Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supporting Information

Anion-dependent dynamic structure and tunable luminescence of Zn-MOFs with carboxyphenyl-terpyridine ligands

Runzhong Guo[§], Yuchen Liu[§], Zhibin Wang, Haiying Wang* and Huiyan Liu*

School of Chemistry & Materials Science, Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou 221116, P. R. China

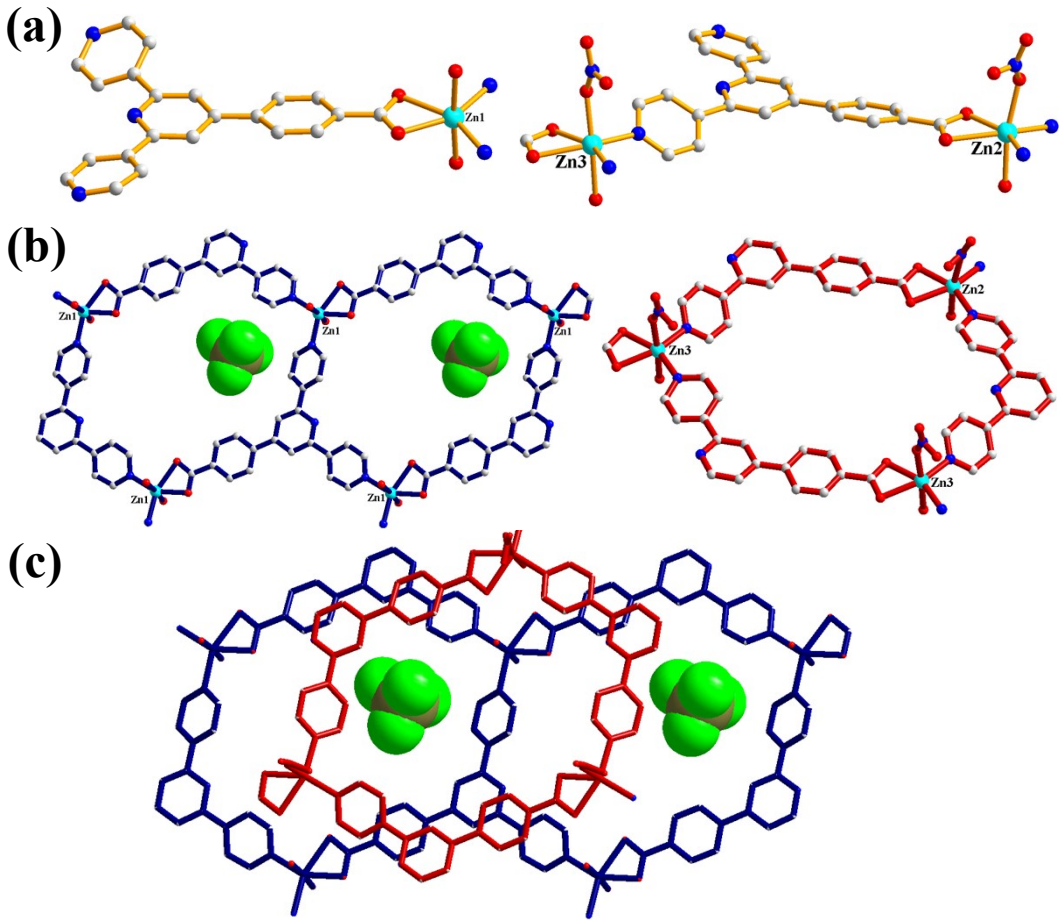

Fig. S1 Crystal structure of **1⊃BF_4^-**. (a) Coordination environment of Zn(II) ions. (b) The two layers comprised of Zn1 centers (left) and Zn2/3 centers (right). (c) The packed double-layers viewed along the *b* axis with free BF_4^- anions shown in space-filling mode.

