

Supporting Information

Carbon dots@metal–organic frameworks as dual-functional fluorescent sensors for Fe³⁺ ions and nitro explosives

Yufang Tao,^{a,b,†} Yansong Jiang,^{a,†} Yating Huang,^a Junning Liu,^c Ping Zhang,^a

Xiaodong Chen,^a Yong Fan,^a Li Wang^{*a} and Jianing Xu^{*a}

a College of Chemistry, Jilin University, Changchun 130012, P. R. China

b Shanghai New Epoch High School, Ruian 325206, P. R. China

c State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, P. R. China

[†] These authors contributed equally to this work.

Email: lwang99@jlu.edu.cn; xujn@jlu.edu.cn

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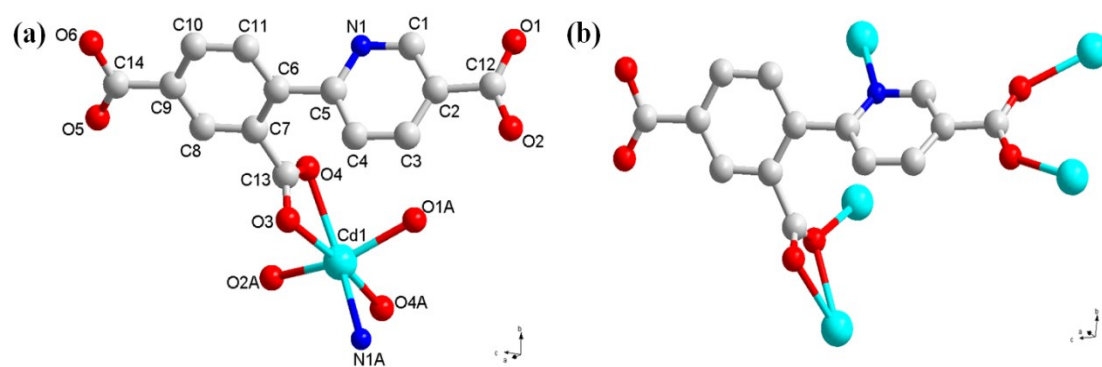


Fig. S1 (a) The coordination environment of Cd²⁺ ion center in **1**. (b) The coordination mode of HL²⁻ ligand.

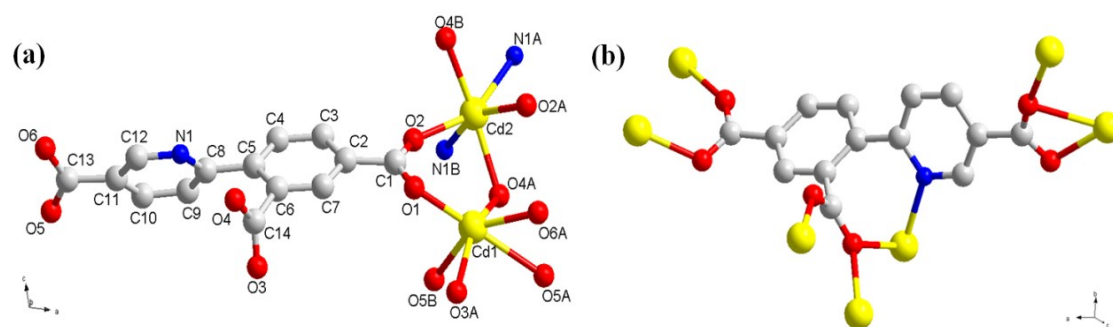


Fig. S2 (a) The coordination environment of Cd1²⁺ ion and Cd2²⁺ ion in **2**. (b) The coordination mode of L³⁻ ligand.

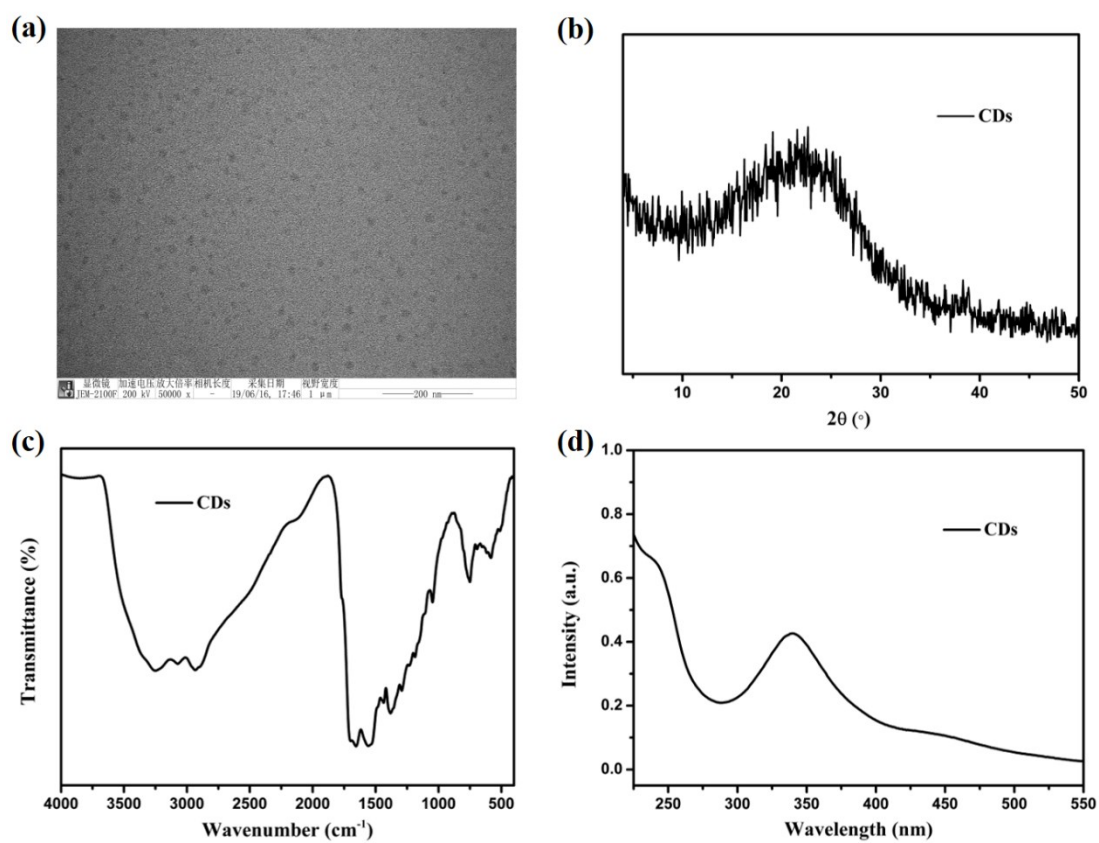


Fig. S3 TEM image (a), PXRD pattern (b), FT-IR spectrum (c) and UV-vis spectrum (d) of CDs.

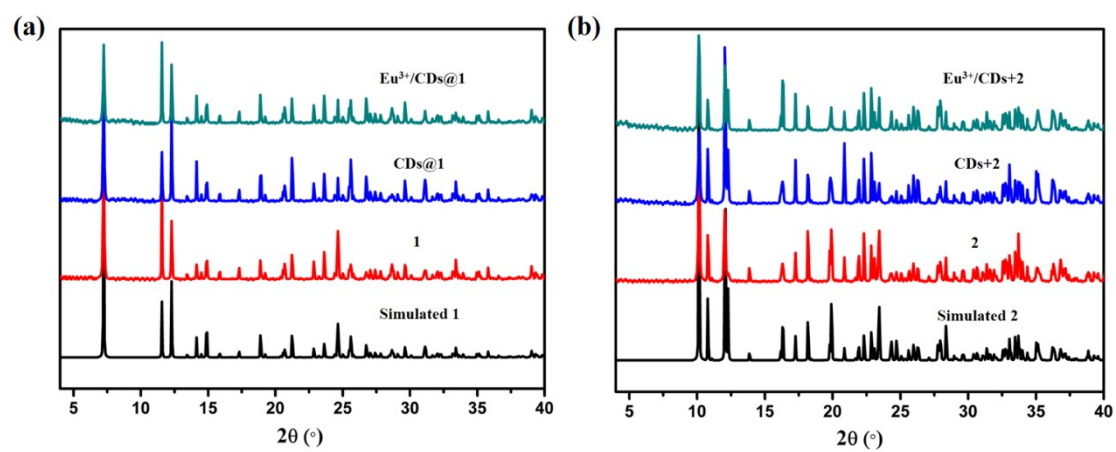


Fig. S4 Powder X-ray diffraction patterns of compounds.

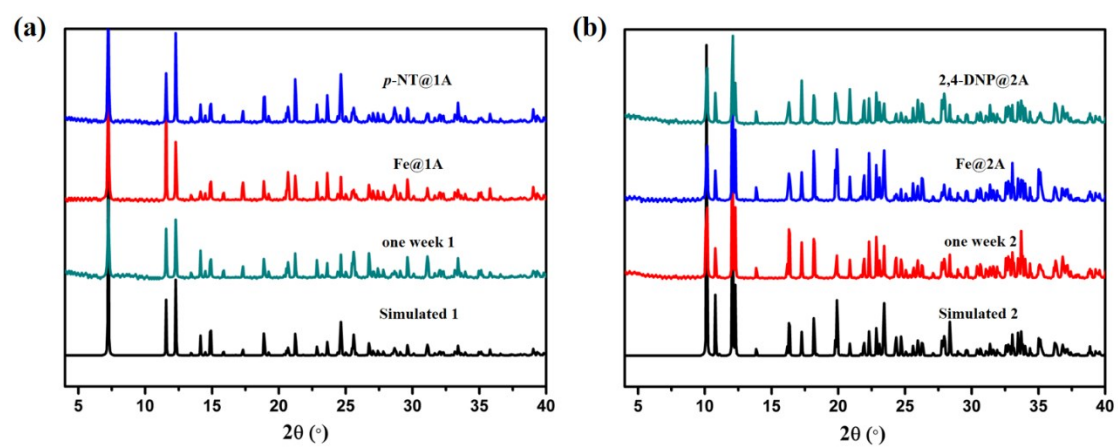


Fig. S5 Powder X-ray diffraction patterns of compounds.

