Electronic Supplementary Material (ESI) for RSC Advances.

Metal-Organic Framework Bearing New Violet Ligand for Ammonia and $Cr_2O_7^{2-}$ Sensing

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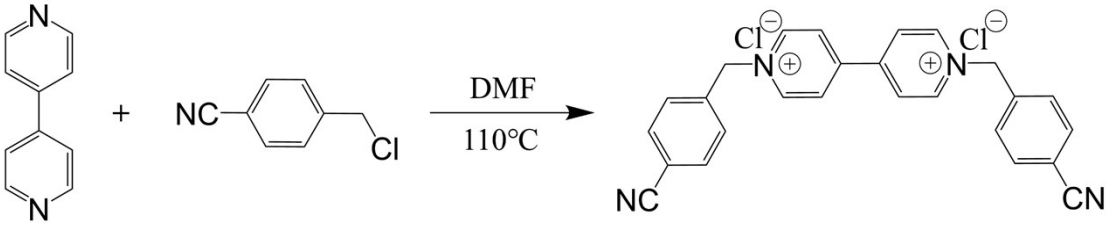
Synthesis of 4-BCBPY·2Cl.

4-BCBPY·2Cl: Dissolve 4,4'-bipyridine (10 mmol, 1.56 g) and 4-cyanobenzyl chloride (20 mmol, 3.92 g) in 25mL of N, N'-dimethylformamide (DMF), and stir at 110°C for 6h. Filtration yielded a yellow product. The obtained product was washed 3 times with hot DMF and recrystallized with methanol to finally obtain a yellow solid. The yield was 90%.



Scheme S1. The synthetic method of 4-BCBPY·2Cl.

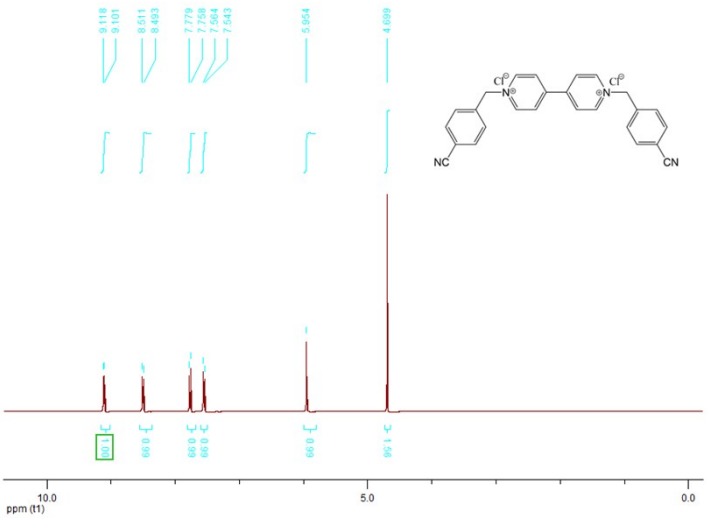


Figure S1. The ^{1}H NMR spectrum of 4-BCBPY·2Cl in D_2O (600 MHz).

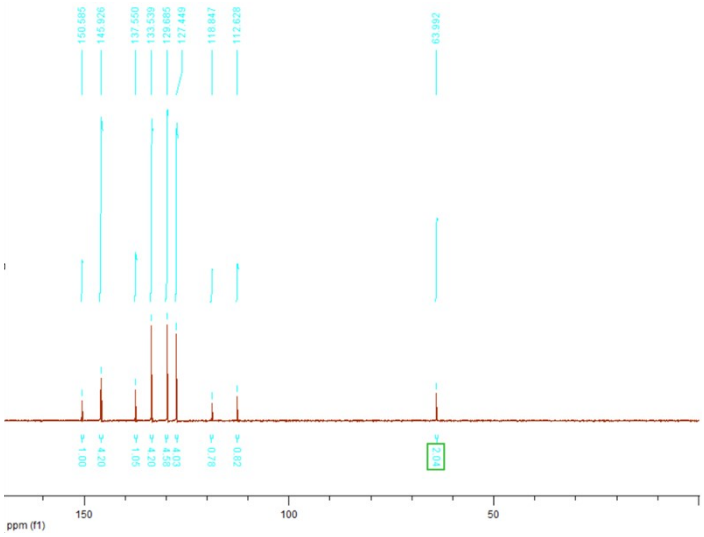


Figure S2. The ^{13}C NMR spectrum of 4-BCBPY·2Cl in D_2O (600 MHz).

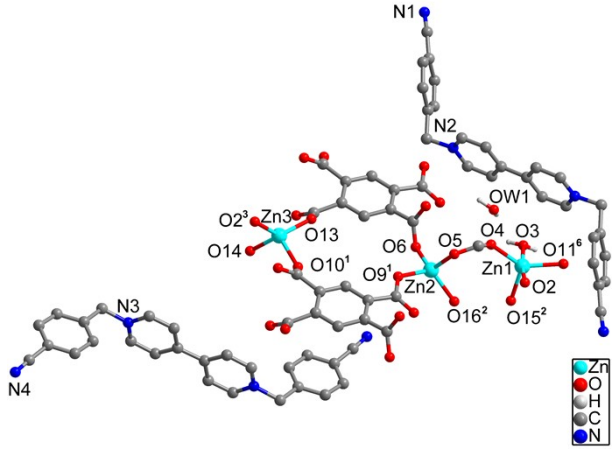


Figure S3. The selected structural unit of compound **1** (Symmetry codes: [1]+x, 1+y, +z; [2]+x, 1-y, -1/2+z; [3]+x, 1-y, 1/2+z; [4]+x, -y, -1/2+z; [5]+x, -1+y, +z; [6]+x, -y, 1/2+z).

