Electronic Supplementary Information (ESI)

Fluorescent Zn(II) frameworks with multicarboxylate and pyridyl N-donor ligands for sensing specific anions and organic molecules

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EXPERIMENTAL

X-ray crystallography

The crystallographic data of **1**–**3** were obtained on Bruker D8 VENTURE and Bruker smart apex II CCD area detector diffractometers with graphite-monochromated Ga Kα (λ = 1.34139 Å) and Mo Kα (λ = 0.71073 Å) radiations. The integration of the diffraction data and the intensity correction for Lorentz and polarization effects were performed using the SAINT program. Semi-empirical absorption correction was carried out using SADABS program. SHELXT-2014 was used to solve the structures of **1**–**3** through the direct method, and SHELXL-2018 program was used to refine the structures by the full matrix least square method.[1] The hydrogen atoms were generated in geometric forms and refined isotropically. Due to the highly disordered solvent molecules in **1**–**3**, SQUEEZE subroutine of PLATON software was applied to remove them. Finally, the crystal parameters, data collection and refinements are summarized in **Table 1**, and the selected bond lengths and angles were listed in **Table S1**.

Table S1. Selected bond lengths (Å) and angles (º) for **1**–**3**.

1			
Zn(1)-O(4)#1	1.9710(18)	Zn(1)-O(1)	1.9313(18)
Zn(1)-N(1)	2.052(2)	Zn(1)-N(2)	2.052(2)
O(1)-Zn(1)-O(4)#1	109.76(8)	O(4)#1-Zn(1)-N(1)	124.07(9)
O(1)-Zn(1)-N(2)	96.95(9)	N(2)-Zn(1)-N(1)	101.49(9)
Symmetry transformations used to generate equivalent atoms: #1 +X, -Y, 1/2+Z			
2			
Zn(1)-O(4)	2.048(4)	Zn(1)-O(5)#1	2.054(4)
Zn(1)-O(6)	2.023(4)	Zn(1)-O(7)#1	2.062 (4)
Zn(1)-N(3)	2.031(4)	Zn(2)-O(1)#2	2.021(3)
Zn(2)-O(2)	2.056(4)	Zn(2)-O(9)#3	2.053(4)
Zn(2)-O(10)#4	2.043(4)	Zn(2)-N(1)	2.028(4)
O(4)-Zn(1)-O(6)	87.18(15)	O(4)-Zn(1)-O(7)#1	88.50(16)
O(5)#1-Zn(1)-O(4)	159.80(13)	O(5)#1-Zn(1)-O(6)	89.86(18)
O(5)#1-Zn(1)-O(7)#1	87.29(17)	O(7)#1-Zn(1)-O(6)	159.42(14)
N(3)-Zn(1)-O(4)	103.14(16)	N(3)-Zn(1)-O(5)#1	97.00(17)
N(3)-Zn(1)-O(6)	103.18(16)	N(3)-Zn(1)-O(7)#1	97.39(17)
O(1)#2-Zn(2)-O(2)	159.89(13)	O(1)#2-Zn(2)-O(9)#3	87.33(15)
O(1)#2-Zn(2)-O(10)#4	89.37(17)	O(9)#3-Zn(2)-O(2)	87.92(17)
O(10)#4-Zn(2)-O(2)	88.25(18)	O(10)#4-Zn(2)-O(9)#3	159.45(13)
O(1)#2-Zn(2)-N(1)	102.60(15)	N(1)-Zn(2)-O(2)	97.51(16)
N(1)-Zn(2)-O(9)#3	103.61(16)	N(1)-Zn(2)-O(10)#4	96.91(17)
Symmetry transformations used to generate equivalent atoms:			
#1 1-X, 1-Y, 2-Z; #2 1-X, -Y, 1-Z; #3 1-X, 1-Y, 1-Z; #4 +X, -1+Y, +Z;			

3

Zn(1)#1-O(1)#1	2.474(3)	Zn(1)#1-O(2)#1	2.060(2)
Zn(1)-O(5)	2.025(3)	Zn(1)-O(6)	2.297(3)
Zn(1)-N(2)	2.087(3)	Zn(1)-N(4)	2.036(3)
N(2)-Zn(1)-O(1)#1	154.88(11)	N(2)-Zn(1)-O(6)	92.89(14)
N(4)-Zn(1)-N(2)	97.95(12)	N(4)-Zn(1)-O(1)#1	86.81(12)
N(4)-Zn(1)-O(2)#1	101.28(11)	N(4)-Zn(1)-O(6)	93.98(12)
O(2)#1-Zn(1)-N(2)	98.04(11)	O(2)#1-Zn(1)-O(1)#1	56.89(10)
O(2)#1-Zn(1)-O(6)	159.75(11)	O(5) -Zn(1)-N(2)	100.97(13)
O(5)-Zn(1)-N(4)	148.06(15)	O(5)-Zn(1)-O(1)#1	86.85(12)
O(5)-Zn(1)-O(2)#1	101.27(11)	O(5)-Zn(1)-O(6)	59.72(12)
O(6)-Zn(1)-O(1)#1	111.45(13)		

Symmetry transformations used to generate equivalent atoms:

#1 1+X, +Y, 1+Z;

Table S2 Hydrogen bonding data for **3**.

