

Electronic Supplementary Information

Guanidine-based dual-responsive 'turn on' fluorometric probes for the selective detection of Zn²⁺ cation and F⁻ anion: Spectral and theoretical investigations, smartphone assisted colorimetric detection, and applications in bio-imaging of *Artemia salina* animal model and molecular logic gate operation

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Table S1 Selected bond length (Å) values of the probe P1, and upon interaction with Zn²⁺ and F⁻ ions (P1 + Zn²⁺/F⁻).

Parameters	P1	P1 + Zn ²⁺	P1 + F ⁻
C5–O11	1.365	1.321	–
C9–N13	1.290	1.689	–
C16–N36	1.282	1.702	–
N19–C20	1.301	1.687	–
C23–O30	1.373	1.582	–
N14–H15	1.015	–	1.019
N17–H18	1.012	–	1.540

Table S2 Selected bond length (Å) values of the probe P2, and upon interaction with Zn^{2+} and F^- ions ($\text{P2} + \text{Zn}^{2+}/\text{F}^-$).

Parameters	P2	$\text{P2} + \text{Zn}^{2+}$	$\text{P2} + \text{F}^-$
C3–O7	1.381	1.322	–
C8–N9	1.298	1.669	–
C11–N13	1.277	1.775	–
N14–C15	1.301	1.698	–
C17–O22	1.369	1.551	–
N10–H26	1.014	–	1.546
N12–H27	1.015	–	1.021

Table S3 Selected bond angle ($^\circ$) values of the probe P1, and upon interaction with Zn^{2+} and F^- ions ($\text{P1} + \text{Zn}^{2+}/\text{F}^-$).

Parameters	P1	$\text{P1} + \text{Zn}^{2+}$	$\text{P1} + \text{F}^-$
C6–C5–O11	118.805	126.044	–
C9–N13–N14	118.787	126.085	–
N14–C16–N36	128.463	126.083	–
N17–N19–C20	122.414	127.654	–
N13–N14–H15	123.674	–	122.851
N19–N17–H18	123.689	–	136.572
C16–N17–H18	114.981	–	115.118
C16–N14–H15	118.297	–	119.838

Table S4 Selected bond angle ($^{\circ}$) values of the probe P2, and upon interaction with Zn^{2+} and F^{-} ions ($\text{P2} + \text{Zn}^{2+}/\text{F}^{-}$).

Parameters	P2	$\text{P2} + \text{Zn}^{2+}$	$\text{P2} + \text{F}^{-}$
C4–C3–O7	122.462	126.028	–
C8–N9–N10	120.613	126.142	–
N10–C11–N13	121.392	127.326	–
N12–N14–C15	119.924	126.320	–
N9–N10–H26	119.334	–	130.633
N14–N12–H27	119.304	–	121.022
C11–N10–H26	118.600	–	114.623
C11–N12–H27	119.057	–	118.915

Table S5 Absolute energies (in Hartree units) of the probe molecules (P1 and P2) and $\text{P1/P2} + \text{Zn}^{2+}/\text{F}^{-}$ complexes.

Parameters	Absolute energy
P1	–6151.6781
$\text{P1} + \text{Zn}^{2+}$	–9708.5758
$\text{P1} + \text{F}^{-}$	–8251.5056
P2	–1312.3711
$\text{P2} + \text{Zn}^{2+}$	–4869.2505
$\text{P2} + \text{F}^{-}$	–3412.2146

Table S6 Limit of detection of the probes (P1 and P2) towards Cu^{2+} and Fe^{3+} cations.

S. No	Probe + Cations	Limit of detection (μM)
1	P1 + Cu^{2+}	9.10
2	P1 + Fe^{3+}	4.70
3	P2 + Cu^{2+}	3.03
4	P2 + Fe^{3+}	1.97

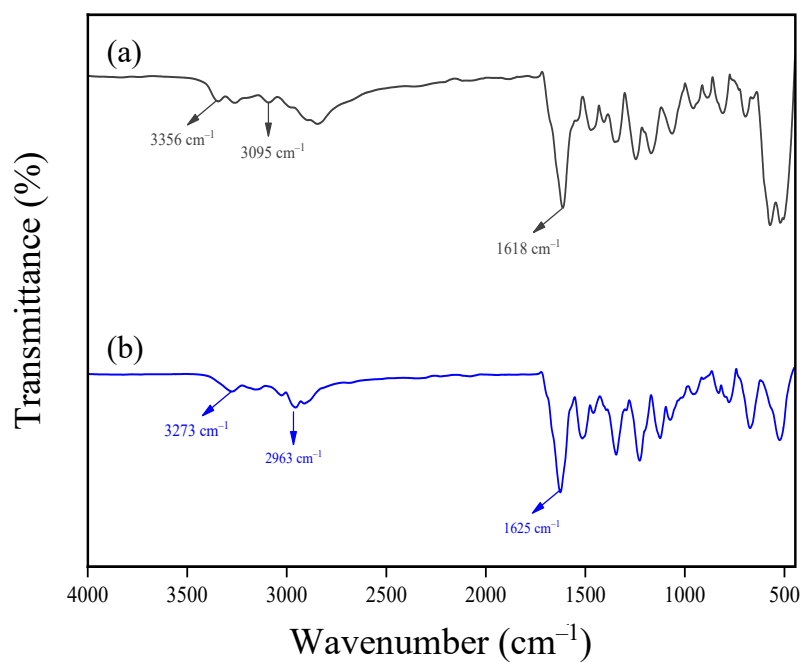


Fig. S1 FT IR spectra of the probes P1 (a) and P2 (b).

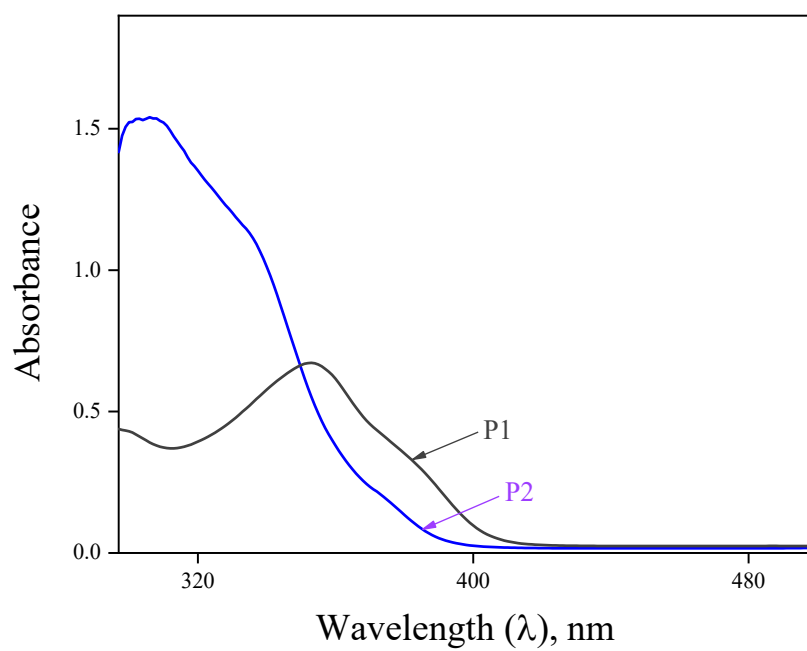


Fig. S2 UV-Vis spectra of the probes (P1 and P2).

