Limit of detection (LOD) calculations

The standard deviation (σ) from repeated fluorescence intensity measurements in blank solutions 10 times was calculated using the following equation.

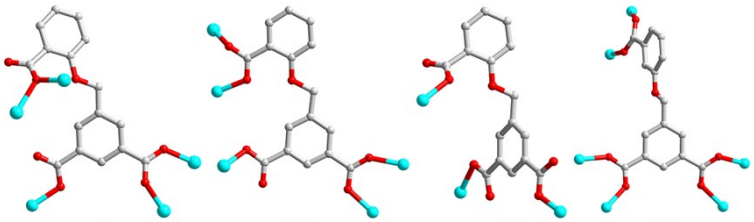
$$\sigma = \sqrt{\frac{\sum (1-\frac{I_0}{I_1})^2}{N-1}} \quad (N = 10)$$

where σ is the standard deviation for repeated detections of blank solutions, and I_1 is the average of I_0.

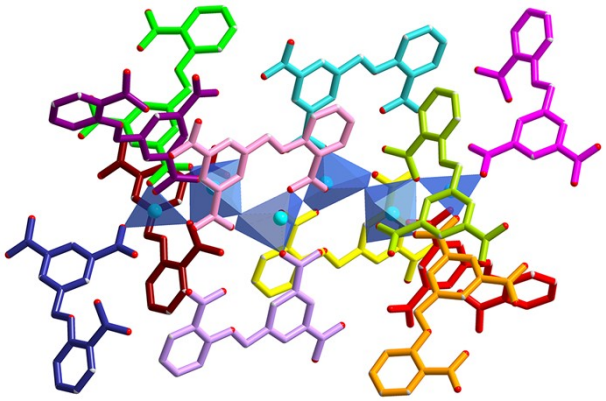
The LOD value was calculated using the following equation.

$$LOD = \frac{3\sigma}{K_{SV}}$$

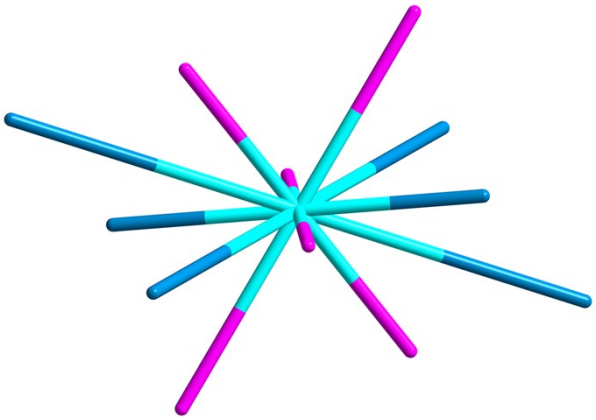
where LOD is the limit of detection, and K_{sv} is the Stern-Volmer constant.



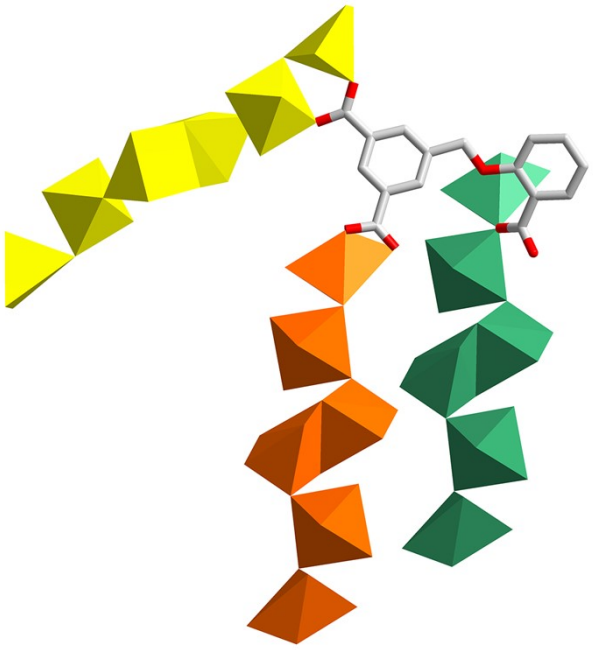
Scheme S1 Coordination modes of $L1^{3-}$ and $L2^{3-}$.



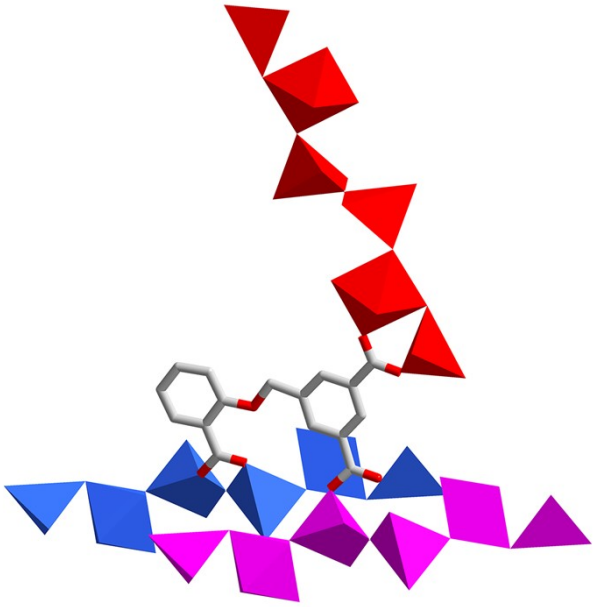
(a)



(b)

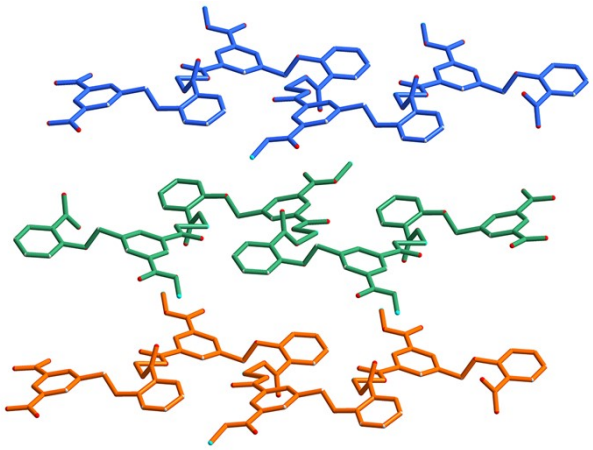


(c)