D-H···A	D-H	H···A	D···A	D-H···A
O(3)-H(3) ···O(2)#1	0.84	1.81	2.619(4)	160
C(24)-H(24) ···O(2)#2	0.95	2.48	3.362(7)	155
C(32)-H(32) ···O(4)#3	0.95	2.52	3.467(5)	176
C(35)-H(35) ···O(4)#4	0.93	2.39	3.208(6)	144

Symmetry codes: #1 +X, -1+Y, +Z; #2 1-X, 2-Y, -Z; #3 1-X, 1-Y, 1-Z; #4 1+X, 1+Y, 1+Z

Table S3 The related parameter for fluorescence detection of analytes by **1**–**3** and various reported MOFs

MOF	Analytes	K_{SV}	Working range	LOD	Ref.
$\{[Zn(IPA)(L_2)]\}_n$	CrO_4^{2-}	1.00×10^3 M^{-1}	0–1 mM	1.83×10^{-5} M	2
	$Cr_2O_7^{2-}$	1.37×10^3 M^{-1}	0–1 mM	1.20×10^{-5} M	
$[Tb_2(H_3L)(C_2O_4)_3(H_2O)_4]\cdot2H_2O$	CrO_4^{2-}	3.63×10^3 M^{-1}	0-0.44 mM	3.7×10^{-6} M	3
	$Cr_2O_7^{2-}$	7.78×10^3 M^{-1}	0-0.44 mM	4.2×10^{-6} M	
Eu_4L_3	CrO_4^{2-}	-	-	--	4
	$Cr_2O_7^{2-}$	1526 M^{-1}	0-0.5 mM		
$[Zn(btz)]_n$	CrO_4^{2-}	3.19×10^3 M^{-1}	0.010-1.8 Mm	1.0×10^{-5} M	5
	$Cr_2O_7^{2-}$	4.23×10^3 M^{-1}	0.020-1.8 mM	2.0×10^{-6} M	
$[EuL(CH_3COO)Cl]_n$	CrO_4^{2-}	2.52×10^4 M^{-1}	0.00074-0.022 mM	8.54×10^{-5} M	6
	$Cr_2O_7^{2-}$	1.15×10^4 M^{-1}	0.0037-0.13 mM	8.63×10^{-5} M	
$[Cd_3(H_2O)_3(L)(tib)_2]\cdot5DMA\cdot3H_2O$	TNP	1.16×10^4 M^{-1}	0-0.12 mM	7.4×10^{-5} M	7
$\{[Cd(IPA)(L)]\}_n$	TNP	1.35×10^4 M^{-1}	-	4.15×10^{-5} M	2
$\{[NaCd_2(\mathbf{L_4})(DMF)_3]\cdot(Me_2NH_2)(3DMF)\}_n$	TNP	1.56×10^4 M^{-1}	0-0.5 mM	6×10^{-8} M	8
$[\{Zn(BINDI)_{0.5}(bpe)\}\cdot3H_2O]_n$	TNP	1.29×10^4 M^{-1}	0-0.03 mM	1.5 ppm	9
$[Cd(tib)(H_2dhbqdc)0.5(NO_3)]\cdot6H_2O$	TNP	1.7×10^3 M^{-1}	-	-	10
$[Zn_2(tphn)(2,6\text{-}NDC)_2]$	TNP	2.4×10^3 M^{-1}	-	19 ppm	11
$[\{Eu(SIP)(H_2O)_4\}]_n$	Benzaldehyde	9.80×103 M^{-1}	-	1×10^{-6} M	12
$[Co(TBTA)(L_3)_{1.5}]_n$	Benzaldehyde	3471 M^{-1}	0-0.3 mM	3.11×10^{-6} M	13
$[Cd_{0.5}(TBC)]_n$	Benzaldehyde	5.02×102 M^{-1}	-	-	14
$[Zn(DTBDA)]\text{-}(DMA)(MeOH)_2(H_2O)_{3.5}$	Benzaldehyde	-	0-0.35%	-	15
$\{[Sm_2Zn(abtc)_2(H_2O)_4]\cdot2H_2O\}_\infty$	Benzaldehyde	13.62 M^{-1}	0-0.2 M	-	16
$[Zn(DPA)(NDA)]_2\cdot2DMF$ (**1**)	TNP	1.40×10^4 M^{-1}	0-0.061 mM	7.7×10^{-5} M	This work
$[Zn_2(DPA)(OBA)_2]\cdot2DMF\cdot4H_2O$ (**2**)	TNP	1.54×10^4 M^{-1}	0-0.061 mM	6.4×10^{-5} M	This work
	Benzaldehyde	27.79 M^{-1}	0-20 mM	3.8×10^{-3} M	This work
$[Zn(DPA)(HNTB)]\cdot H_2O$ (**3**)	TNP	1.22×10^4 M^{-1}	0-0.061 mM	9.0×10^{-5} M	This work
	CrO_4^{2-}	4.05×10^3 M^{-1}	0-0.38 mM	1.48×10^{-4} M	This work
	$Cr_2O_7^{2-}$	4.03×10^3 M^{-1}	0-0.38 mM	2.58×10^{-4} M	This work

Table S4 The QY of **1**–**3** before and after the sensing of analytes

MOF	Analyte	QY of MOF (%)	QY of MOF after sensing of analytes (%)
1	TNP	40.95	39.43
2	TNP	6.64	7.69
	Benzaldehyde		7.99
3	TNP	7.04	9.46
	CrO_4^{2-}		7.72
	$Cr_2O_7^{2-}$		7.52

Table S5 Fluorescence lifetime for **1**–**3** before and after addition of CrO_4^{2-}, $Cr_2O_7^{2-}$, TNP and benzaldehyde.

MOF	Analyte	MOF (ns)		MOF + analyte (ns)	
		Lifetime (ns)	R^2	Lifetime (ns)	R^2
1	TNP	7.44	0.99952	7.13	0.99948
2	TNP	5.15	0.99947	6.53	0.99947
	Benzaldehyde	5.46	0.99938	3.91	0.99943
3	TNP	4.62	0.99947	5.80	0.99943
	CrO_4^{2-}	3.38	0.99947	3.23	0.99948
	$Cr_2O_7^{2-}$	3.32	0.99955	3.36	0.99934

