

Supplementary material

Turn-on fluorescent probe toward glyphosate and Cr³⁺ based on Cd(II)-metal organic framework with Lewis basic sites

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Parameter	1	1-NH₂
Empirical formula	C ₁₈ H ₁₂ CdN ₄ O ₄	C ₁₈ H ₁₃ CdN ₅ O ₄
Formula weight	460.72	475.73
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Cmca</i>	<i>Cmca</i>
a (Å)	13.6401(5)	13.7017(6)
b (Å)	20.7509(7)	20.9274(8)
c (Å)	14.4681(5)	14.7410(7)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å ³)	4095.1(2)	4226.8(3)
Z	8	8
D _{calc} (gcm ⁻³)	1.495	1.495
Data/res/parameters	2538/173/151	2258/183/157
GOF on F ²	0.794	0.902
R ₁ ^a , wR ₂ ^b [I > 2σ(I)]	0.0375/0.1063	0.0449/0.1419
R ₁ ^a , wR ₂ ^b (all data)	0.0448/0.1117	0.0614/0.1518

Table S1 Crystallographic data and structural refinement for **1** and **1-NH₂**

$${}^aR_1 = \sum \|F_0\| - \|F_c\| / \sum \|F_0\|, {}^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

Table S2 Selected bond distances (Å) and angle (°) for compound **1**

	Distances (Å)
Cd1—O2	2.300(3)
Cd1—N1	2.320(3)
Cd1—N1 ¹	2.320(3)
Cd1—O1 ²	2.346(4)
Cd1—O4 ³	2.365(3)
Cd1—O3 ³	2.393(3)
Cd1—O3 ³	2.607(3)
	Angles (°)
O2—Cd1—N1	92.97(9)
O2—Cd1—N1 ¹	92.97(9)
N1—Cd1—N1 ¹	170.43(17)
O2—Cd1—O1 ²	130.10(11)
N1—Cd1—O1 ²	85.22(8)
N1 ¹ —Cd1—O1 ²	85.21(8)
O2—Cd1—O4 ³	84.71(12)
N1—Cd1—O4 ³	94.01(8)
N1 ¹ —Cd1—O4 ³	94.01(8)
O1 ² —Cd1—O4 ³	145.18(11)
O2—Cd1—O3 ³	139.75(11)
N1—Cd1—O3 ³	90.16(8)
N1 ¹ —Cd1—O3 ³	90.15(8)
O1 ² —Cd1—O3 ³	90.15(10)
O4 ³ —Cd1—O3 ³	55.03(11)
O2—Cd1—O1	52.76(11)
N1—Cd1—O1	88.81(8)
N1 ¹ —Cd1—O1	88.81(8)
O1 ² —Cd1—O1	77.34(12)
O4 ³ —Cd1—O1	137.47(11)
O3 ³ —Cd1—O1	167.49(11)

Symmetry codes: (1) $I-x, +y, +z$; (2) $I-x, I-y, I-z$; (3) $+x, -I/2+y, I/2-z$; (4) $+x, I/2+y, I/2-z$

Table S3 Selected bond distances (Å) and angle (°) for compound **1-NH₂**

	Distances (Å)
Cd1—O1	2.242(5)
Cd1—O2 ¹	2.326(6)
Cd1—O4 ²	2.327(5)
Cd1—N1 ³	2.340(5)
Cd1—N1	2.340(5)
Cd1—O3 ²	2.423(5)
	Angles (°)
O1—Cd1—O2 ¹	128.61(18)
O1—Cd1—O4 ²	142.39(18)
O2 ¹ —Cd1—O4 ²	89.00(16)
O1—Cd1—N1 ³	91.69(11)
O2 ¹ —Cd1—N1 ³	85.73(11)
O4 ² —Cd1—N1 ³	91.17(10)
O1—Cd1—N1	91.69(11)
O2 ¹ —Cd1—N1	85.73(11)
O4 ² —Cd1—N1	91.17(10)
N1 ³ —Cd1—N1	171.1(2)
O1—Cd1—O3 ²	88.19(18)
O2 ¹ —Cd1—O3 ²	143.20(17)
O4 ² —Cd1—O3 ²	54.20(17)
N1 ³ —Cd1—O3 ²	94.16(11)
N1—Cd1—O3 ²	94.16(11)

Symmetry codes: (1) $I-x, -y, I-z$; (2) $+x, -I/2+y, I/2-z$; (3) $I-x, +y, +z$; (4) $+x, I/2+y, I/2-z$

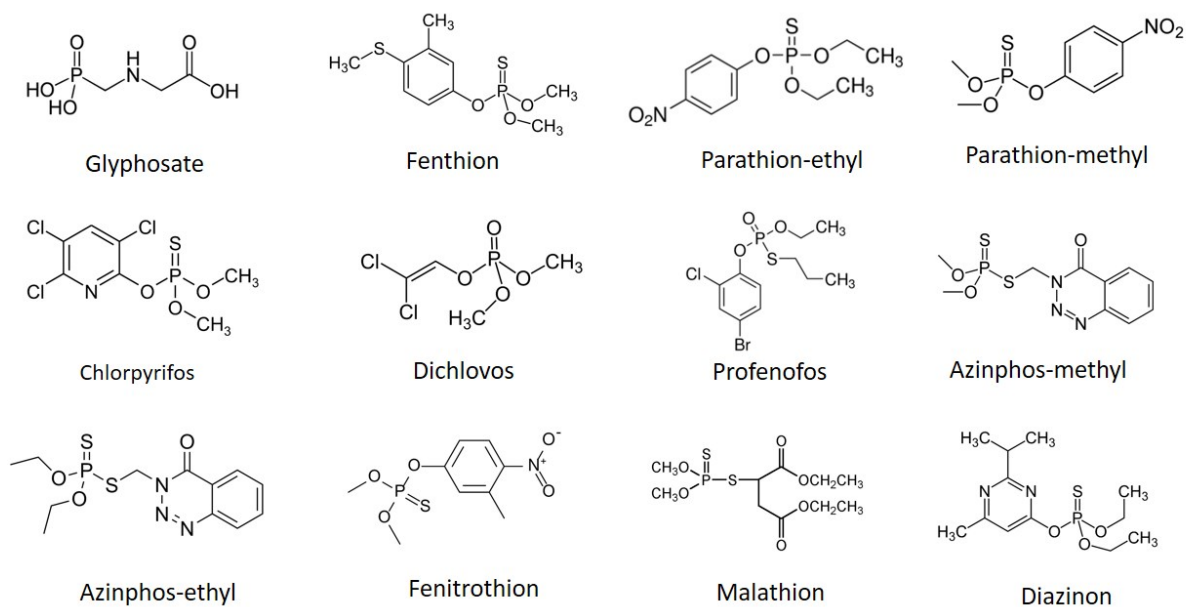


Fig. S1 Chemical structures of the selected pesticides.