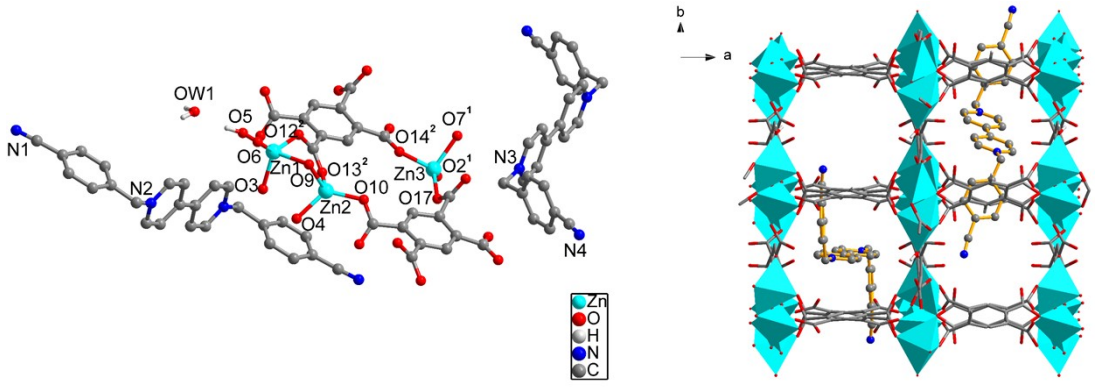


Figure S4. The selected structural unit (a) and 3D packing structure (b) of compound **2** (Symmetry codes: [1]+x, 1-y, 1/2+z; [2]+x, -1+y, +z).

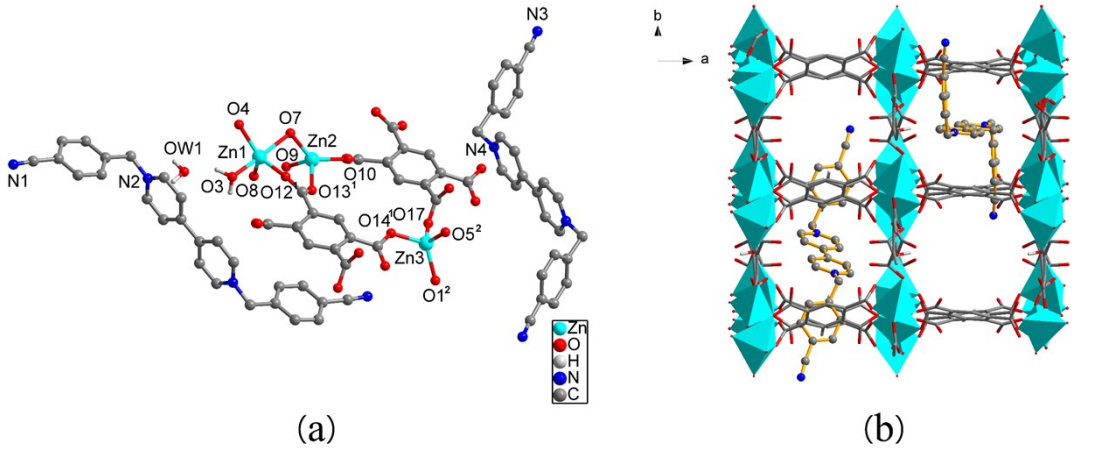


Figure S5. The selected structural unit (a) and 3D packing structure (b) of compound **3** (Symmetry codes: ^{1}+x, -1+y, +z; ^{2}+x, 1-y, 1/2+z).

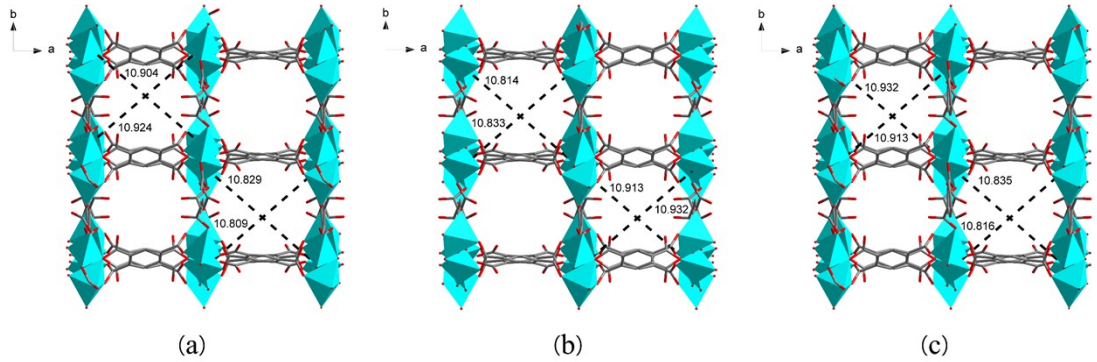


Figure S6. Estimated channel size for compounds **1**(a), **2**(b) and **3**(c).