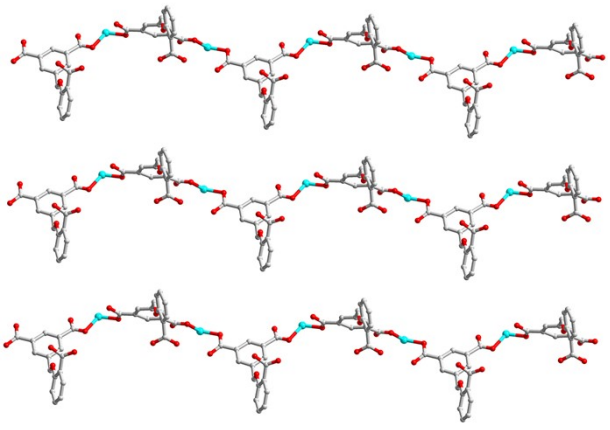


(d)

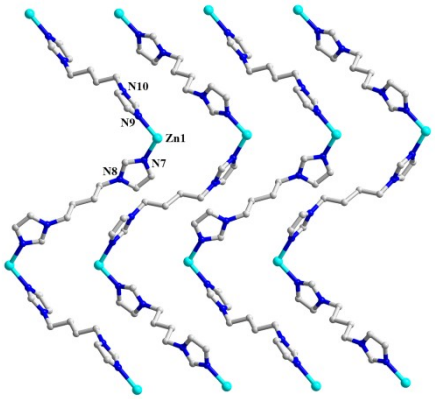
Fig. S1 (a) View of the hexanuclear Zn(II) cluster. (b) View of the 12-connected node simplified by the hexanuclear Zn(II) cluster. (c) and (d) View of the $L1^{3-}$ ligand surrounded by three hexanuclear Zn(II) clusters.



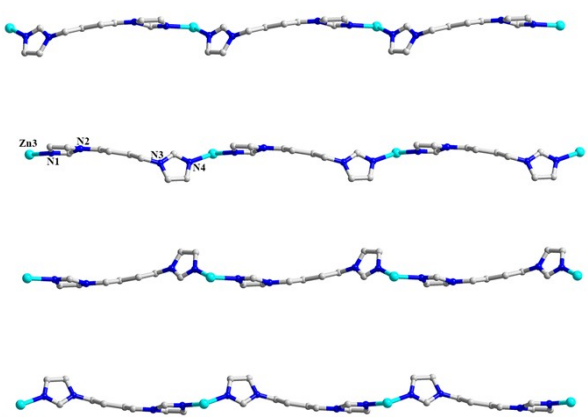
(a)



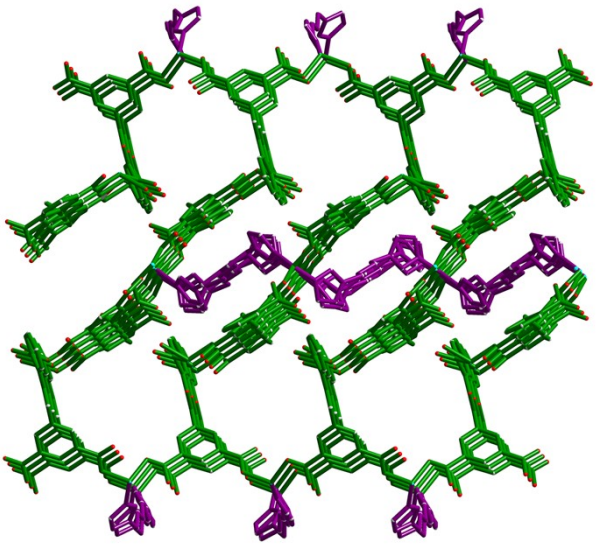
(b)



(c)

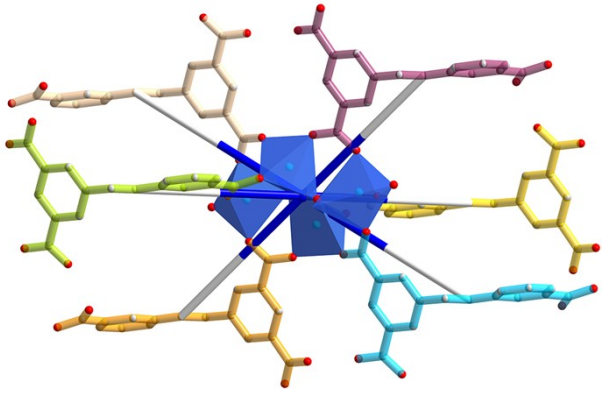


(d)

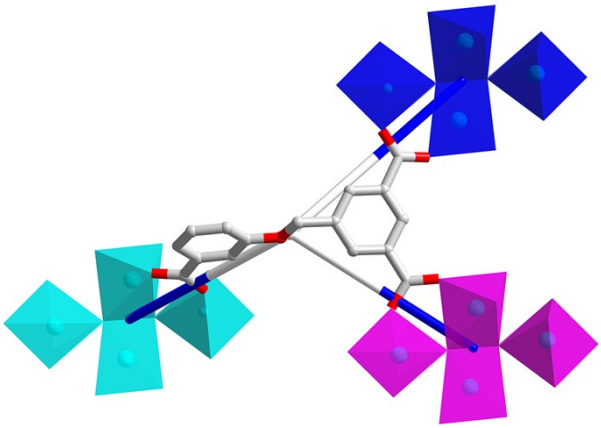


(e)

Fig. S2 (a-d) View of the 1D chains constructed by Zn(II) ions and different ligands. (e) View of the 2D framework.

