Electronic Supplementary Information

A Xanthene-Based Novel Colorimetric and Fluorometric Chemosensor for the Detection of Hydrazine and Its Application in Bio-Imaging of Live Cells

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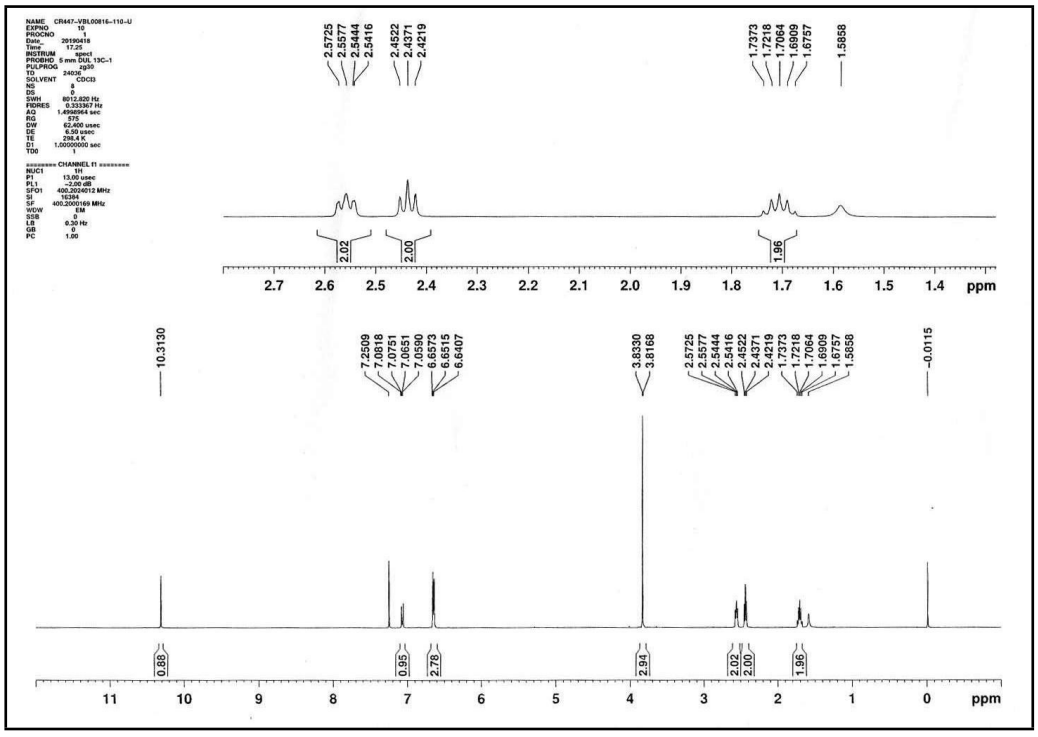

Figure S1. ^{1}H -NMR spectrum of compound **2** in $CDCl_3$.