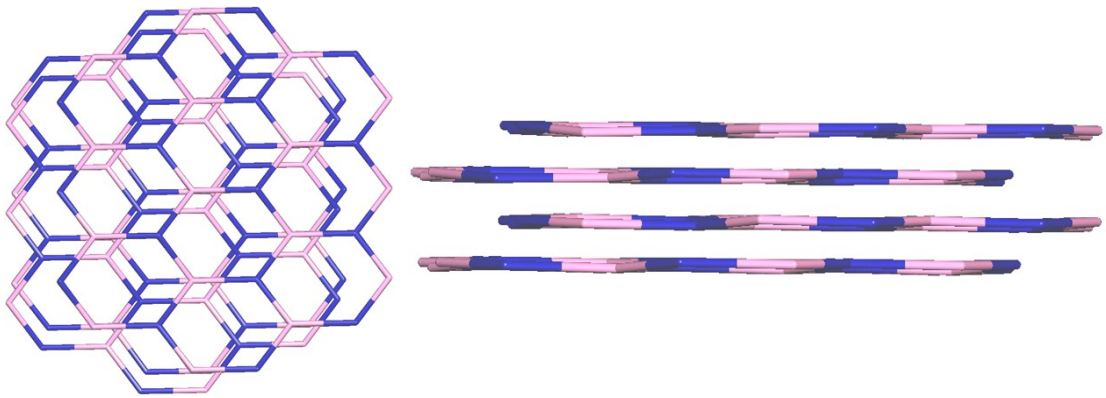

Fig. S2 The 3-connected ***hcb*** topological representation of **1** (**1⊃ClO_4^-** and **1⊃BF_4^-**) viewed along the *b* axis (left) and *c* axis (right).

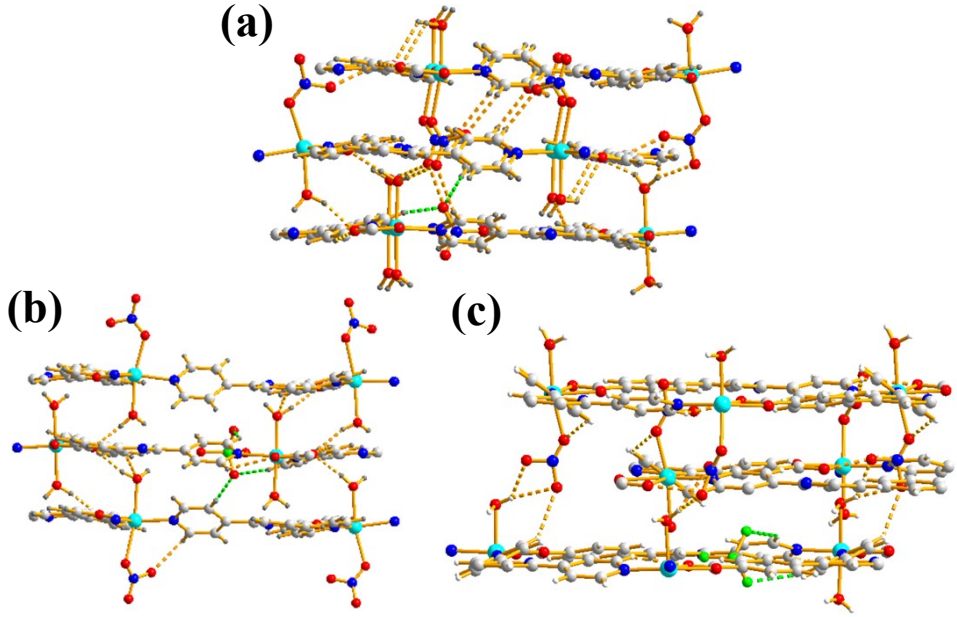

Fig. S3 The hydrogen bonds between the coordination nitrate ions and the coordination water within the framework (oranage dotted lines), and between C–H of HL linkers and lattice anions (greeen dotted lines) in **1⊃NO_3^-**(a), **1⊃ClO_4^-** (b) and **1⊃BF_4^-** (c).

