

NiS₂-Integrated Cd-Oxalate MOF: A Multifunctional Platform for Selective 2,4-D Amine Sensing and Efficient NR/EBT Photodegradation

Azaz Ahmed^a, Musheer Ahmad^b, Chandrakant Thakur^c, Astakala Anil Kumar^d, Nohyun Lee^d,
Nazrul Haq^e, Kafeel Ahmad Siddiqui^a

^a Department of Chemistry, National Institute of Technology Raipur, G. E. Road Raipur –
492010, Chhattisgarh, India.

^b Department of Applied Chemistry, Faculty of Engineering and Technology, ZHCET, Aligarh
Muslim University, Aligarh, UP (India) – 202002.

^c Department of Chemical Engineering, National Institute of Technology Raipur, G. E.
Road Raipur - 492010, Chhattisgarh, India.

^d School of Advanced Materials Engineering, Kookmin University, Seoul 02707, South Korea.

^e Department of Pharmaceutics, College of Pharmacy, King Saud University, Riyadh
11451, Saudi Arabia.

^a Corresponding Author: Dr. Kafeel Ahmad Siddiqui

^a e-mail: kasiddiqui.chy@nitrr.ac.in

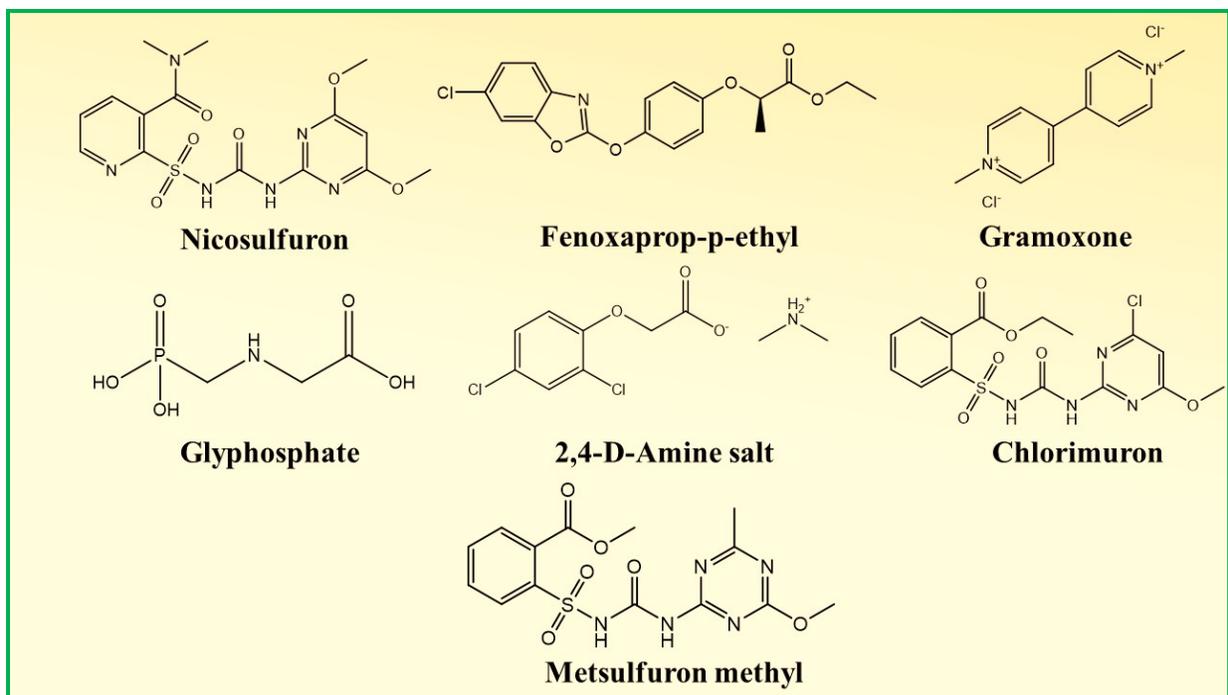
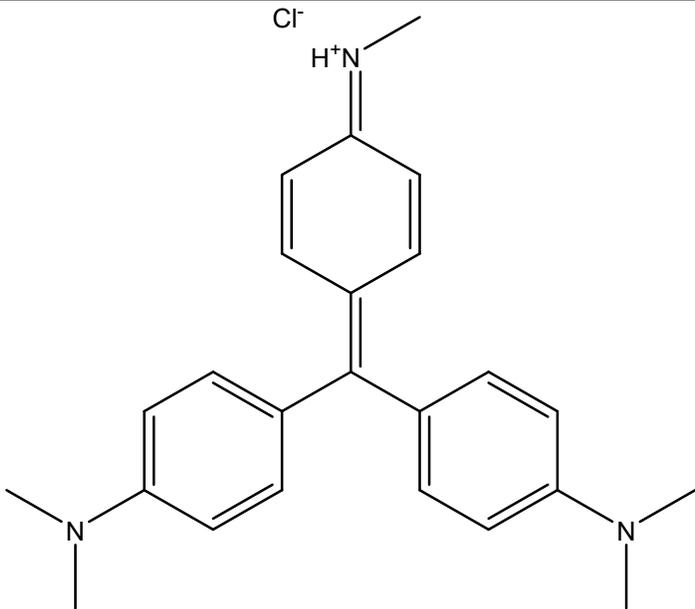
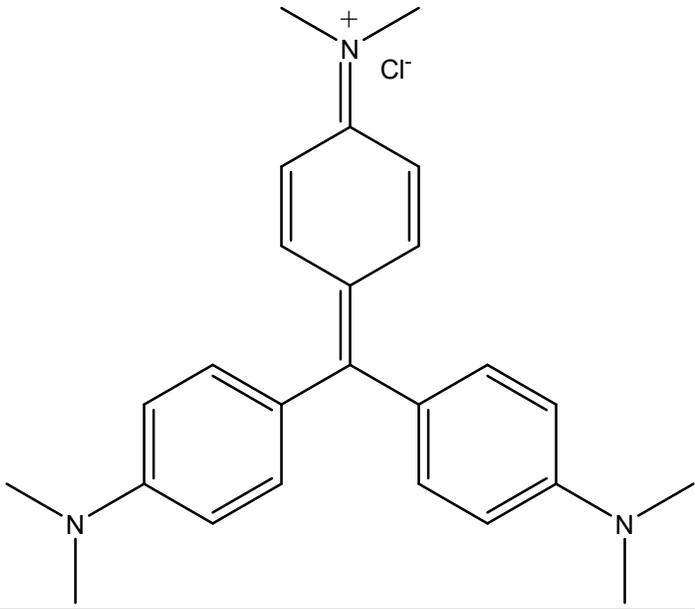
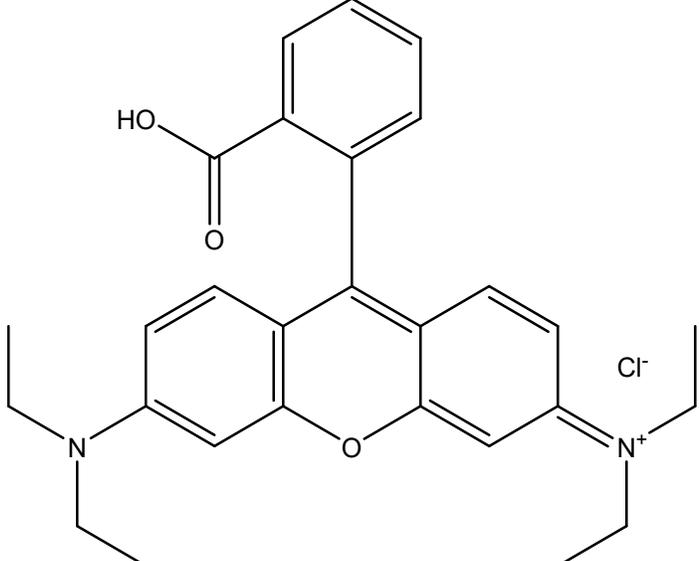
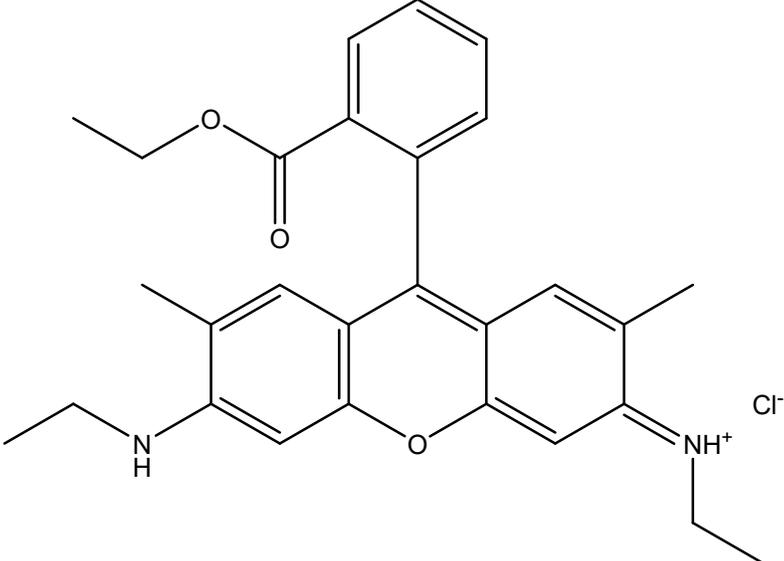
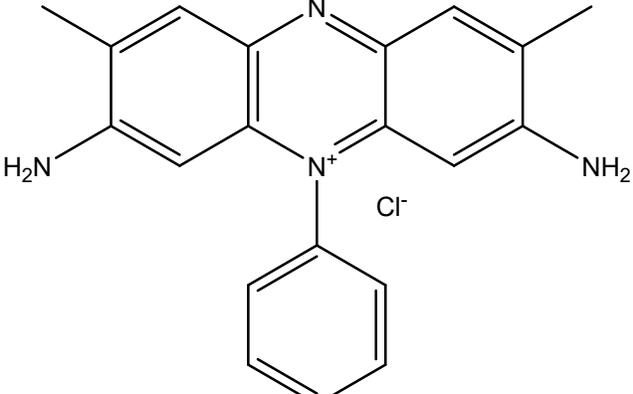
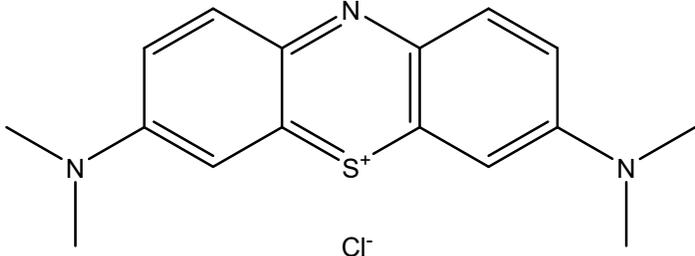
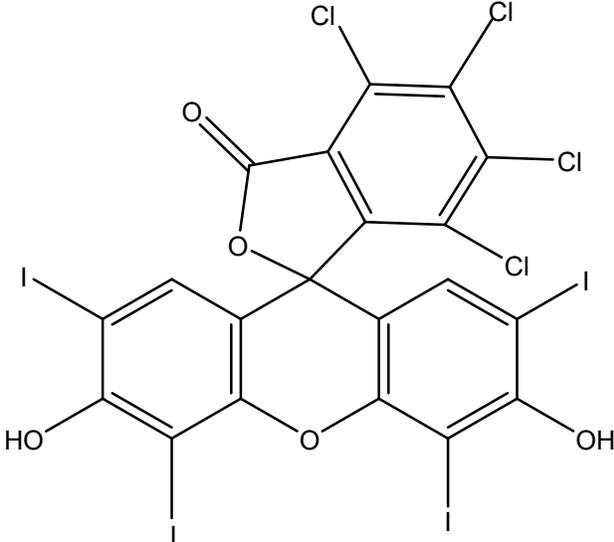
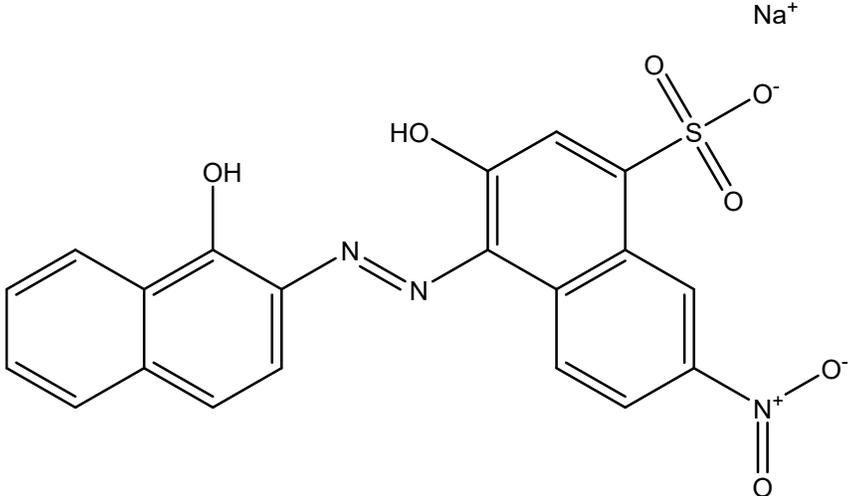