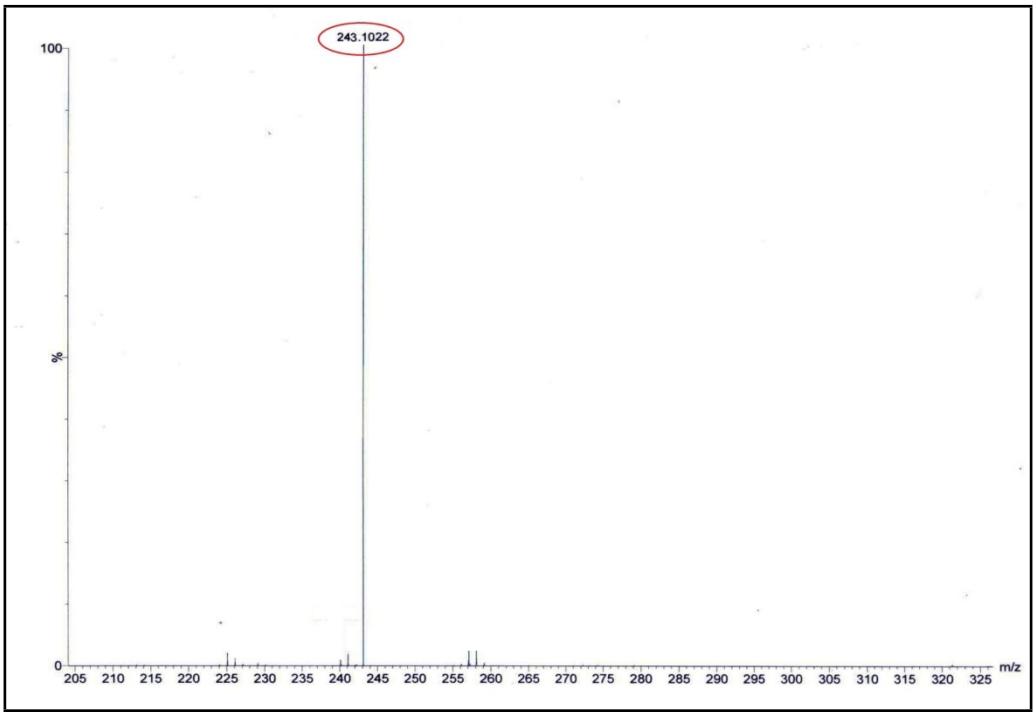

Figure S2. HRMS Mass spectrum of compound **2**.

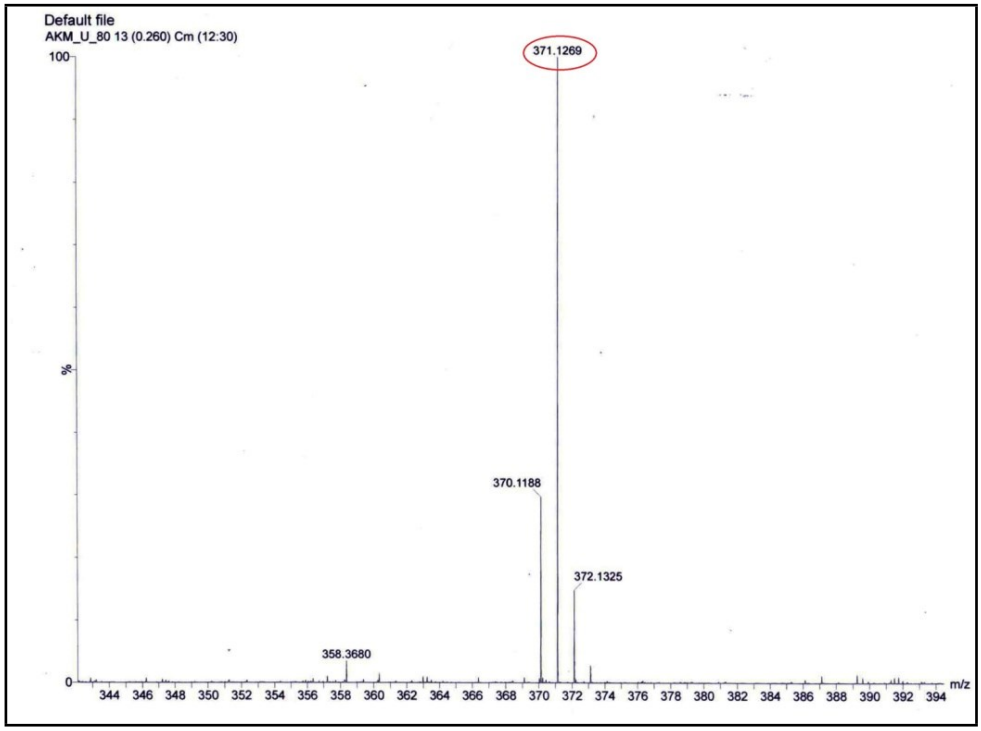

Figure S3. HRMS Mass spectrum of **MXI**.