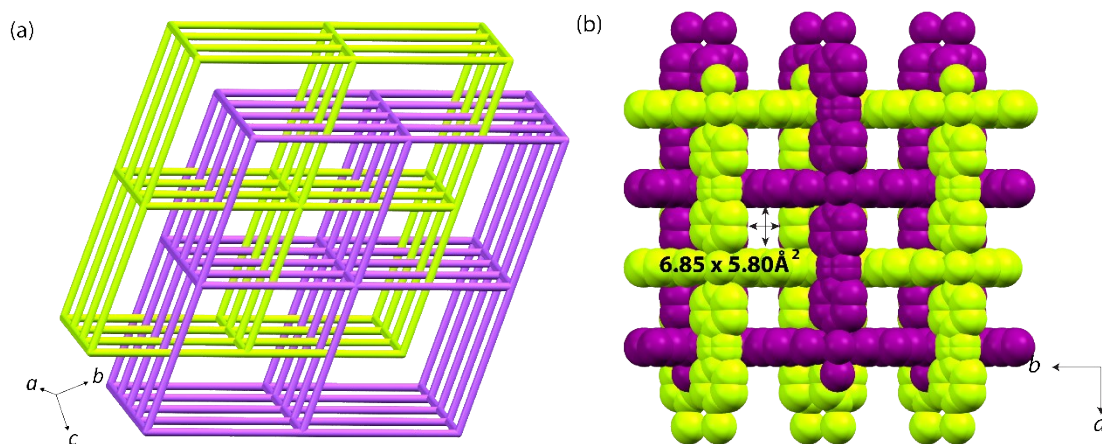


Fig. S2 (a) Topological feature of 1-NH_2 along a axis. (b) 2-fold interpenetrated 3D framework of 1-NH_2 in space filling mode.

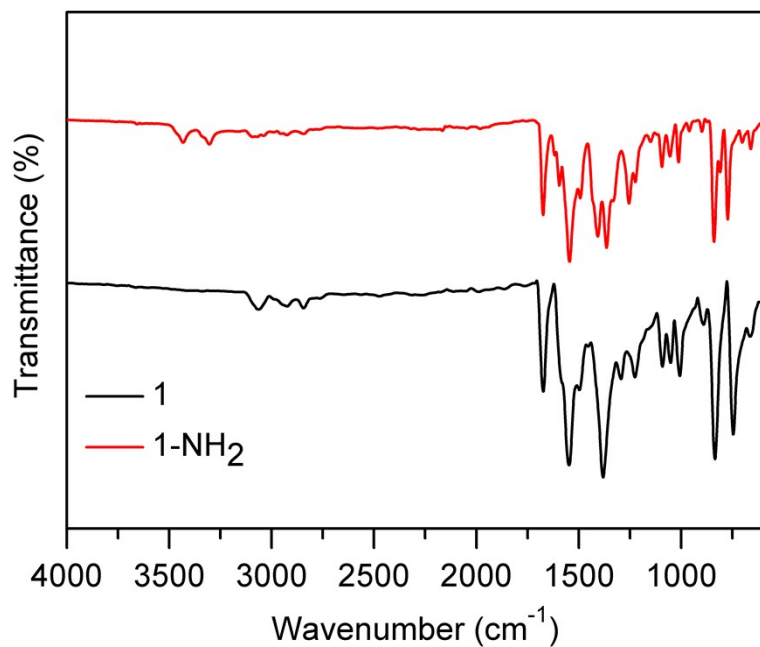


Fig. S3 FT-IR spectra of **1** and **1-NH₂**.

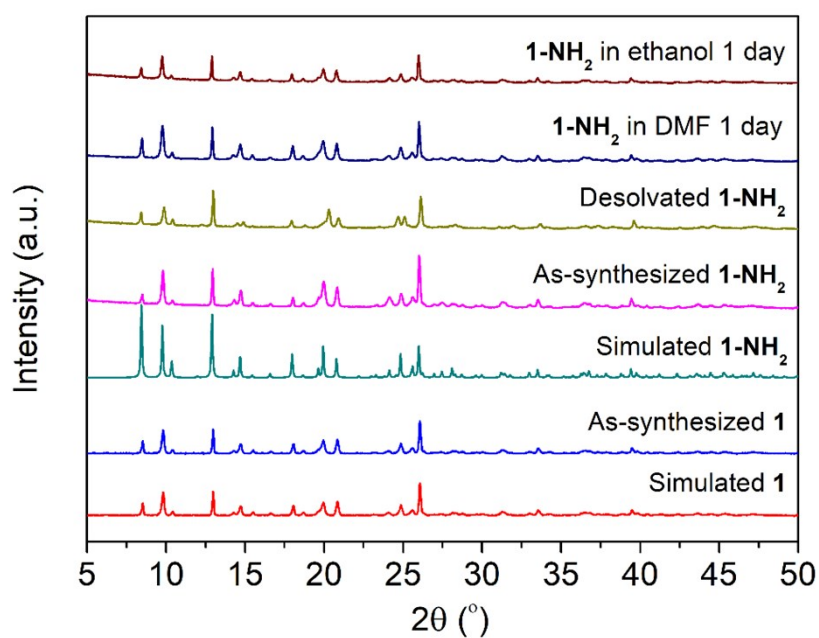


Fig. S4 PXRD patterns for the simulated and as-synthesized **1** and **1-NH₂**.