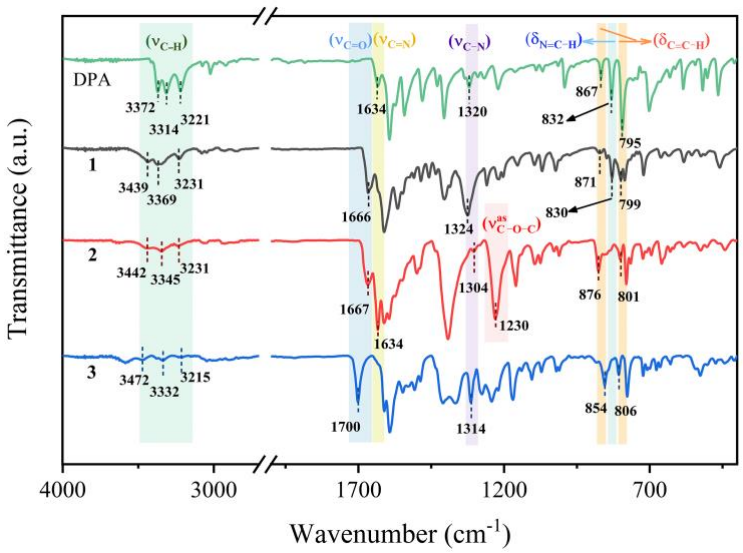


Fig. S1 IR spectra of **1**–**3** and DPA.

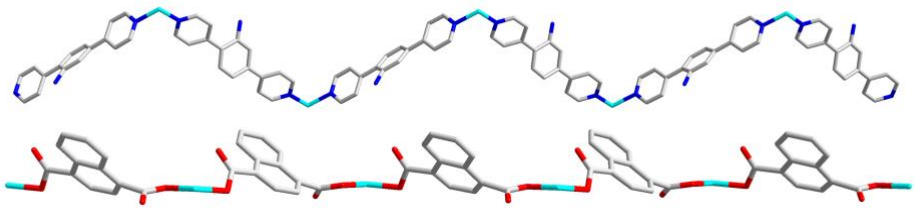


Fig. S2 1D chains of Zn(II)-DPA (upper) and Zn(II)-NDA^{2-} (below) in **1**.

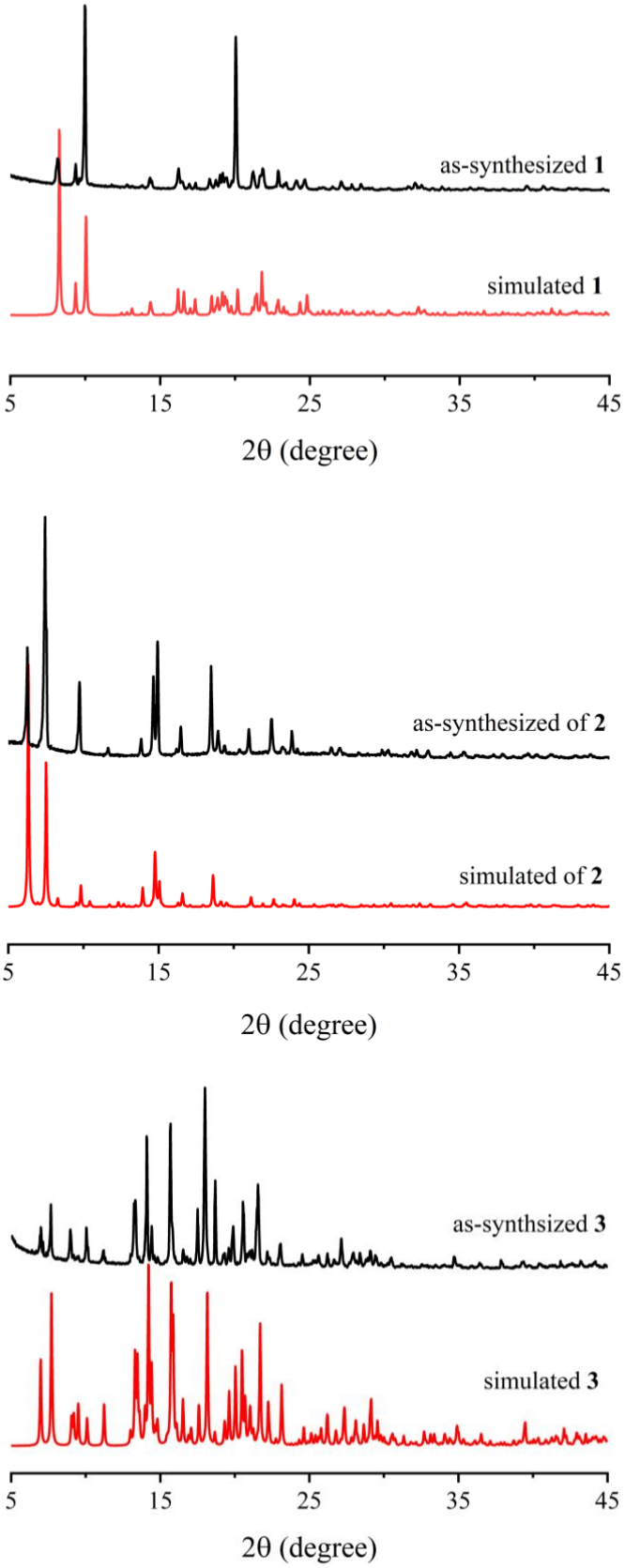


Fig. S3 PXRD patterns of **1**–**3**.

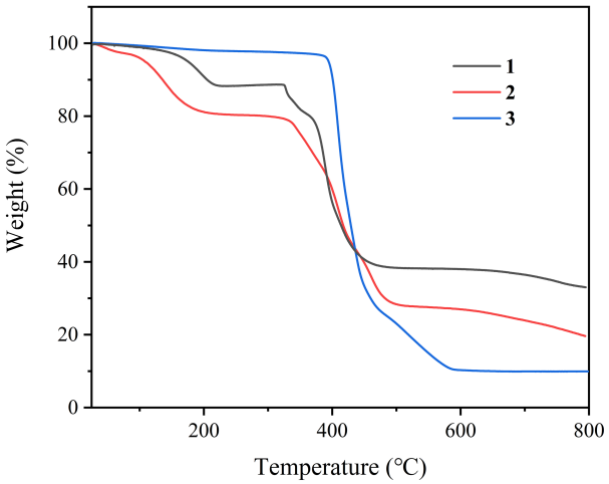


Fig. S4 TG curves of **1**–**3**.