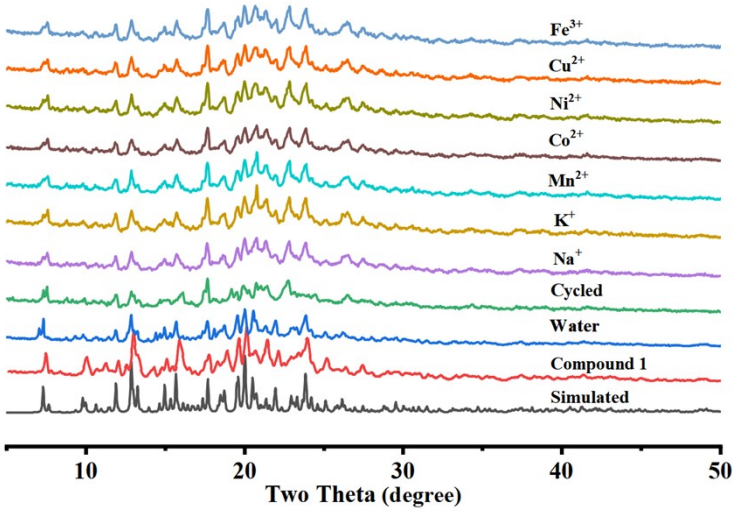


(a)

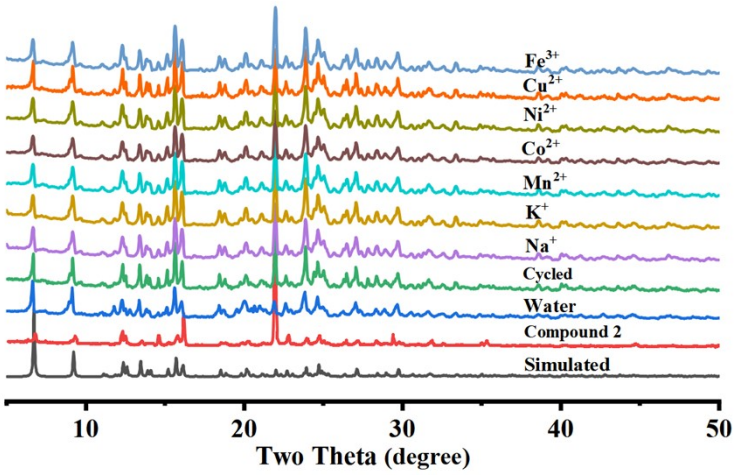


(b)

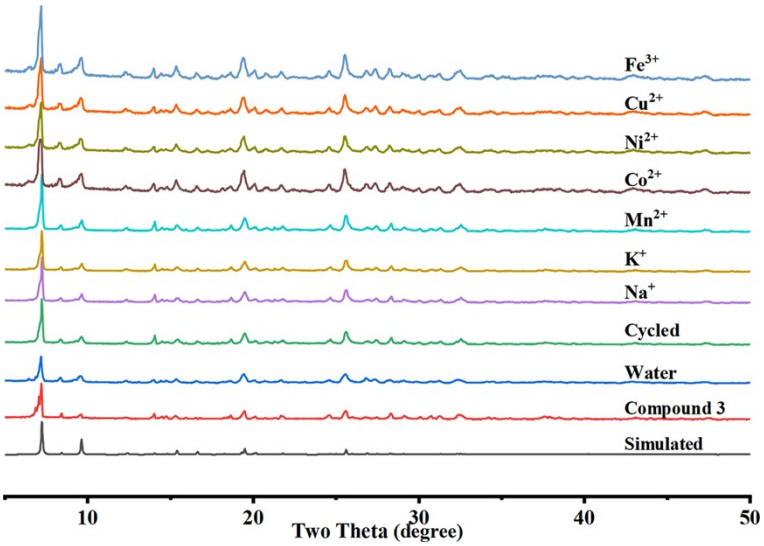
Fig. S3 (a) and (b) Representation of 3- and 6-connected nodes.



(a)

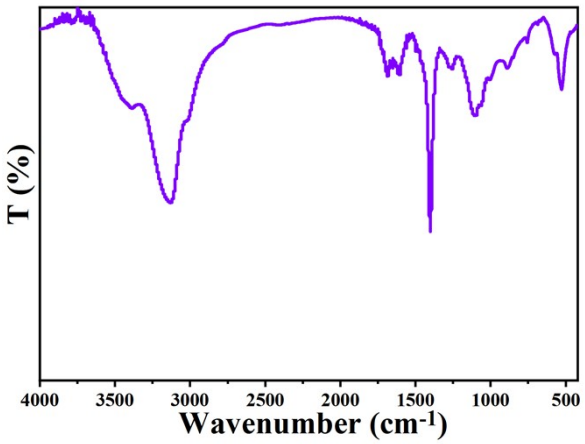


(b)

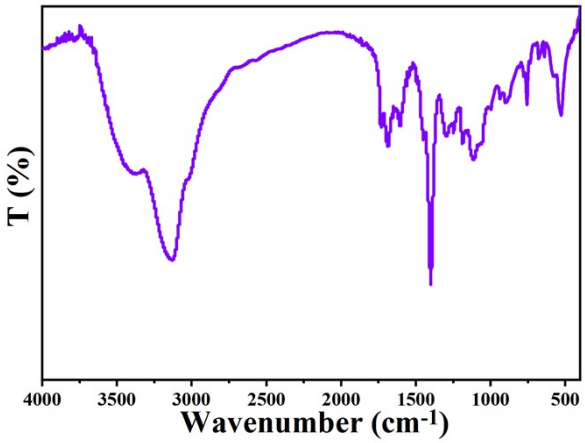


(c)

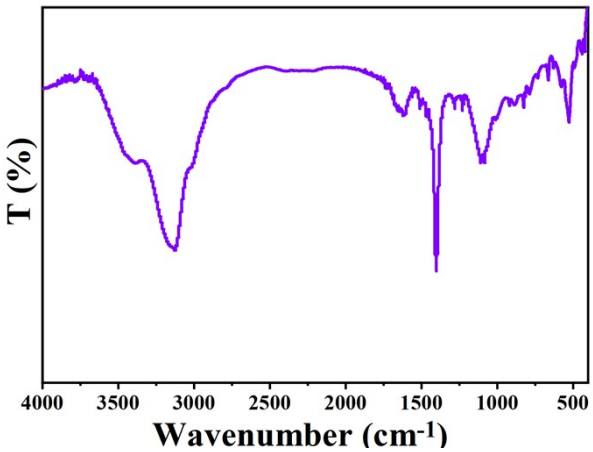
Fig. S4 Simulated PXRD patterns of **1-3** (black) and PXRD patterns of the as-synthesized samples (red).