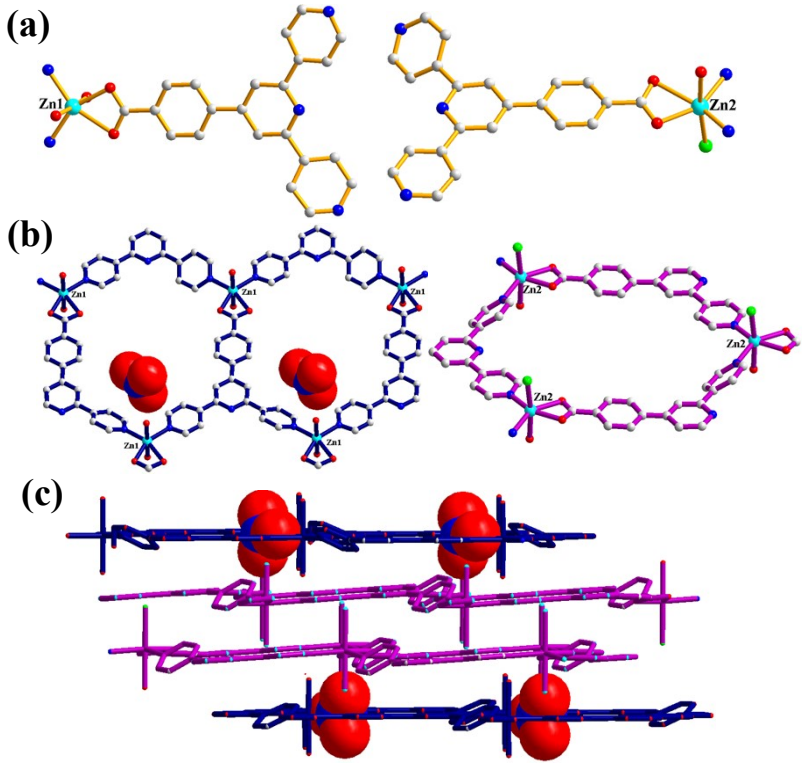

Fig. S4 Crystal structure of **2**. (a) Coordination environment of Zn(II) ions. (b) The two layers comprised of Zn1 centers (left) and Zn2 centers (right). (c) The packed double-layers viewed along the *c* axis with uncoordinated NO_3^- anions (space-filling mode) located within the framework.

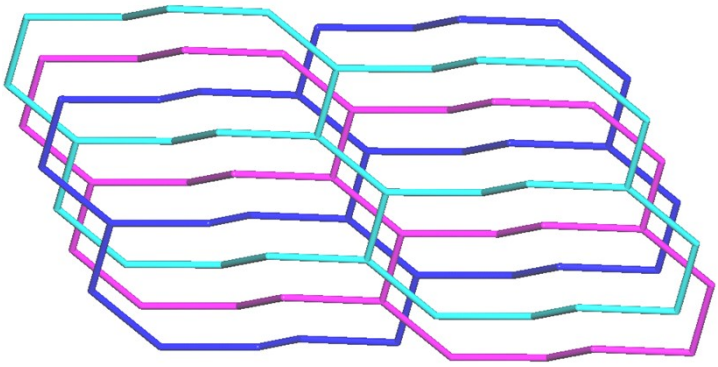

Fig. S5 The 3-fold interpenetrating 3D framework of **3** with ***ths*** topology.

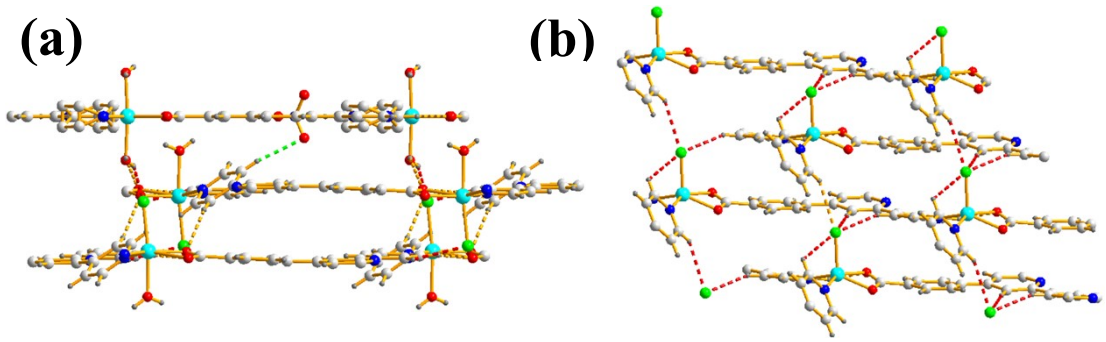

Fig. S6 The hydrogen bonds between the coordination chloride ions and framework (red dotted lines), and between C–H of HL linker and lattice anions (greeen dotted line) in **2** (a) and **3** (b).