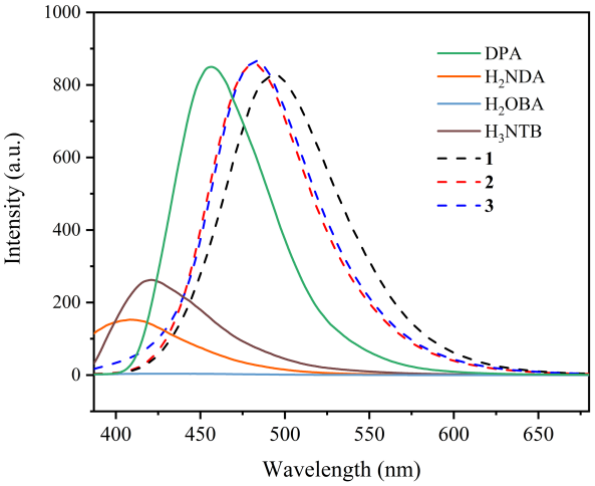
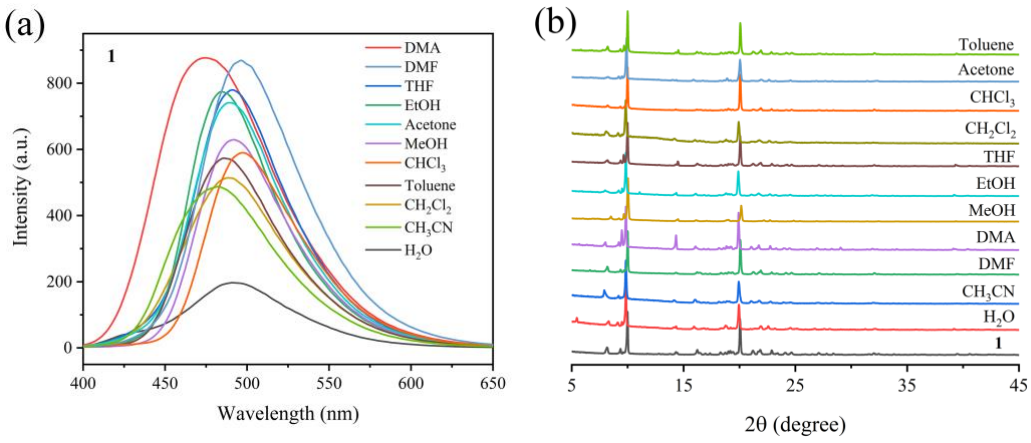


Fig. S5 Emission spectra of **1**–**3** and ligands in DMF at room temperature (λex = 367 nm).



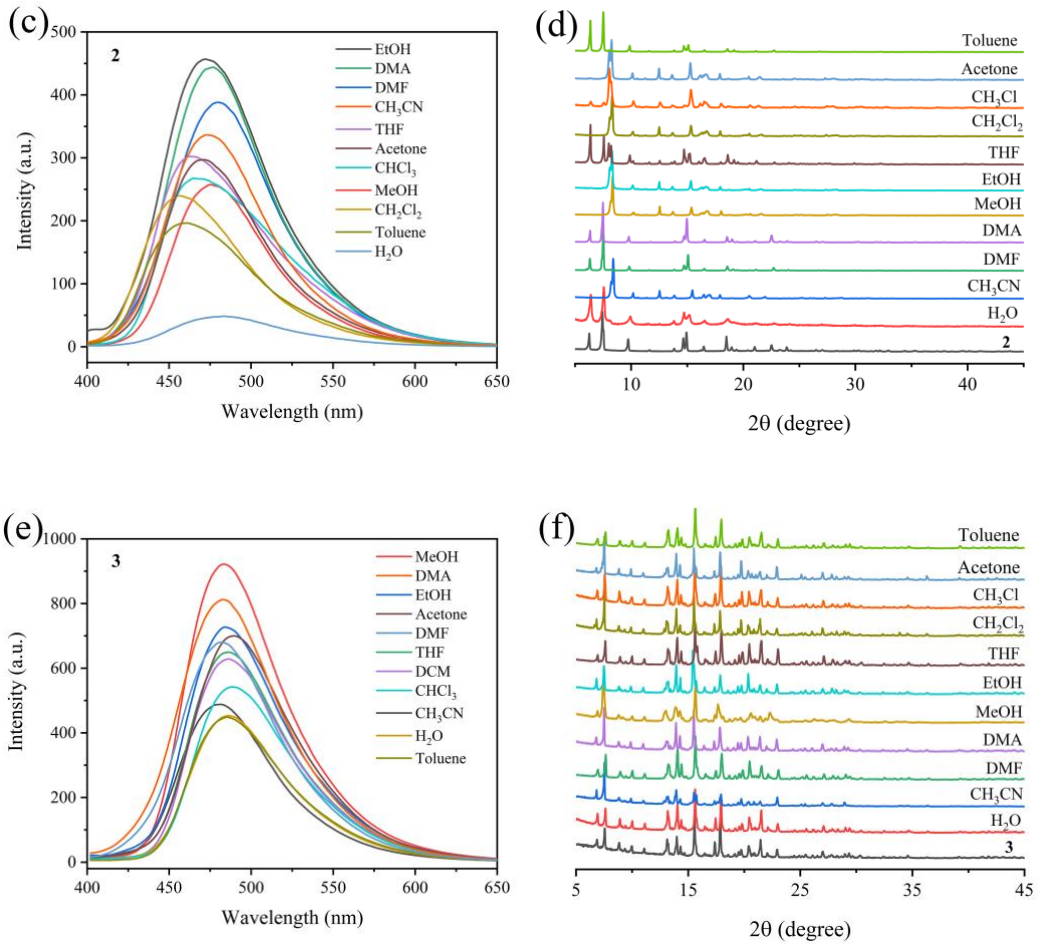
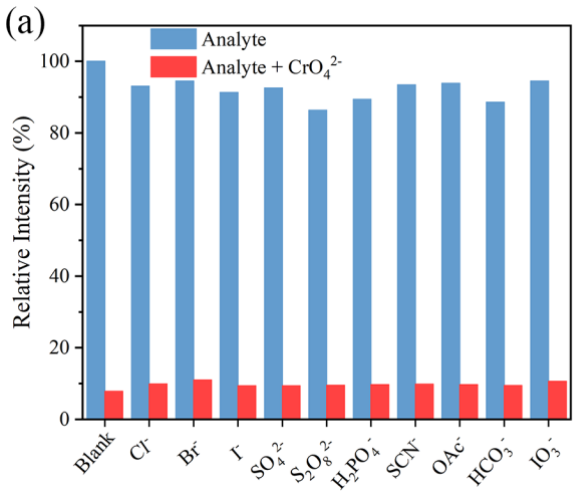