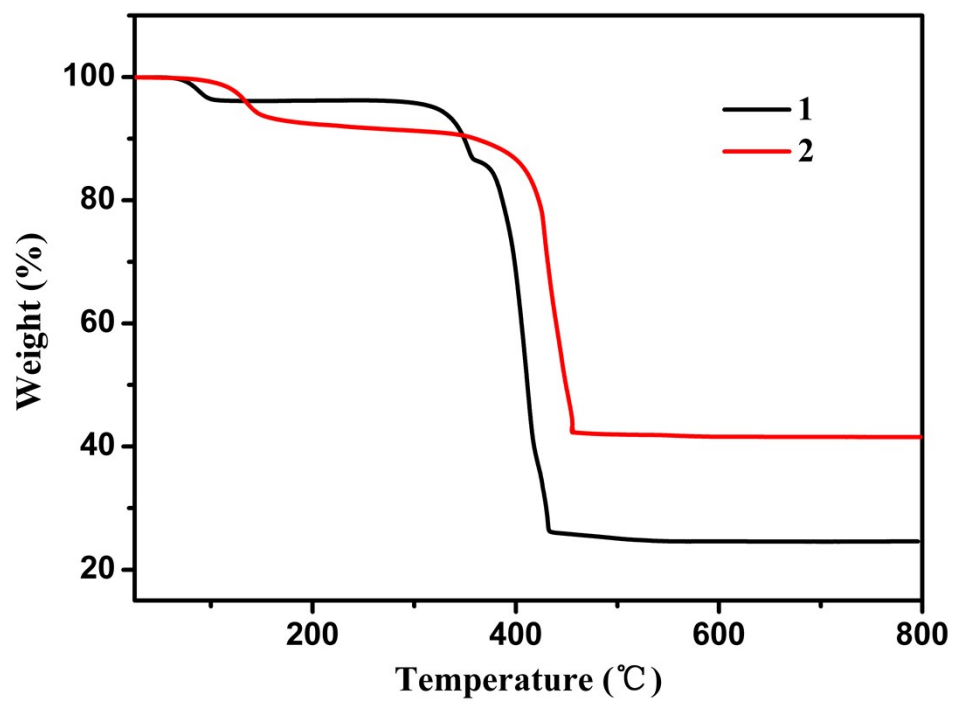


Fig. S6 TGA curve of **1** and **2** measured in air atmosphere.

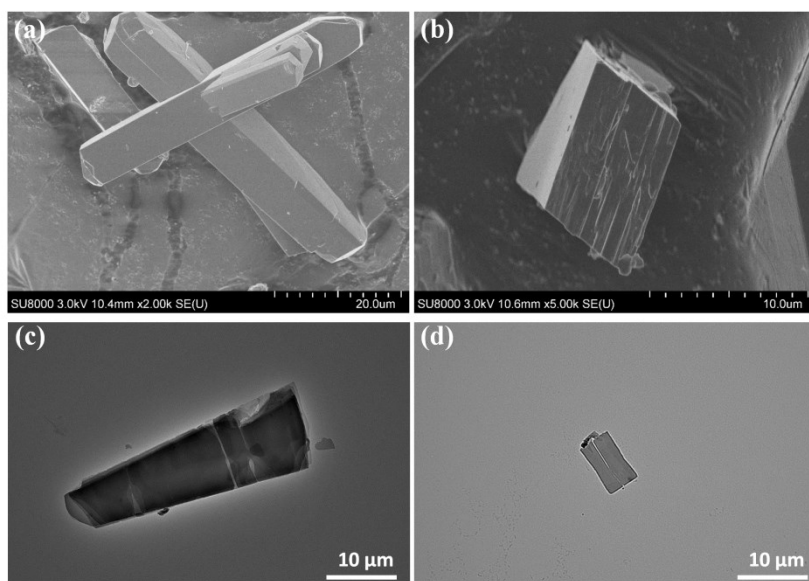


Fig. S7 SEM images of **1** (a) and **2** (b). TEM images of Eu³⁺/CDs@**1** (c) and Eu³⁺/CDs+**2** (d).

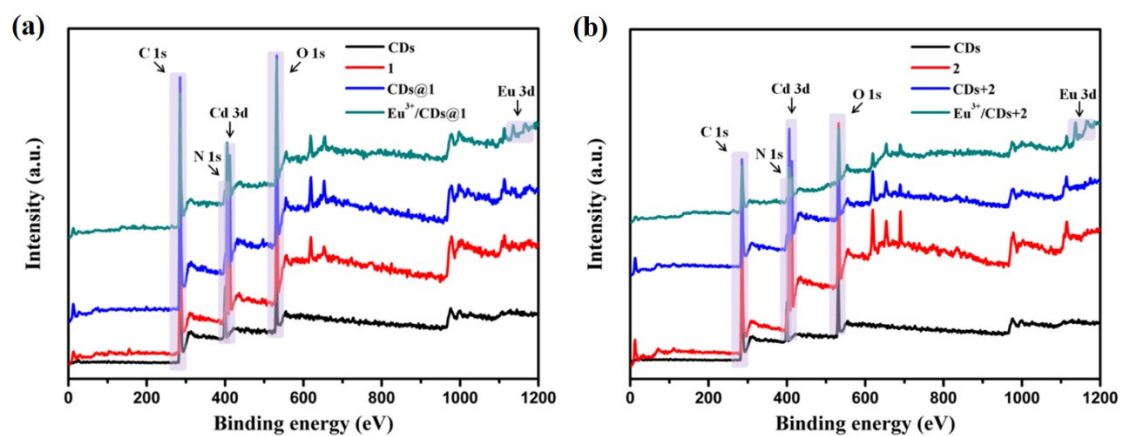


Fig. S8 The XPS spectra of CDs, **1**, CDs@**1**, Eu³⁺/CDs@**1** (a) and CDs, **2**, CDs@**2**, Eu³⁺/CDs+**2** (b).

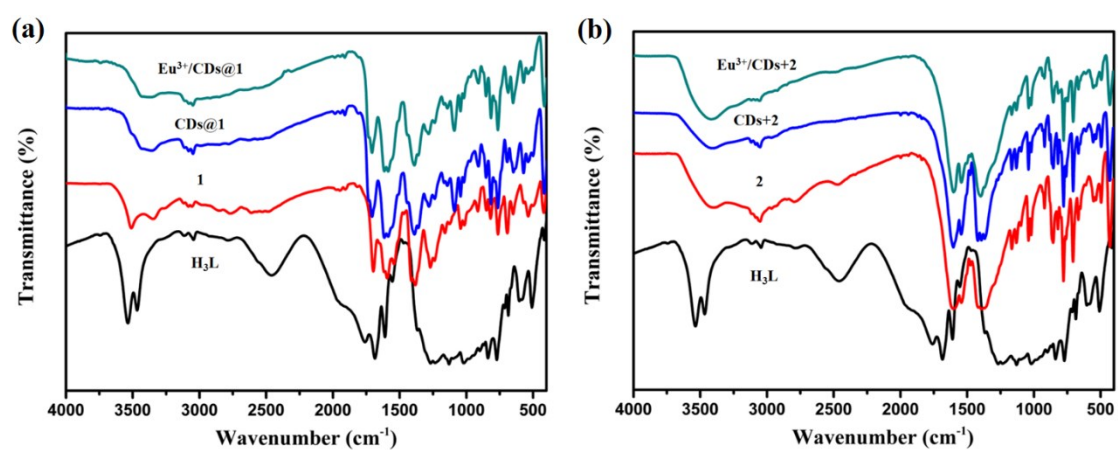


Fig. S9 FT-IR spectra of compounds.

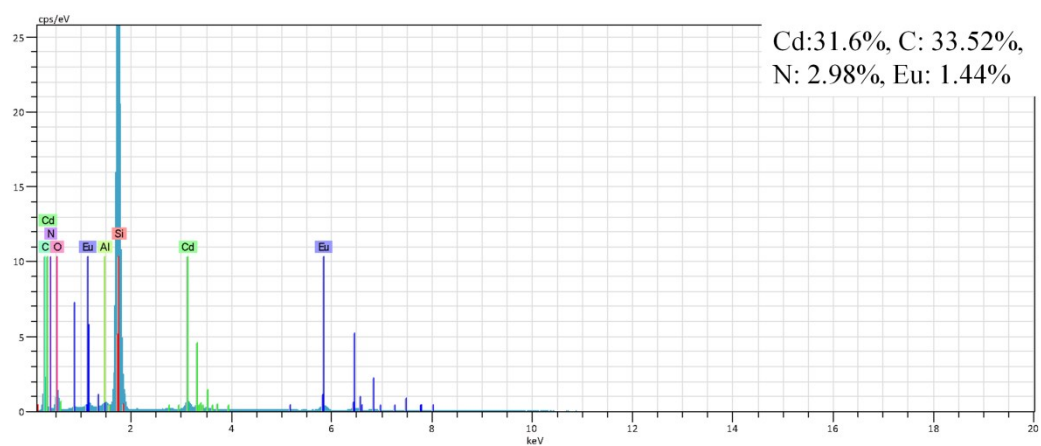


Fig. S10 Representative EDS plot of **1A**.