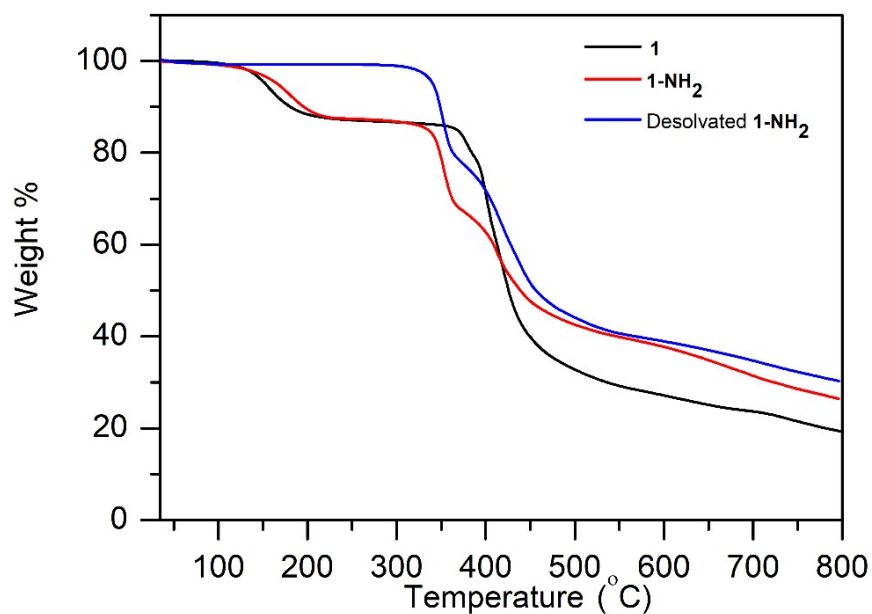


Fig. S5 TGA curves for as-synthesized **1** and **1-NH₂** and desolvated **1-NH₂**.

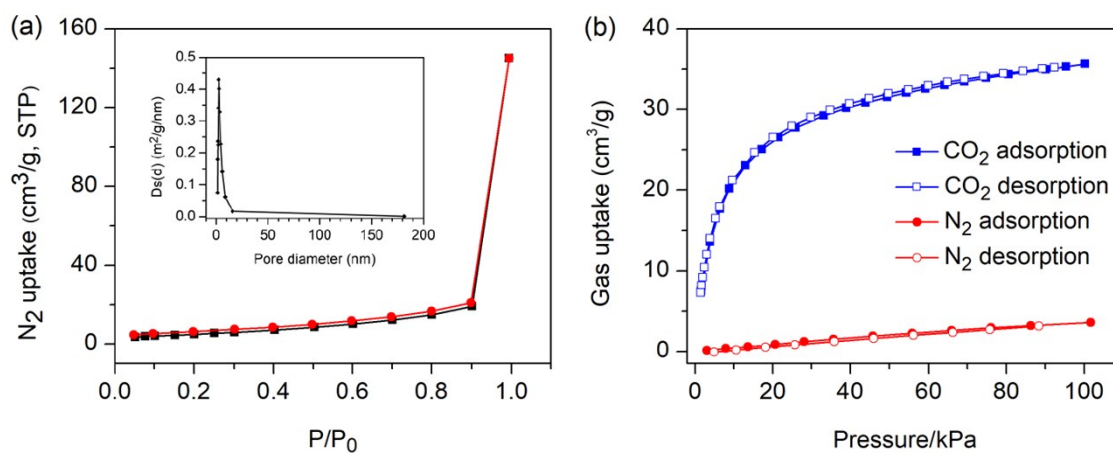


Fig. S6 (a) N₂ adsorption isotherm of desolvated **1-NH₂** at 77 K (inset: pore size distribution of desolvated **1-NH₂**) (b) Gas adsorption isotherms of desolvated **1-NH₂** at 295 K.

Table S4 Calculation of standard deviation of fluorescence intensity for glyphosate sensing

Blank reading (only 1-NH₂)	Fluorescent intensity at 434 nm
Reading 1	4437.849
Reading 2	4614.951
Reading 3	4526.954
Reading 4	4558.367
Reading 5	4460.107
Reading 6	4387.441
Reading 7	4377.512
Reading 8	4462.322
Reading 9	4533.827
Reading 10	4670.202
Standard deviation (δ)	95.4051
Slope from calibration graph (m)	11375.0506
LOD ($3\delta/m$)	0.025 μ M

Table S5 Fluorescent sensor for glyphosate detection based on MOF and other fluorescent materials

Fluorescent material	Fluorescent response	Mechanism	LOD	Ref.
MOFs				
Fe ₃ O ₄ @SiO ₂ @UiO-67	Enhancement	Electron transfer	1 μM	[1]
[Cd(NH ₂ -bdc)(azp)]·DMF	Enhancement	Structural dissociation inhibited PET	25 nM	This work
Other fluorescent materials				
IgG-Carbon dot	Enhancement	Immune Reaction	47 nM	[2]
Carbon dot	Enhancement	Competitive affinity	95 nM	[3]
Carbon dot	Quenching	Fluorescent-resonance energy transfer	0.6 μM	[4]
Graphene quantum dots-silver nanoparticles	Quenching	Reduction of metal-enhanced fluorescence	53 nM	[5]
Calixarene-grafted Ruthenium(II)bipyridine Doped Silica NPs	Enhancement	Switch on FRET	0.79 μM	[6]

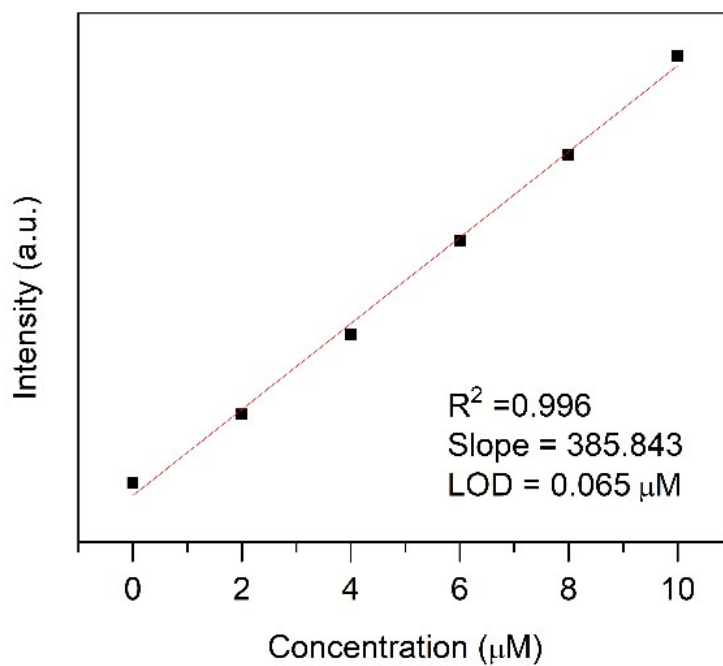


Fig. S7 The linear enhancement response of bulk phase **1-NH₂** toward glyphosate.