Fig. S6 Fluorescence spectra and PXRD patterns of **1**–**3** in different solvent.



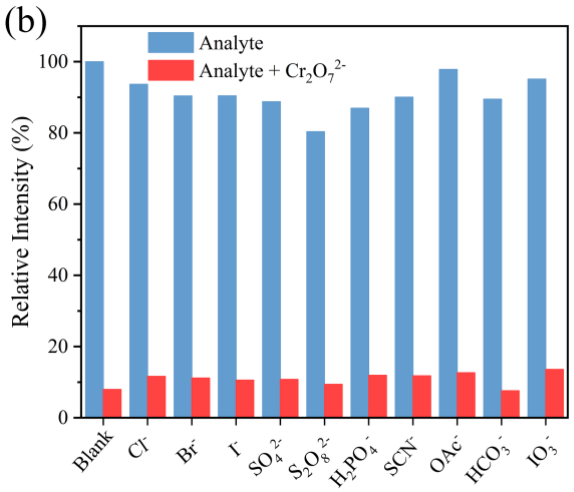


Fig. S7 Luminescent responses of **3** exposed to different anions in water.

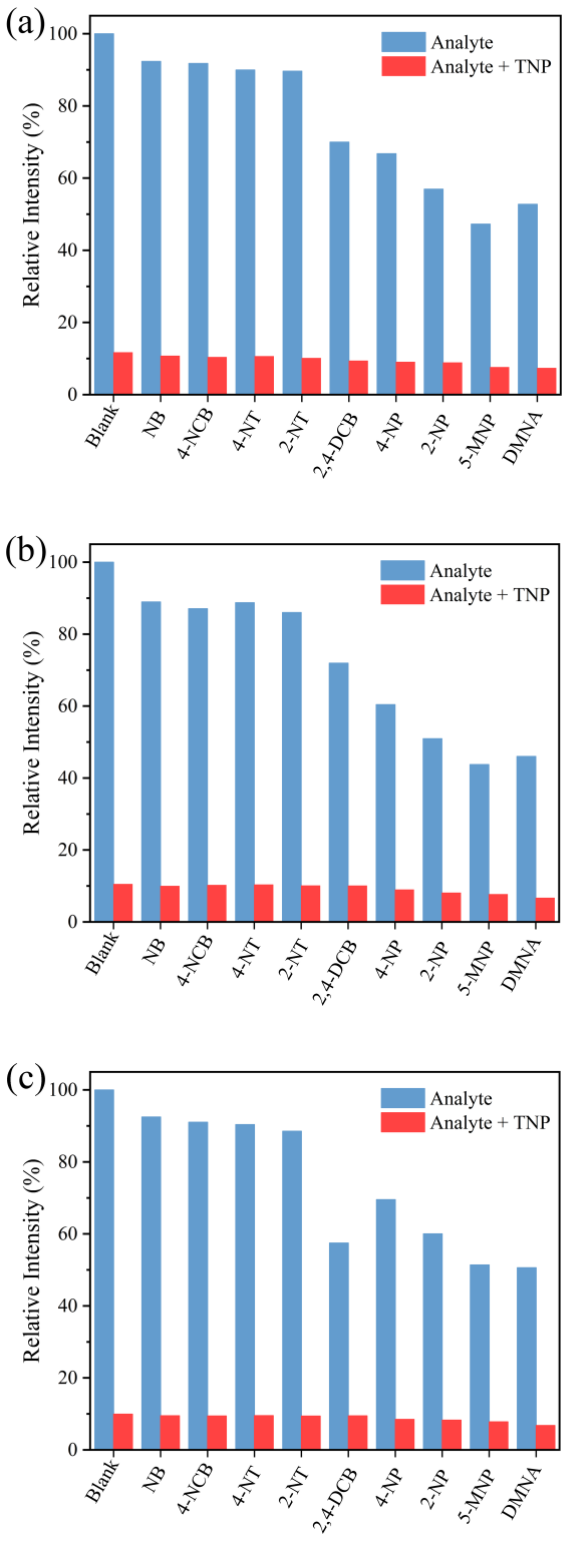


Fig. S8 Luminescent responses of **1**–**3** exposed to different NACs in DMF solvent.