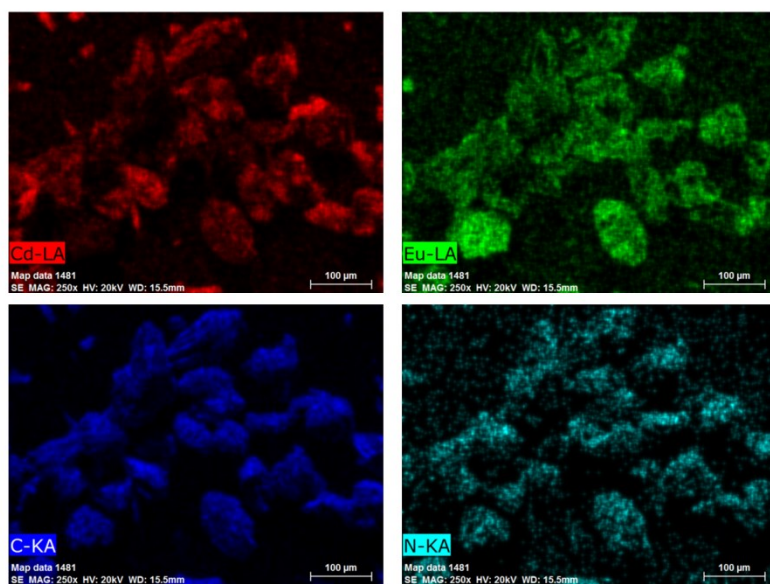


Fig. S11 EDS mapping images of **1A**.

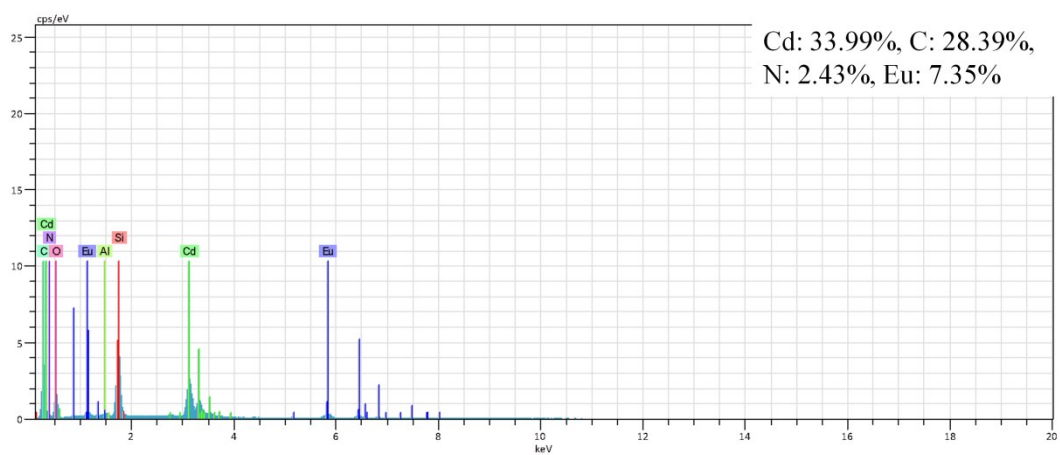


Fig. S12 Representative EDS plot of **2A**.

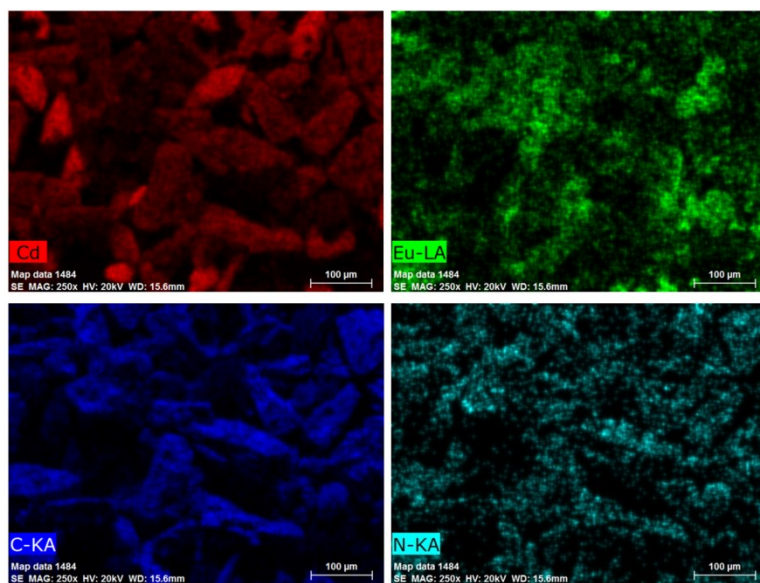


Fig. S13 EDS mapping images of **2A**.

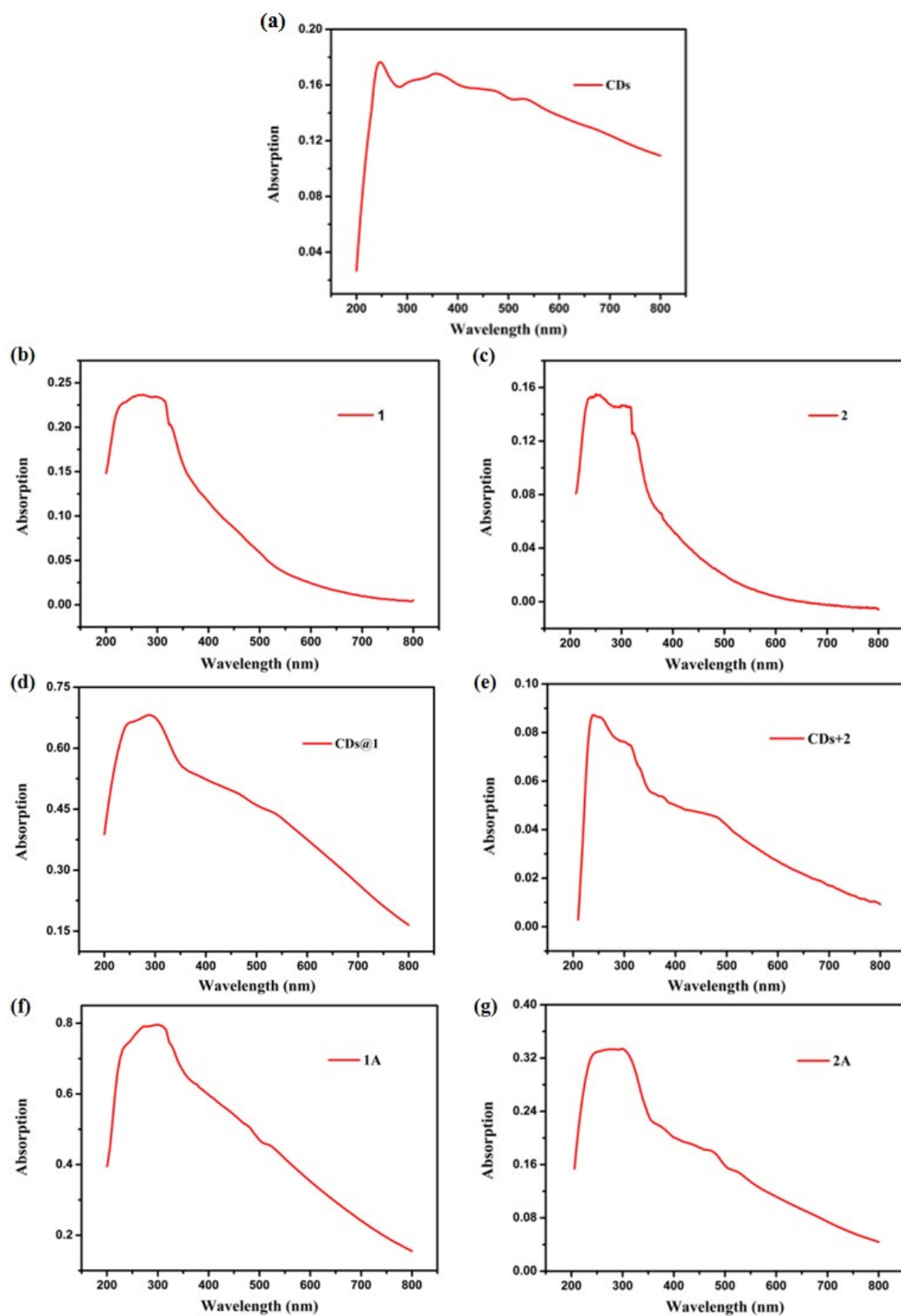


Fig. S14 Solid-state UV-vis absorption spectra of CDs (a), **1** (b), **2** (c), CDs@**1** (d), CDs+**2** (e), **1A** (f) and **2A** (g) at room temperature.