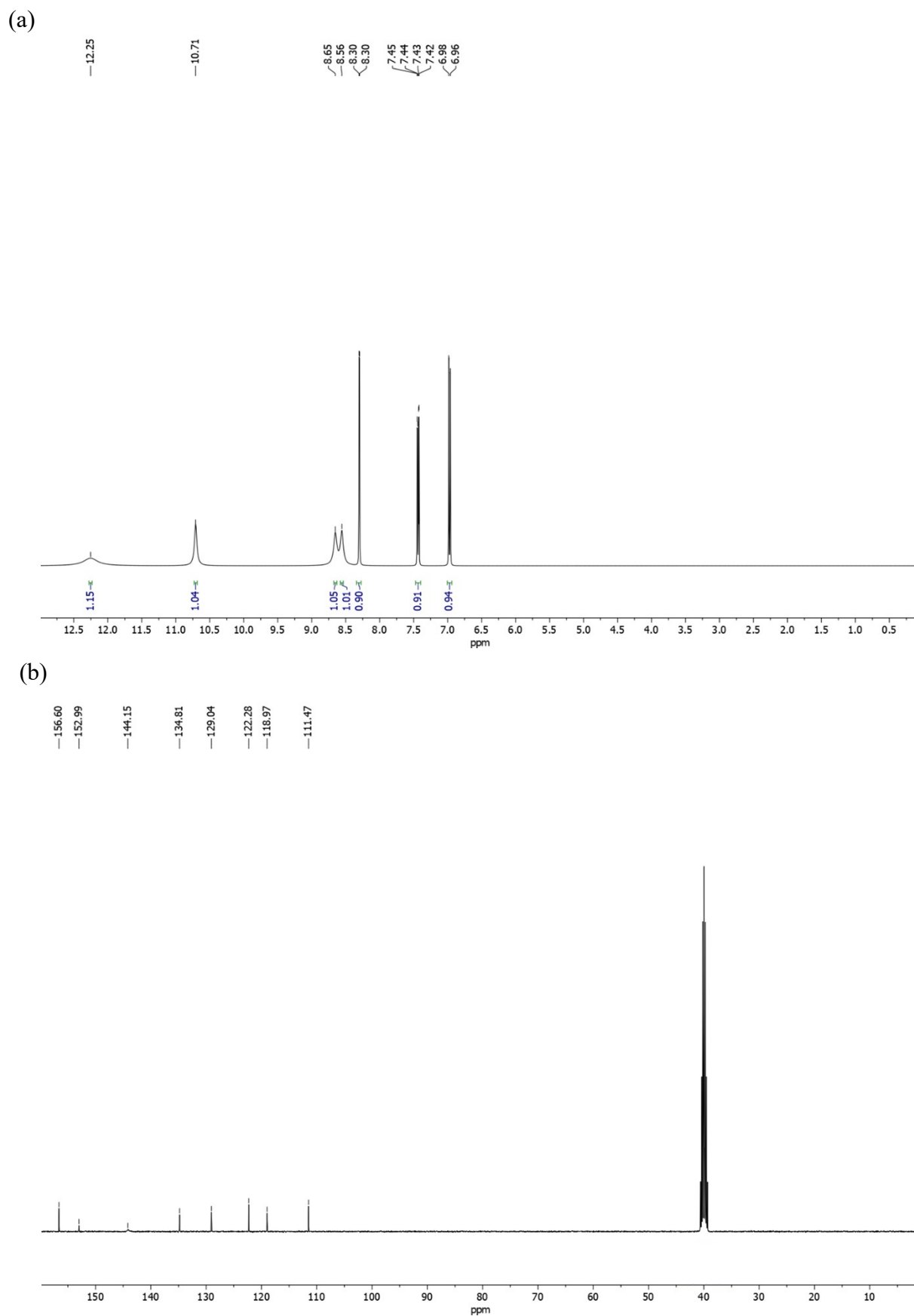
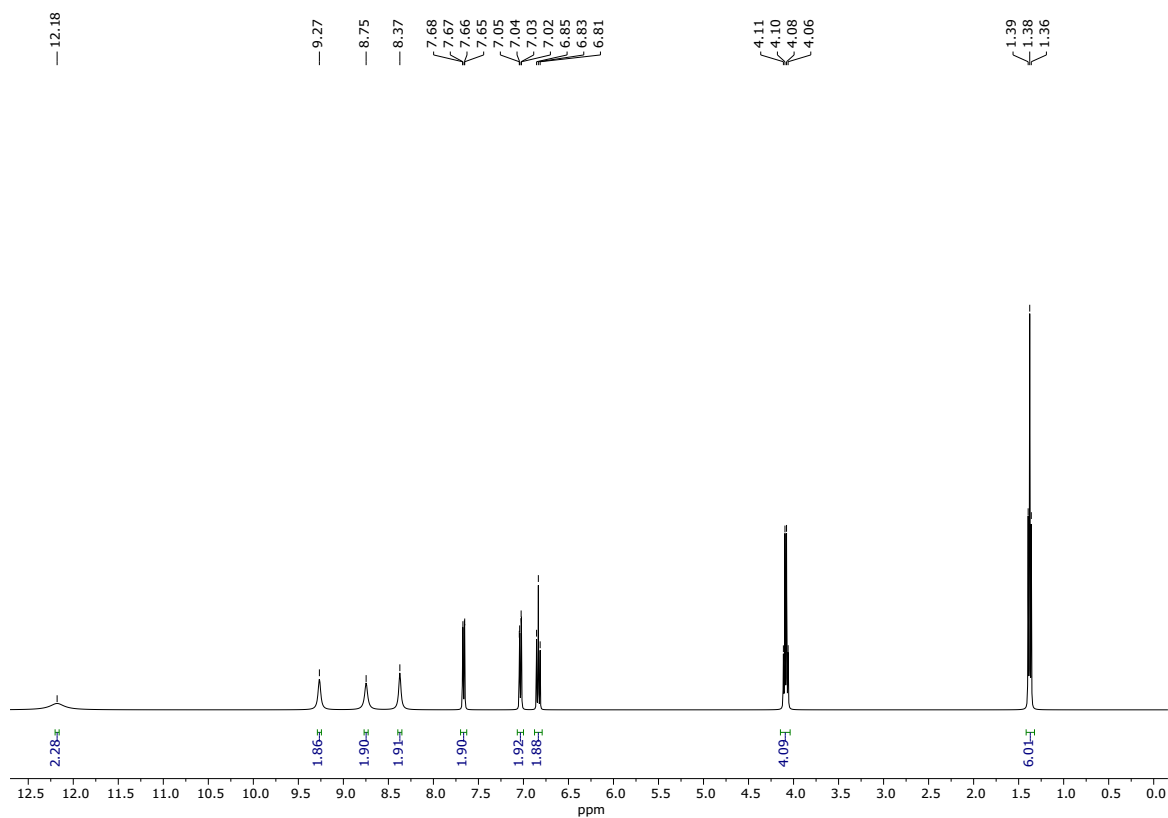


Fig. S3 ^1H (a) and ^{13}C NMR (b) spectra of the probe P1.

(a)



(b)

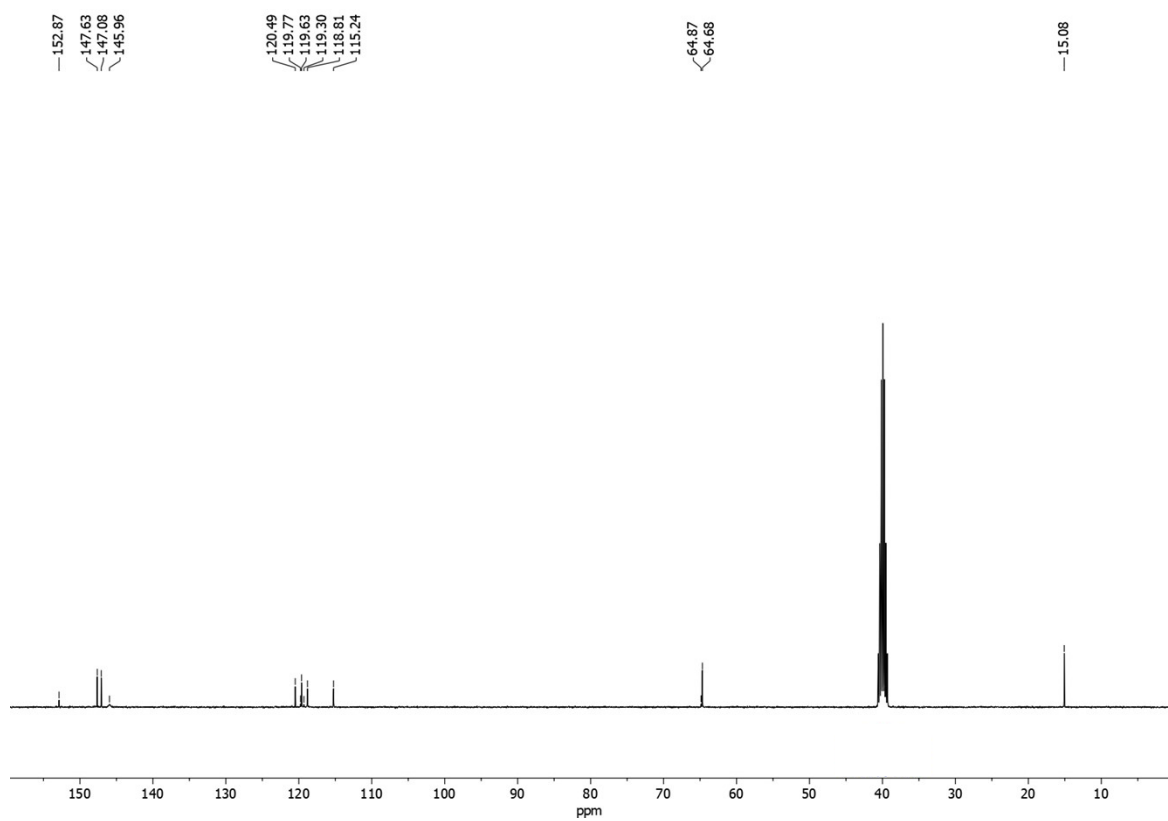
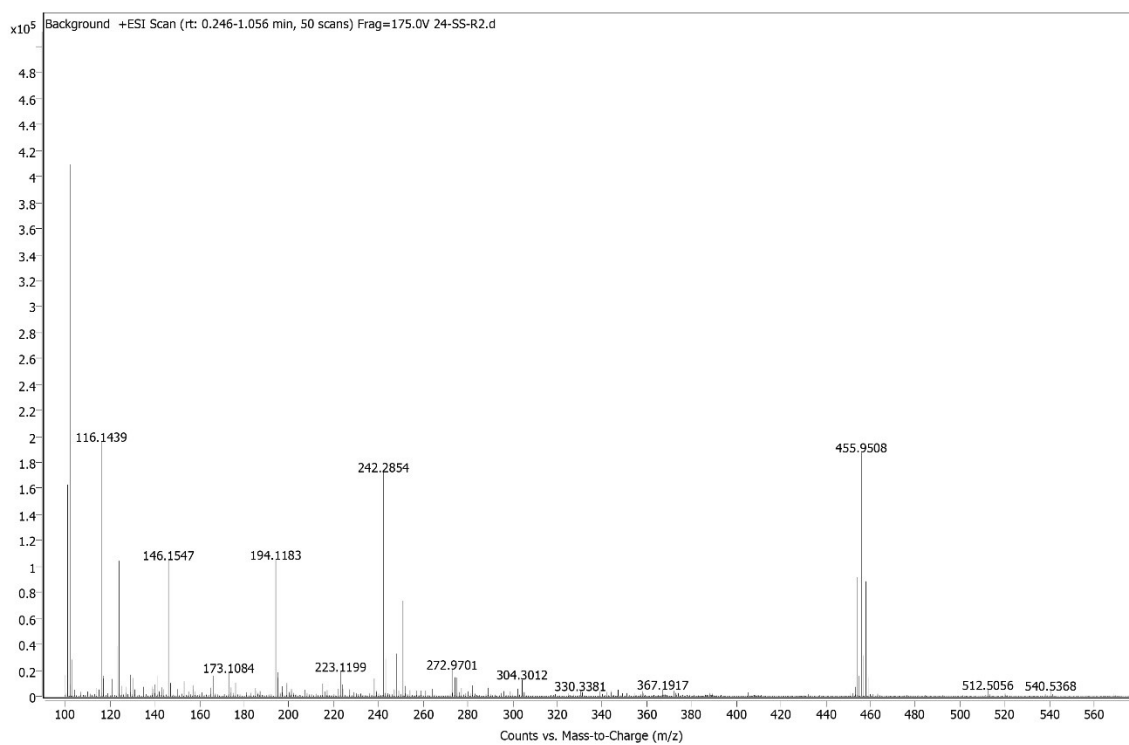


Fig. S4 ¹H (a) and ¹³C NMR (b) spectra of the probe P2.