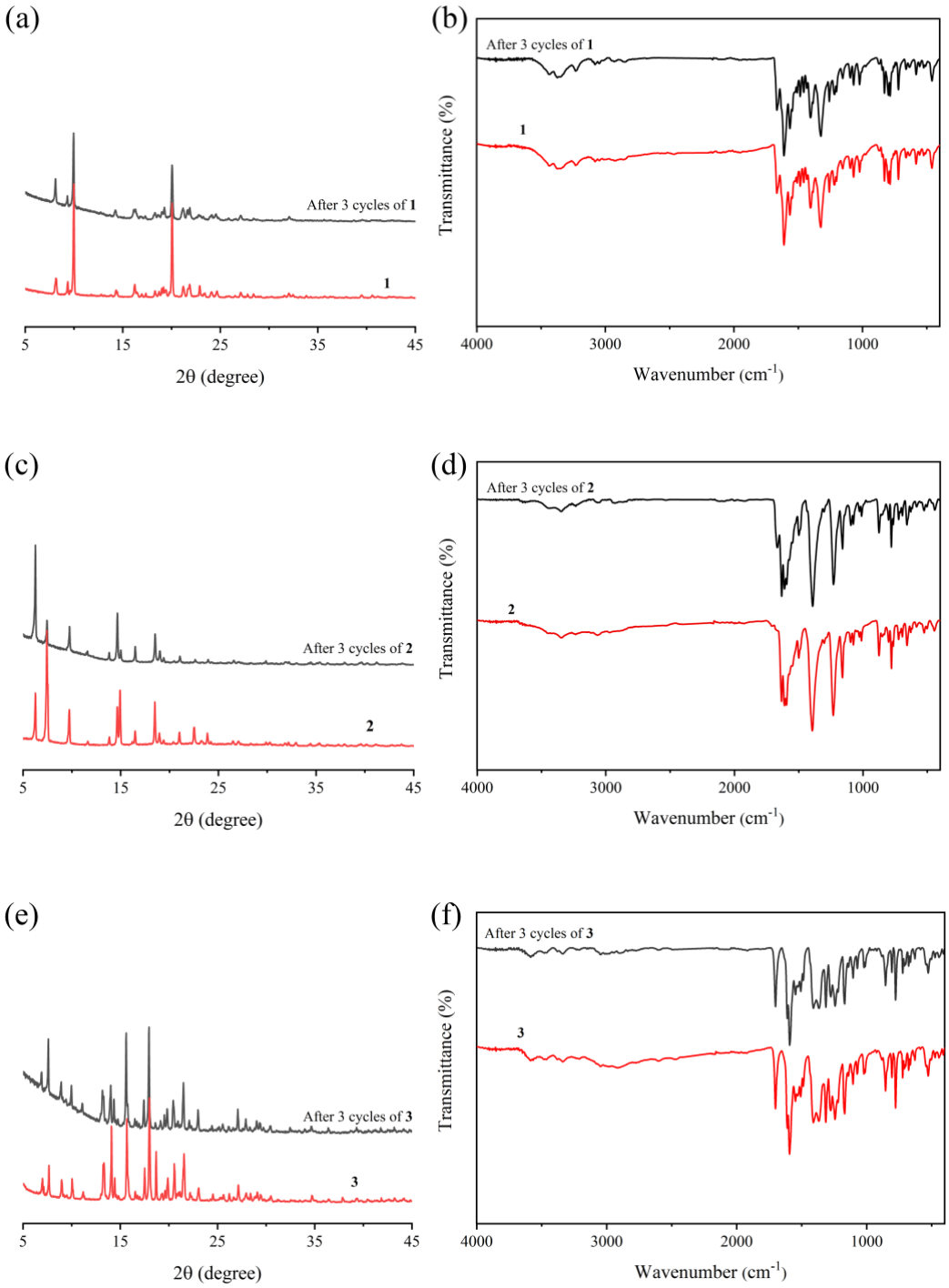


Fig. S9 XRD patterns and IR spectra of **1**–**3** after three cycles for sensing TNP.