T (%)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

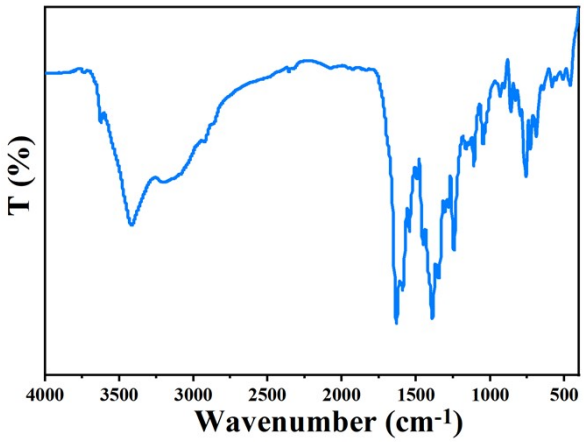
(a)


T (%)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

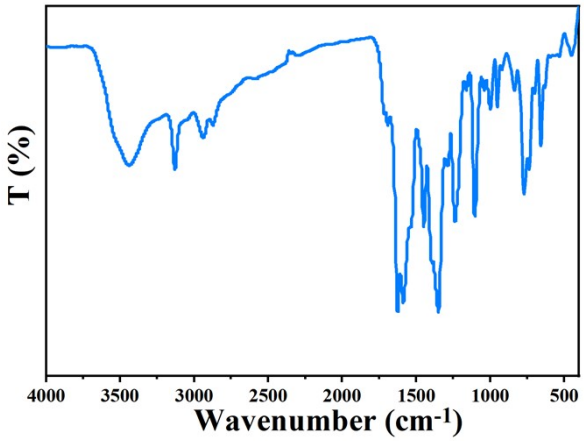
(b)


T (%)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

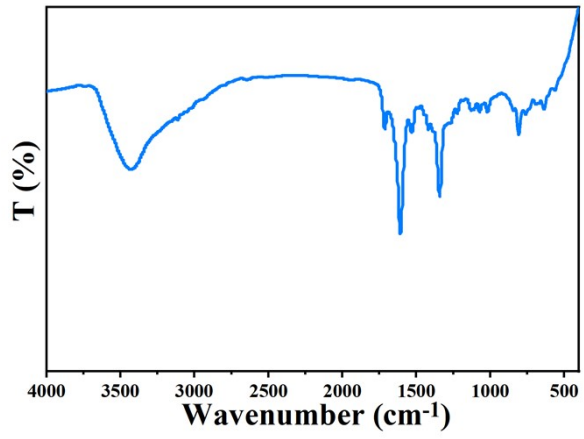
(c)



(d)

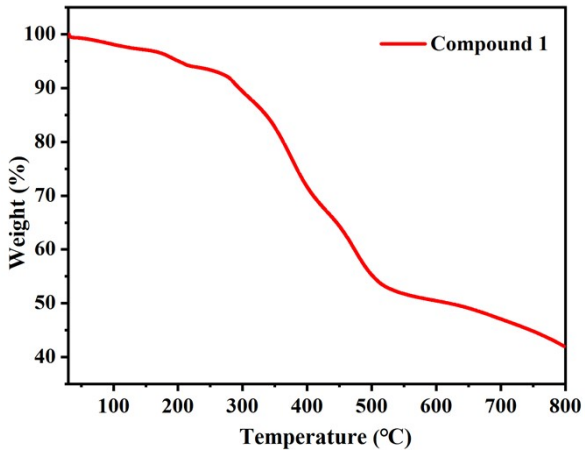


(e)

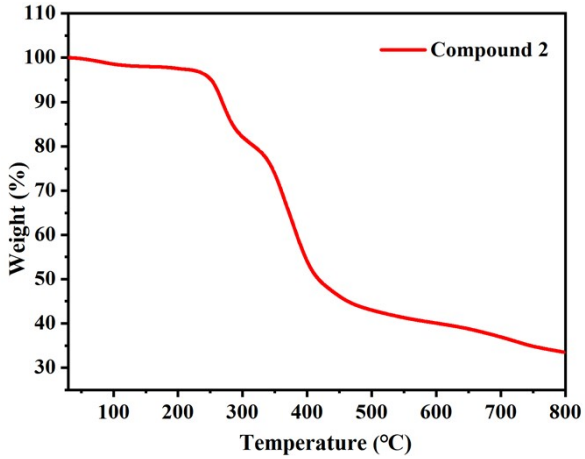


(f)

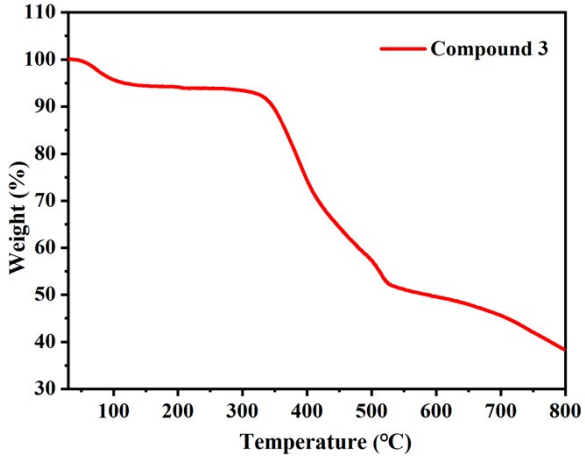
Fig. S5 IR spectra of H3L1 (a), H3L2 (b), dib (c), and compounds **1**-**3** (d-f).



(a)

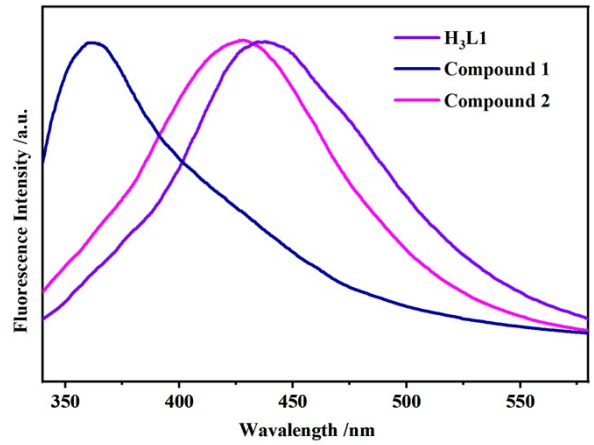


(b)

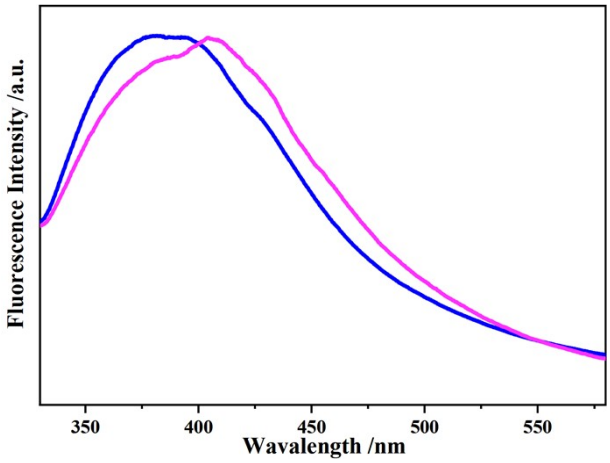


(c)

Fig. S6 TG curves of compounds **1**-**3**.