(a)



(b)

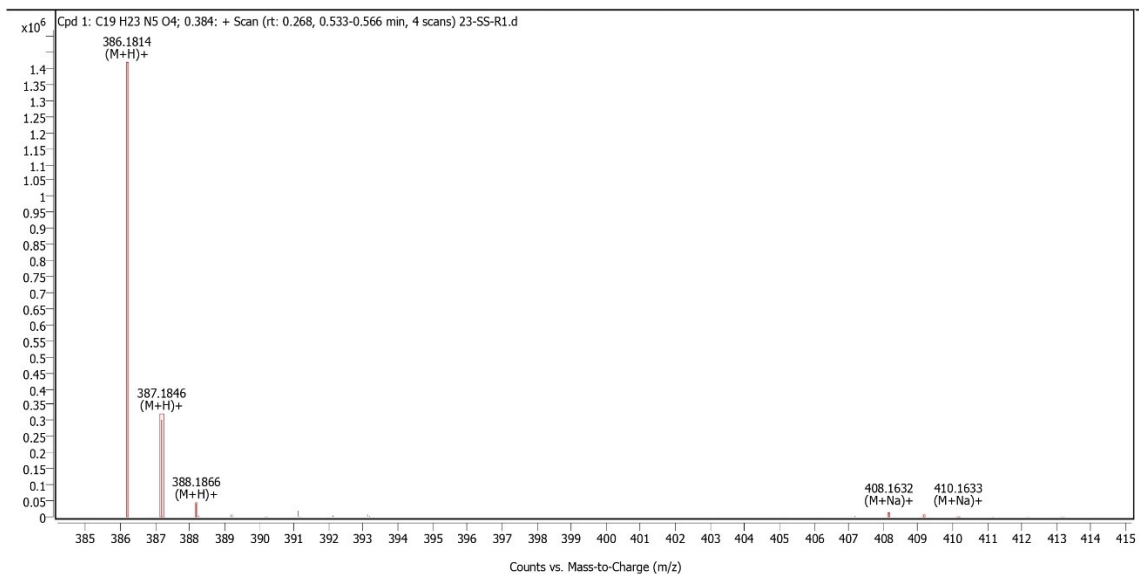


Fig. S5 ESI-MS spectra of the probes P1 (a) and P2 (b).

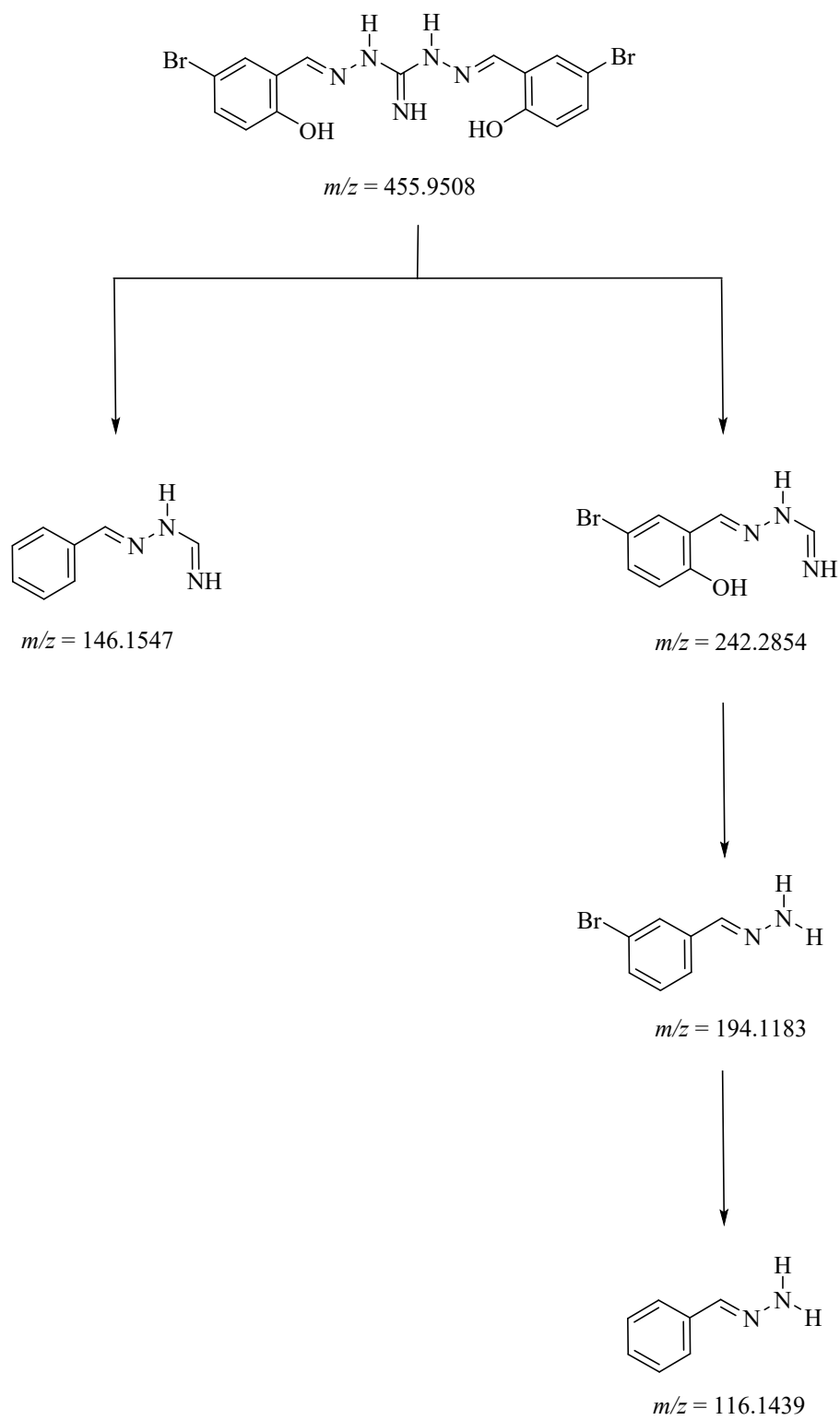


Fig. S6 Mass fragmentation pattern for the probe P1.



Fig. S7 Visual responses of P1 upon addition of different cations under ambient (a) and UV light (b) conditions, and anions under ambient (c) and UV light (d) conditions, in $\text{CH}_3\text{CN}:\text{DMSO}$ (9:1, v/v; pH 7.1) solution.



Fig. S8 Visual responses of P1 upon the addition of Cu^{2+} (a) and Fe^{3+} (b) cations, and P2 upon the addition of Cu^{2+} (c) and Fe^{3+} (d) cations in the presence of various competing metal ions under ambient light condition, in $\text{CH}_3\text{CN}:\text{DMSO}$ (9:1, v/v; pH 7.1) solution.

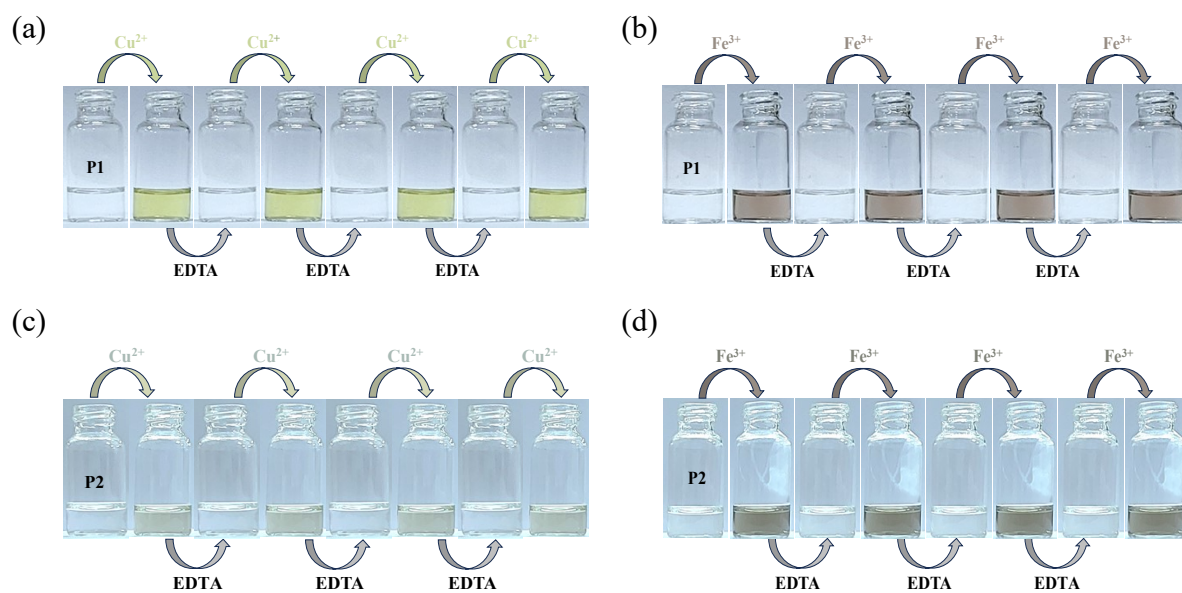


Fig. S9 Photograph showing the alternative addition of sensed ions ($\text{Cu}^{2+}/\text{Fe}^{3+}$) and EDTA: P1 upon alternative addition of Cu^{2+} (a) and Fe^{3+} (b) cations with EDTA, and P2 upon alternative addition of Cu^{2+} (c) and Fe^{3+} (d) cations with EDTA, under ambient light condition, in $\text{CH}_3\text{CN}:\text{DMSO}$ (9:1, v/v; pH 7.1) solution.