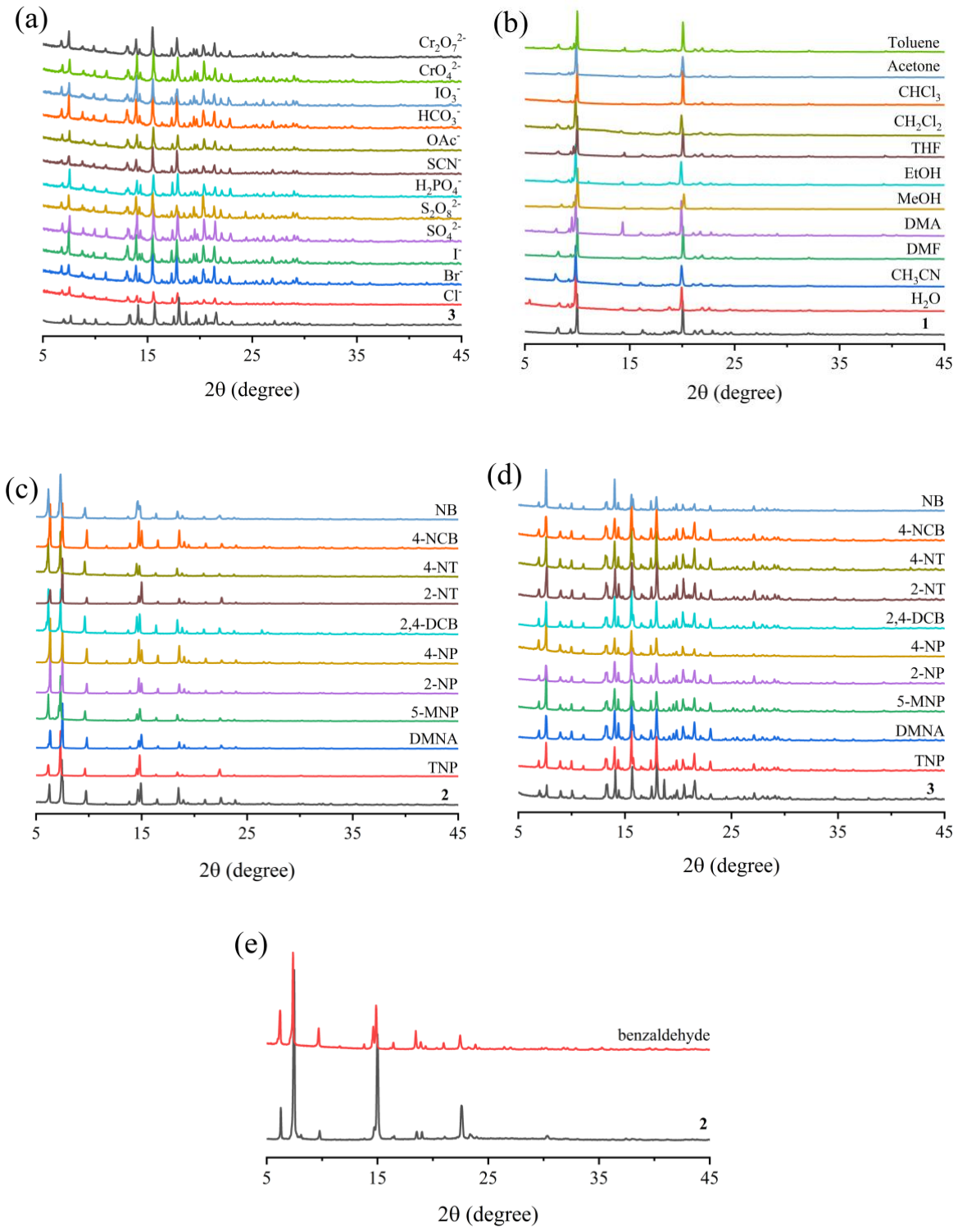


Fig. S10 XRD patterns of **1**–**3** after immersion in various anions, NAC and benzaldehyde solutions.

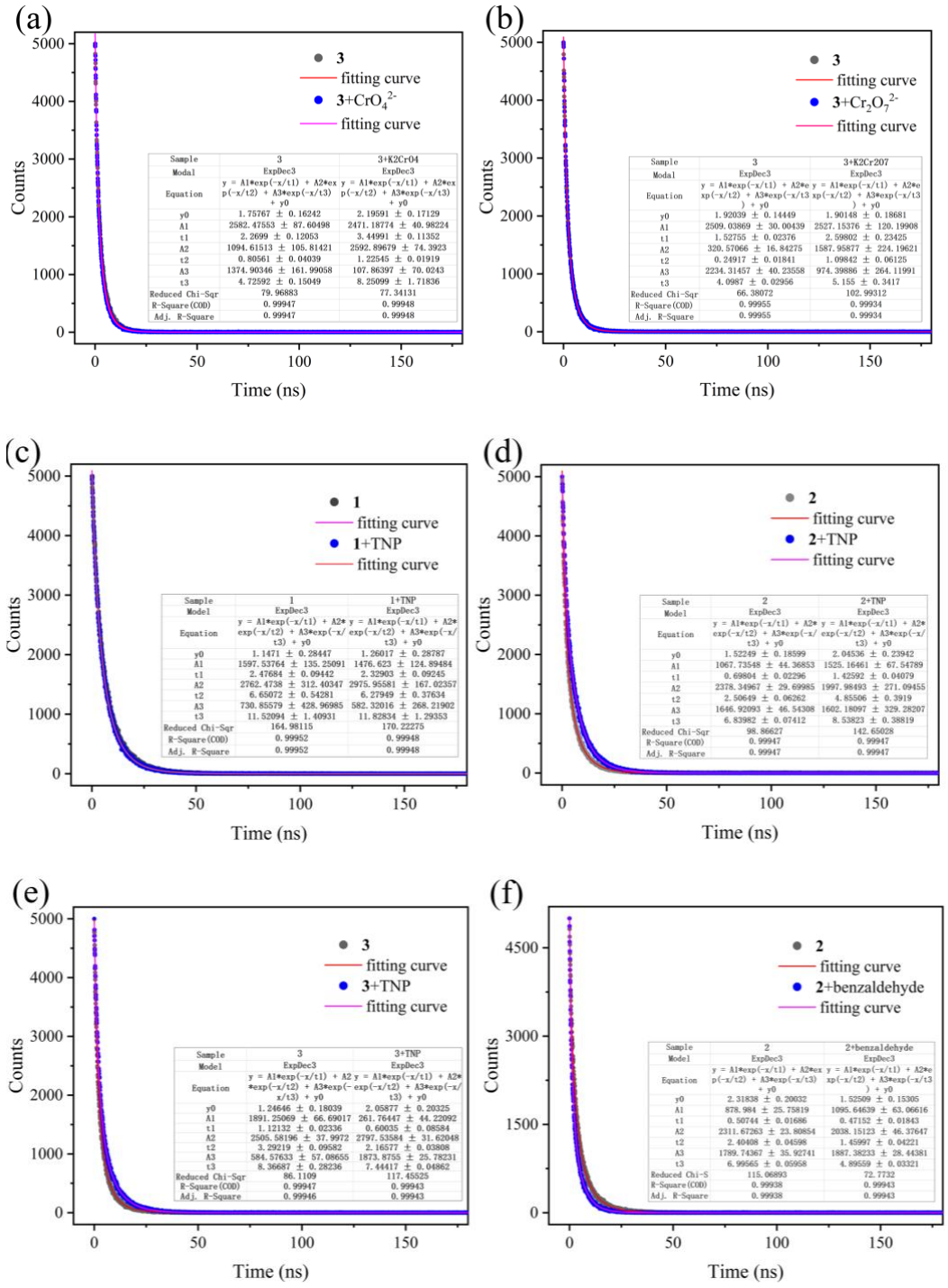


Fig. S11 Experimental and fitting lifetime curves of the suspension of **1**–**3** before and after addition of CrO_4^{2-}, $Cr_2O_7^{2-}$, TNP and benzaldehyde.