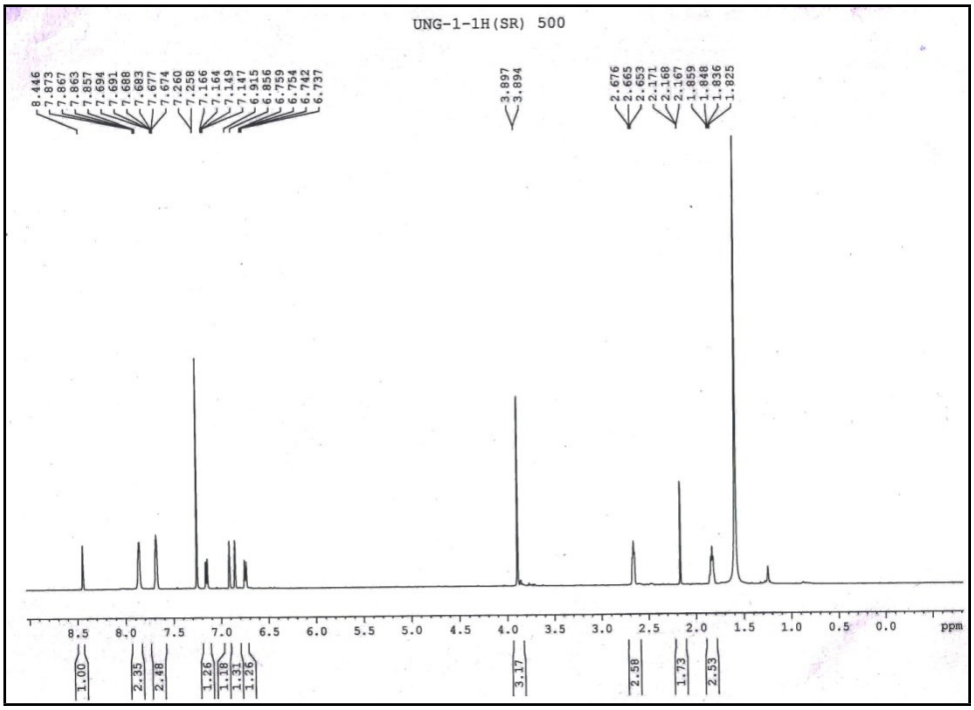

Figure S4. ^{1}H -NMR spectrum of **MXI** in $CDCl_3$.