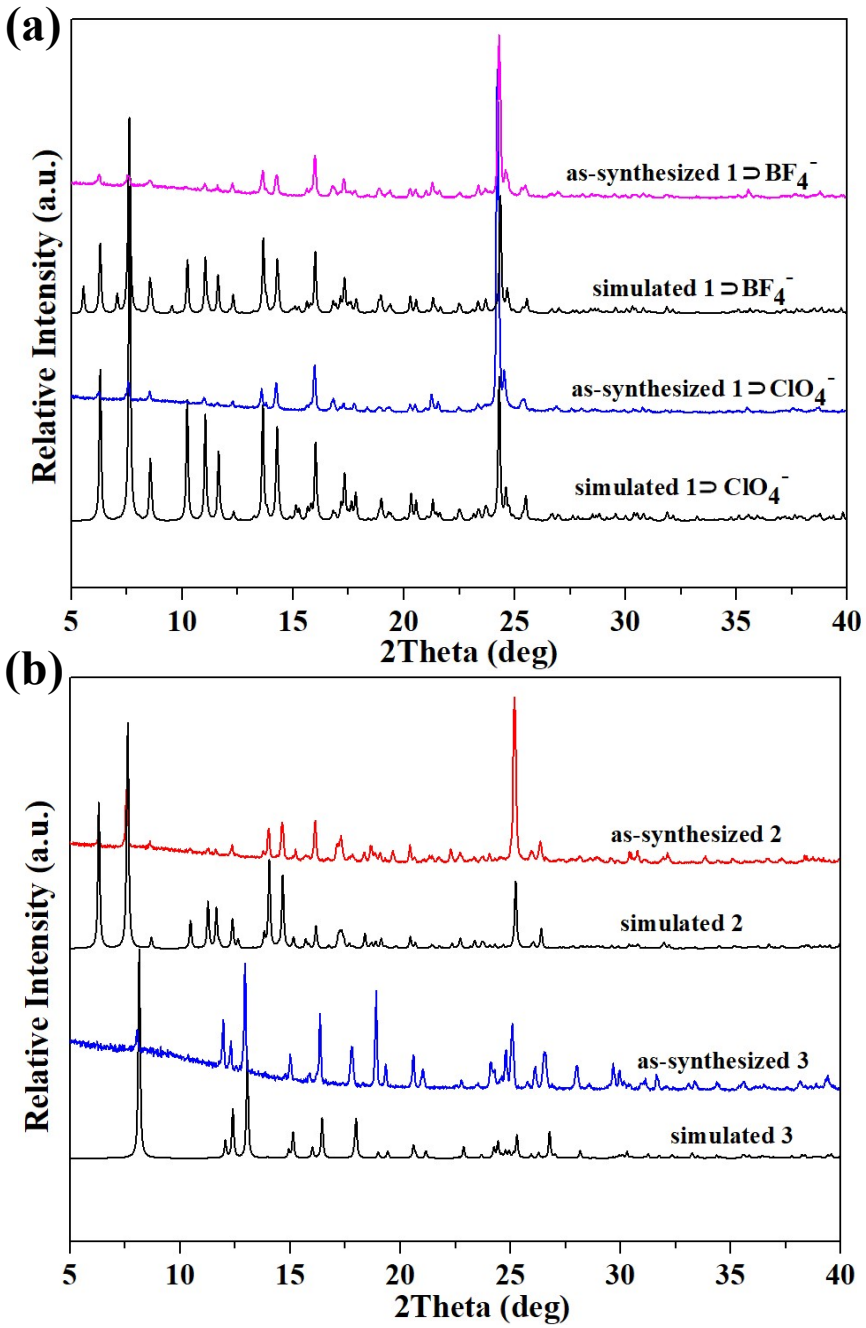

Fig. S7 PXRD patterns for **1** (**1⊃ClO_4^-** and **1⊃BF_4^-**) (a), **2** and **3** (b): a simulated PXRD pattern from the single-crystal structure and as-synthesized samples, respectively.