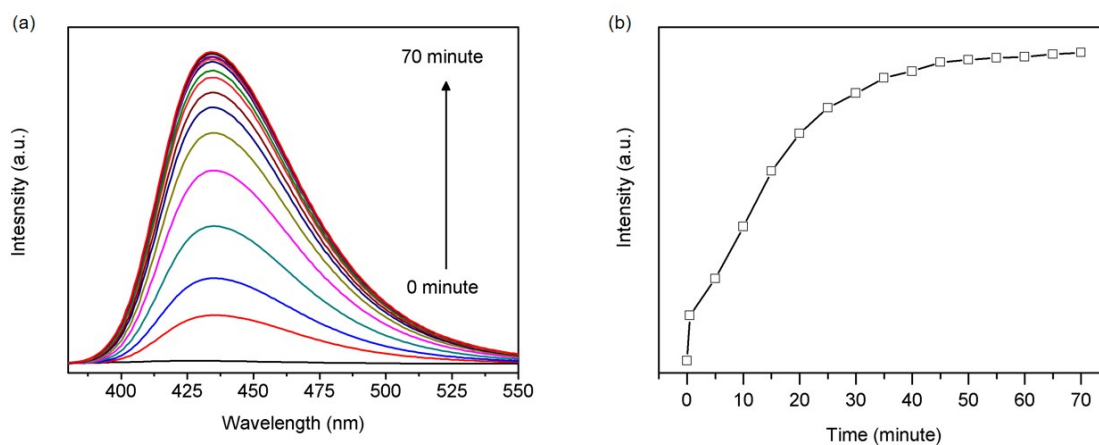


Fig. S8 (a) Fluorescence response of **1-NH₂** toward glyphosate at different times.

b) Plot of time dependent fluorescence intensity at 434 nm.

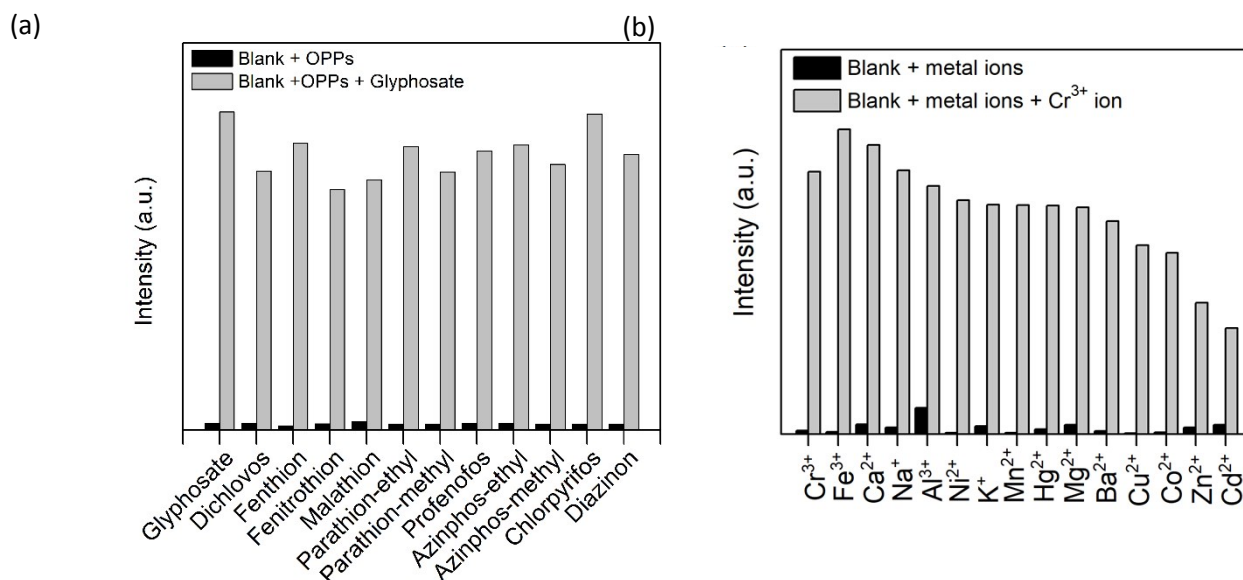


Fig. S9 (a) Fluorescent intensity response of **1-NH₂** at 434 nm in the presence of the selected OPPs (black bar) and **1-NH₂** + glyphosate upon the addition of interferent OPPs (gray bar) (total concentration of OPPs is 50 μ M). (b) Fluorescent intensity response of **1-NH₂** at 434 nm in the presence of the selected metal ions (black bar) and **1-NH₂** + Cr³⁺ upon the addition of interferent cations (gray bar) (total concentration of metal ions is 50 μ M).

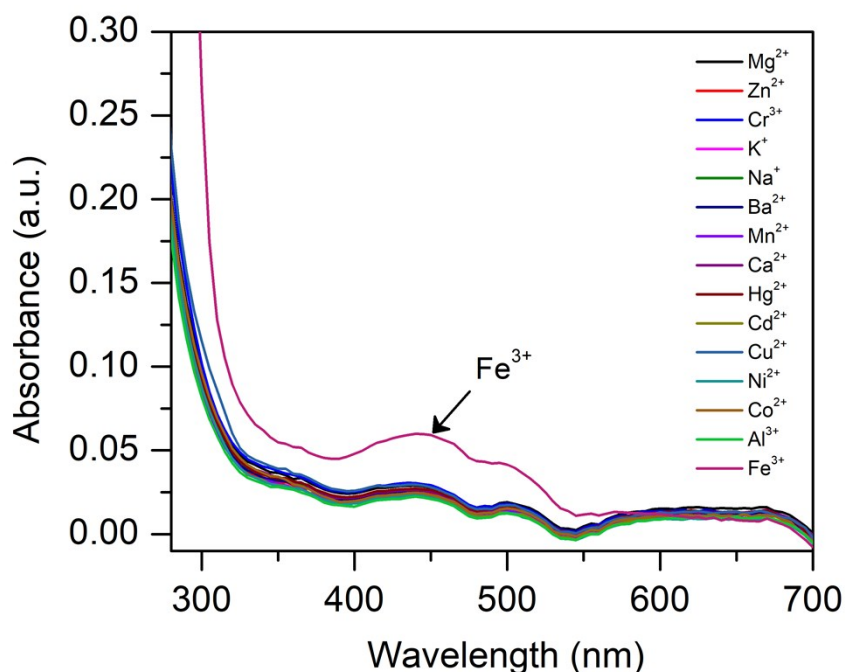


Fig. S10 UV-Vis absorption spectra of different metal ions in DMF.