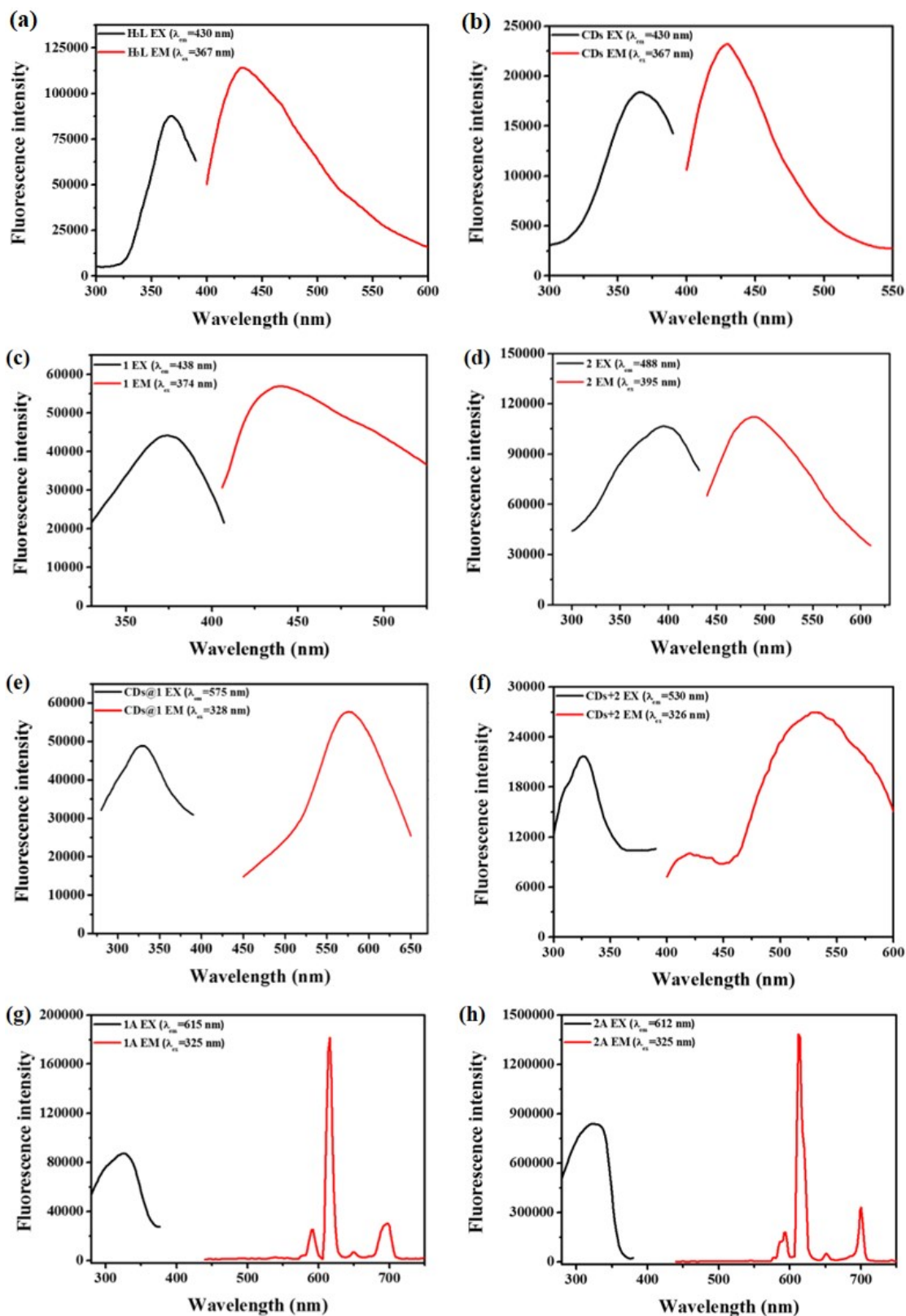


Fig. S15 Solid-state excitation and emission spectra of H₃L (a), CDs (b), **1** (c), **2** (d), CDs@**1** (e), CDs+**2** (f), **1A** (g) and **2A** (h) at room temperature.

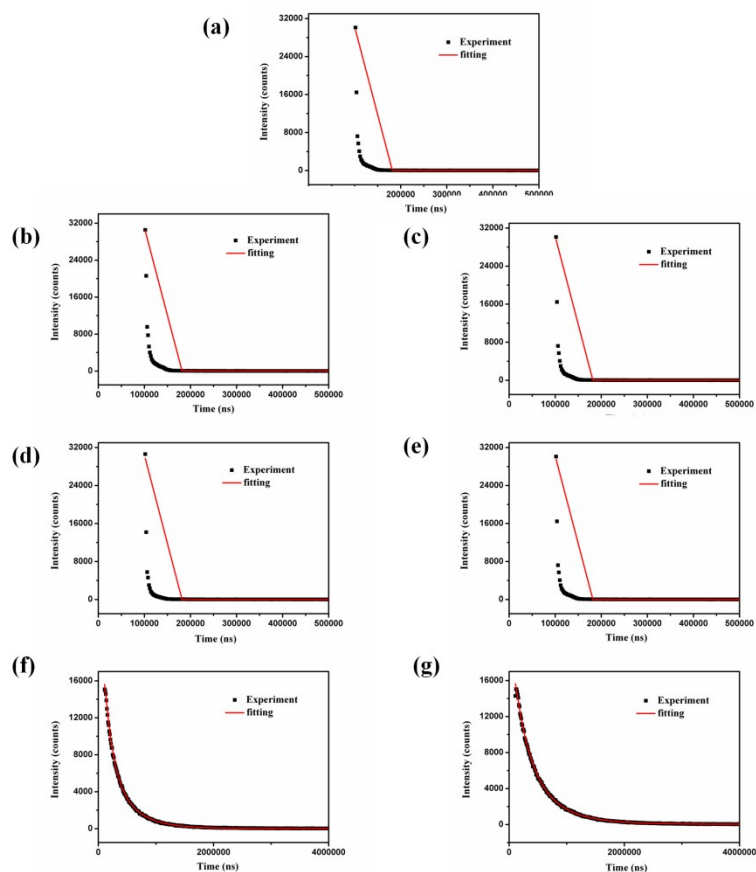


Fig. S16 Fluorescence decay profiles of CDs (a), **1** (b), **2** (c), CDs@**1** (d), CDs+**2** (e), **1A** (f) and **2A** (g) recorded at room temperature.

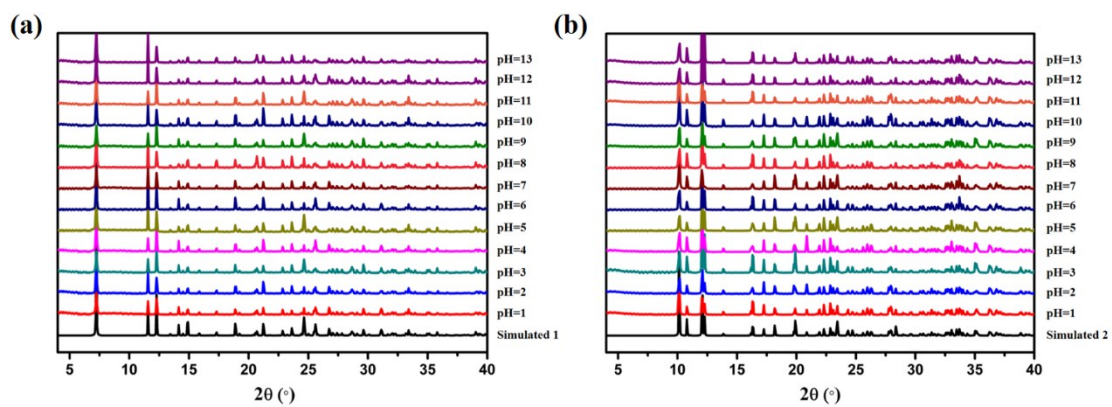


Fig. S17 Powder X-ray diffraction patterns of **1A** and **2A** after the treatment in different pH conditions.

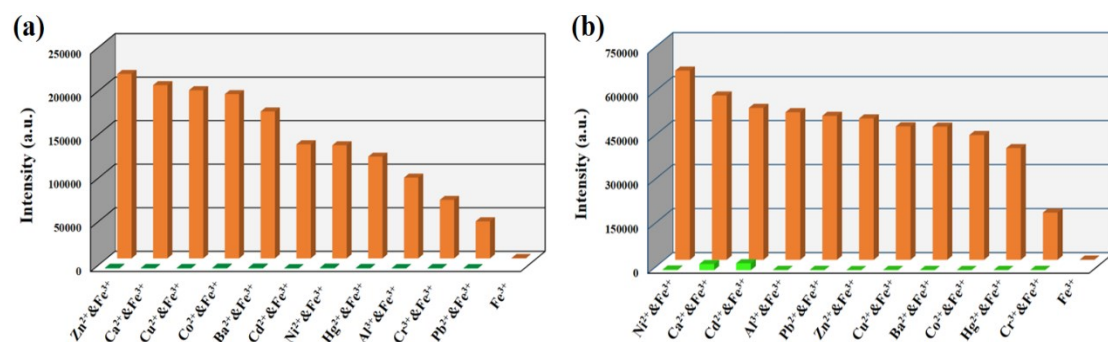


Fig. S18 (a) and (b) The fluorescence intensities of **1A** and **2A** at 612 nm at the addition of various metal ions followed by Fe³⁺ ions. The orange bars represent the intensities in different metal ion aqueous solutions, the green bars represent the intensities in the mixed solutions of Fe³⁺ and other metal ions.