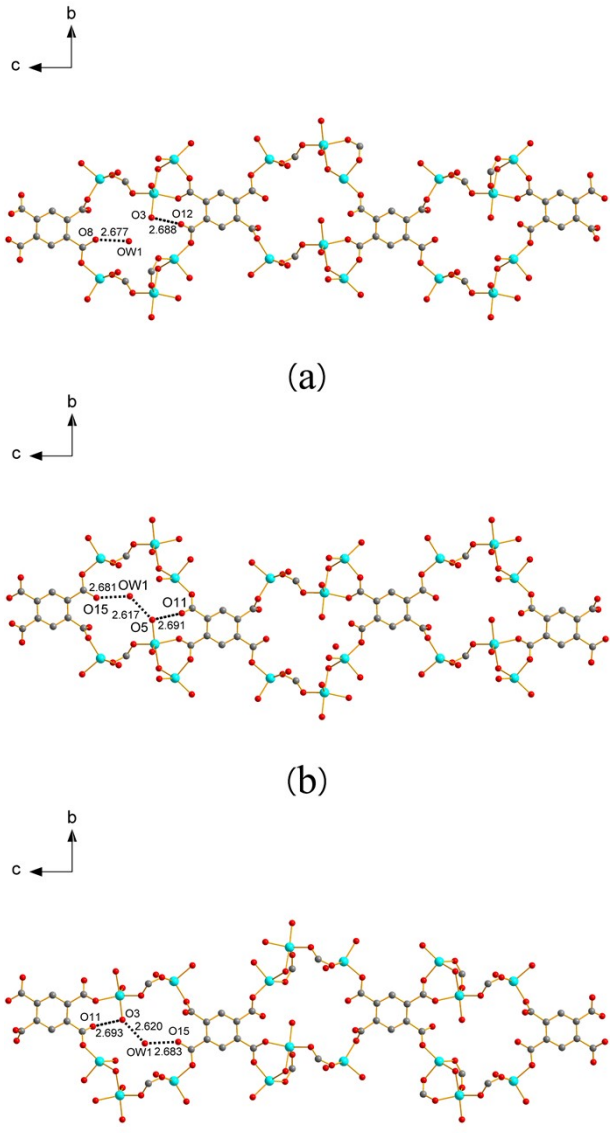


Figure S7. The hydrogen bonding interaction of compounds **1**(a), **2**(b) and **3**(c).

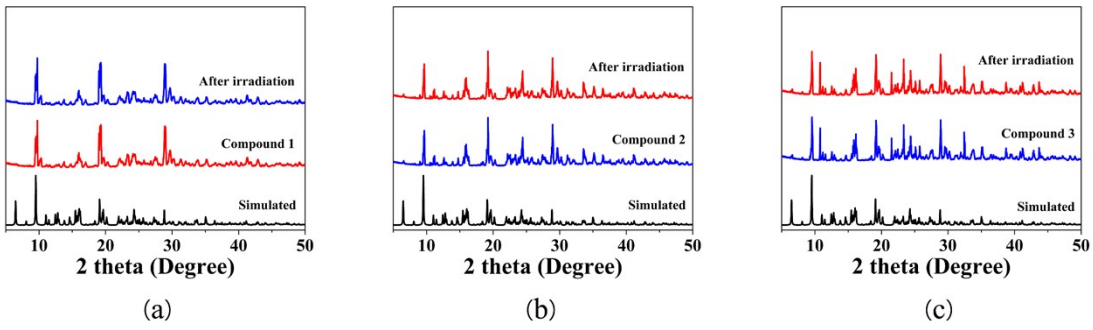


Figure S8. PXRD patterns of compounds **1**(a), **2**(b) and **3**(c).

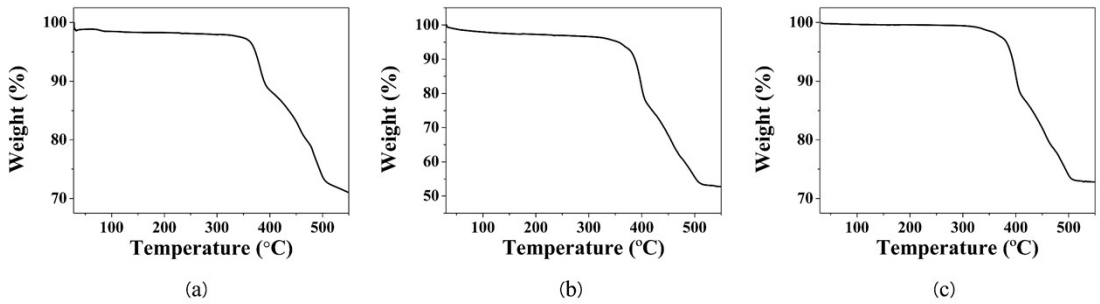


Figure S9. TGA curves of compounds **1**(a), **2**(b) and **3**(c).

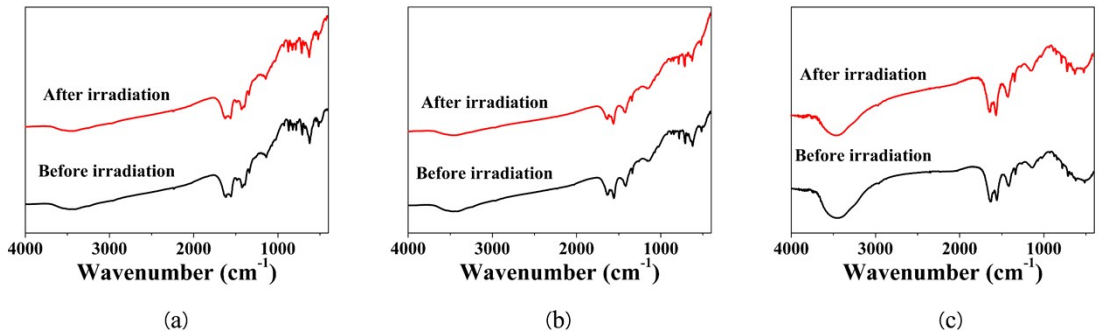


Figure S10. FT-IR spectra of compounds **1**(a), **2**(b) and **3**(c).