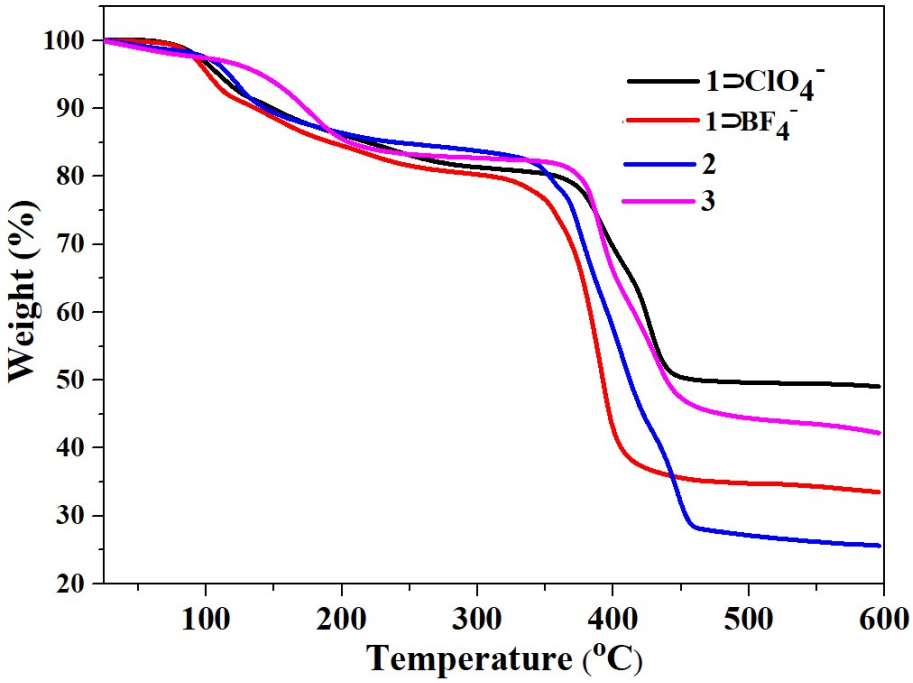

Fig. S8 TGA data of as-synthesized **1** (**1⊃ClO$_4^-$** and **1⊃BF$_4^-$**), **2** and **3**.

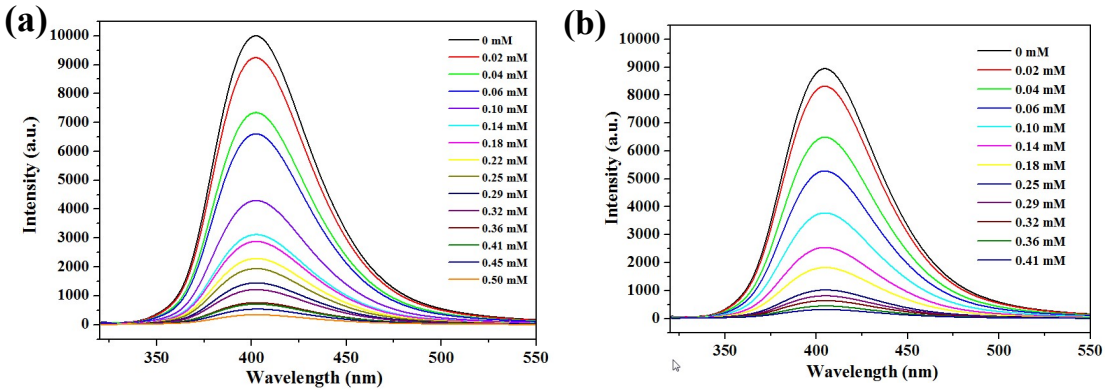

Fig. S9 The fluorescence emission spectra of **1⊃ClO$_4$** (a) and **1⊃BF$_4^-$** (b) with 4-NT of different concentrations.

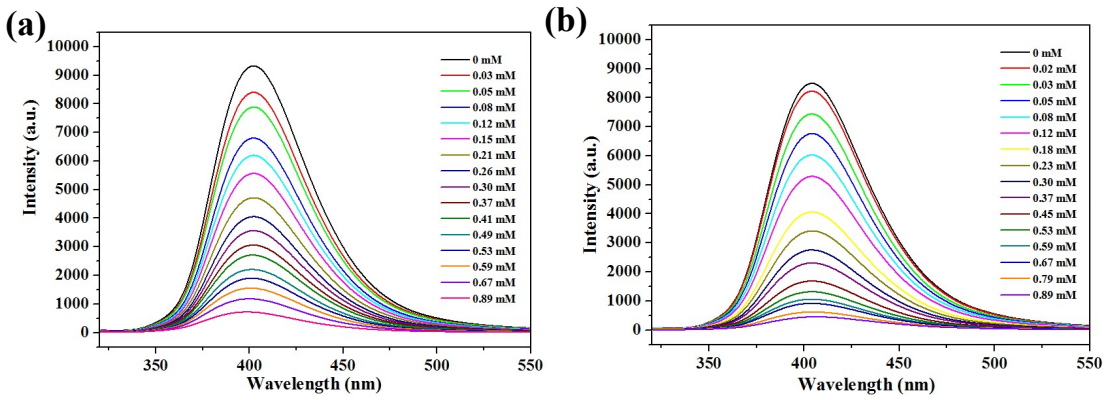

Fig. S10 The fluorescence emission spectra of **1⊃ClO$_4$** (a) and **1⊃BF$_4^-$** (b) with 1,3-DNB of different concentrations.