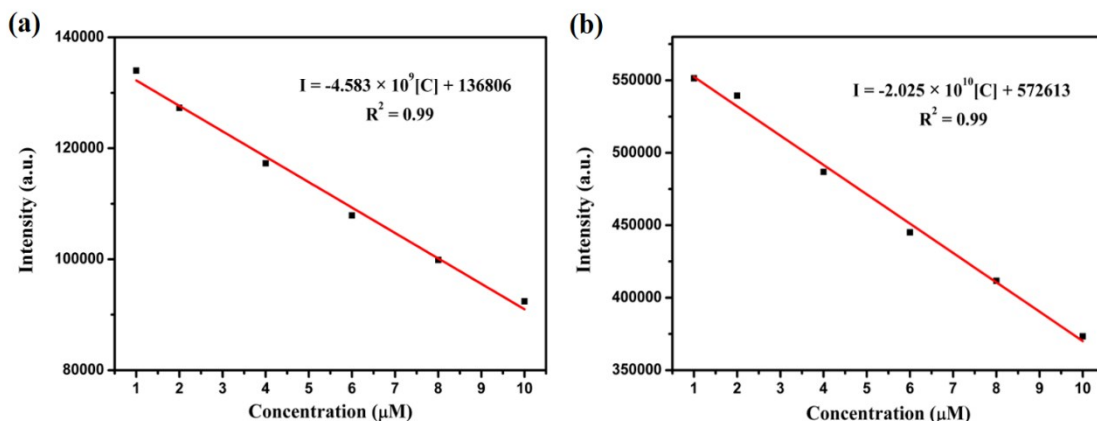


Fig. S19 (a) Relation of fluorescence intensity against Fe^{3+} added into **1A** suspension and their linear fitting curve for the estimation of LOD ($\sigma = 52.42$, $k = 4.583 \times 10^9 \text{ M}^{-1}$).

$$\text{Detection Limit} = 3\sigma/k$$

$$= (3 \times 52.42)/4.583 \times 10^9$$

$$= 0.034 \mu\text{M}$$

Multiple number of fluorescence spectra ($n = 10$) were recorded for the blank sample of **1A** suspension. Sample standard deviation σ for the blank probe without the addition of analyte was calculated to be 52.42.

(b) Relation of fluorescence intensity against Fe^{3+} added into **2A** suspension and their linear fitting curve for the estimation of LOD ($\sigma = 65$, $k = 2.025 \times 10^{10} \text{ M}^{-1}$).

$$\text{Detection Limit} = 3\sigma/k$$

$$= (3 \times 65)/2.025 \times 10^{10}$$

$$= 0.0096 \mu\text{M}$$

Multiple number of fluorescence spectra ($n = 10$) were recorded for the blank sample of **2A** suspension. Sample standard deviation σ for the blank probe without the addition of analyte was calculated to be 65.

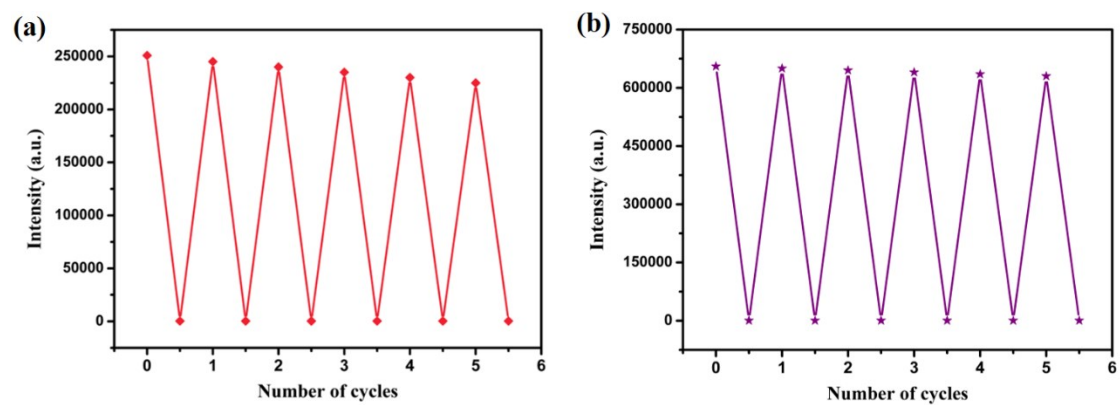


Fig. S20 Cyclic response of **1A** and **2A** for sensing Fe³⁺ (fluorescence intensity at 612 nm).

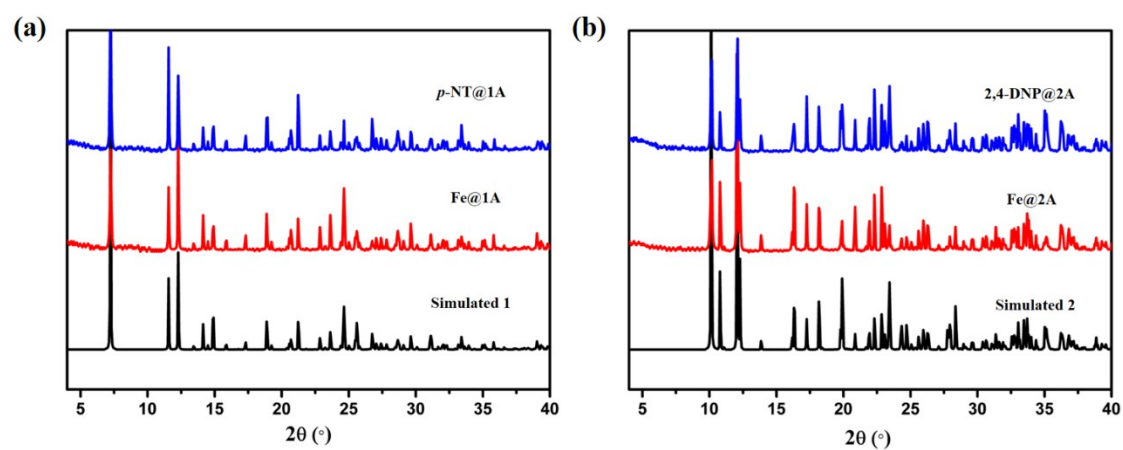


Fig. S21 PXRd patterns of **1A** and **2A** after cyclic sensing Fe^{3+} ions and nitro explosives.

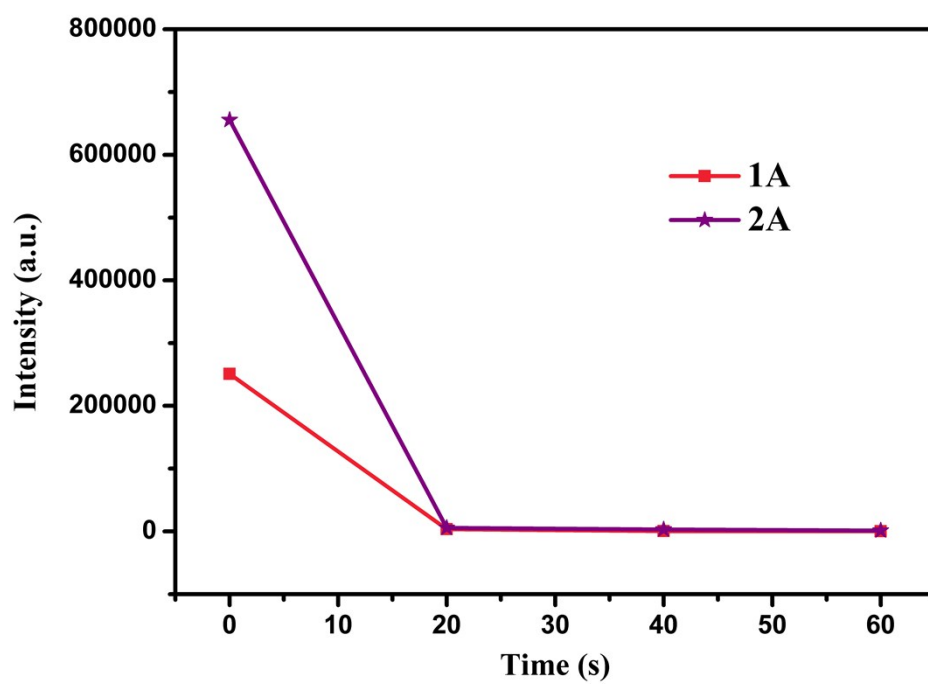


Fig. S22 Variation of fluorescence intensity of **1A** and **2A** with immersion time in analyte solution of Fe^{3+} ($1 \times 10^{-2} \text{ M}^{-1}$).

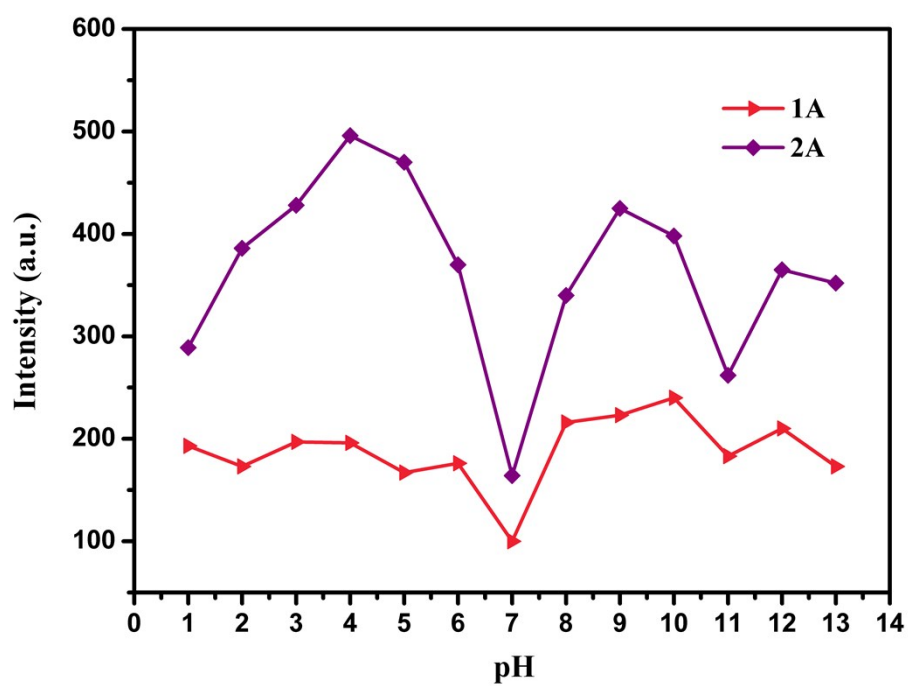


Fig. 23 Effect of pH on the emission intensity of **1A** and **2A** in the presence of Fe^{3+} ions.