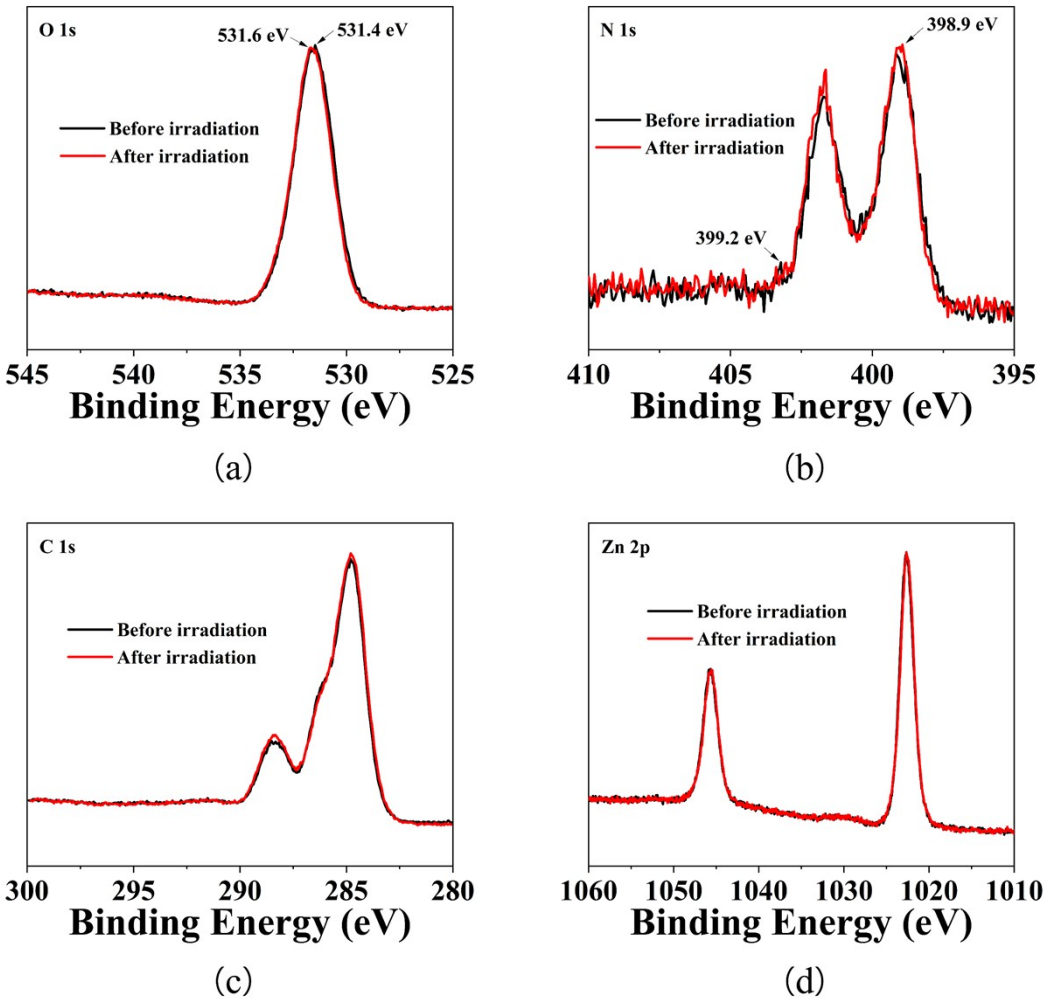


Figure S11. O 1s (a), N 1s (b), C 1s (c), Zn 2p (d) XPS for compound 1 before and after irradiation.