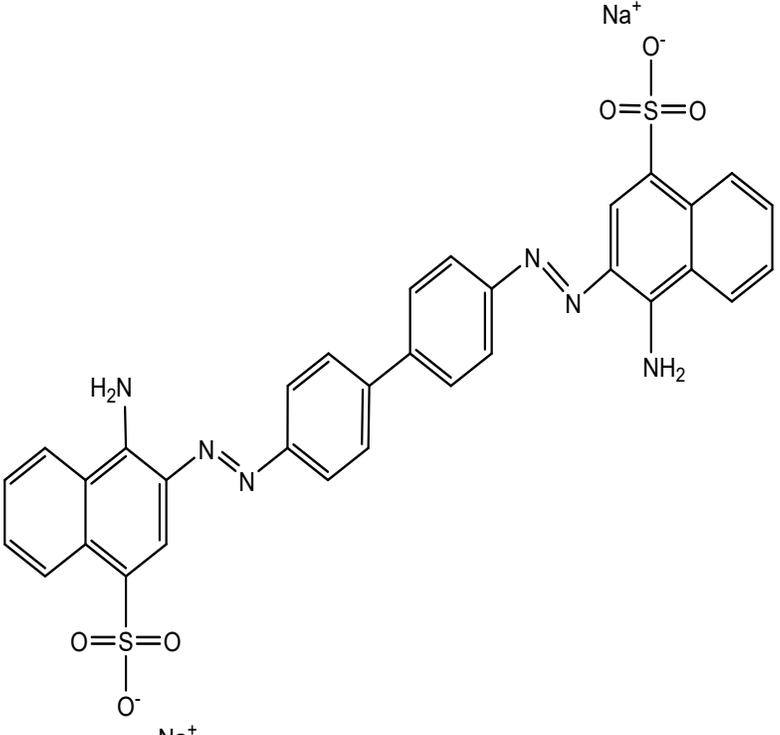
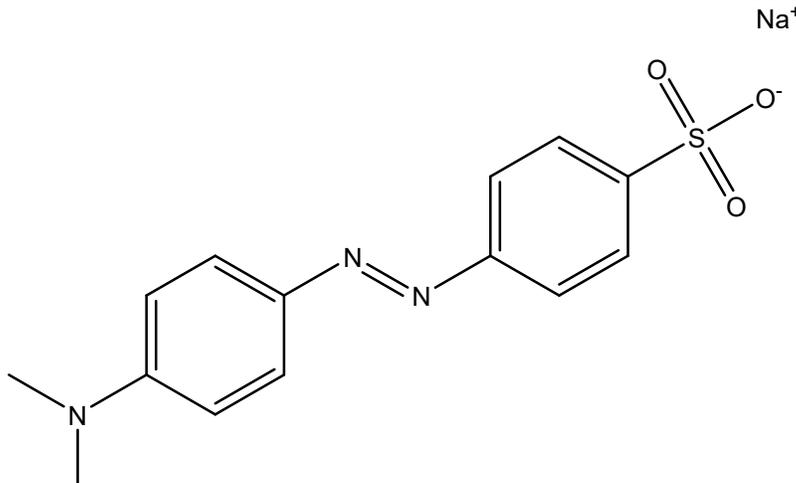
Fig.S1. Chemical structure of Herbicides.