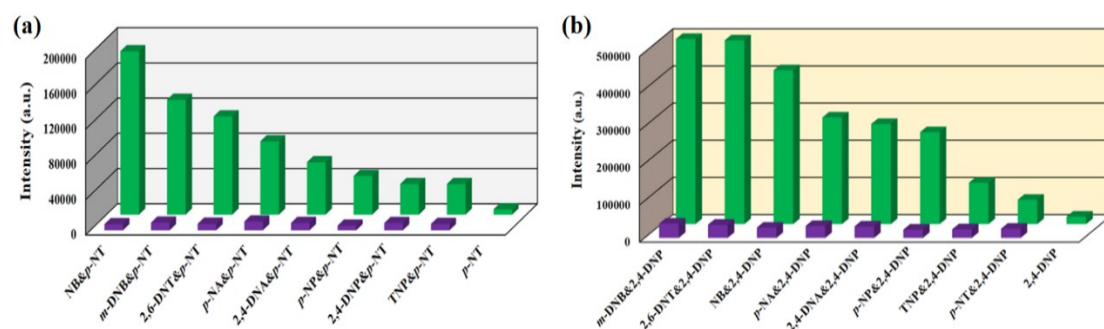


Fig. S24 (a) and (b) The fluorescence intensities of **8A** and **9A** at 612 nm at the addition of various nitro explosives followed by *p*-NT and 2,4-DNP, respectively. The green bars represent the intensities in different nitro explosive aqueous solutions, the purple bars represent the intensities in the mixed solutions of other nitro explosives and *p*-NT and 2,4-DNP, respectively.

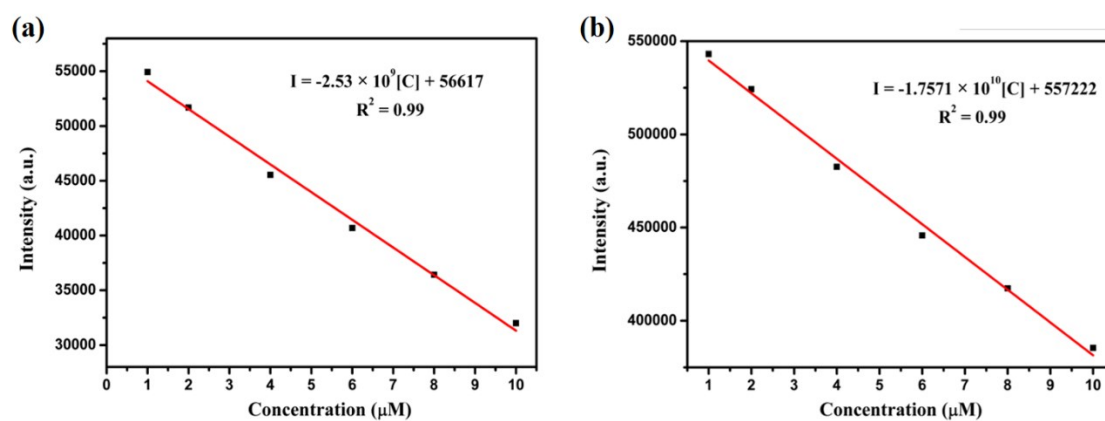


Fig. S25 (a) Relation of fluorescence intensity against *p*-NT added into **8A** suspension and their linear fitting curve for the estimation of LOD ($\sigma = 52.42$, $k = 2.53 \times 10^9 \text{ M}^{-1}$).

$$\text{Detection Limit} = 3\sigma/k$$

$$= (3 \times 52.42)/2.53 \times 10^9$$

$$= 0.062 \mu\text{M}$$

(b) Relation of fluorescence intensity against 2,4-DNP added into **9A** suspension and their linear fitting curve for the estimation of LOD ($\sigma = 65$, $k = 1.757 \times 10^{10} \text{ M}^{-1}$).

$$\text{Detection Limit} = 3\sigma/k$$

$$= (3 \times 65)/1.757 \times 10^{10}$$

$$= 0.0111 \mu\text{M}$$

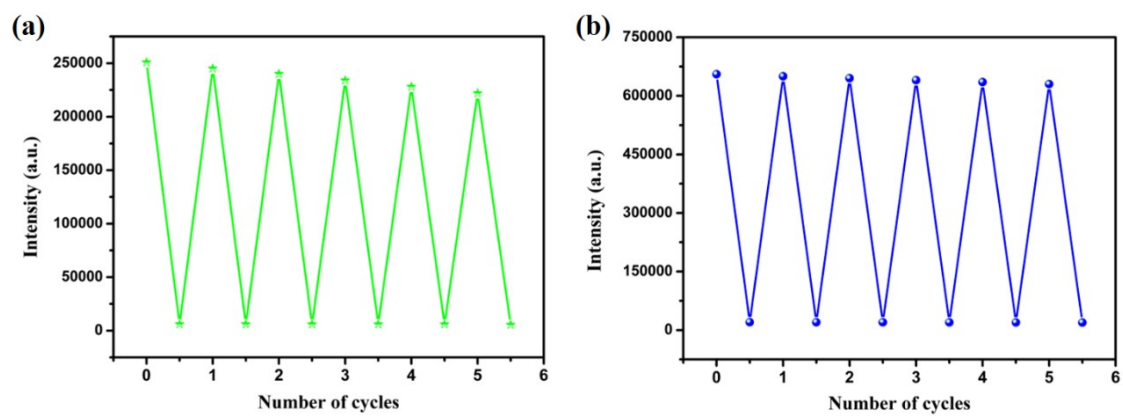


Fig. S26 Cyclic response of **1A** and **2A** for sensing *p*-NT and 2,4-DNP, respectively. (fluorescence intensity at 612 nm).

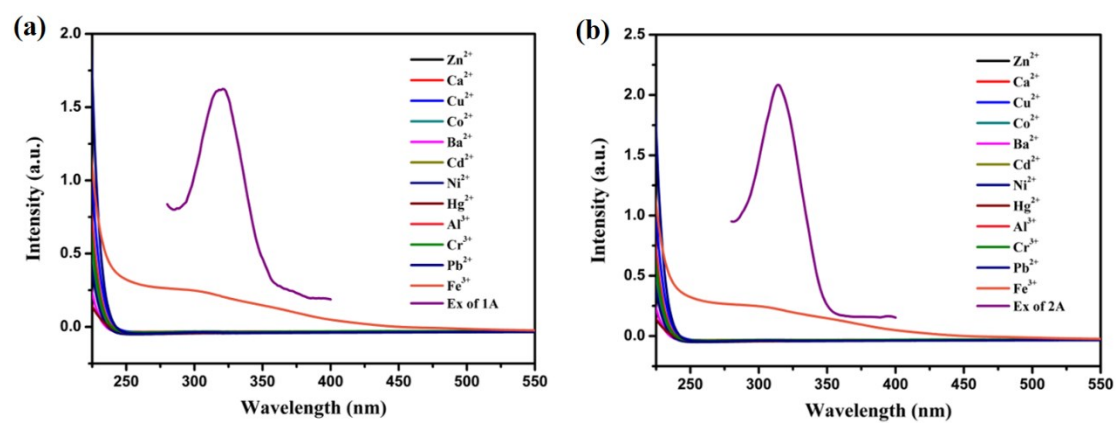


Fig. S27 (a) and (b) The absorption spectra of different cations and the excitation spectrum of **1A** and **2A**.