Table S6 Calculation of standard deviation of fluorescence intensity for Cr^{3+} sensing

Blank reading (only 1-NH₂)	Fluorescent intensity at 434 nm
Reading 1	751.551
Reading 2	745.172
Reading 3	726.349
Reading 4	753.238
Reading 5	707.114
Reading 6	722.223
Reading 7	726.112
Reading 8	717.274
Reading 9	728.123
Reading 10	770.443
Standard deviation (δ)	19.4889
Slope from calibration graph (m)	98.7274
LOD ($3\delta/m$)	0.60 μM

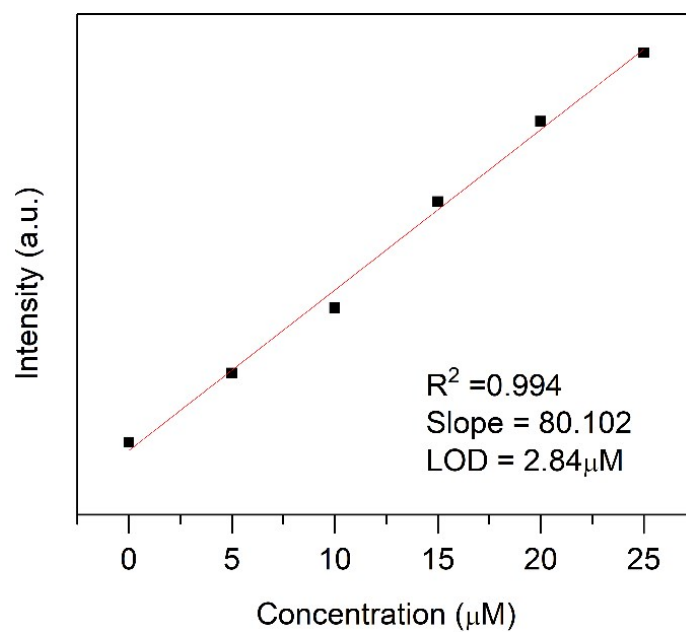


Fig. S11 The linear enhancement response of bulk phase 1-NH_2 toward Cr^{3+} .

Table S7 Fluorescent sensor for Cr³⁺ detection based on various MOFs and other fluorescent materials

Fluorescent material	Fluorescent response	Mechanism	LOD	Ref.
MOFs				
[Zn(L)(H ₂ O)]·H ₂ O	Quenching	Inner filter affect	2.44 μM	[7]
[Eu ₂ (tpbpc) ₄ ·CO ₃ ·H ₂ O]·DMF	Quenching	Inner filter affect & antenna effect inhibition	70 μM	[8]
[Zn ₂ (tpeb) ₂ (2,3-ndc) ₂]·H ₂ O	Quenching	Weak coordination	16 nM	[9]
Tb@[Cd ₄ (NDIC) ₄ (DMF) ₅ (H ₂ O)]·DMF	Quenching	Collapse of the structure	0.075 μM	[10]
[Zn ₃ (bpdc) ₂ (pdc) (DMF)]·6DMF	Quenching	Coordination inhibited energy transfer	25.1 μM	[11]
[Zn ₂ (TPOM)(NH ₂ -bdc) ₂]·4H ₂ O	Enhancement	Chelation enhanced fluorescence	4.9 μM	[12]
[Co ₃ (BIBT) ₃ (BTC) ₂ (H ₂ O) ₂]·solvents	Enhancement	Absorbance caused enhancement (ACE)	0.1 μM	[13]
[Cd(NH ₂ -bdc)(azp)]·DMF	Enhancement	Structural dissociation inhibited PET	0.6 μM	This work
Other fluorescent materials				
TGA-CdSe QDs	Quenching	Coordination modified valence band and conduction band energies	11.3 nM	[14]
RDC-1	Enhancement	Internal charge transfer	17.8 nM	[15]
Coumarin–Pyrazolone	Quenching	Nonfluorescent complex formation	37 pM	[16]
Gold nanoparticle	Enhancement	Aggregation induced emission	0.02 μM	[17]
PIN/CDS nanocomposite	Enhancement	Chelation enhanced fluorescence	0.47 μM	[18]

L = 5-(2-methylpyridin-4-yl)isophthalate; tpbpc = 4'-[4,2';6',4'']-terpyridin-4'-yl-biphenyl-4-carboxylate; tpeb = 1,3,5-tri-4-pyridyl-1,2-ethenylbenzene; 2,3-ndc = 2,3-naphthalenedicarboxylic acid; NDIC = 5-(5-norbornene-2,3-dicarboximide)isophthalic acid; bpdc = 4,4'-biphenyldicarboxylic acid; pdc = pyridine-3,5-dicarboxylate, TPOM = tetrakis(4-pyridyloxymethylene)methane)