Table S1. The names and corresponding chemical structures of the dyes employed in this study are provided.

S.No.	Dye	Dye Structure	λ_{\max} (nm)
Cationic			
1.	Methyl Violet	 <p>Chemical structure of Methyl Violet dye. It features a central carbon atom double-bonded to a nitrogen atom (H⁺N) and single-bonded to two para-substituted benzene rings. Each benzene ring has a dimethylamino group (-N(CH₃)₂). The nitrogen atom is also bonded to a methyl group. A chloride ion (Cl⁻) is shown above the nitrogen atom.</p>	589.49
2.	Crystal Violet	 <p>Chemical structure of Crystal Violet dye. It features a central carbon atom double-bonded to a nitrogen atom (N⁺) and single-bonded to two para-substituted benzene rings. Each benzene ring has a dimethylamino group (-N(CH₃)₂). The nitrogen atom is also bonded to two methyl groups. A chloride ion (Cl⁻) is shown to the right of the nitrogen atom.</p>	590.67

3.	Rhodamine B	 <p>The structure shows a rhodamine core consisting of a central oxygen atom bonded to two benzene rings. The left ring has a diethylamino group (-N(CH₂CH₃)₂) at the 4-position. The right ring has an iminium group (=N⁺CH₂CH₃) at the 4-position. A chlorine ion (Cl⁻) is shown as a counterion. A 4-phenylbenzoic acid group (-C₆H₄-COOH) is attached to the 6-position of the central oxygen.</p>	553.24
4.	Rhodamine 6G	 <p>The structure shows a rhodamine core with a central oxygen atom. The left ring has a methyl group (-CH₃) at the 2-position and an ethylamino group (-NHCH₂CH₃) at the 4-position. The right ring has a methyl group (-CH₃) at the 2-position and an iminium group (=NH⁺CH₂CH₃) at the 4-position. A chlorine ion (Cl⁻) is shown as a counterion. A 4-phenylbenzoic acid ethyl ester group (-C₆H₄-COOCH₂CH₃) is attached to the 6-position of the central oxygen.</p>	525.31
5.	Safranin O	 <p>The structure shows a safranin core consisting of a central nitrogen atom bonded to two benzene rings. The left ring has a methyl group (-CH₃) at the 2-position and an amino group (-NH₂) at the 4-position. The right ring has a methyl group (-CH₃) at the 2-position and an amino group (-NH₂) at the 4-position. A chlorine ion (Cl⁻) is shown as a counterion. A phenyl group (-C₆H₅) is attached to the central nitrogen atom.</p>	519.58

6.	Methyl Blue		662.63
Anionic			
7.	Rose Bengal		549.44
8.	Eriochrome Black T		529.23

9.	Congo Red		497.82
10.	Methyl Orange		463.43

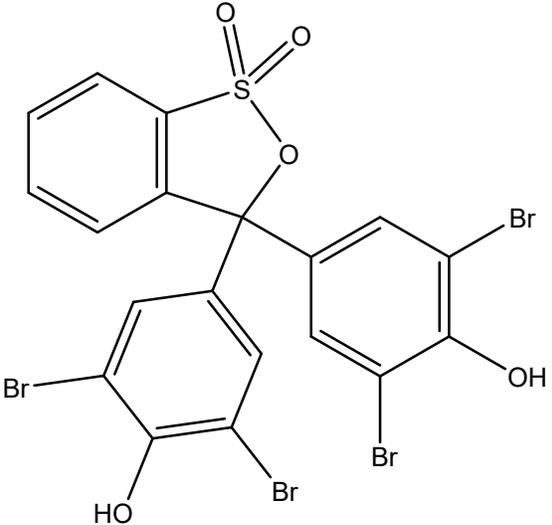
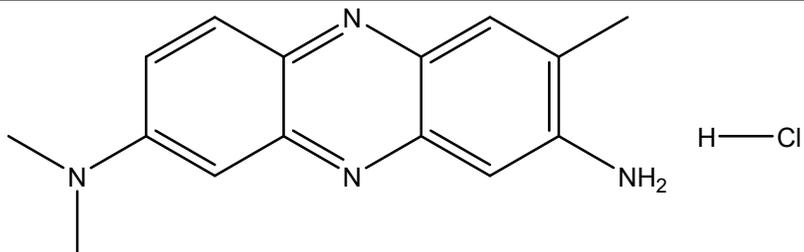
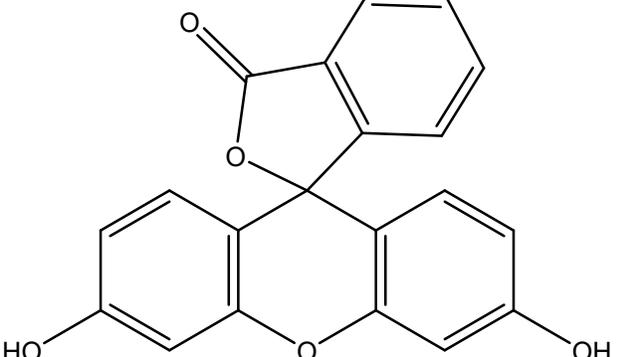
11.	Bromophenol Blue		591.75
Neutral			
12.	Neutral Red		532.86
13.	Fluorescein		483.51