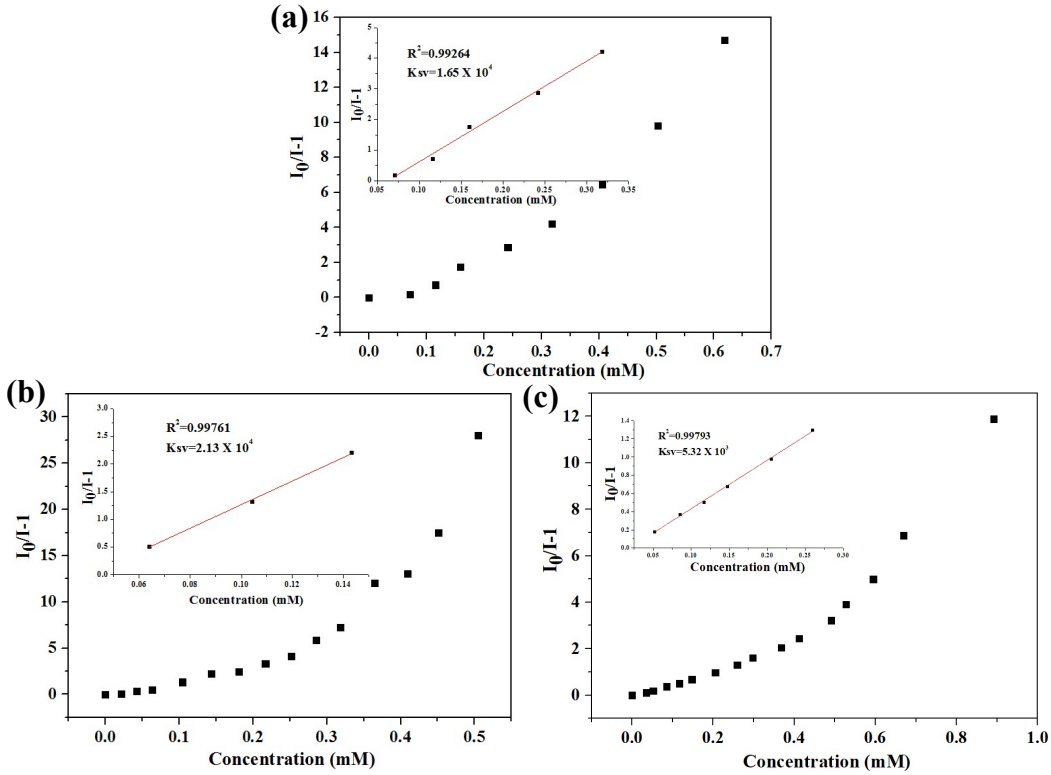

Fig. S11 The Stern-Volmer plots for **1⊃ClO$_4^-$** with NB (a), 4-NT (b) and 1,3-DNB (c).