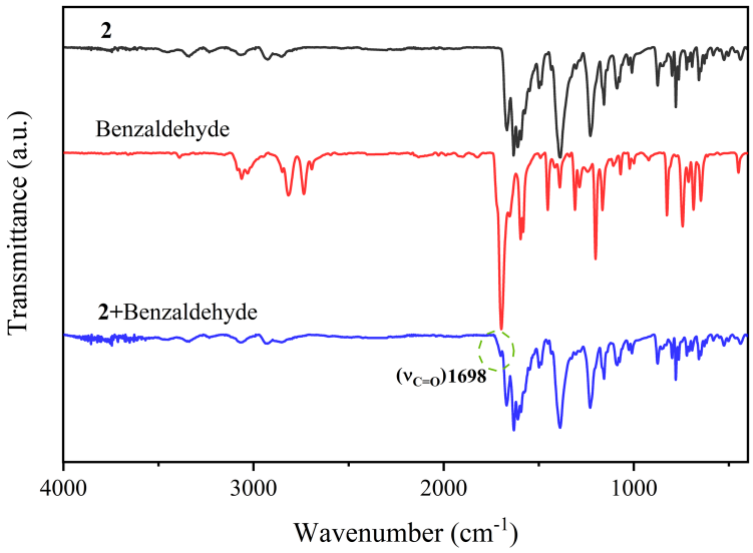


Fig. S12 IR spectra of benzaldehyde, MOF **2** and MOF **2** after detection for benzaldehyde.

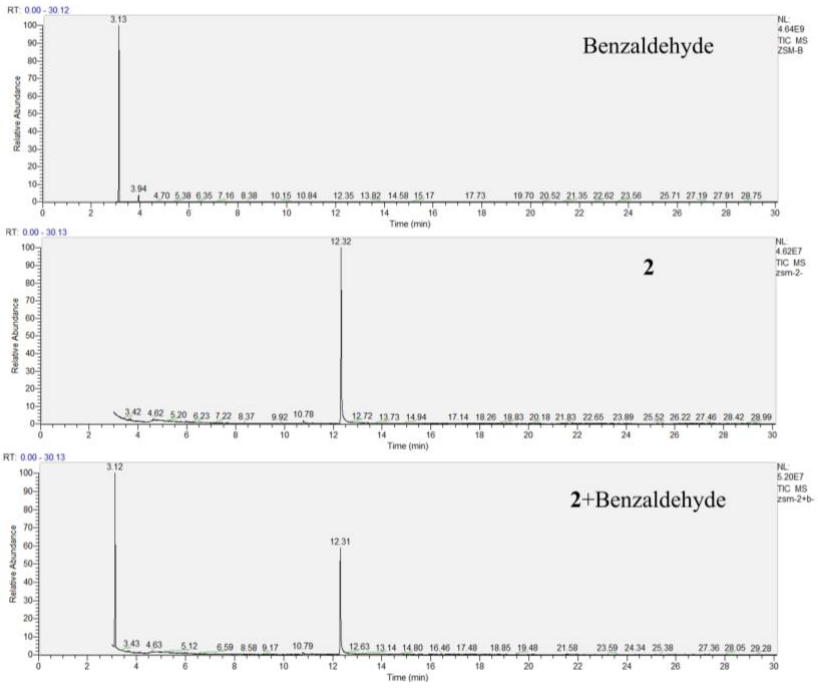


Fig. S13 Gas chromatography-mass spectra of benzaldehyde, MOF **2** and MOF **2** after detection for benzaldehyde

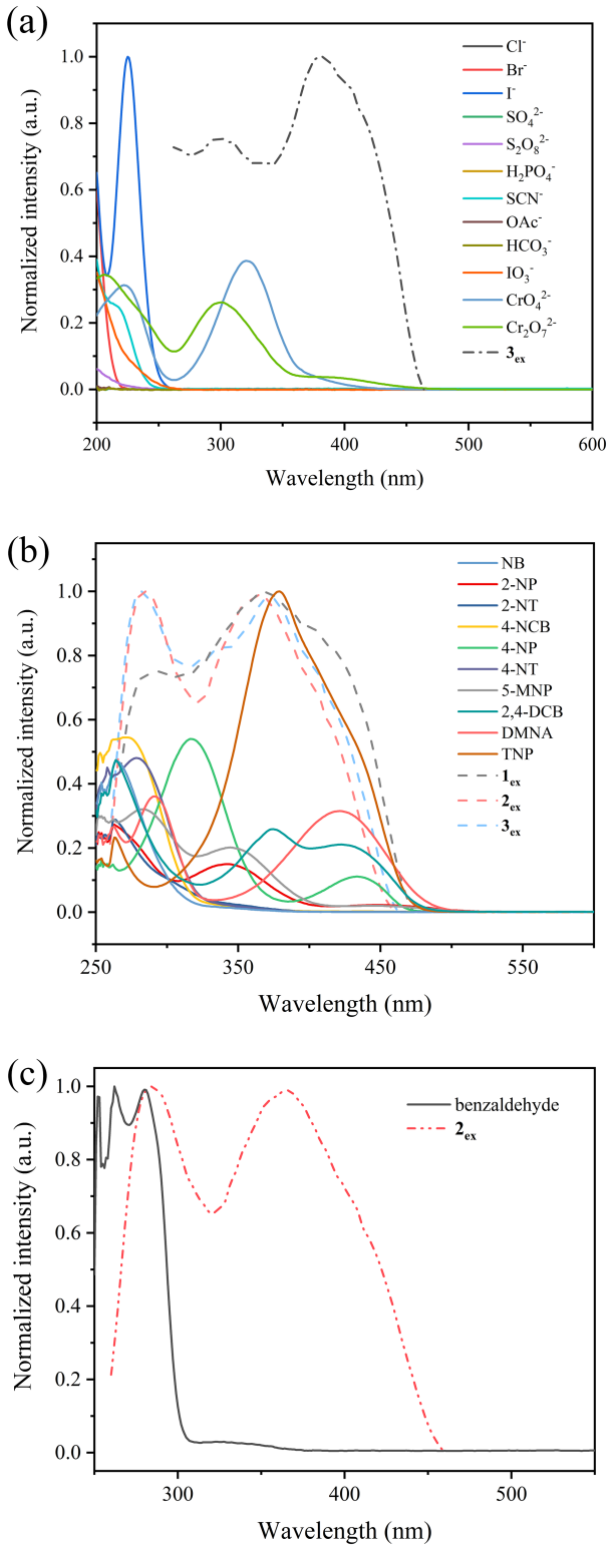


Fig. S14 Spectral overlap between the absorption spectra of analytes with the normalized excitation spectra of **1**–**3**

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