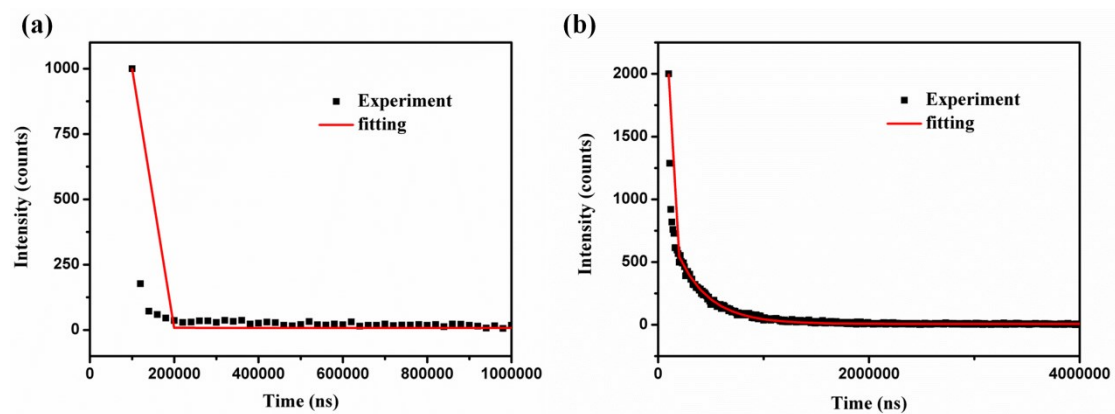


Fig. S28 Fluorescence decay profiles of $\text{Fe}^{3+}\text{@1A}$ (a) and $\text{Fe}^{3+}\text{@2A}$ (b) recorded at room temperature. The $^5\text{D}_0$ decay curve of $\text{Fe}^{3+}\text{@1A}$ with emission was monitored at 616 nm ($\lambda_{\text{ex}} = 328$ nm), $\tau_1 = 0.012$ ms. The $^5\text{D}_0$ decay curve of $\text{Fe}^{3+}\text{@2A}$ with emission was monitored at 612 nm ($\lambda_{\text{ex}} = 334$ nm), $\tau_1 = 0.013$ ms and $\tau_2 = 0.300$ ms.

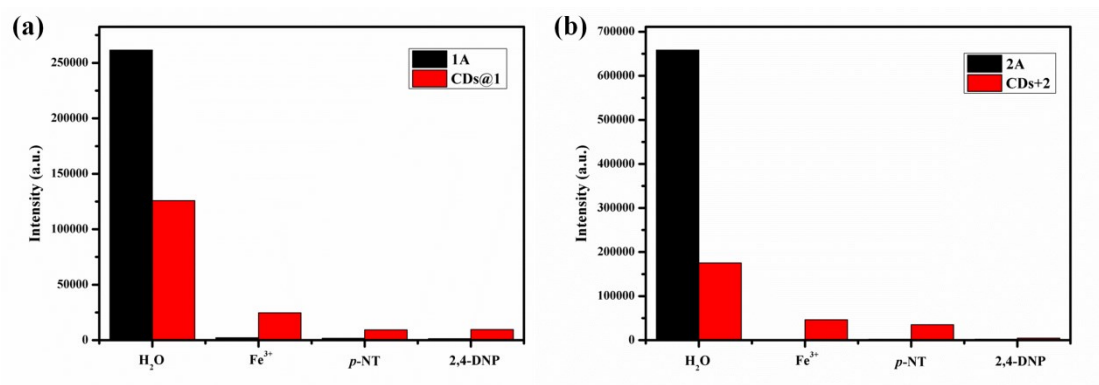


Fig. S29 Sensitivity of (a) **1A** and CDs@1, (b) **2A** and CDs+2.

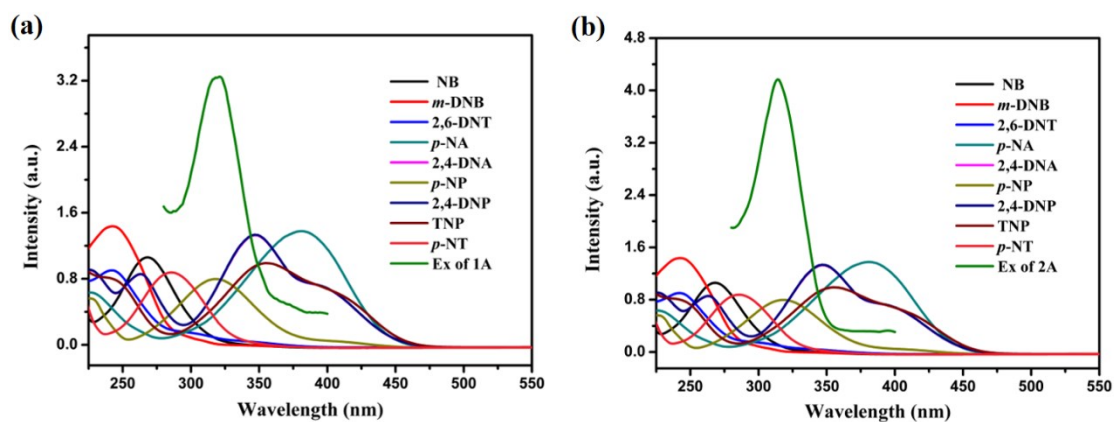


Fig. S30 (a) and (b) The absorption spectra of different nitro explosives and the excitation spectrum of **1A** and **2A**.

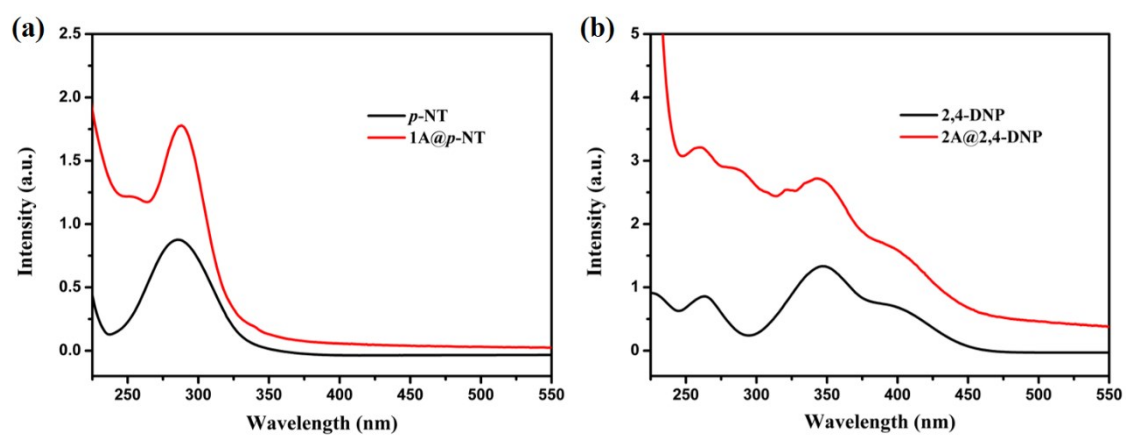


Fig. S31 The UV-vis absorption spectra of **1A** and *p*-NT@**1A** (a), **2A** and 2,4-DNP@**2A** (b).

Table S1. Crystal data and structure refinement for compounds **1-2**.

	1	2
Formula	C ₁₄ H _{8.6} O _{6.8} NCd	C ₂₈ H ₁₈ O ₁₅ N ₂ Cd ₃
Fw (g mol ⁻¹)	412	959.63
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	12.501(3)	15.1651(3)
<i>b</i> (Å)	7.2941(15)	10.8557(2)
<i>c</i> (Å)	15.655(3)	16.4832(3)
<i>V</i> (Å ³)	1395.6(5)	2623.47(9)
<i>Z</i>	4	4
<i>D</i> _{Calc} (mg·cm ⁻³)	1.888	2.293
<i>F</i> (000)	772	1736
<i>θ</i> range (°)	3.09 – 25.00	2.56 – 28.31
Limiting indices	-14 ≤ <i>h</i> ≤ 14	-15 ≤ <i>h</i> ≤ 20
	-8 ≤ <i>k</i> ≤ 8	-11 ≤ <i>k</i> ≤ 14
	-18 ≤ <i>l</i> ≤ 18	-21 ≤ <i>l</i> ≤ 21
Refl.Collectd / unique	7208/2264	9336/3115
<i>R</i> _{int}	0.0266	0.0161
Data / restraints / parameters	2264/0/199	3115/0/204
GOF	1.160	1.125
<i>R</i> _{<i>I</i>} [<i>I</i> > 2σ(<i>I</i>)]	0.0262	0.0186
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0757	0.0435
<i>R</i> _{<i>I</i>} (all data)	0.0292	0.0190
<i>wR</i> ₂ (all data)	0.0778	0.0437
Largest diff.peak and hole(e·Å ⁻³)	1.020 and -0.477	0.460 and -0.460
CCDC No.	1891845	2073945

Table S2. Selected bond lengths [Å] and angles [°] for compounds **1-2**.

1			
O(4)-Cd(1)#1	2.299(3)	O(1)-Cd(1)#3	2.232(3)
O(4)-Cd(1)	2.445(3)	N(1)-Cd(1)#4	2.317(4)
O(2)-Cd(1)#2	2.194(3)	Cd(1)-O(3)	2.354(3)
Cd(1)-O(2)#5	2.194(3)	Cd(1)-O(1)#3	2.232(3)
Cd(1)-O(4)#6	2.299(3)	Cd(1)-N(1)#7	2.317(4)
O(2)#5-Cd(1)-O(1)#3	153.48(14)	O(2)#5-Cd(1)-O(4)#6	83.71(12)
O(1)#3-Cd(1)-O(4)#6	87.80(12)	O(2)#5-Cd(1)-N(1)#7	109.87(13)
O(1)#3-Cd(1)-N(1)#7	93.80(12)	O(4)#6-Cd(1)-N(1)#7	82.60(12)
O(2)#5-Cd(1)-O(3)	89.45(13)	O(1)#3-Cd(1)-O(3)	99.40(13)
O(4)#6-Cd(1)-O(3)	172.76(11)	N(1)#7-Cd(1)-O(3)	97.56(12)
O(2)#5-Cd(1)-O(4)	82.26(12)	O(1)#3-Cd(1)-O(4)	82.94(11)
O(4)#6-Cd(1)-O(4)	126.98(6)	N(1)#7-Cd(1)-O(4)	149.85(12)
O(3)-Cd(1)-O(4)	53.95(10)		