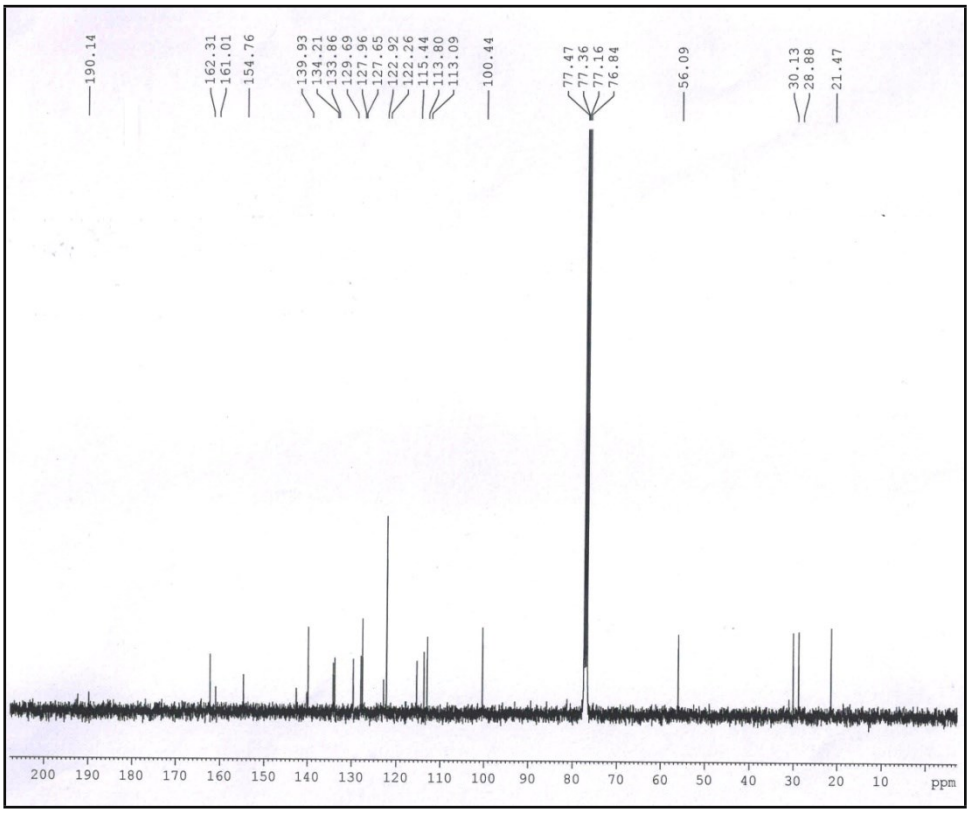

Figure S5. ^{13}C-NMR spectrum of **MXI** in $CDCl_3$.

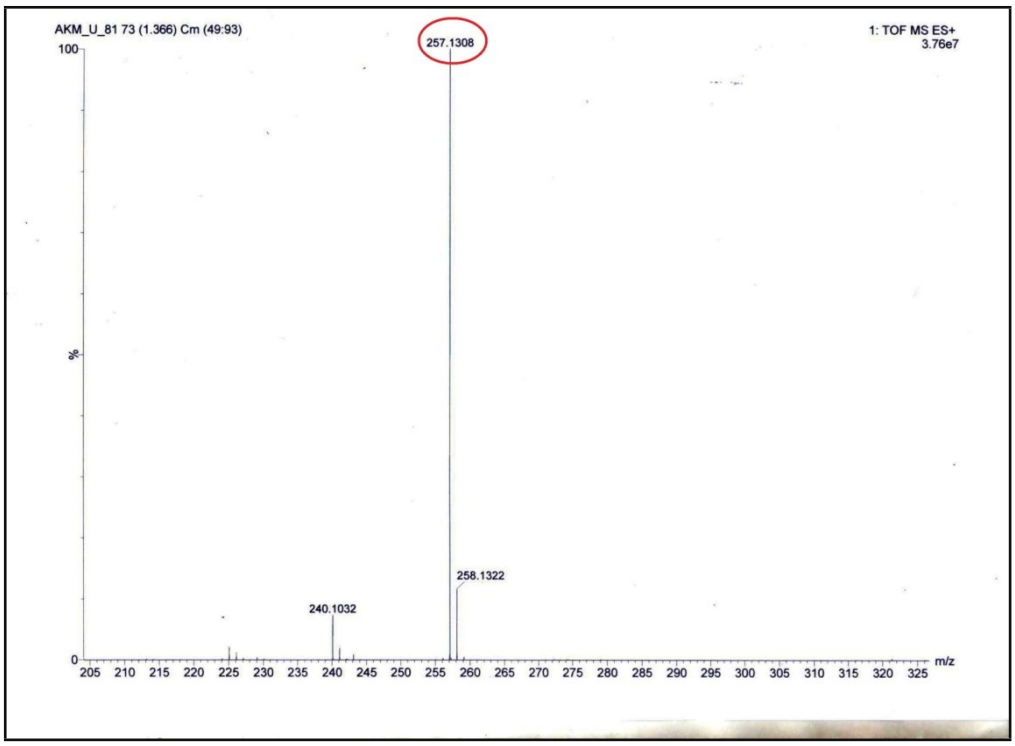

Figure S6. HRMS mass spectrum of **MXH**.