Table S2. Crystal data and structure refinement for **Cd-MOF**

Identification code	Cd-MOF
Empirical formula	C ₂ H ₆ CdO ₇
Formula weight	254.48
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	6.00275(8)
b/Å	6.65883(6)
c/Å	8.48721(10)

$\alpha/^\circ$	74.6832(9)
$\beta/^\circ$	74.3039(11)
$\gamma/^\circ$	81.0102(9)
Volume/ \AA^3	313.678(6)
Z	2
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	2.6941
μ/mm^{-1}	3.465
F(000)	242.6
Crystal size/ mm^3	$0.47 \times 0.29 \times 0.17$
Radiation	Mo K α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	5.12 to 54.84
Index ranges	$-7 \leq h \leq 7, -8 \leq k \leq 8, -10 \leq l \leq 10$
Reflections collected	18351
Independent reflections	1380 [$R_{\text{int}} = 0.1007, R_{\text{sigma}} = 0.0373$]
Data/restraints/parameters	1380/0/97
Goodness-of-fit on F^2	1.071
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0268, wR_2 = 0.0707$
Final R indexes [all data]	$R_1 = 0.0280, wR_2 = 0.0745$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.99/-0.86
CCDC number	2484446

Table S3. Bond Lengths for Cd-MOF

Atom	Atom	Length/ \AA	Atom	Atom	Length/ \AA
Cd1	O2 ¹	2.354 (2)	O2	C1	1.243 (5)
Cd1	O4 ²	2.368 (3)	O4	C2	1.245 (5)
Cd1	O3	2.377 (2)	O3	C2	1.255 (4)
Cd1	O3 ³	2.360 (3)	O1	C1	1.257 (4)
Cd1	O1	2.296 (3)	C1	C1 ¹	1.562 (7)
Cd1	O6	2.350 (3)	C2	C2 ⁴	1.544 (7)
Cd1	O5	2.288 (4)			

Table S4. Bond Angles for Cd-MOF

Atom	Atom	Atom	Angle/ $^\circ$	Atom	Atom	Atom	Angle/ $^\circ$
O4 ¹	Cd1	O2 ²	73.66 (9)	O5	Cd1	O3 ³	100.17 (12)
O3	Cd1	O2 ²	146.41 (9)	O5	Cd1	O3	93.61 (11)
O3 ³	Cd1	O2 ²	126.21 (10)	O5	Cd1	O1	175.18 (10)
O3 ³	Cd1	O4 ¹	69.02 (9)	O5	Cd1	O6	84.90 (12)
O3	Cd1	O4 ¹	136.76 (9)	C1	O2	Cd1 ²	116.4 (2)
O1	Cd1	O2 ²	71.25 (9)	C2	O4	Cd1 ⁴	117.7 (2)

O1	Cd1	O4 ¹	105.74 (11)	C2	O3	Cd1 ³	117.5 (2)
O1	Cd1	O3 ³	83.12 (10)	C2	O3	Cd1	132.9 (2)
O1	Cd1	O3	84.13 (10)	C1	O1	Cd1	117.8 (3)
O6	Cd1	O2 ²	76.78 (10)	O1	C1	O2	125.4 (3)
O6	Cd1	O4 ¹	139.08 (10)	C1 ²	C1	O2	117.2 (4)
O6	Cd1	O3 ³	151.51 (9)	C1 ²	C1	O1	117.4 (4)
O6	Cd1	O3	81.08 (9)	O3	C2	O4	126.0 (3)
O6	Cd1	O1	90.54 (11)	C2 ⁵	C2	O4	117.0 (4)
O5	Cd1	O2 ²	109.07 (11)	C2 ⁵	C2	O3	117.0 (4)
O5	Cd1	O4 ¹	78.82 (12)				

Table S5. Comparison of Cd-MOF and NiS₂/Cd-MOF with reported probes for 2,4-D amine salt (DAS)

S. No.	MOF-based Sensors	Objective	LOD	Reference
1	[H ₂ BTC] ²⁻ . [Zn (H ₂ O) ₆] ²⁺	DAS	0.351 ppm	9
2	Cd-MOF	DAS	0.665 ppm	This work
3	NiS ₂ /Cd-MOF	DAS	0.510 ppm	This work

detection in terms of sensitivity, selectivity, and detection limits.