Symmetry transformations used to generate equivalent atoms:

#1 $-x, y+1/2, -z+1/2$; #2 $x, -y+1/2, z-1/2$; #3 $-x, -y+1, -z$; #4 $x, y+1, z$; #5 $x, -y+1/2, z+1/2$; #6 $-x, y-1/2, -z+1/2$; #7 $x, y-1, z$

Cd(1)-O(1)	2.1716(16)	Cd(1)-O(3)#1	2.2627(16)
Cd(1)-O(6)#2	2.2658(16)	Cd(1)-O(5)#3	2.3225(17)
Cd(1)-O(4)#4	2.3260(15)	Cd(1)-O(5)#2	2.545(2)
Cd(2)-O(2)#6	2.2358(16)	Cd(2)-O(2)#6	2.2358(16)
Cd(2)-O(4)#7	2.3329(14)	Cd(2)-O(4)#4	2.3329(14)
Cd(2)-N(1)#7	2.3394(17)	Cd(2)-N(1)#4	2.3394(17)
O(3)-Cd(1)#1	2.2627(16)	O(4)-Cd(1)#8	2.3260(15)
O(4)-Cd(2)#8	2.3329(14)	O(5)-Cd(1)#3	2.3225(17)
O(5)-Cd(1)#9	2.545(2)	O(6)-Cd(1)#9	2.2658(16)
N(1)-Cd(2)#8	2.3394(17)		
O(1)-Cd(1)-O(3)#1	91.18(7)	O(1)-Cd(1)-O(6)#2	120.66(7)
O(3)#1-Cd(1)-O(6)#2	92.87(7)	O(1)-Cd(1)-O(5)#3	92.66(7)
O(3)#1-Cd(1)-O(5)#3	78.24(7)	O(6)#2-Cd(1)-O(5)#3	145.89(7)
O(1)-Cd(1)-O(4)#4	110.63(7)	O(3)#1-Cd(1)-O(4)#4	151.03(5)
O(6)#2-Cd(1)-O(4)#4	92.00(6)	O(5)#3-Cd(1)-O(4)#4	81.80(7)
O(1)-Cd(1)-O(5)#2	171.91(7)	O(3)#1-Cd(1)-O(5)#2	83.36(7)
O(6)#2-Cd(1)-O(5)#2	53.99(6)	O(5)#3-Cd(1)-O(5)#2	92.06(6)
O(4)#4-Cd(1)-O(5)#2	76.57(6)	O(2)-Cd(2)-O(2)#6	107.31(11)
O(2)-Cd(2)-O(4)#7	78.24(7)	O(2)#6-Cd(2)-O(4)#7	85.97(7)
O(2)-Cd(2)-O(4)#4	85.97(7)	O(2)#6-Cd(2)-O(4)#4	78.24(7)
O(4)#7-Cd(2)-O(4)#4	153.26(8)	O(2)-Cd(2)-N(1)#7	152.91(7)
O(2)#6-Cd(2)-N(1)#7	86.11(7)	O(4)#7-Cd(2)-N(1)#7	79.41(6)
O(4)#4-Cd(2)-N(1)#7	120.31(6)	O(2)-Cd(2)-N(1)#4	86.11(7)
O(2)#6-Cd(2)-N(1)#4	152.91(7)	O(4)#7-Cd(2)-N(1)#4	120.31(6)
O(4)#4-Cd(2)-N(1)#4	79.41(6)	N(1)#7-Cd(2)-N(1)#4	92.12(9)

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1/2, -y+1/2, -z$; #2 $x+1, y, z$; #3 $-x, -y+1, -z$; #4 $x+1/2, y+1/2, z$; #5 $-x+1, -y+1, -z$; #6 $-x+1, y, -z+1/2$; #7 $-x+1/2, y+1/2, -z+1/2$; #8 $x-1/2, y-1/2, z$; #9 $x-1, y, z$

Table S3. Fluorescence lifetimes of CDs, **1**, **2**, CDs@**1**, CDs+**2**, **1A**, **2A**, Fe³⁺@**1A** and Fe³⁺@**2A**.

Compounds	Fluorescence lifetimes	
CDs	$\tau_1 = 3.607 \mu\text{s}$	$\tau_2 = 3.270 \mu\text{s}$
1	$\tau_1 = 3.585 \mu\text{s}$	$\tau_2 = 5.022 \mu\text{s}$
2	$\tau_1 = 3.924 \mu\text{s}$	$\tau_2 = 12.283 \mu\text{s}$
CDs@ 1	$\tau_1 = 2.935 \mu\text{s}$	-
CDs+ 2	$\tau_1 = 2.552 \mu\text{s}$	-
1A	$\tau_1 = 0.413 \text{ ms}$	$\tau_2 = 0.144 \text{ ms}$
2A	$\tau_1 = 0.584 \text{ ms}$	$\tau_2 = 0.261 \text{ ms}$
Fe ³⁺ @ 1A	$\tau_1 = 0.012 \text{ ms}$	-
Fe ³⁺ @ 2A	$\tau_1 = 0.013 \text{ ms}$	$\tau_2 = 0.300 \text{ ms}$

Table S4. The comparison of K_{SV} and detection limit between **1A** and **2A** and other reported fluorescent chemosensors for detecting of Fe^{3+} ions.

MOFs	K_{SV} (M^{-1})	Detection limits (μM)	Reference
1A	9.269×10^4	0.034	This work
2A	6.329×10^4	0.0096	This work
$[Zn_3(L_1)_2(bipy)(\mu_3-OH)_2] \cdot 3H_2O$	2.3×10^4	-	[1]
$[Zr_6O_4(OH)_8(H_2O)_4(L_2)_2]$	1.66×10^4	0.0396	[2]
$[Zn_2(bptc)(H_2O)] \cdot (4,4'-bipy)_{0.5}$	2.826×10^4	8.5	[3]
$[Cd(L_3)-(BPDC)] \cdot 2H_2O$	3.64×10^4	2.21	[4]
$[Cd(L_3)(SDBA)(H_2O)] \cdot 0.5H_2O$	3.59×10^4	7.14	[4]
$[Cd(5-asba)(bimb)]$	1.78×10^4	-	[5]

H_2L_1 = 9H-carbazolyl-3,6-dicarboxylic acid;

H_2L_2 = 4,4',4'',4'''-(4,4'-(1,4-phenylene)bis(pyridine-6,4,2-triyl))-tetrabenzoate;

H_4bptc = 2,4,4',6-biphenyl tetracarboxylic acid;

L_3 = 4,4'-(2,5-bis(methylthio)-1,4-phenylene)dipyridine;

H_2BPDC = 4,4'-biphenyldicarboxylic acid;

H_2SDBA = 4,4'-sulfonyldibenzoic acid;

$H_25-asba$ = 2-amino-5-sulfobenzoic acid;

$bimb$ = 1,4-bis(1H-imidazol-1-yl)butane.

Table S5. The comparison of K_{SV} and detection limit between **1A** and other reported fluorescent chemosensors for detecting of *p*-NT.

MOFs	K_{SV} (M^{-1})	Detection limits (μM)	Reference
1A	3.57×10^5	0.062	This work
[Cd(DBCD)(1,3-bib)]·(H ₂ O) ₂	6.8×10^4	-	[6]
[Zn(DBCD)(1,4-bib)]·(H ₂ O) ₂	1.5×10^5	-	[6]
[Cd _{1/2} (L ₄) _{1/3} (bib) _{1/2} (H ₂ O)]	1.7×10^5	-	[7]
[Cd ₂ (HL ₄) ₂ (bibp) ₂]·3H ₂ O	1.0×10^5	-	[7]
534-MOF-Tb	7.90×10^4	320	[8]
[Zn(tta) _{0.5} (<i>m</i> -bimb)]·H ₂ O	1.78×10^4	-	[9]

H₂DBCD = N,N'-dioxide 3,3'-benzo(c)cinnoline dicarboxylic acid;

H₃L₄ = tris[*p*-carboxyphenyl]phosphane oxide;

bib = 1,4-bis[imidazol-1-yl]benzene;

bibp = 4,4'-bis[imidazol-1-yl]biphenyl;

H₄tta = terphenyl-4,2'',5'',4'-tetracarboxylic acid;

m-bimb = 1,3-bis(imidazol-1-ylmethyl)benzene.

Table S6. The comparison of K_{SV} and detection limit between **2A** and other reported fluorescent chemosensors for the detecting of 2,4-DNP.

MOFs	K_{SV} (M^{-1})	Detection limits (μM)	Reference
2A	5.456×10^4	0.0111	This work
$(CH_3)_2NH_2)_6[Cd_5(L_5)_4] \cdot H_2O \cdot 3DMF$	2.37×10^4	4.56	[10]
$(NH_2(CH_3)_2)[Zn_4(ddn)_2(COO)(H_2O)_4] \cdot solvent$	8.93×10^3	6.08	[11]
$[Nd(L^1)(NO_3)_3] \cdot 2DMF$	7.00×10^3	0.72	[12]
$[Sm(L^1)(NO_3)_3] \cdot 2DMF$	5.90×10^3	0.70	[12]
$(PFBHC)_2Ir(acac)$	1.58×10^3	89	[13]

H_4L_5 = terphenyl-3,3'',5,5''-tetracarboxylic acid;

H_4ddn = 3,5-di(3,5-dicarboxylphenyl)nitrobenzene;

PFBHC = 9,90-((2-(pyridin-2-yl)-9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl))bis(9H-carbazole).

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