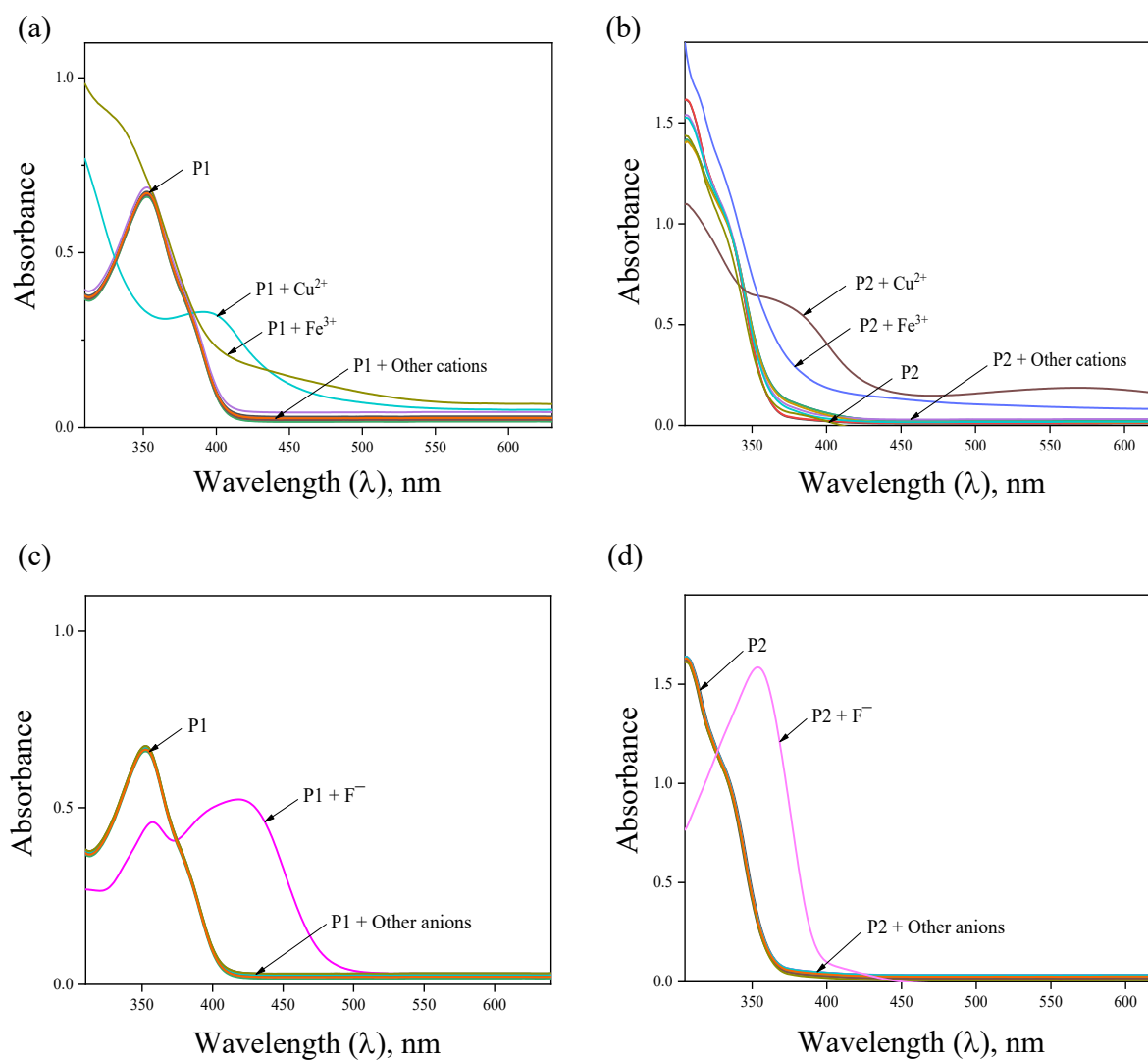


Fig. S10 Absorbance spectral changes of the probe molecules upon addition of 5 μL of different cations and anions: P1 + cations (a), P2 + cations (b), P1 + anions (c) and P2 + anions (d), in $\text{CH}_3\text{CN}:\text{DMSO}$ (9:1, v/v; pH 7.1) solution.

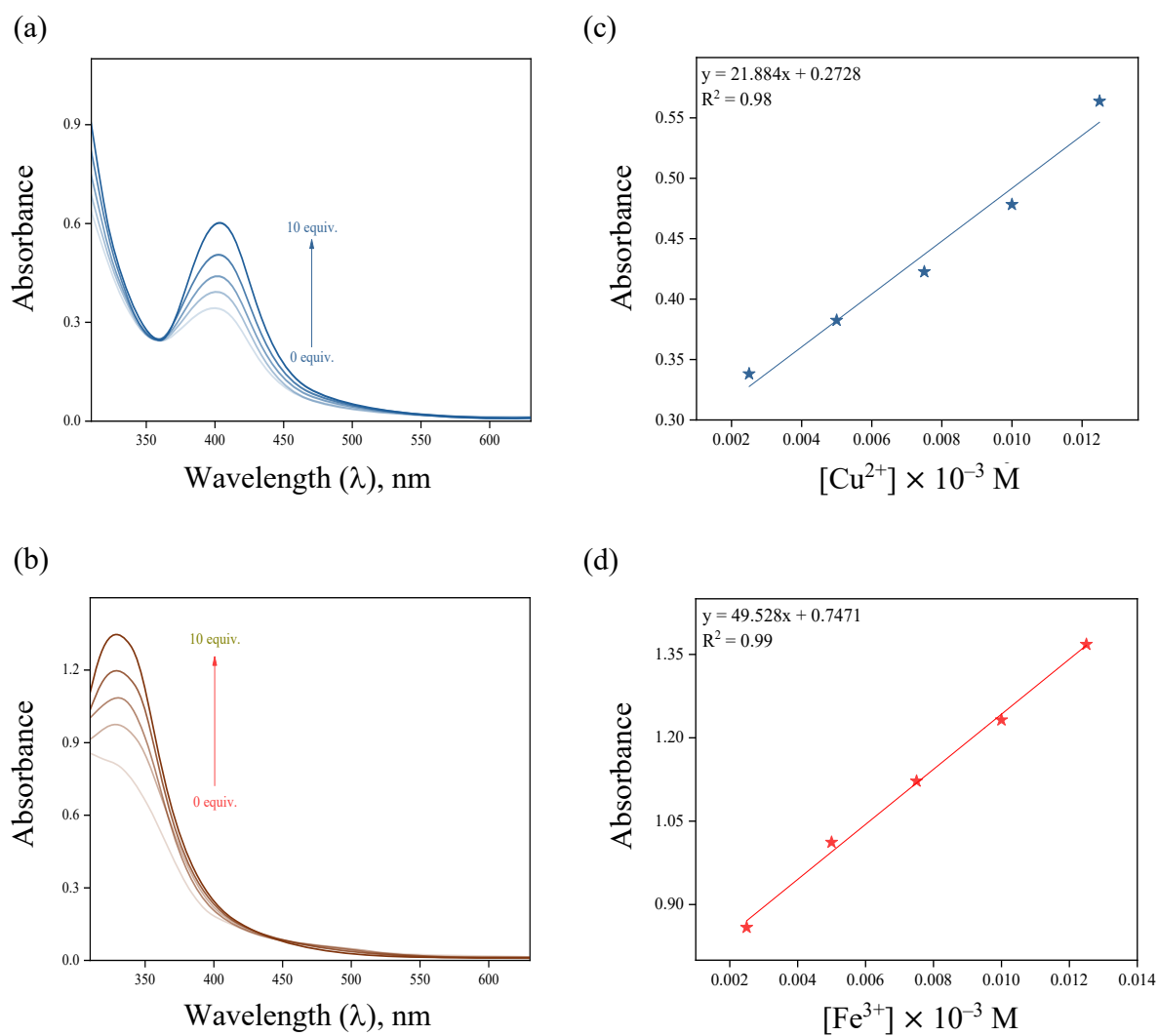


Fig. S11 Absorption spectral titrations of the probe molecule P1 on incremental addition of Cu^{2+} (a) and Fe^{3+} (b) cations, and their corresponding calibration plots (c) and (d), in $\text{CH}_3\text{CN}:\text{DMSO}$ (9:1, v/v; pH 7.1) solution.