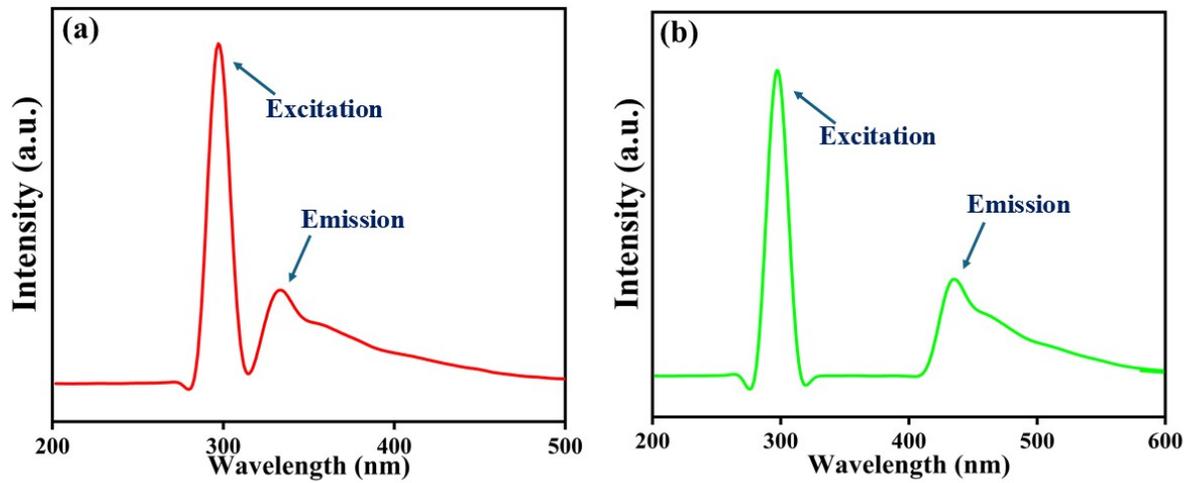


Fig.S2. Excitation and emission spectra of Cd-MOF and NiS₂/Cd-MOF in aqueous suspension, illustrating the strong fluorescence emission of (a) Cd-MOF at 332.65 nm and the red-shifted emission of (b) NiS₂/Cd-MOF at 433.26 nm upon excitation at 300 nm.

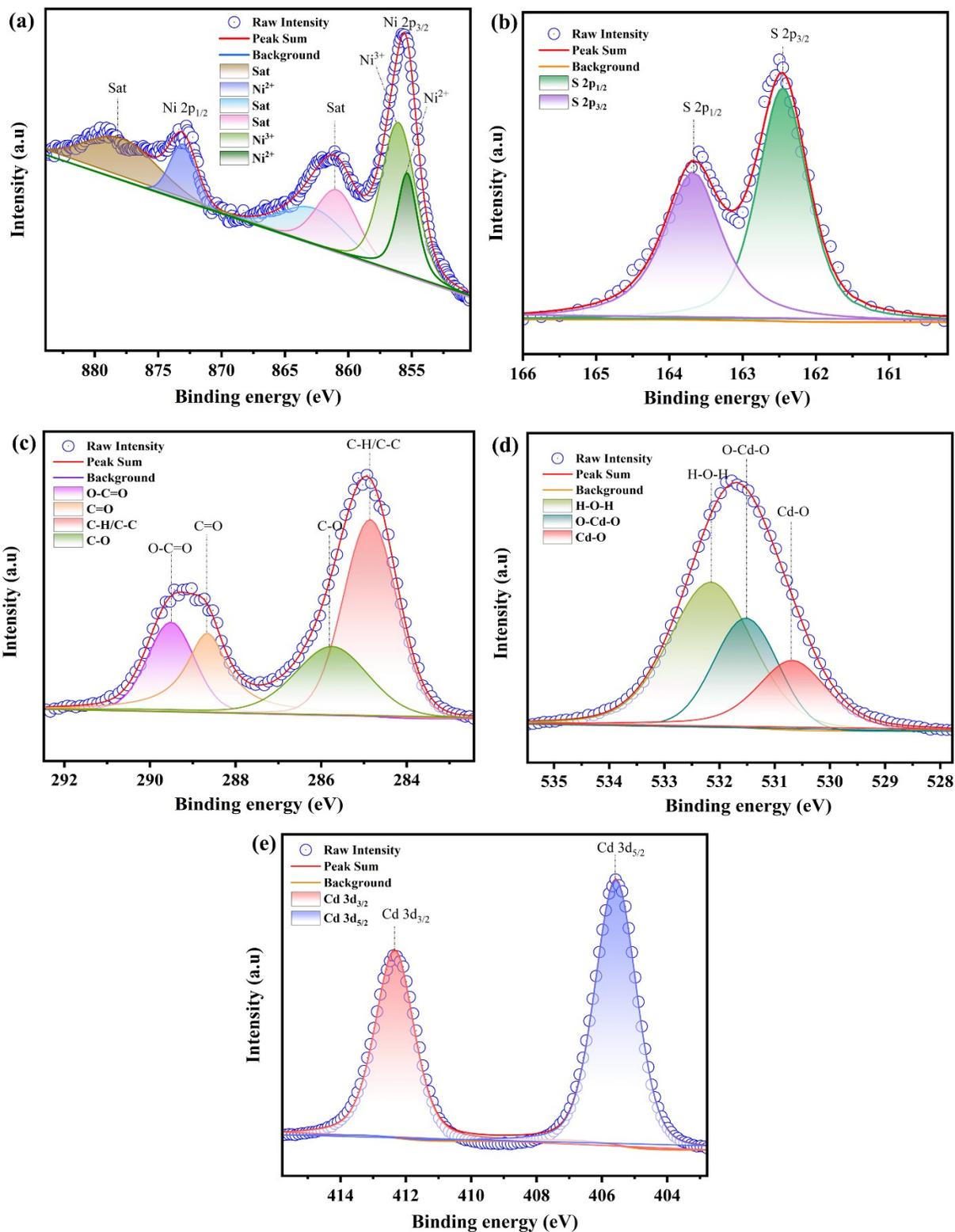


Fig. S3. High-resolution XPS spectra of pristine materials: (a) Ni 2p spectrum of NiS₂, (b) S 2p spectrum of NiS₂, (c) C 1s spectrum of Cd-MOF, (d) O 1s spectrum of Cd-MOF, and (e) Cd 3d

spectrum of Cd-MOF, confirming the chemical states and coordination environments of the constituent elements.