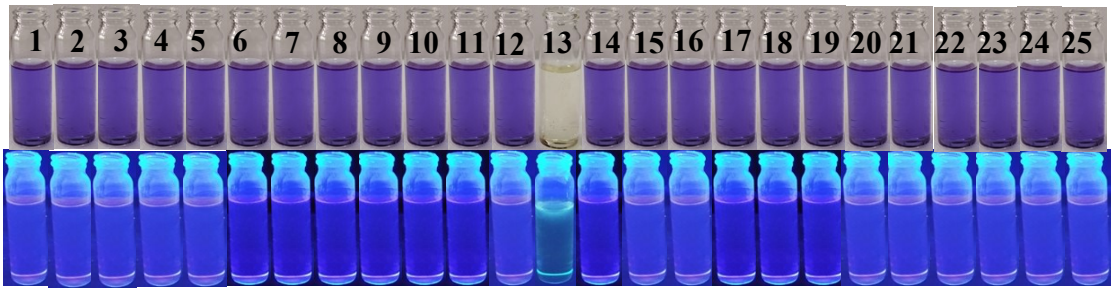

Figure S7. Absorbance (top) and fluorescence(bottom) color changes of receptor **MXI** (in aqueous DMSO solution) upon addition of various analytes[1. CO_3^{2-}, 2. SO_4^{2-}, 3. HPO_4^{2-}, 4. AcO^-, 5. NO_3^-, 6. N_3^-, 7. I^-, 8. DIPEA, 9. phenol, 10. TEA, 11. urea, 12. PhSH, 13. N_2H_4, 14. $PhNH_2$, 15. Thiourea, 16. Br^-, 17. Cl^-, 18. Cys, 19. Lys, 20. GSH, 21. His, 22. Zn^{2+}, 23. Cr^{3+}, 24. Na^+, 25. Cu^{2+}].

Calculation of detection limit of the probe BBHO:

The detection limit (DL) of **MXI** for N_2H_4 were determined from the following equation:

DL = K* Sb1/S

Where K = 2 or 3 (we take 3 in this case); Sb1 is the standard deviation of the blank solution; S is the slope of the calibration curve.

From graph S = 610930.9346, Sb1=0.01538. DL=75 nM

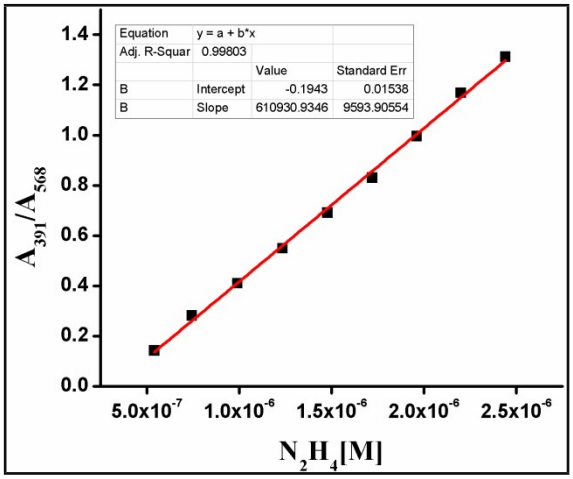

Figure S8. Linearship of absorption intensity ratio (A_{568nm}/A_{391nm}) of **MXI** (1.0 µM) to N_2H_4.

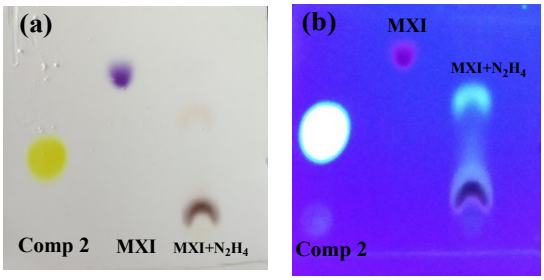

Figure S9. Progress of the reaction monitored by the TLC (thin layer chromatography) plate.