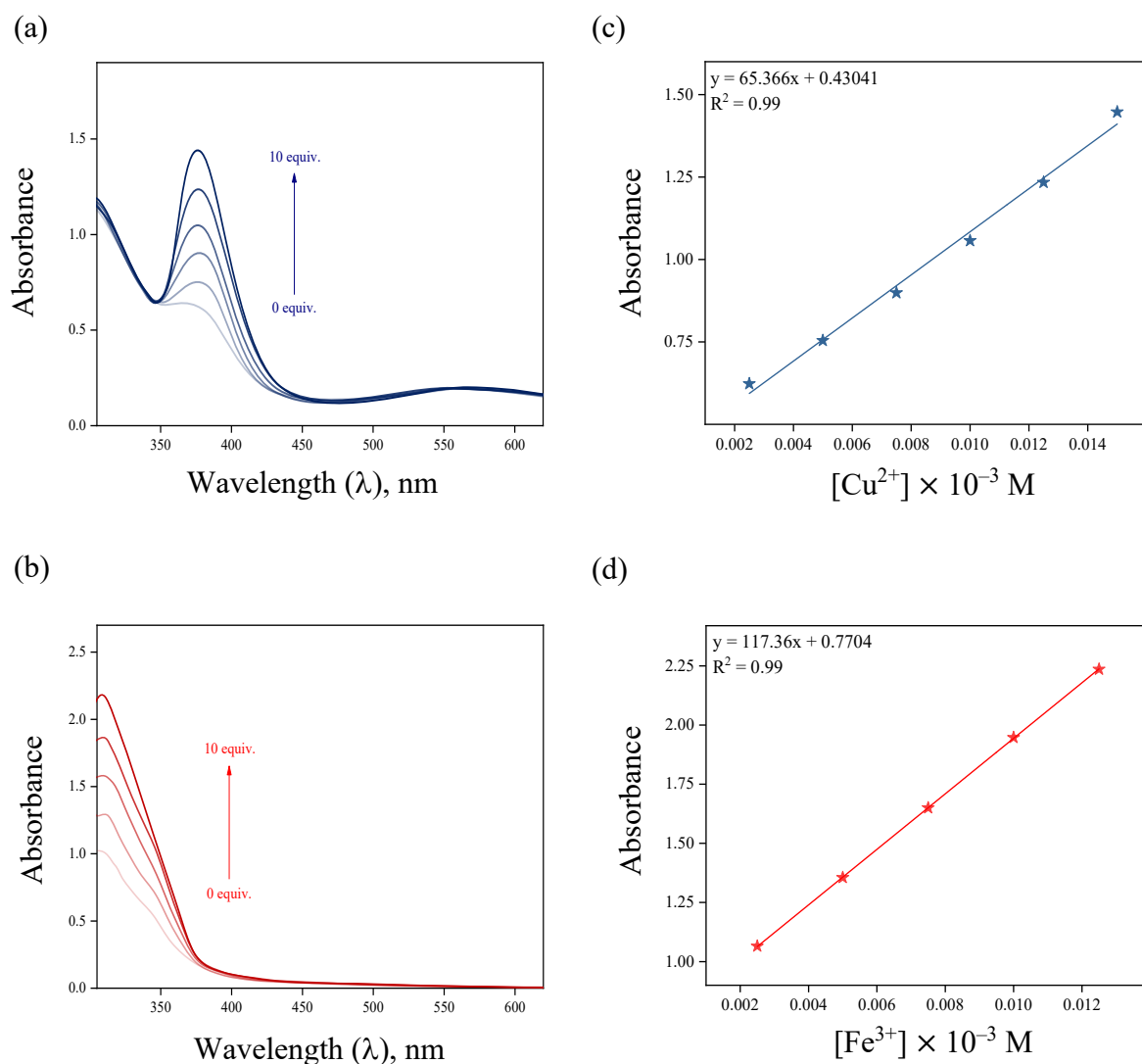


Fig. S12 Absorption spectral titrations of the probe molecule P2 on incremental addition of Cu^{2+} (a) and Fe^{3+} (b) cations, and their corresponding calibration plots (c) and (d), in $\text{CH}_3\text{CN}:\text{DMSO}$ (9:1, v/v; pH 7.1) solution.

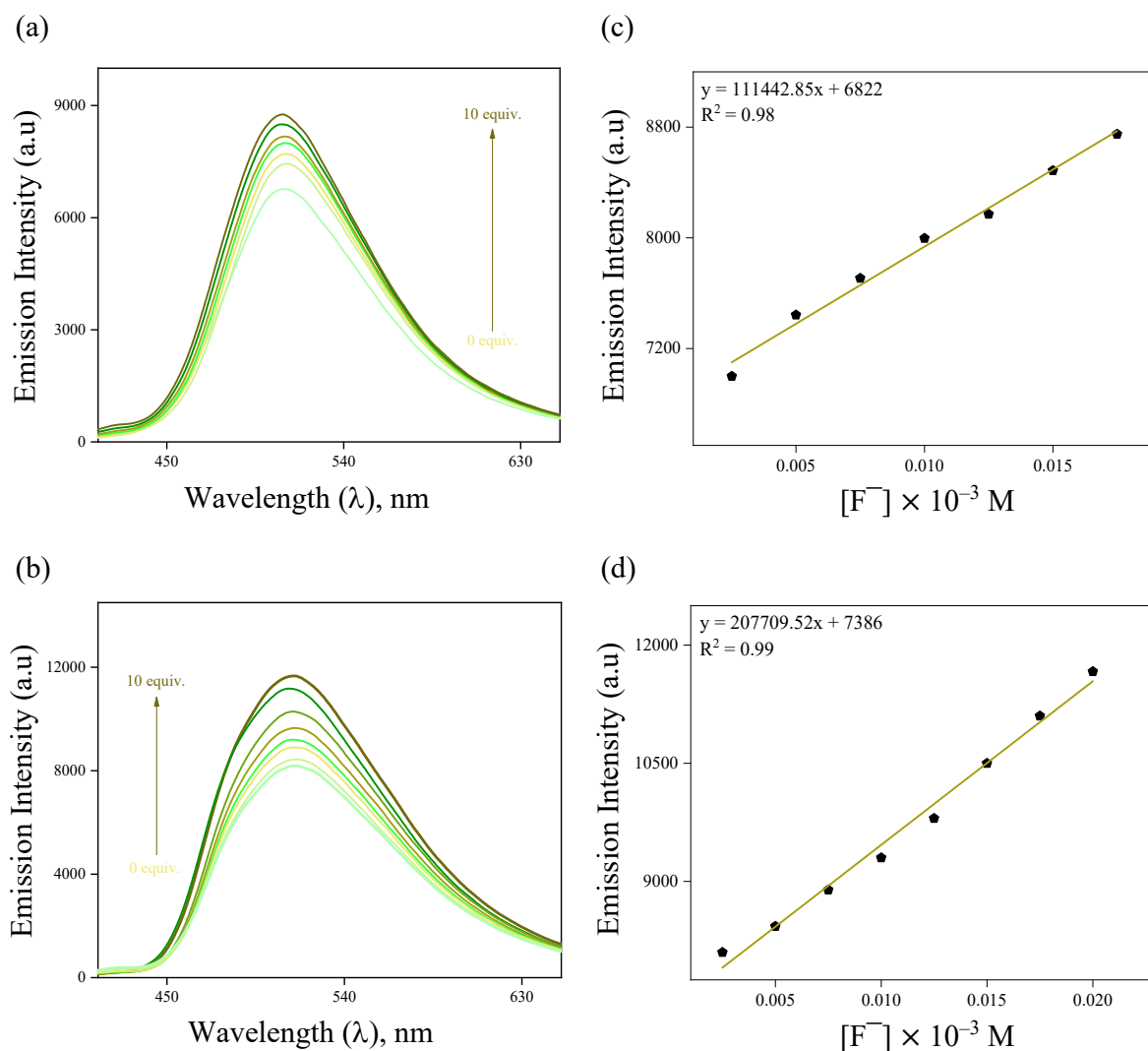


Fig. S13 Fluorescence spectral titrations of the probe molecules P1 (a) and P2 (b) on incremental addition of F^- anion, and their corresponding calibration plots (c) and (d), in $\text{CH}_3\text{CN}:\text{DMSO}$ (9:1, v/v; pH 7.1) solution.

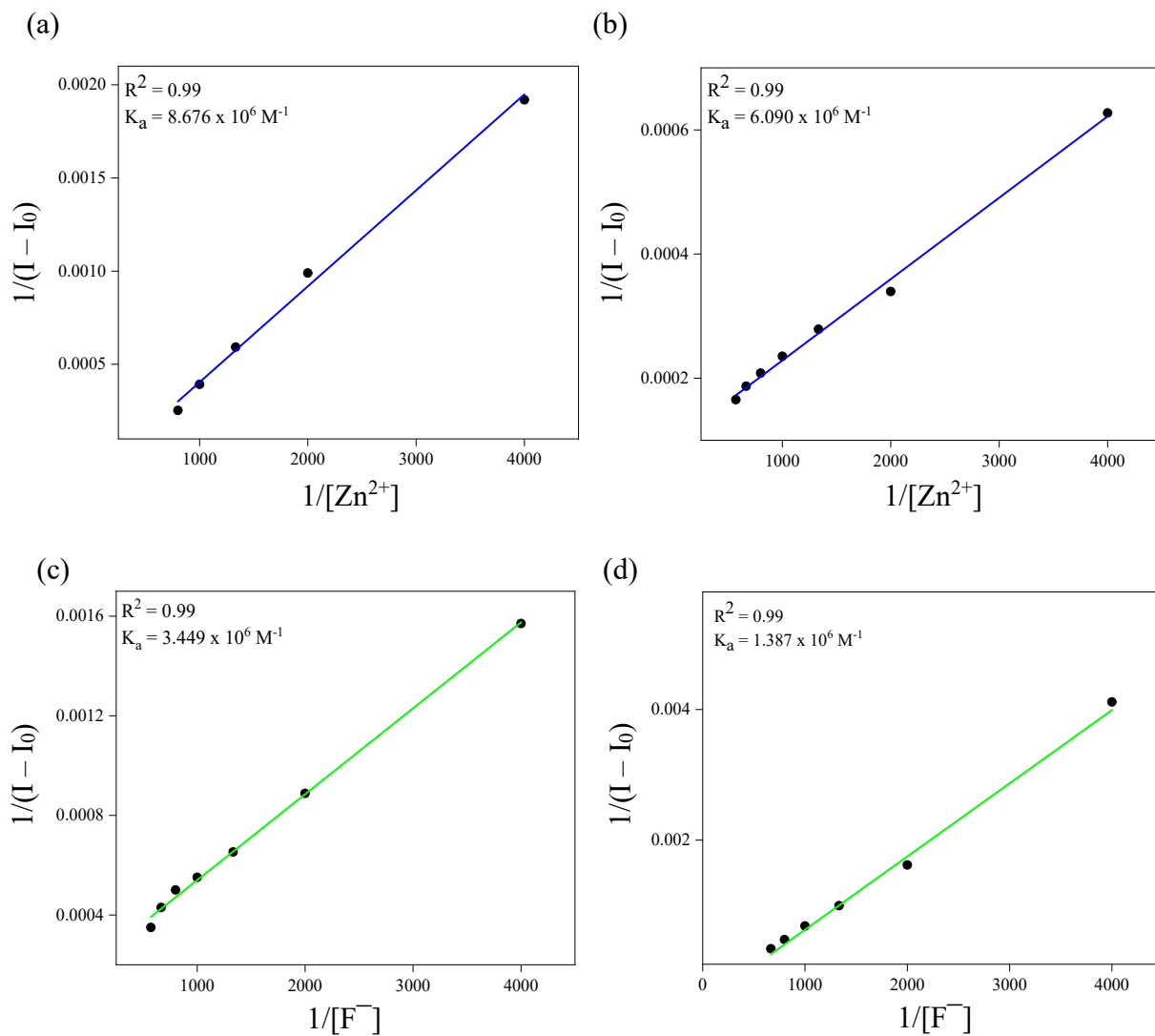


Fig. S14 Benesi-Hildebrand plots for association constant calculation of probes with Zn^{2+} cations and F^- anions: P1 + Zn^{2+} (a), P2 + Zn^{2+} (b), P1 + F^- (c) and P2 + F^- (d).