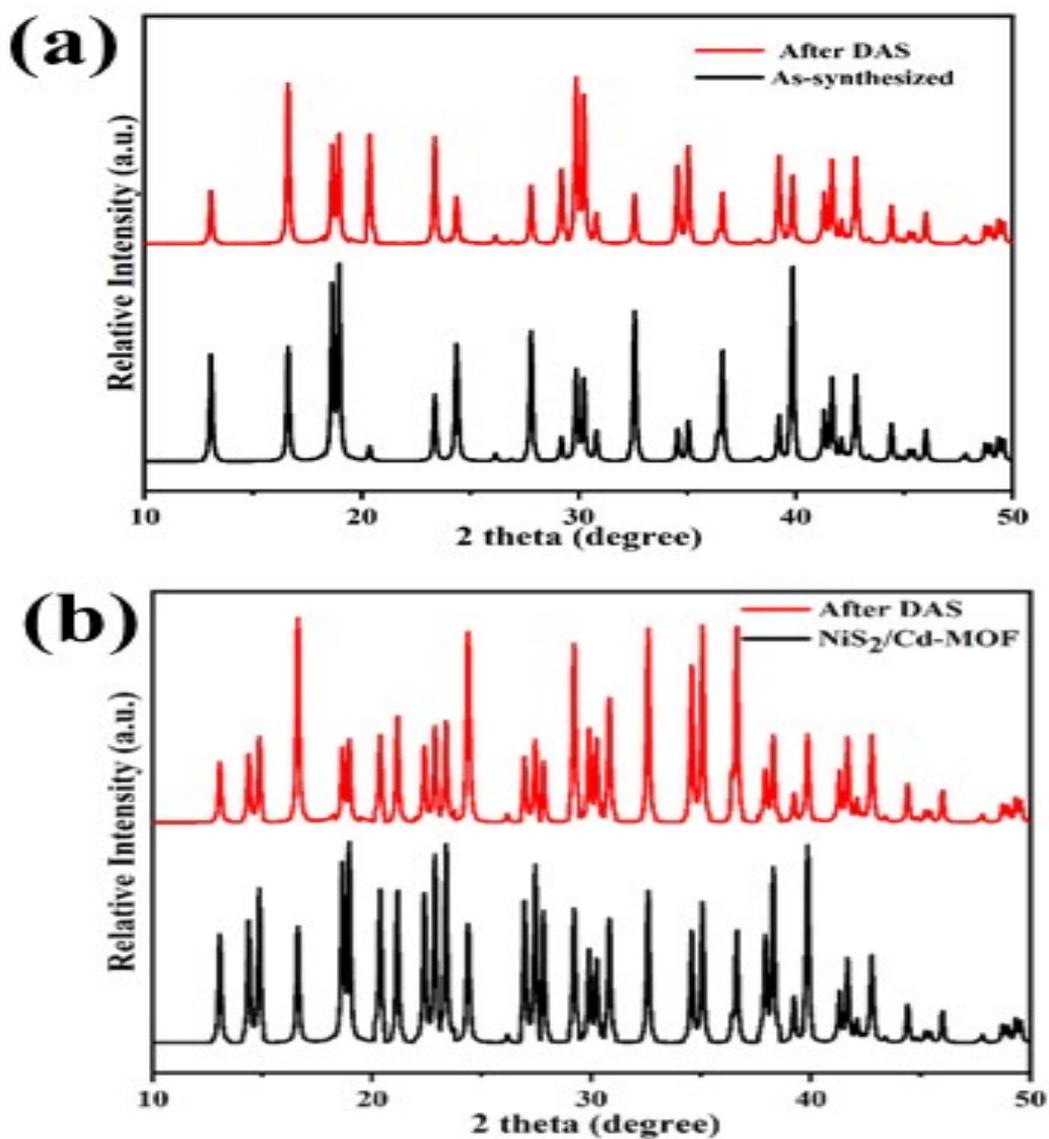


Fig.S4. PXRd patterns of the as-synthesized Cd-MOF and NiS₂/Cd-MOF, along with those recorded after sensing of (a) DAS and (b) DAS.

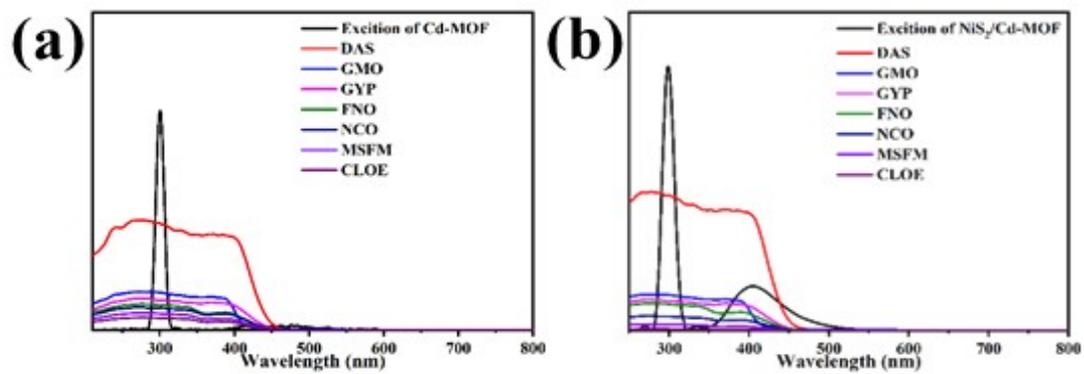


Fig.S5. Proposed fluorescence(FL) sensing mechanism of DAS using (a) **Cd-MOF** and (b) **NiS₂/Cd-MOF**