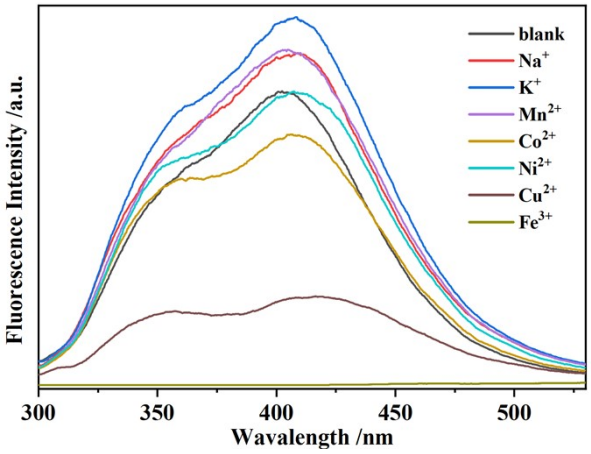


(a)

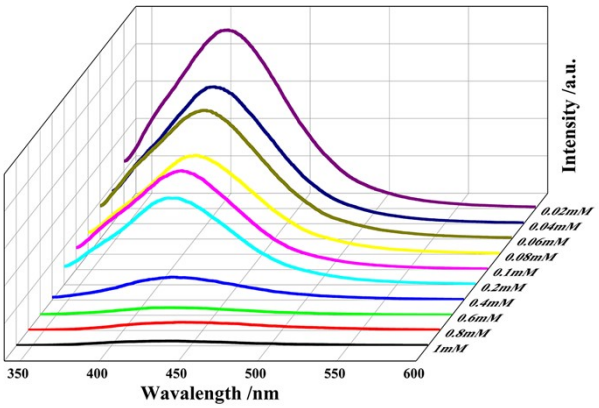


(b)

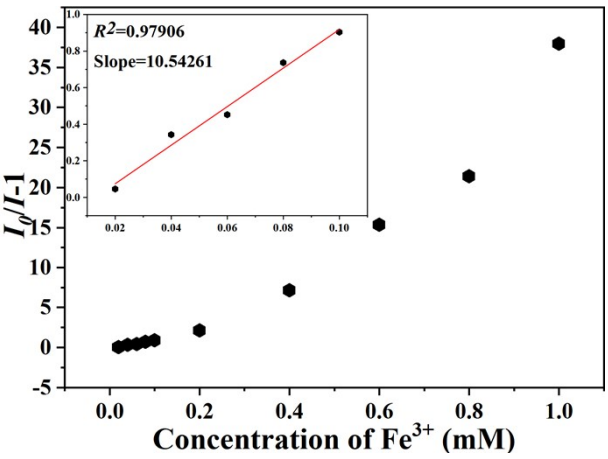
Fig. S7 Solid-state emission spectra of compounds **1-3** and organic ligands at room temperature.



(a)

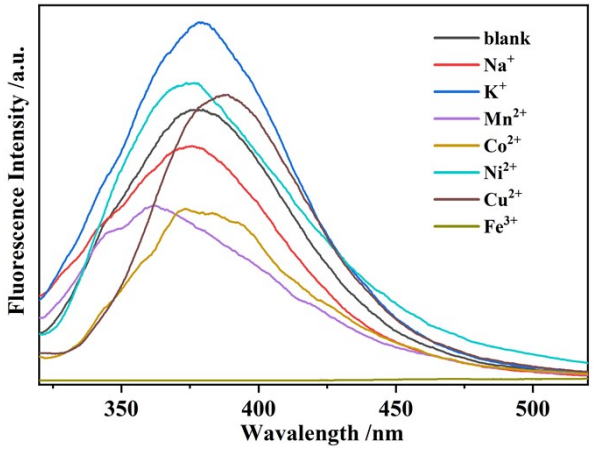


(b)

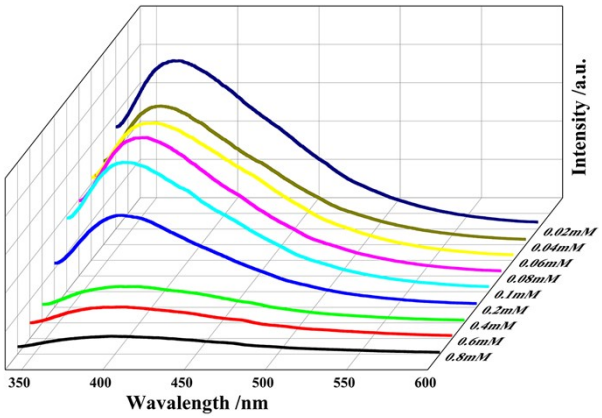


(c)

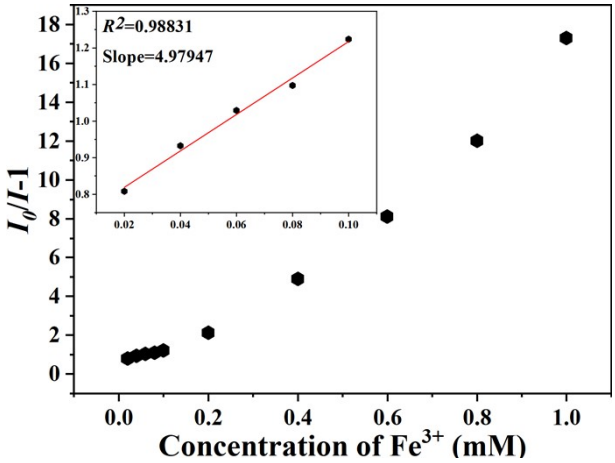
Fig. S8 (a) Emission spectra of compound **2** in different cationic solutions at room temperature. (b) Emission intensity spectra of compound **2** under different Fe^{3+} ion concentrations. (c) Stern-Volmer plots (inset: Stern-Volmer plots at low concentrations).