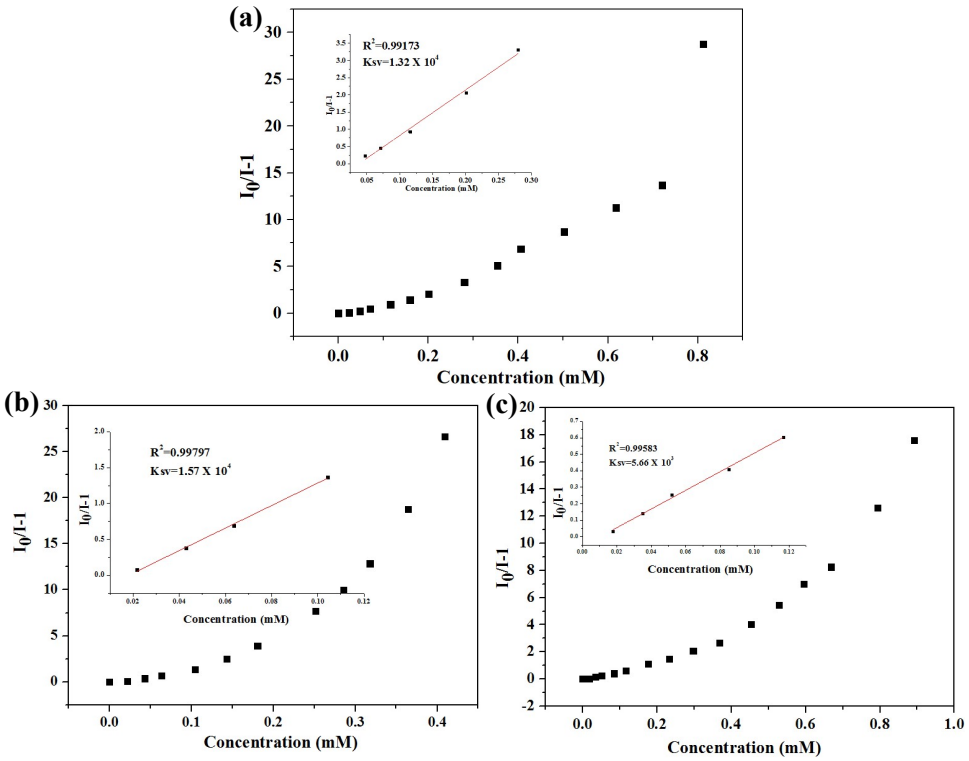

Fig. S12 The Stern-Volmer plots for **1⊃BF_4^-** with NB (a), 4-NT (b) and 1,3-DNB (c).

Table S1 Parameters of hydrogen bonding interactions involving in C-H of HL and anions in **1** (**1⊃NO_3^-**, **1⊃ClO_4^-** and **1⊃BF_4^-**)

D-H···A	***d*(D-H)**	***d*(H···A)**	***d*(D···A)**	**∠(DHA)**
1⊃NO_3^-				
C17-H17···O18	0.93	2.479	3.404	173.14
C39-H39···O19#7	0.93	2.590	3.510	170.42
C64-H64···O18#8	0.93	2.664	3.364	132.62
1⊃ClO_4^-				
C21-H21···O20#7	0.93	2.591	3.301	133.48
C58-H58···O20#1	0.93	2.601	3.529	175.94
1⊃BF_4^-				
C15-H15···F2	0.93	2.522	3.243	134.55
C21-H21···F1#11	0.93	2.600	3.293	131.70

Symmetry codes: **1⊃NO_3^-**: #7: x-1, -y+3/2, z-1/2 ; #8: x, -y+3/2, z+1/2 ; **1⊃ClO_4^-**: #7: -x+1, -y+1, -z+1; #1: x+1/2, -y+1/2, z-1/2; **1⊃BF_4^-**: #11: x-1/2, -y+1/2, z-1/2.

Table S2 Parameters of hydrogen bonding interactions involving in O-H/C-H and chloride ions in **2** and **3**

D-H···A	***d*(D-H)**	***d*(H···A)**	***d*(D···A)**	**∠(DHA)**
2				
O2-H2B···Cl1#7	0.85	2.474	3.230	148.57
C17-H17···Cl1#10	0.93	2.935	3.638	133.51
3				
C22-H22···Cl2#6	0.93	2.733	3.5958	154.56
C16-H16···Cl2#3	0.93	2.836	3.363	117.12
C15-H15···Cl2#8	0.93	2.871	3.614	137.72
O3-H3A···Cl2	0.85	2.476	3.245	150.83

Symmetry codes: **2**: #7: -x, -y+1, -z; #10: -x, -y+1, -z; **3**: #6: x, y+1, z; #3: x-1/2, -y+1/2, z+1/2; #8: x, -y, z+1/2.

Table S3 Fluorescence test data related to three MOFs

MOFs	I_0	*K*sv (M^{-1})		
		NB	4-NT	1,3-DNB
1⊃NO_3^-	6500	1.33×10^4	1.48×10^4	2.53×10^3
1⊃ClO_4^-	9400	1.65×10^4	2.13×10^4	5.32×10^3
1⊃BF_4^-	8600	1.32×10^4	1.57×10^4	5.66×10^3