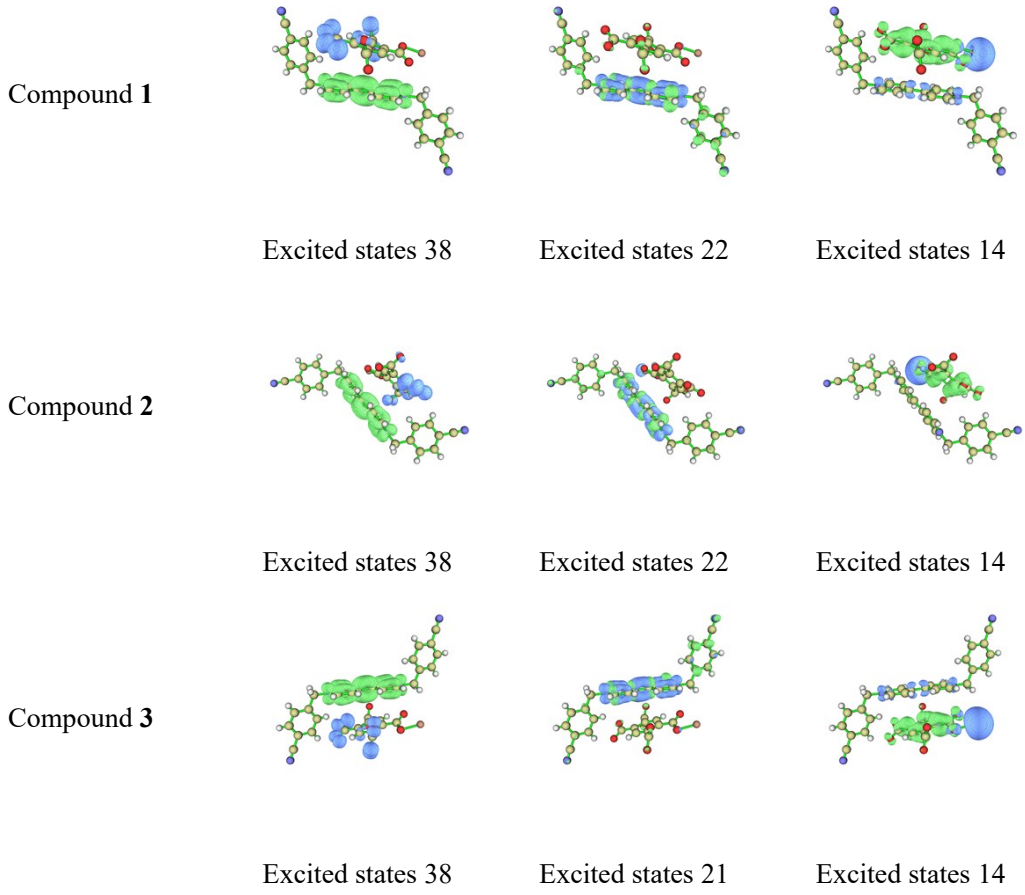


Figure S12. The charge density difference diagrams of compounds **1**, **2** and **3**.

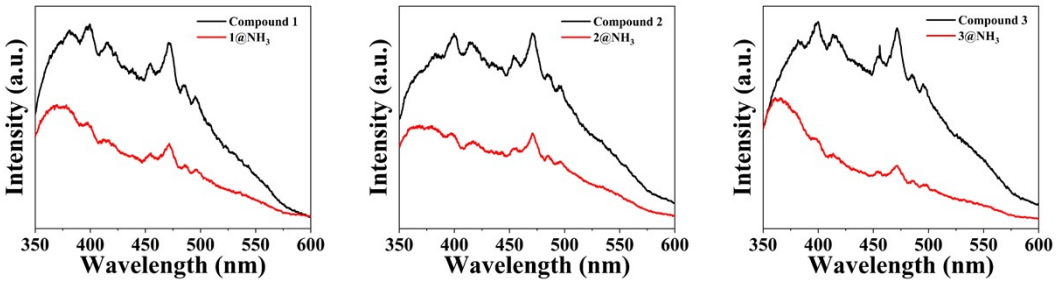


Figure S13. Compounds **1**(a), **2**(b) and **3**(c) have different fluorescence quenching phenomena for ammonia.

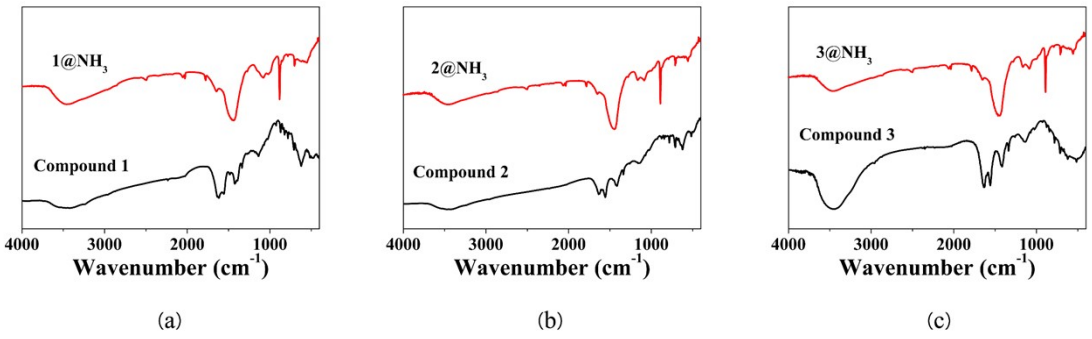


Figure S14. FT-IR spectra of **1**@NH_3(a), **2**@NH_3(b) and **3**@NH_3(c).

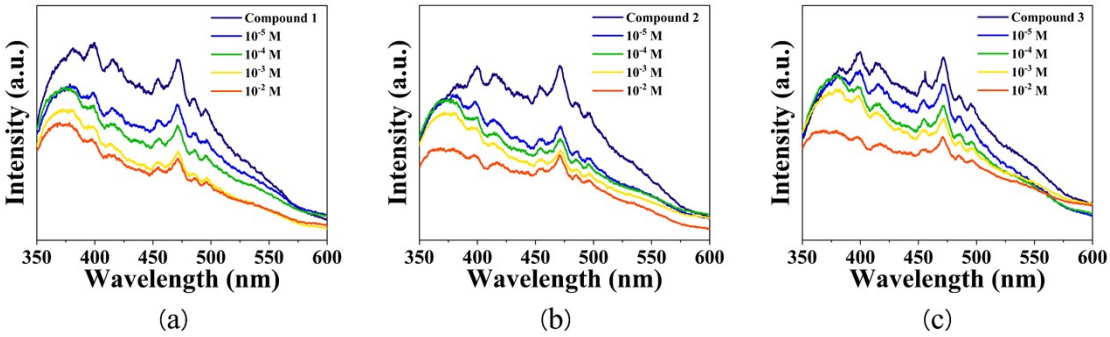


Figure S15. The fluorescence quenching of compounds 1(a), 2(b), and 3(c) in the presence of different concentrations of $Cr_2O_7^{2-}$.