(a)

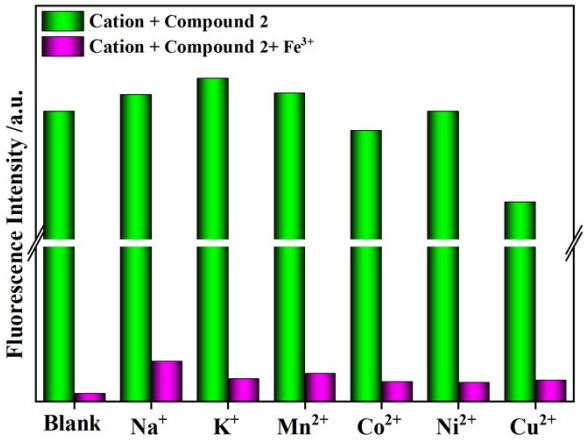


(b)

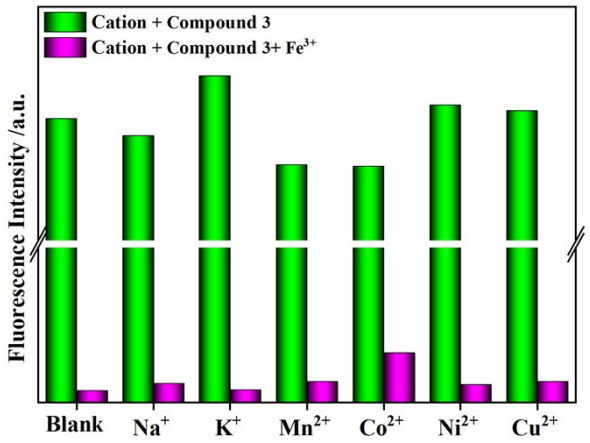


(c)

Fig. S9 (a) Emission spectra of compound **3** in different cationic solutions at room temperature. (b) Emission intensity spectra of compound **3** under different Fe^{3+} ion concentrations. (c) Stern-Volmer plots (inset: Stern-Volmer plots at low concentrations).

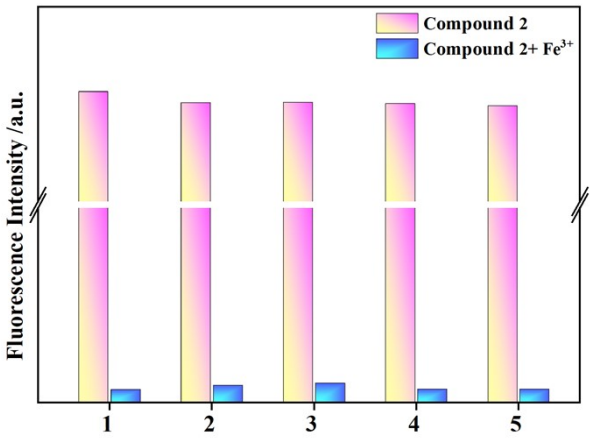


(a)

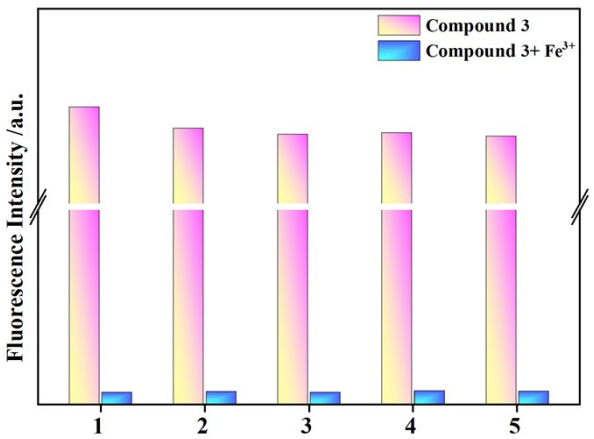


(b)

Fig. S10 The anti-interference performance of compounds **2** and **3** for Fe^{3+} detection in the presence of different anions.



(a)



(b)

Fig. **S11** Recyclability tests of compounds **2** and **3** for Fe^{3+} detection.

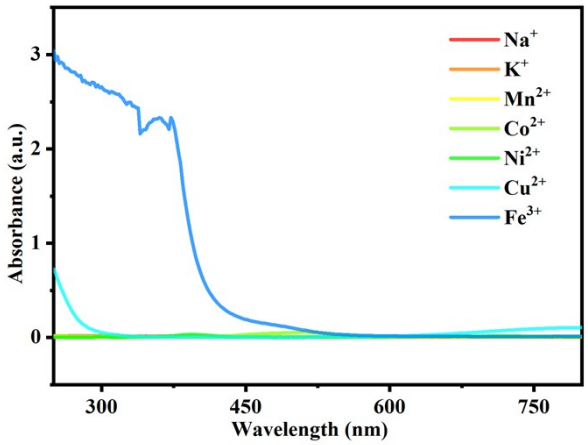
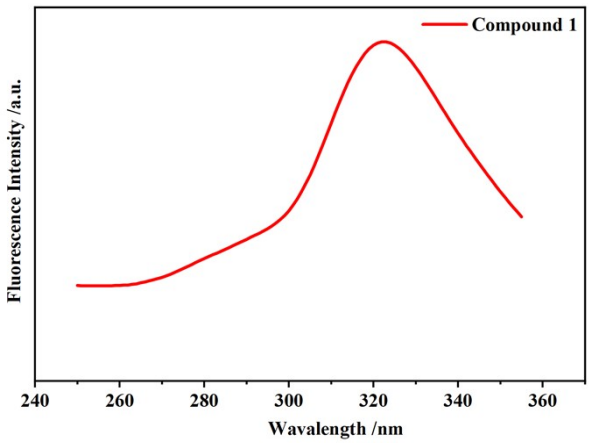
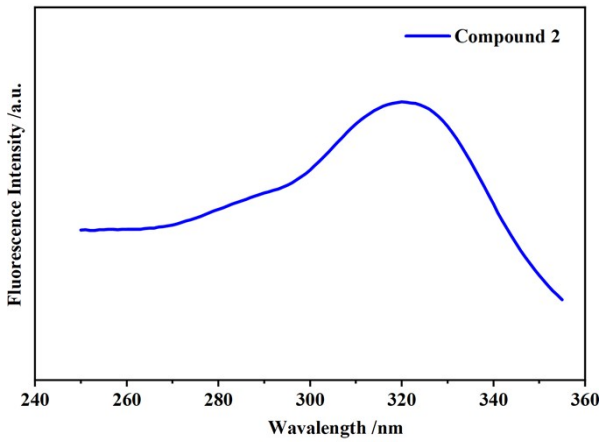