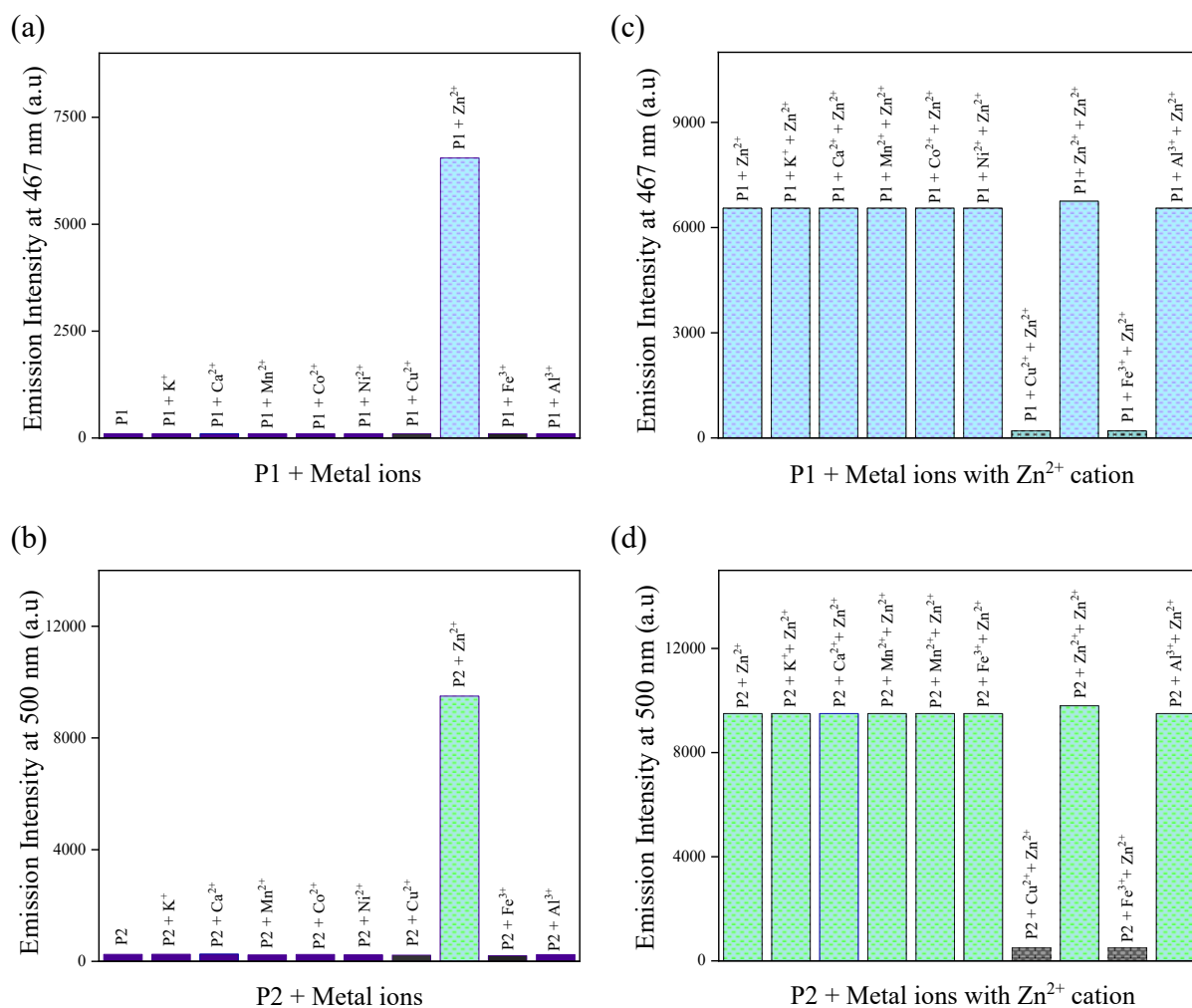


Fig. S15 Bar plots of the probes P1 (a) and P2 (b) upon addition of 10 equiv. of various metal ions, and P1 with Zn²⁺ (c) and P2 with Zn²⁺ (d) in the presence of competitive metal ions (1:1 equiv.), in CH₃CN:DMSO (9:1, v/v; pH 7.1) solution.

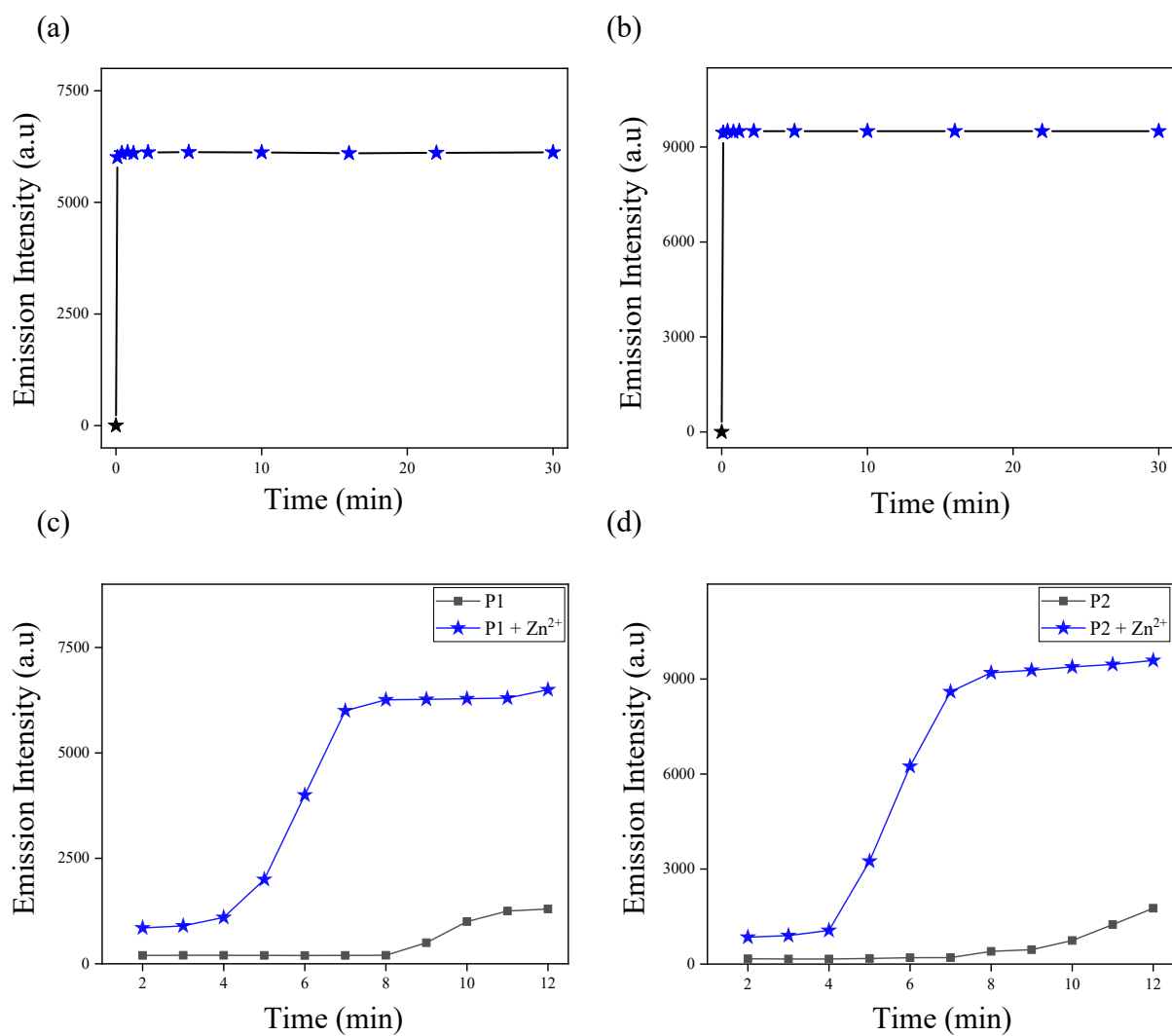


Fig. S16 Effect of the response time of P1 (a) and P2 (b) upon addition of the Zn²⁺ cations, and the effect of pH of P1 (c) and P2 (d) in the absence and presence of the Zn²⁺ cations, in relation to fluorescence intensity, in CH₃CN:DMSO (9:1, v/v) solution.