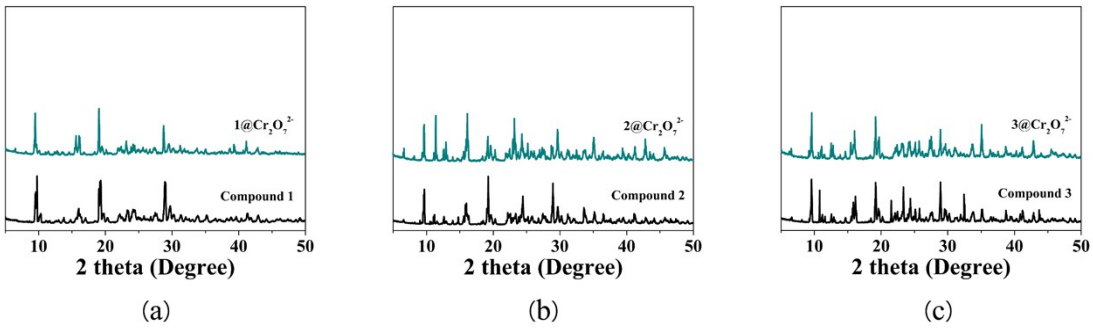


Figure S16. PXRD patterns of **1**@$Cr_2O_7^{2-}$(a), **2**@$Cr_2O_7^{2-}$(b) and **3**@$Cr_2O_7^{2-}$(c).

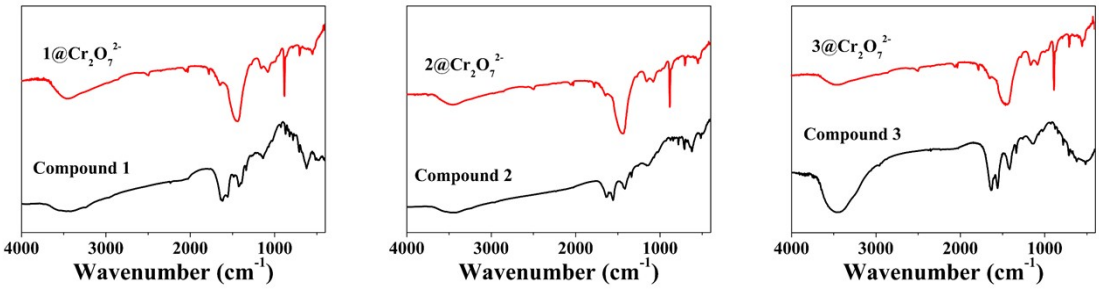


Figure S17. FT-IR spectra of **1**@$Cr_2O_7^{2-}$(a), **2**@$Cr_2O_7^{2-}$(b) and **3**@$Cr_2O_7^{2-}$(c).

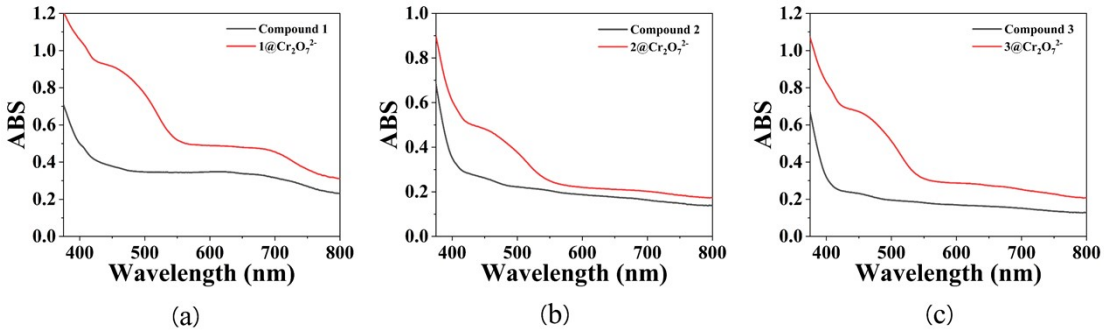


Figure S18. UV-Vis spectra of **1**@$Cr_2O_7^{2-}$(a), **2**@$Cr_2O_7^{2-}$(b) and **3**@$Cr_2O_7^{2-}$(c).

Table S1. Crystal data and structure refinement for **1**, **2** and **3**.

Compound	**1**	**2**	**3**
Empirical formula	$C_{46}H_{28}N_4O_{18}Zn_3$	$C_{46}H_{28}N_4O_{18}Zn_3$	$C_{46}H_{28}N_4O_{18}Zn_3$
Formula weight	1120.89	1120.89	1120.89
Temperature/K	296.15	296.15	296.15
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*P2/c*	*P2/c*	*P2/c*
a/Å	18.566(2)	18.5619(16)	18.5787(17)
b/Å	8.0029(9)	8.0153(7)	8.0072(8)
c/Å	27.231(3)	27.220(2)	27.240(2)
α/°	90	90	90
β/°	90.472(2)	90.5820(10)	90.531(2)
γ/°	90	90	90
Volume/Å^3	4045.9(8)	4049.6(6)	4052.1(6)
Z	4	4	4
ρ_{calc}g/cm^3	1.840	1.839	1.837
μ/mm^{-1}	1.858	1.856	1.855
2*θ* range for data collection/°	3.696 to 55.23	5.338 to 55.42	5.088 to 55.22
Goodness-of-fit on F^2	1.091	1.013	1.006
Final R indexes	R_1 = 0.0693,	R_1 = 0.0355,	R_1 = 0.0486,
[$I \geq 2\sigma$ (I)]	wR_2 = 0.1396	wR_2 = 0.0776	wR_2 = 0.0853
Final R indexes	R_1 = 0.1187,	R_1 = 0.0535,	R_1 = 0.1029,
[all data]	wR_2 = 0.1551	wR_2 = 0.0838	wR_2 = 0.1016

Table S2. Selected bond Lengths (Å) and bond angles (°) for **1**.