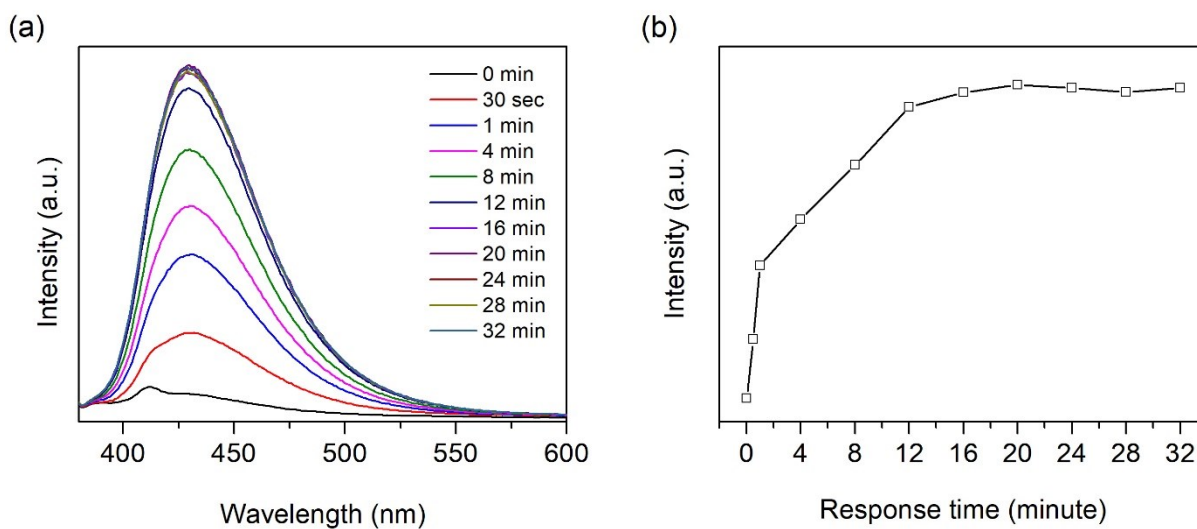


Fig. S12 (a) Fluorescence response of **1-NH₂** toward Cr³⁺ ion (20 μ M) at 0-32 min.
 (b) Plot of time dependent fluorescence intensity at 434 nm.

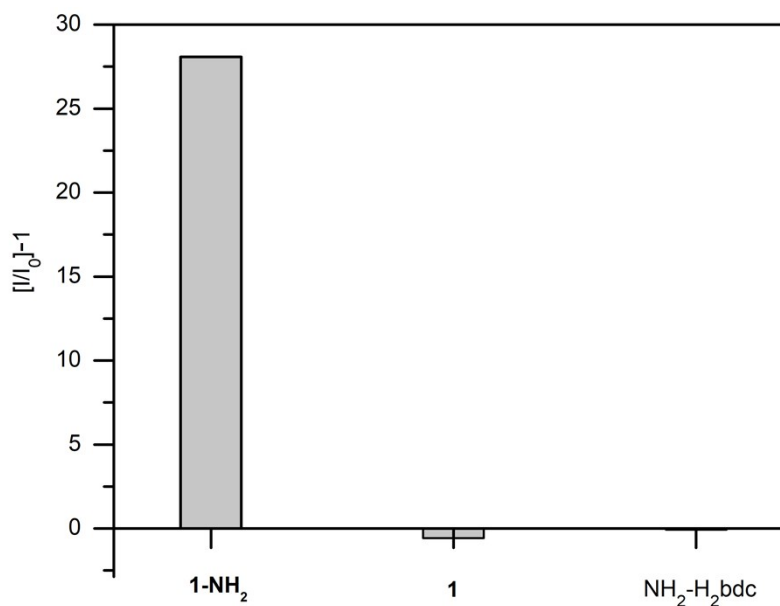


Fig. S13 The fluorescent response of **1-NH₂**, **1** and free NH₂-H₂bdc with the addition of 50 μ M Cr³⁺ ion.

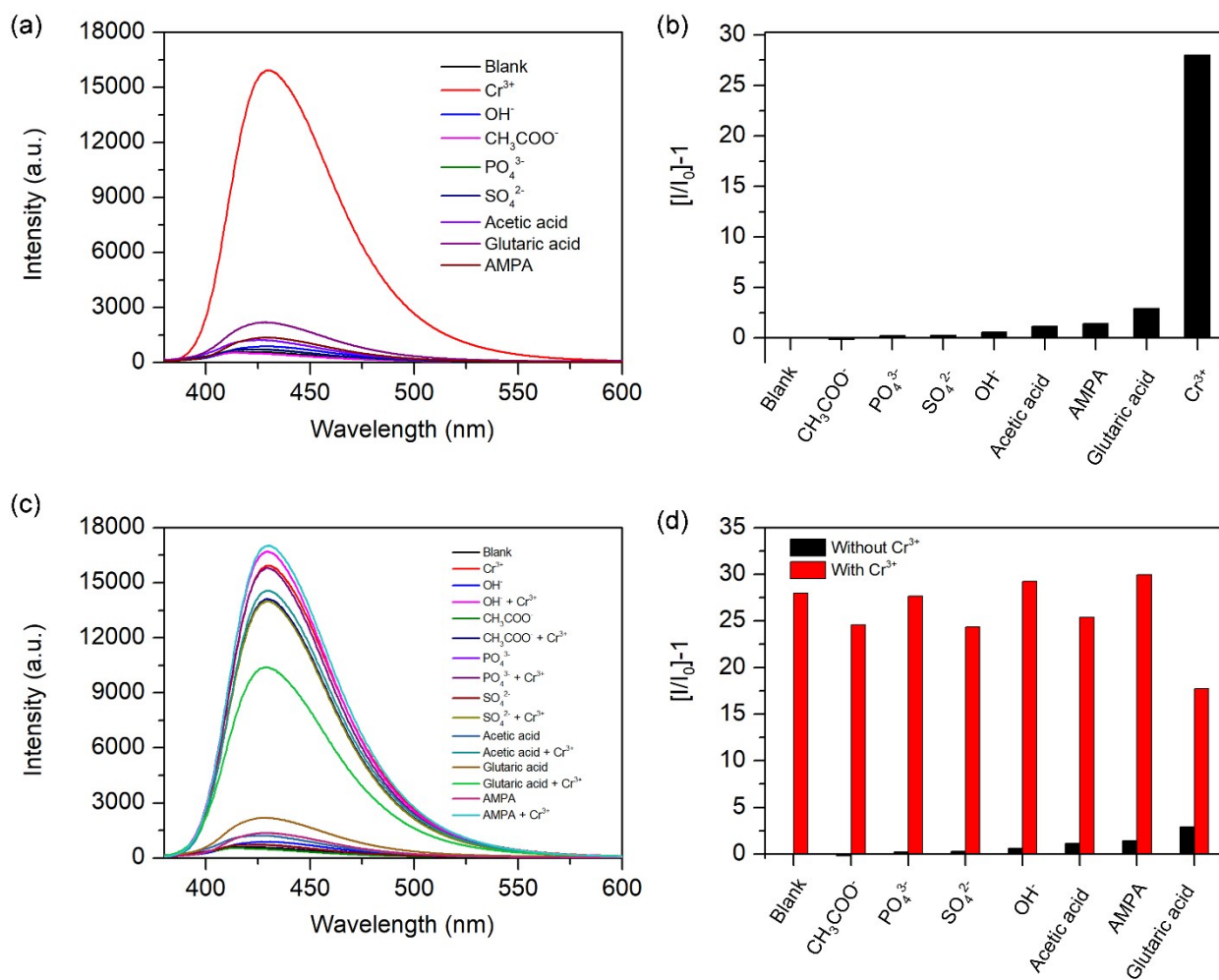


Fig. S14. (a) Fluorescent spectra and (b) fluorescent intensities of 1-NH₂ in the presence of 50 μM of different interfering species with respect to the emission at 434 nm in DMF media. (c) Fluorescent spectra and (d) fluorescent intensities of 1-NH₂ the presence of the interfering species without Cr³⁺ (black bar) and with Cr³⁺ (red bar).