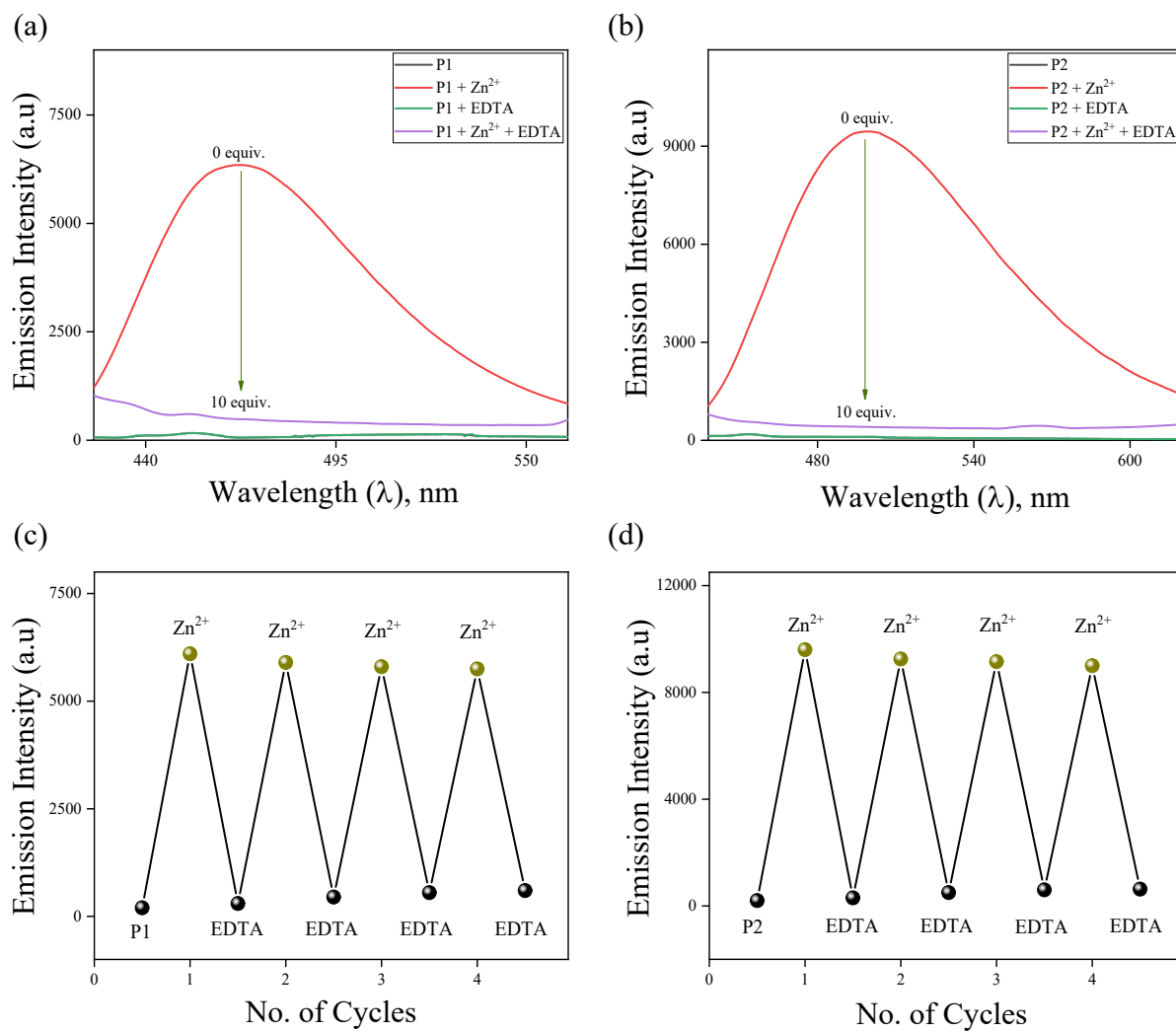


Fig. S17 Fluorescence reversibility responses of the probe molecules P1 (a) and P2 (b) upon alternate addition of Zn^{2+} cations and EDTA (10 equiv.), and the corresponding reversible cycles for fluorescence responses of P1 (c) and P2 (d), in $\text{CH}_3\text{CN}:\text{DMSO}$ (9:1, v/v; pH 7.1) solution.

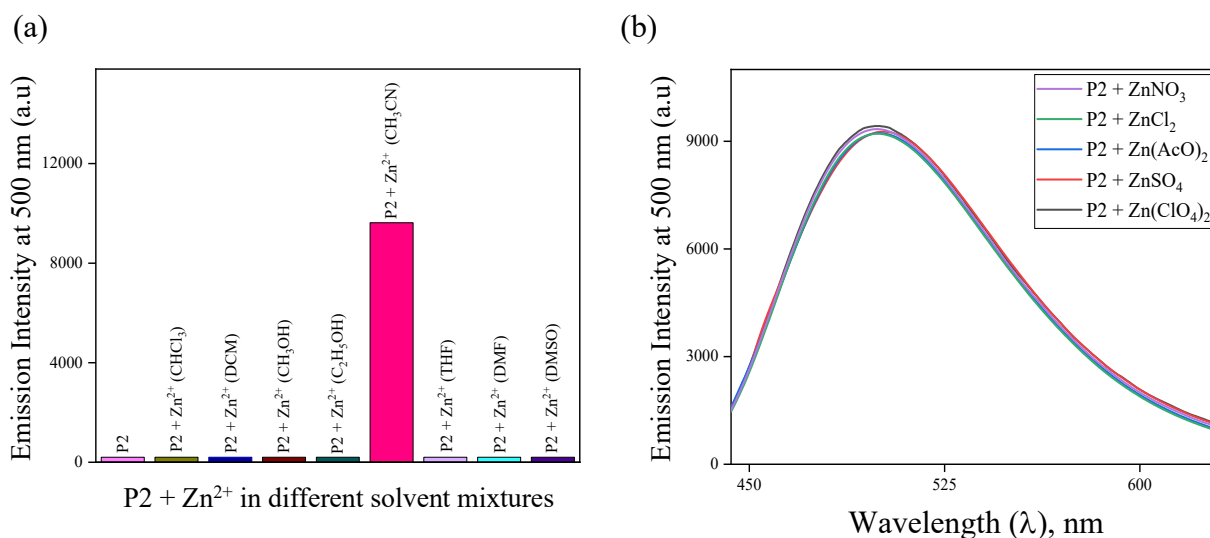


Fig. S18. Effect of solvent on fluorescence intensity of the probe P2 in the presence of Zn²⁺ cations in different solvent (a) and counter ion effect on fluorescence intensity of the probe P2 in the presence of various zinc salts (b), in CH₃CN:DMSO (9:1, v/v; pH 7.1) solution.

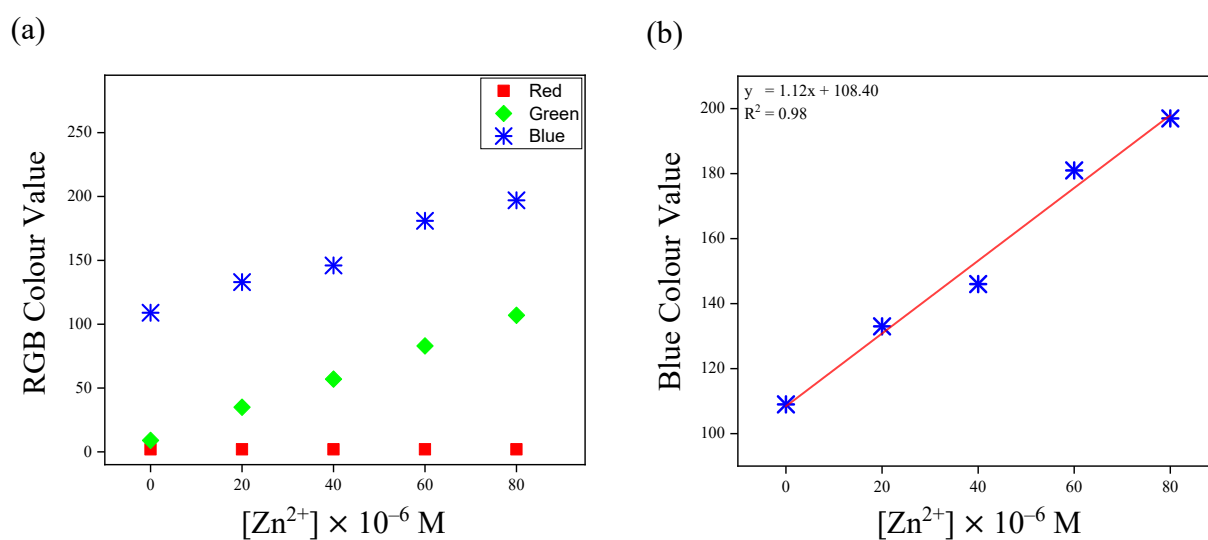


Fig. S19 Plots of red, green and blue colour channel (a) and blue colour channel level (b) of signal images of P2 obtained from smartphone using RGB values.

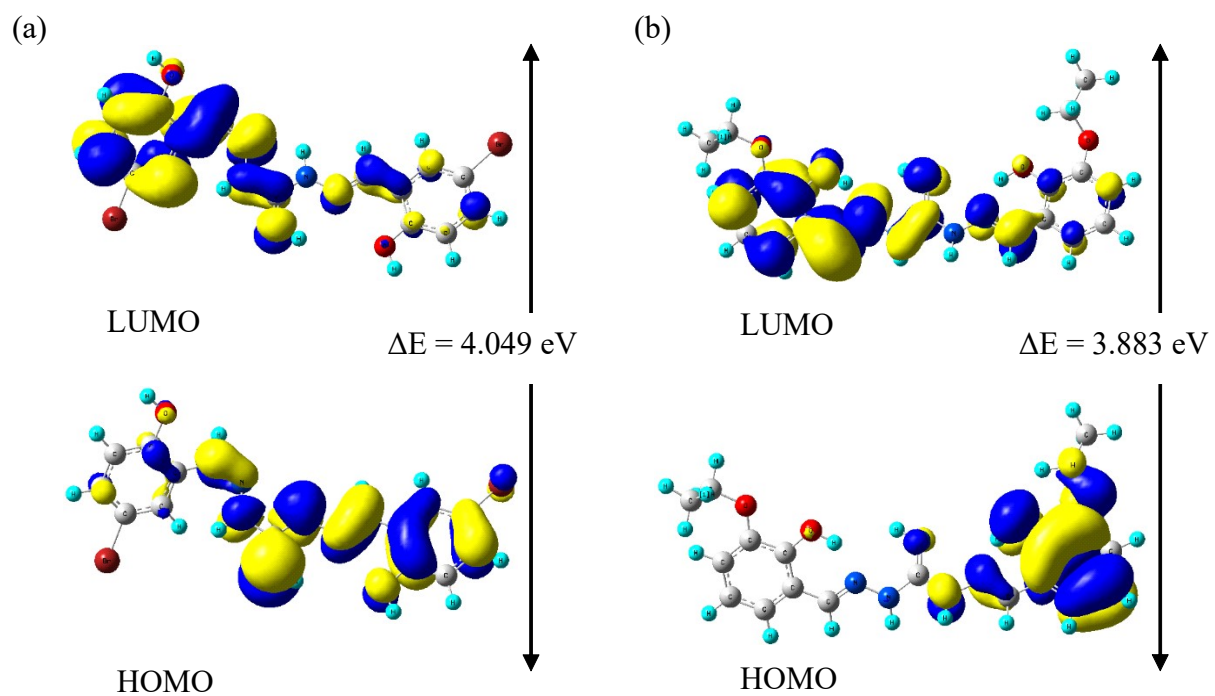


Fig. S20 Frontier molecular orbitals of the probe molecules P1 (a) and P2 (b).