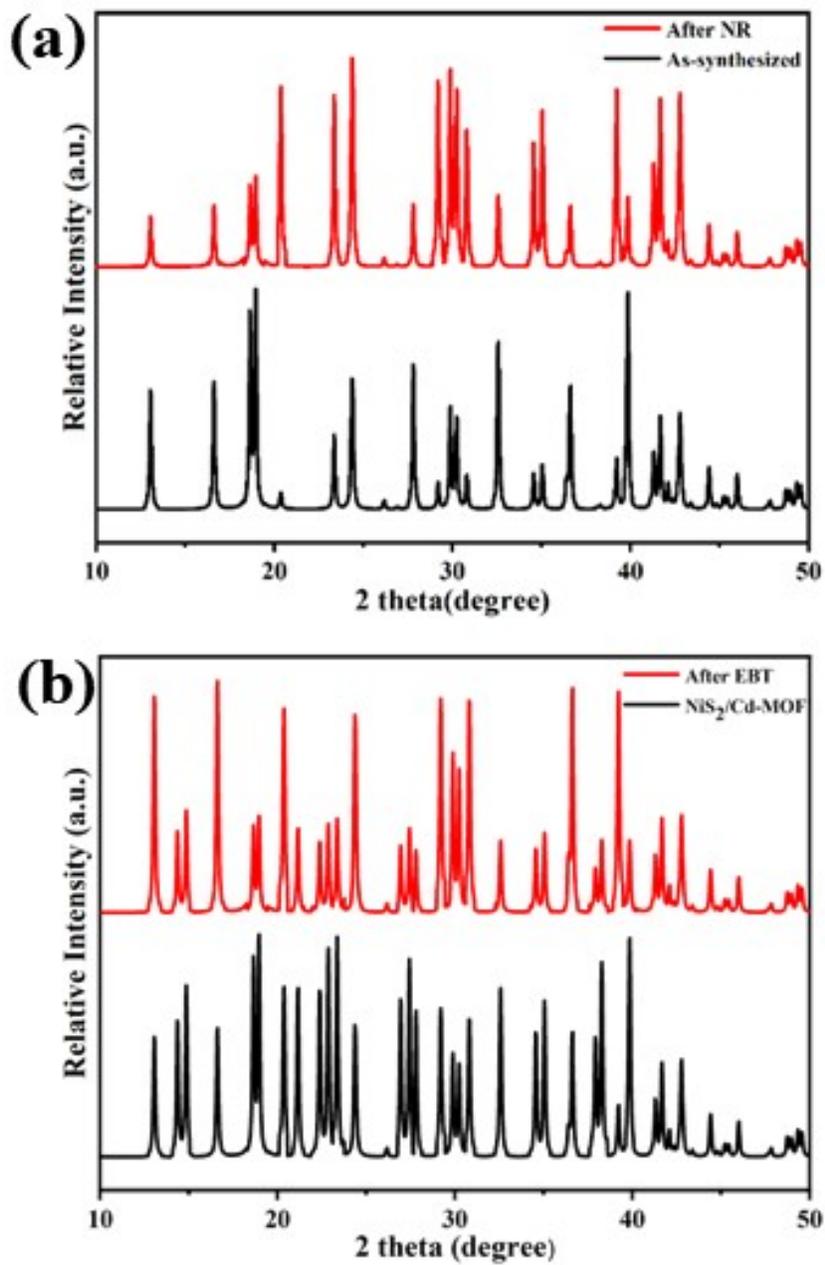


Fig.S6. PXRD patterns of (a) Cd-MOF after the degradation of NR and (b) NiS₂/Cd-MOF after the degradation of EBT.

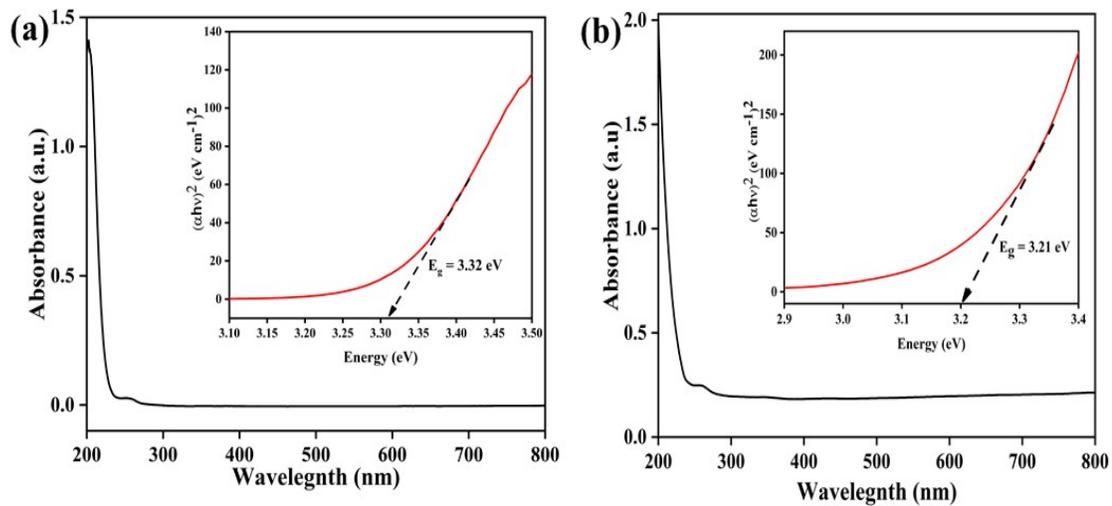


Fig.S7. UV-vis absorption spectra of (a) Cd-MOF and (b) NiS₂/Cd-MOF, with the corresponding Tauc plots shown in the insets.