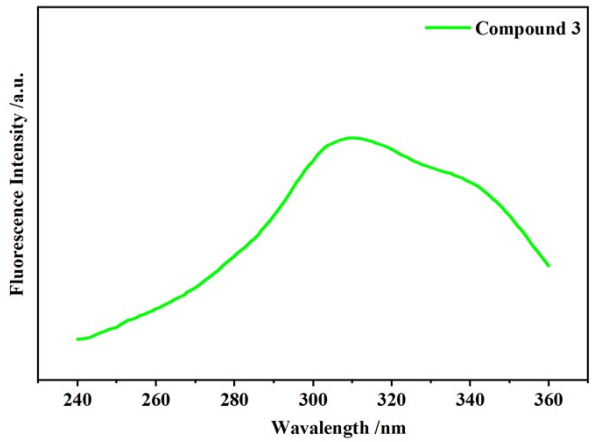
Fig. S12 The UV-Vis absorption spectra of cation solvents.



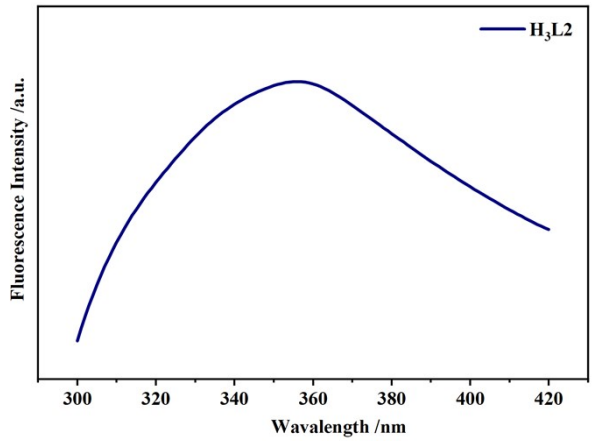
(a)



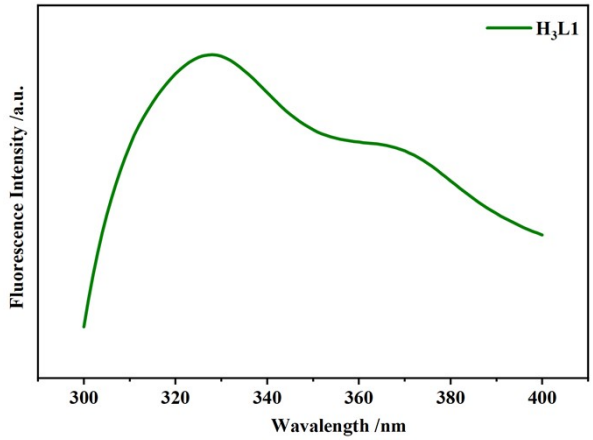
(b)



(c)



(d)



(e)

Fig. S13 The excitation spectra of compounds **1-3**, H_3L1, and H_3L2 in the solid state.

Table S1 Crystallographic data for compounds **1-3**

Compound	1	2	3
Empirical	$C_{32}H_{25}O_{17.5}Zn_3$	$C_{57}H_{55}N_{10}O_{15.5}Zn_3$	$C_{16}H_{13}O_{9.50}Zn_2$

formula			
Formula weight	885.63	1325.22	488.00
Temperature/K	293.15	293.15	293.15
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	P-1
a/Å	8.4102(2)	24.416(2)	7.1877(3)
b/Å	24.2114(6)	13.1343(13)	10.8583(4)
c/Å	15.6405(4)	18.2143(19)	12.6345(5)
α/°	90	90	104.4760(10)
β/°	91.320(1)	97.684(3)	91.4000(10)
γ/°	90	90	94.0910(10)
Volume/Å^3	3183.92(14)	5788.7(10)	951.42(7)
Z	4	4	2
ρ_{calc}g/cm^3	1.85	1.519	1.703
μ/mm^{-1}	2.329	1.311	2.569
Independent reflections	5818 [R_{int} = 0.0432, R_{sigma} = 0.0309]	10556 [R_{int} = 0.0482, R_{sigma} = 0.0349]	3471 [R_{int} = 0.0165, R_{sigma} = 0.0087]
Goodness-of-fit on F^2	1.07	1.044	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0355, wR_2 = 0.0984	R_1 = 0.0606, wR_2 = 0.1598	R_1 = 0.0248, wR_2 = 0.0841
Final R indexes [all data]	R_1 = 0.0443, wR_2 = 0.1048	R_1 = 0.0843, wR_2 = 0.1741	R_1 = 0.0254, wR_2 = 0.0846

Table S2 Selected bond lengths (Å) and bond angles (°) for 1

Bond	**Dist.**	**Bond**	**Dist.**
Zn1-O1	1.925(3)	Zn2-O1W	2.031(3)
Zn1-O4#3	1.985(3)	Zn2-O2W	2.083(3)
Zn1-O6#1	1.969(2)	Zn2-O3W#2	2.277(3)
Zn1-O8	1.969(3)	Zn3-O11#1	1.930(3)
Zn2-O3#3	2.011(3)	Zn3-O13	1.926(3)
Zn2-O6#1	2.252(2)	Zn3-O14#3	1.994(3)
Zn2-O9	2.016(3)	Zn3-O3W	2.060(3)
Angle	**(°)**	**Angle**	**(°)**
O4#3-Zn1-O1	112.41(12)	O2W-Zn2-O9	96.51(14)
O6#1-Zn1-O1	130.42(11)	O2W-Zn2-O1W	93.71(15)
O6#1-Zn1-O4#3	104.75(11)	O3W#2-Zn2-O3#3	90.81(10)
O8-Zn1-O1	98.54(12)	O3W#2-Zn2-O6#1	83.31(9)
O8-Zn1-O4#3	99.54(12)	O3W#2-Zn2-O9	174.10(12)
O8-Zn1-O6#1	106.59(11)	O3W#2-Zn2-O1W	85.79(10)