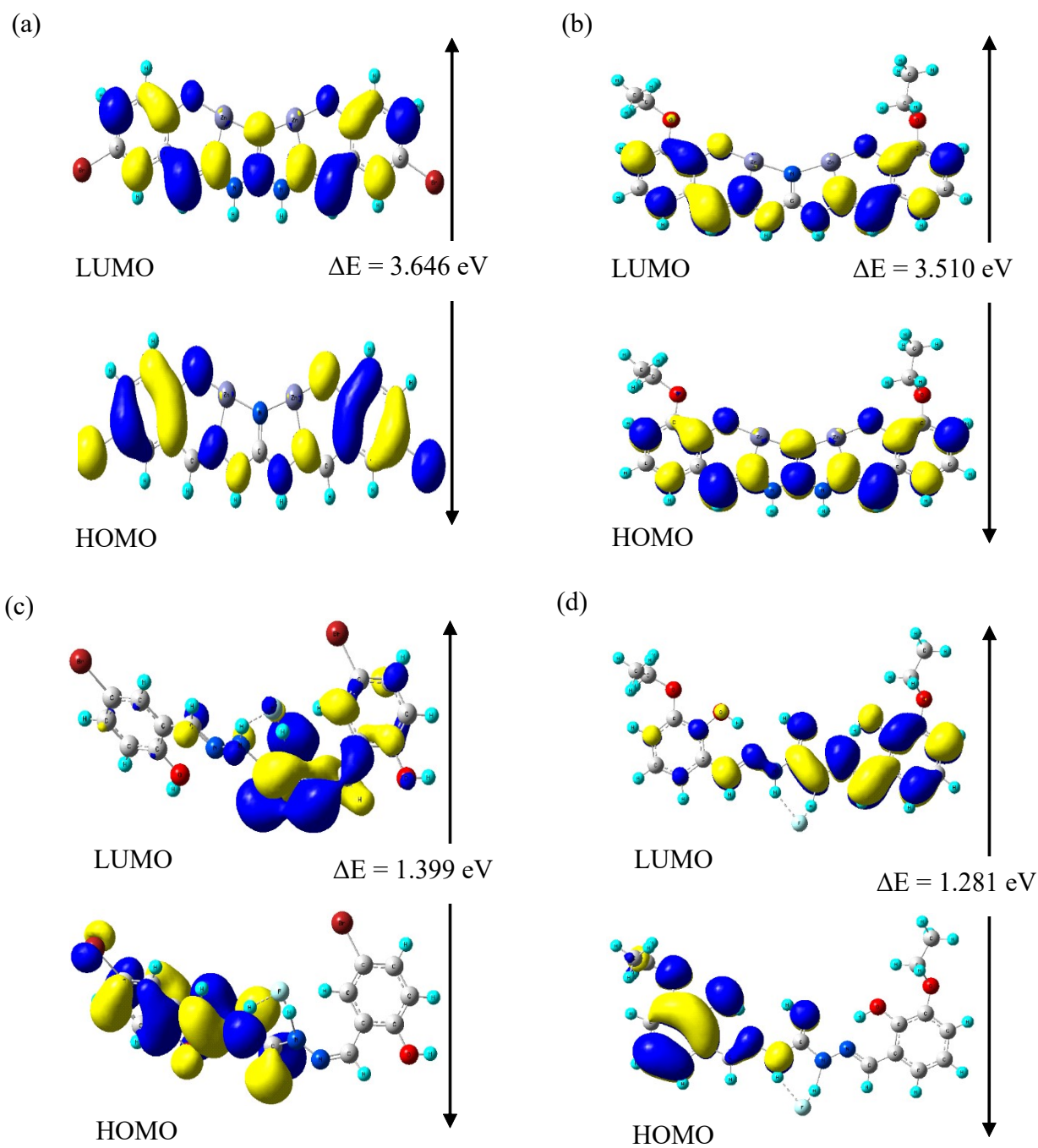


Fig. S21 Frontier molecular orbitals of the probe molecules upon binding with Zn^{2+} cations and F^- anions: P1 + Zn^{2+} (a), P2 + Zn^{2+} (b), P1 + F^- (c) and P2 + F^- (d).

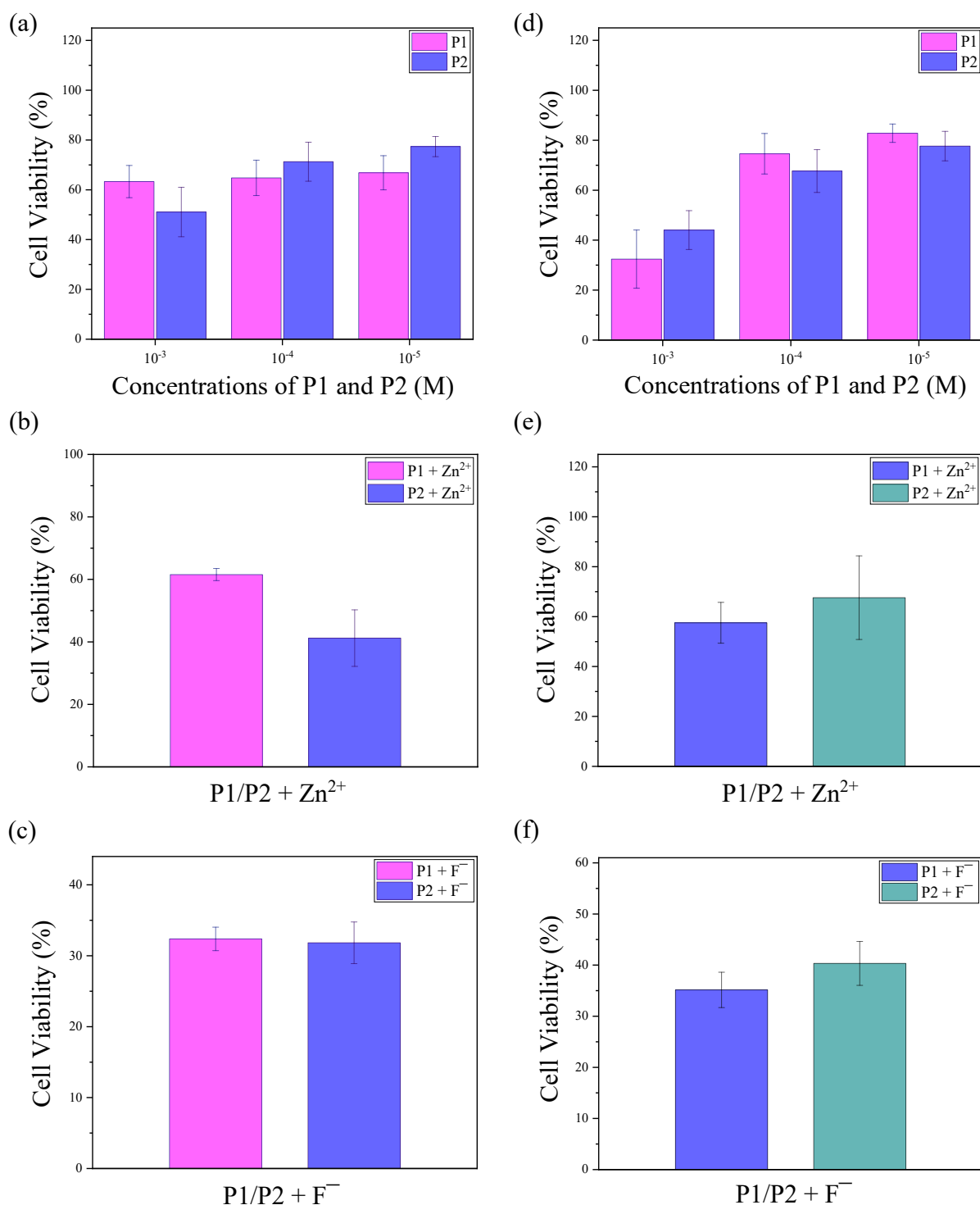


Fig. S22 Cell viability of P1 and P2 at various concentrations (a), cell viability of P1/P2 (10^{-3} M) + Zn^{2+} (10^{-1} M) (b) and cell viability of P1/P2 (10^{-3} M) + F^- (20 μ L) (c) on HaCaT cells; Cell viability of P1 and P2 at various concentrations (d), cell viability of P1/P2 (10^{-3} M) + Zn^{2+} (10^{-1} M) (e) and cell viability of P1/P2 (10^{-3} M) + F^- (20 μ L) (f) on MDA-MB 231 cells.

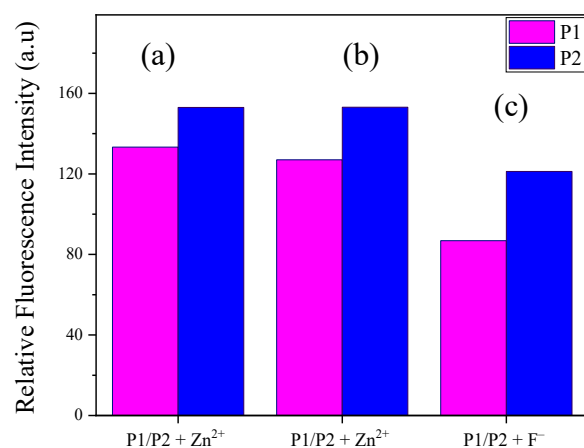


Fig. S23 Relative fluorescence intensity of the probe molecules (P1 and P2) with various concentrations of Zn²⁺ and F⁻ ions on *A. Salina*: Probes (10⁻³ M) + Zn²⁺ (10⁻¹ M) (a), Probes (10⁻³ M) + Zn²⁺ (10⁻³ M) (b) and Probes (10⁻³ M) + F⁻ (20 μL) (c).