Atom	Length/Å	Angle/°
Zn2-O5	1.999(5)	
Zn2-O6	1.943(4)	
Zn2-O9[1]	1.980(4)	
Zn2-O16[2]	1.982(5)	
Zn3-O13	1.909(5)	
Zn3-O14	1.971(5)	
Zn3-O10[1]	1.985(5)	
Zn3-O2[3]	2.011(5)	
Zn1-O11[4]	2.023(4)	
Zn1-O15[2]	1.988(5)	
Zn1-O4	1.985(4)	
Zn1-O2	2.143(5)	
Zn1-O3	2.013(5)	
O6-Zn2-O5		120.5(2)
O6-Zn2-O9[1]		100.28(19)
O6-Zn2-O16[2]		120.4(2)
O9[1]-Zn2-O5		97.5(2)
O9[1]-Zn2-O16[2]		118.5(2)
O16[2]-Zn2-O5		98.4(2)
O13-Zn3-O14		124.2(2)
O13-Zn3-O10[1]		96.1(2)
O13-Zn3-O2[3]		127.4(2)
O14-Zn3-O10[1]		106.6(2)
O14-Zn3-O23		96.2(2)
O10[1]-Zn3-O2[3]		103.3(2)
O11[4]-Zn1-O2		88.38(19)
O15[2]-Zn1-O11[4]		109.1(2)
O15[2]-Zn1-O2		96.2(2)
O15[2]-Zn1-O3		93.8(2)
O4-Zn1-O11[4]		138.0(2)
O4-Zn1-O15[2]		112.9(2)
O4-Zn1-O2		86.10(19)
O4-Zn1-O3		91.9(2)
O3-Zn1-O11[4]		86.4(2)
O3-Zn1-O2		169.8(2)

Symmetry codes: [1]+x, 1+y, +z; [2]+x, 1-y, -1/2+z; [3]+x, 1-y, 1/2+z; [4]+x, -y, -1/2+z.

Table S3. Selected bond Lengths (Å) and bond angles (°) for **2**.

Atom	Length/Å	Angle/°
Zn3-O2[1]	1.9831(17)	
Zn3-O7[1]	2.0019(18)	
Zn3-O14[2]	1.9825(17)	
Zn3-O17	1.9472(17)	
Zn2-O9	2.0047(17)	
Zn2-O4	1.9728(18)	
Zn2-O10	1.9047(18)	
Zn2-O13[2]	1.9884(18)	
Zn1-O9	2.1424(18)	
Zn1-O12[2]	2.0231(17)	
Zn1-O6	1.9767(16)	
Zn1-O3	1.9931(18)	
Zn1-O5	2.016(2)	
O2[1]-Zn3-O7[1]		98.23(7)
O14[2]-Zn3-O2[1]		118.27(8)
O14[2]-Zn3-O7[1]		96.96(8)
O17-Zn3-O2[1]		120.65(7)
O17-Zn3-O7[1]		120.84(8)
O17-Zn3-O14[2]		100.53(8)
O4-Zn2-O9		96.43(8)
O4-Zn2-O13[2]		106.24(8)
O10-Zn2-O9		127.62(8)
O10-Zn2-O4		123.85(8)
O10-Zn2-O13[2]		96.13(8)
O13[2]-Zn2-O9		103.54(7)
O12[2]-Zn1-O9		88.67(7)
O6-Zn1-O9		86.12(7)
O6-Zn1-O12[2]		137.97(7)
O6-Zn1-O3		112.70(8)
O6-Zn1-O5		91.85(8)
O3-Zn1-O9		95.84(7)
O3-Zn1-O12[2]		109.32(7)
O3-Zn1-O5		94.05(10)
O5-Zn1-O9		169.92(10)
O5-Zn1-O12[2]		86.24(8)

Symmetry codes: [1]+x, 1-y, 1/2+z; [2]+x, -1+y, +z.

Table S4. Selected bond Lengths (Å) and bond angles (°) for **3**.