O6#1-Zn2-O3#3	90.34(10)	O3W#2-Zn2-O2W	86.15(13)
O9-Zn2-O3#3	94.59(12)	O13-Zn3-O11#1	128.97(12)
O9-Zn2-O6#1	94.25(11)	O14#3-Zn3-O11#1	110.51(11)
O1W-Zn2-O3#3	176.48(12)	O14#3-Zn3-O13	115.40(12)
O1W-Zn2-O62	88.37(12)	O3W-Zn3-O11#1	97.95(11)
O1W-Zn2-O9	88.77(12)	O3W-Zn3-O13	97.30(11)
O2W-Zn2-O3#3	86.95(13)	O3W-Zn3-O14#3	97.18(11)
O2W-Zn2-O6#1	169.07(13)		
#1: -x,2-y,1-z; #2: 1/2+x,3/2-y,-1/2+z; #3: -1-x,2-y,1-z ; #4: -1+x,+y,+z; #5: -1/2+x,3/2-y,-1/2+z			

Table S3 Selected bond lengths (Å) and bond angles (°) for 2

Bond	**Dist.**	**Bond**	**Dist.**
Zn1-O1	1.994(4)	Zn2-O7	1.932(4)
Zn1-N9	2.023(4)	Zn2-N5	1.978(5)
Zn1-O4#1	1.970(4)	Zn3-O12	2.057(7)
Zn1-N7	2.004(4)	Zn3-N1	2.037(6)
Zn1-C1	2.565(5)	Zn3-O13#2	1.946(6)
Zn2-O8	1.976(4)	Zn3-N4#3	2.022(7)
Zn2-O1W	1.997(4)		
Angle	**(°)**	**Angle**	**(°)**
O1-Zn1-N9	114.16(16)	O8-Zn2-N5	99.29(19)
O1-Zn1-N7	124.88(16)	O7-Zn2-O8	108.03(16)
O1-Zn1-C1	28.95(16)	O7-Zn2-O1W	111.15(18)
N9-Zn1-C1	105.21(16)	O7-Zn2-N5	125.6(2)
O4-Zn1-O1	102.68(16)	N5-Zn2-O1W	108.8(2)
O4#1-Zn1-N9	95.13(15)	N1-Zn3-O12	103.1(3)
O4#1-Zn1-N7	108.92(17)	O13#2-Zn3-O12	105.9(3)
O4#1-Zn1-C1	131.63(18)	O13#2-Zn3-N1	98.2(3)
N7-Zn1-N9	106.71(16)	O13#2-Zn3-N4#3	107.2(3)
N7-Zn1-C1	106.41(17)	N4#3-Zn3-O12	131.0(4)
O8-Zn2-O1W	100.26(17)	N4#3-Zn3-N1	106.9(3)
#1: -x,1/2+y,3/2-z; #2: +x,1/2-y,1/2+z; #3: +x,-1+y,+z; #4: -x,1-y,2-z; #5: -x,1-y,1-z; #6: -1-x,-y,2-z			

Table S4 Selected bond lengths (Å) and bond angles (°) for 3

Bond	**Dist.**	**Bond**	**Dist.**
Zn1-O1#1	2.0433(19)	Zn2-O1W	2.109(2)
Zn1-O4#2	2.0678(19)	Zn2-O2	1.982(2)
Zn1-O5	1.9560(19)	Zn2-O3#4	2.037(2)

Zn1-O8#1	2.0272(18)	Zn2-O6#3	1.983(2)
Zn1-O8#3	2.1119(18)	Zn2-O8	2.0157(18)
Angle	**(°)**	**Angle**	**(°)**
O1#1-Zn1-O4#2	90.90(9)	O2-Zn2-O1W	102.54(9)
O1#1-Zn1-O8#3	92.17(7)	O2-Zn2-O3#5	96.76(10)
O4#2-Zn1-O8#3	173.94(8)	O2-Zn2-O6#3	101.16(11)
O5-Zn1-O1#1	115.23(9)	O2-Zn2-O8	108.92(8)
O5-Zn1-O4#2	86.00(8)	O3#5-Zn2-O1W	80.07(8)
O5-Zn1-O8#3	97.40(8)	O6#3-Zn2-O1W	81.01(9)
O5-Zn1-O8#1	132.62(9)	O6#3-Zn2-O3#5	156.31(10)
O8#1-Zn1-O1#1	112.14(8)	O6#3-Zn2-O8	96.50(8)
O8#1-Zn1-O4#2	94.31(8)	O8-Zn2-O1W	148.29(9)
O8#1-Zn1-O8#3	79.69(8)	O8-Zn2-O3#5	92.17(8)
#1: 1+x,+y,-1+z; #2: 2-x,1-y,-z; #3: 1-x,2-y,1-z; #4: 1-x,1-y,1-z			

Table S5 A comparison of CP-based luminescent probes for detection of Fe^{3+}

CP	K_{sv} (M^{-1})	Linear range (mM^{-1})	LOD (M)	Ref.
$\{[Cd_3(itp)_2(btc)_2]\cdot 4H_2O\}_n$	5.885×10^4	0-0.006	0.12×10^{-6}	S1
$[Cd(L1)(DCTP)]_n$	6.750×10^3	0-0.1	2.54×10^{-6}	S2
$[Cd(L2)(TPA)]_n$	2.6273×10^4	0-0.004	0.99×10^{-6}	S2
$[Sr_3(BPTC)_{1.5}(H_2O)_{6.5}]_n$	4.12×10^4	0-0.06	1×10^{-6}	S3
$[Zn(L)_2]_n$	1.34×10^4	0-0.15	2.24×10^{-6}	S4
1	13.55634×10^3	0.02-0.10	4.07×10^{-6}	This work
2	10.54261×10^3	0.02-0.10	1.14×10^{-6}	This work
3	4.97947×10^3	0.02-0.10	40.70×10^{-6}	This work

References

S1 T. Zheng, V. A. Blatov, Y. Zhang, C. Yang, L. Qian, K. Li, B. Li and B. Wu, *J. Lumin.*, 2018, **199**, 126-132.

S2 M. Wen, S. Wang, D. Liu and G. Dong, *J. Mol. Struct.*, 2021, **1244**, 130954.

S3 B. Zhao, S. Li, Y. Gu, Q. Sun and H. Liu, *J. Mol. Struct.*, 2022, **1270**, 133944.

S4 T. Xu, H. Nie, J. Li and Z. Shi, *J. Solid State Chem.*, 2020, **287**, 121342.