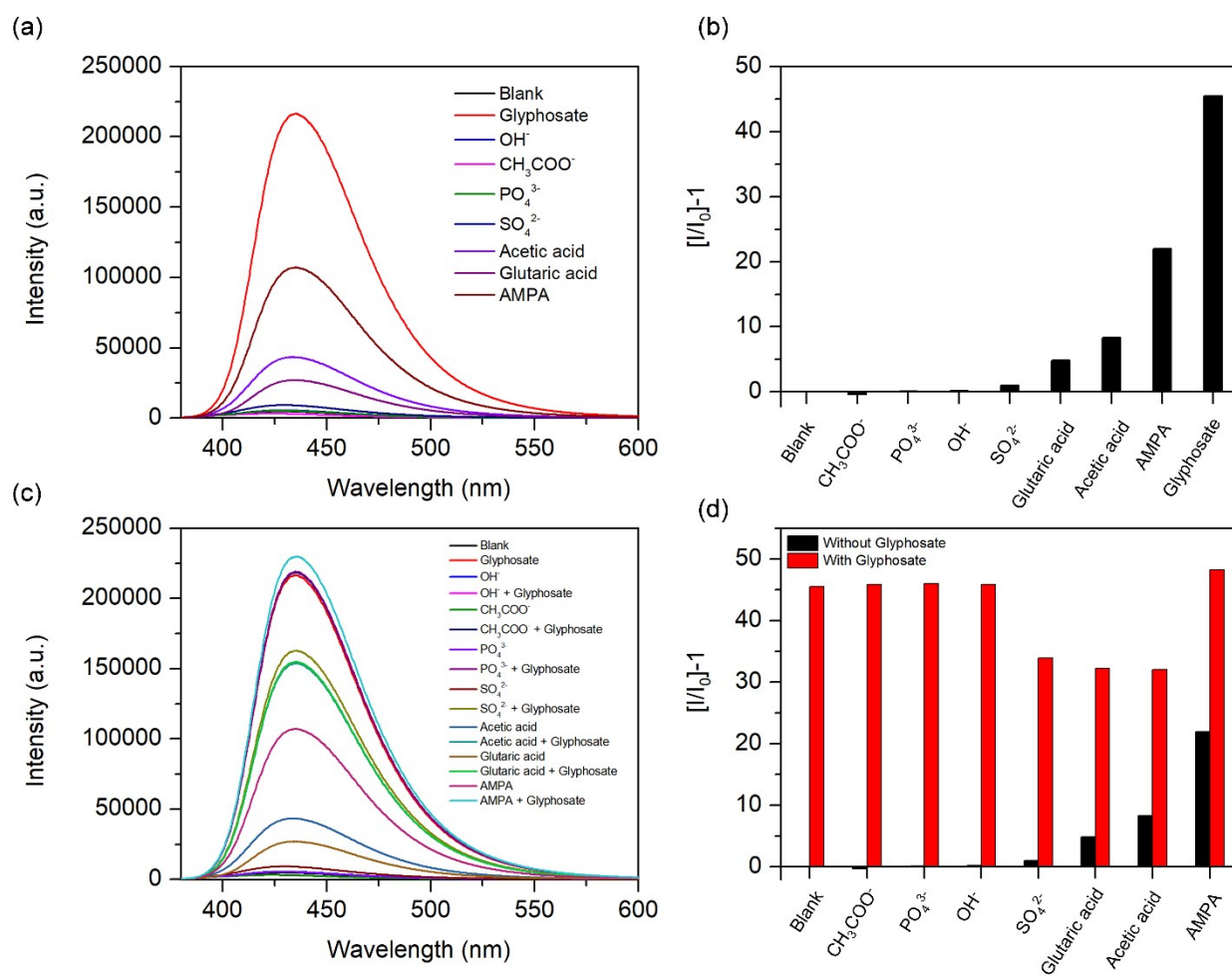


Fig. S15. (a) Fluorescent spectra and (b) fluorescent intensities of **1-NH₂** in the presence of 50 μM of different interfering species with respect to the emission at 434 nm in ethanol media. (c) Fluorescent spectra and (d) fluorescent intensities of **1-NH₂** the presence of the interfering species without glyphosate (black bar) and with glyphosate (red bar).

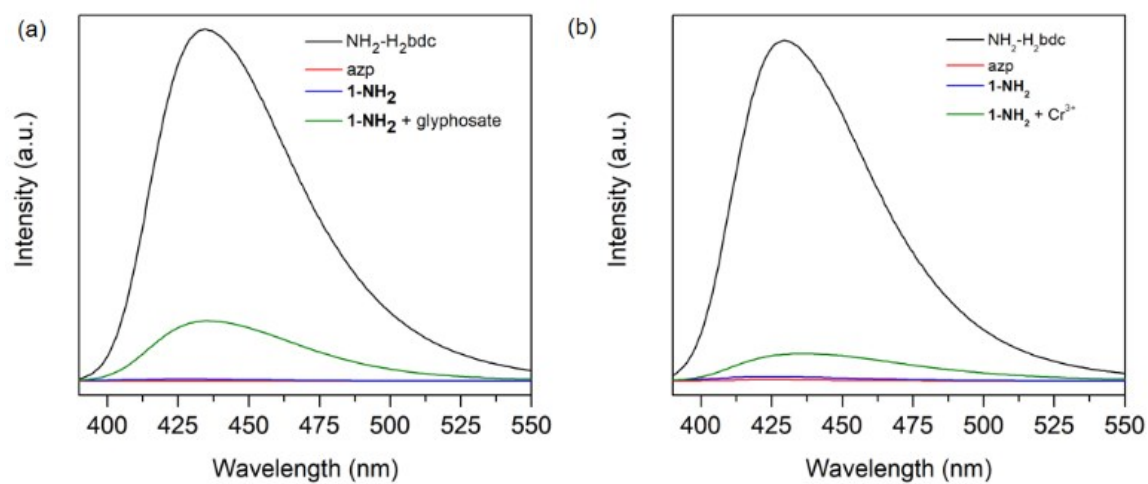


Fig. S16 Fluorescent emission of $\text{NH}_2\text{-H}_2\text{bdc}$, azp ligand, 1-NH_2 , and $1\text{-NH}_2 + \text{glyphosate}$ in ethanol media (a) and $\text{NH}_2\text{-H}_2\text{bdc}$, azp ligand, 1-NH_2 , and $1\text{-NH}_2 + \text{Cr}^{3+}$ in DMF.