Atom	Length/Å	Angle/°
Zn3-O5[1]	2.001(3)	
Zn3-O14[2]	1.983(3)	
Zn3-O17	1.943(3)	
Zn3-O11	1.981(3)	
Zn2-O10	1.902(3)	
Zn2-O9	1.974(3)	
Zn2-O7	2.007(3)	
Zn2-O13[2]	1.989(3)	
Zn1-O12[2]	2.021(2)	
Zn1-O7	2.138(3)	
Zn1-O4	1.979(2)	
Zn1-O8	1.992(3)	
Zn1-O3	2.008(3)	
O14[1]-Zn3-O5[2]		96.95(11)
O17-Zn3-O5[2]		120.61(11)
O17-Zn3-O14[1]		100.59(11)
O17-Zn3-O1[2]		120.55(11)
O12-Zn3-O5[2]		98.41(11)
O12-Zn3-O14[1]		118.36(12)
O10-Zn2-O9		123.65(12)
O10-Zn2-O7		127.77(12)
O10-Zn2-O13[1]		96.12(12)
O9-Zn2-O7		96.36(11)
O9-Zn2-O13[1]		106.38(12)
O13[1]-Zn2-O7		103.62(11)
O12[1]-Zn1-O7		88.66(11)
O4-Zn1-O12[1]		137.94(11)
O4-Zn1-O7		86.13(11)
O4-Zn1-O8		112.67(11)
O4-Zn1-O3		91.81(12)
O8-Zn1-O12[1]		109.38(10)
O8-Zn1-O7		95.87(11)
O8-Zn1-O3		93.98(14)
O3-Zn1-O12[1]		86.30(12)
O3-Zn1-O7		169.98(14)

Symmetry codes: [1]+x, 1-y, 1/2+z; [2]+x, -1+y, +z.

Table S5. O−H···O interactions Geometry (Å, °) for **1**, **2** and **3**.

	D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
Compound 1	O3-H3B…O12[1]	0.90	1.88	2.688(7)	149.1
	OW1-HW1B…O8	0.85	2.00	2.676(7)	135.5
Compound 2	O5-H5A…OW1	0.85	1.78	2.616(3)	167.3
	O5-H5B…O11[1]	0.85	1.93	2.691(3)	147.7
	OW1-HW1A…O15[2]	0.85	1.83	2.681(3)	174.2
Compound 3	O3-H3A…OW1	0.85	1.79	2.620(4)	163.9
	O3-H3B…O11[1]	0.85	1.95	2.694(4)	146.1
	OW1-HW1B…O15[2]	0.85	1.85	2.683(4)	165.5

Symmetry code of **1**: [1]+x, -y, -1/2+z.

Symmetry codes of **2**: [1]+x, -1+y, +z; [2]+x, 1-y, -1/2+z.

Symmetry codes of **3**: [1]+x, -1+y, +z; [2]+x, 1-y, -1/2+z.

Table S6. The main crystal data of **1**, **1P**, **2**, **2P**, **3** and **3P**.

Compound	**1**	**1P**	**2**	**2P**	**3**	**3P**
Space group	*P2/c*	*P2/c*	*P2/c*	*P2/c*	*P2/c*	*P2/c*
a/Å	18.566 (2)	18.5771 (17)	18.5619 (16)	18.577 (2)	18.5787 (17)	18.6073 (15)
b/Å	8.0029 (9)	8.0007 (7)	8.0153 (7)	8.0124 (10)	8.0072 (8)	8.0235 (7)
c/Å	27.231 (3)	27.235 (3)	27.220 (2)	27.266 (4)	27.240 (2)	27.301 (2)
α/°	90	90	90	90	90	90
β/°	90.472 (2)	90.504 (2)	90.5820 (10)	90.554 (2)	90.531 (2)	90.501 (2)
γ/°	90	90	90	90	90	90
Volume/Å^3	4045.9 (8)	4047.8 (7)	4049.6 (6)	4058.3 (9)	4052.1 (6)	4075.8 (6)

Table S7. Results of the TDDFT/B3LYP-lanl2dz calculations related to **1**, **2** and **3**.

	Excited states	λ_{max} / nm		f
		Exp.	Calc.	
Compound **1**	38	404	401	0.0004
	22	615	574	0.2405
	14	740	710	0.0027
Compound **2**	38	404	395	0.0003
	22	615	585	0.2973
	14	734	704	0.0055
Compound **3**	38	405	391	0.0002
	21	615	599	0.3604
	14	739	720	0.0038

Table S8. Comparison of Response Time of Ammonia Sensors.

Materials	Response time	Ref
$\{[Eu_3(Bcbp)_3(NO_3)_7]\cdot NO_3\cdot ClO_4\}_n$	1 min	11
$[Cd_2(Pbpy)(bdc)_2I_2]\cdot 4H_2O$	5 s	25
$[Cd_2(Pbpy)(Bdc)_2Cl_2]\cdot nH_2O$	30 s	37
$[Cd_2Cl(m\text{-}bpybdc)_2(H_2O)_4]\text{-}(NO_3)_3\cdot 7H_2O$	-	38
$\{[Zn_3(BTEC)_2(H_2O)(4\text{-}BCBPY)]\cdot H_2O\}_n$ (1-3)	3s/6s/15s	This work

Table S9. Comparison of $Cr_2O_7^{2-}$ Fluorescence Sensors.

Fluorescent Materials	K_{SV} (M^{-1})	DL (μM)	Ref
$\{[Eu_3(Bcbp)_3(NO_3)_7]\cdot NO_3\cdot ClO_4\}_n$	1.40×10^4	5.6	11
$\{[Eu(BCEbpy)(H_2O)_4](CoIII(CN)_6)\cdot 4H_2O\}_n$	4.31×10^3	9.6	33
$[Eu(ipbp)_2(H_2O)_3]\cdot Br\cdot 6H_2O$	8.98×10^3	5.16	39
$[Zn(TTVTC)]\cdot 4H_2O$	1.38×10^4	0.41	40
$\{[Zn_3(BTEC)_2(H_2O)(4\text{-}BCBPY)]\cdot H_2O\}_n$ (1-3)	9.12×10^3, 1.56×10^4, 8.60×10^3	3.28, 7.69, 10.40	This work