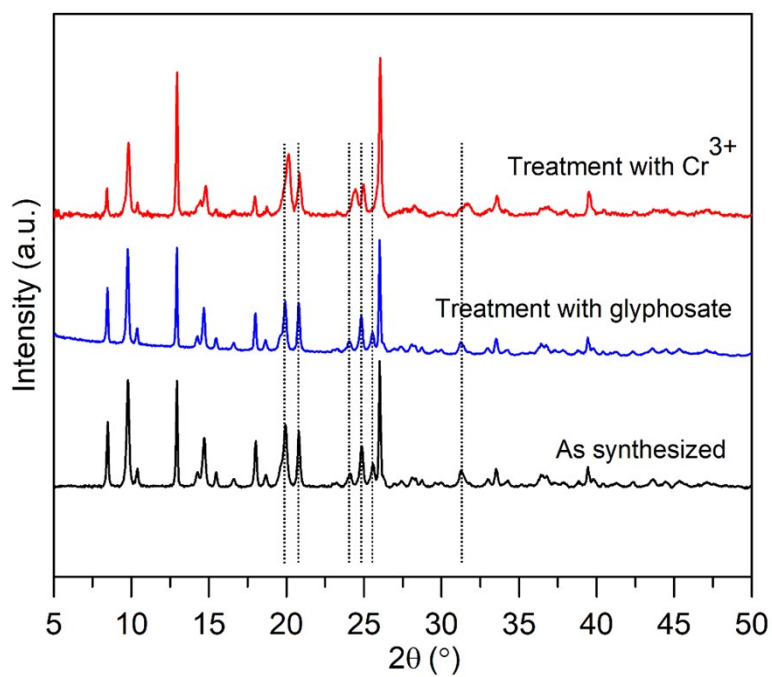


Fig. S17 PXRD patterns of as-synthesized and 1-NH_2 treated with Cr^{3+} for 1 day.

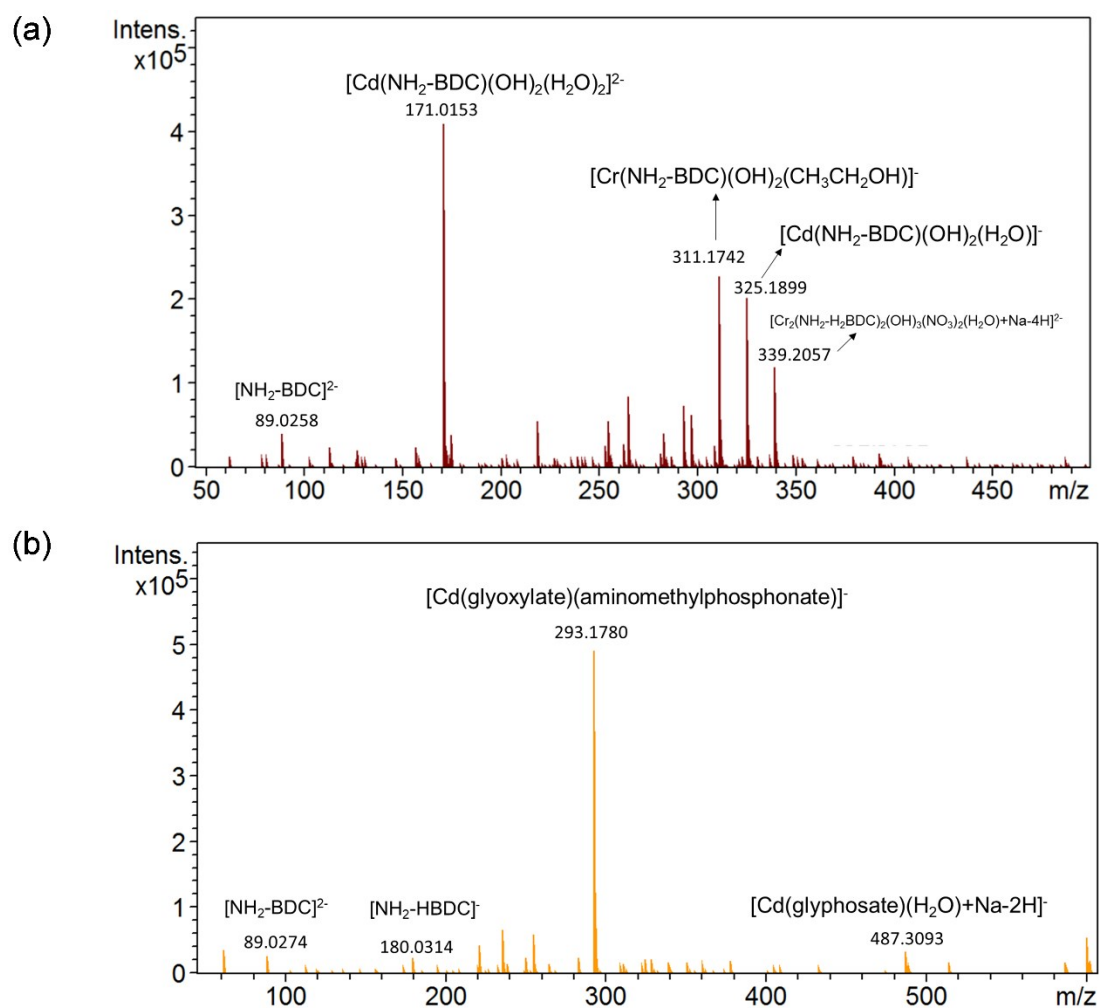


Fig. S18 ESI-MS spectra of **1-NH₂** upon the addition of (a) Cr^{3+} and (b) glyphosate.

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