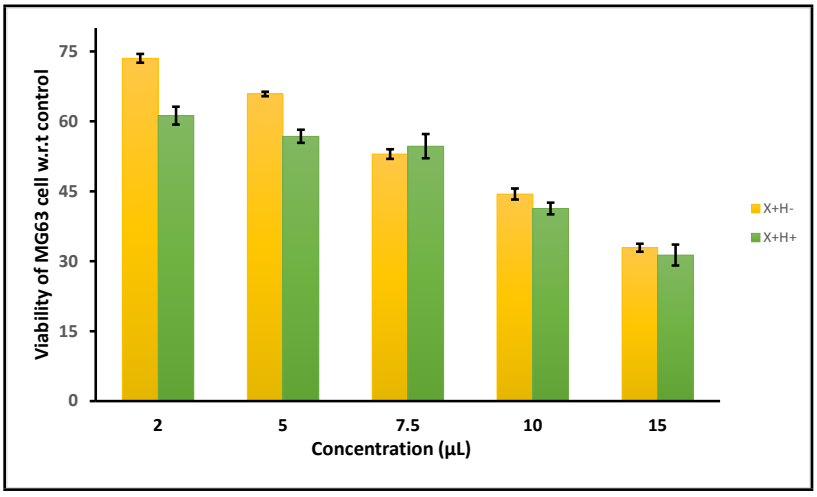

Figure S10. MTT assay to determine the cytotoxic effect of **MXI** and N_2H_4 complex on MG63 (human bone osteosarcoma) cell.

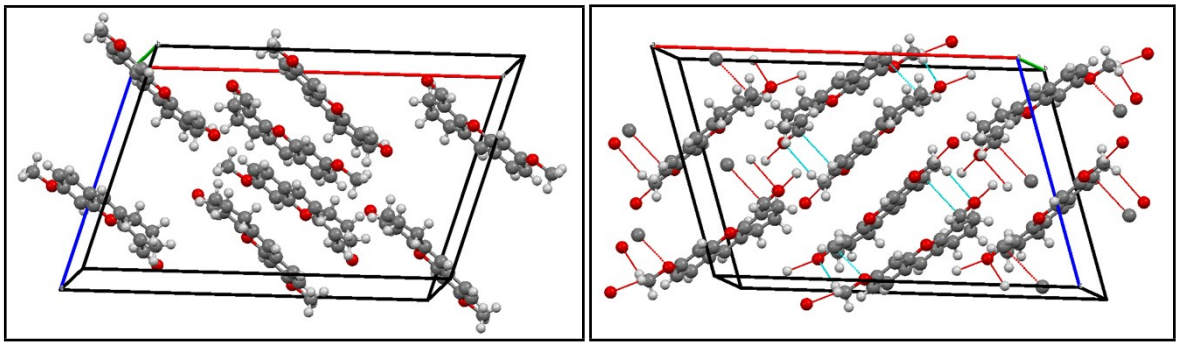

Figure S11. Crystals structure of the aldehyde (**2**).

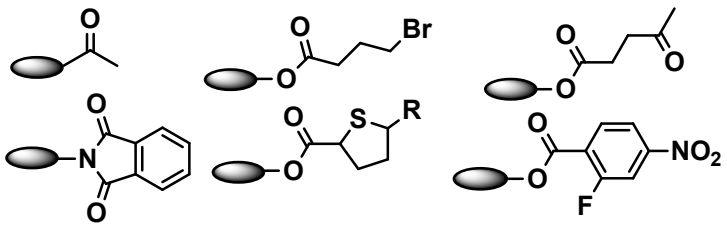

Figure S12. Recent time sensing approaches for hydrazine and the representative sensing moiety.

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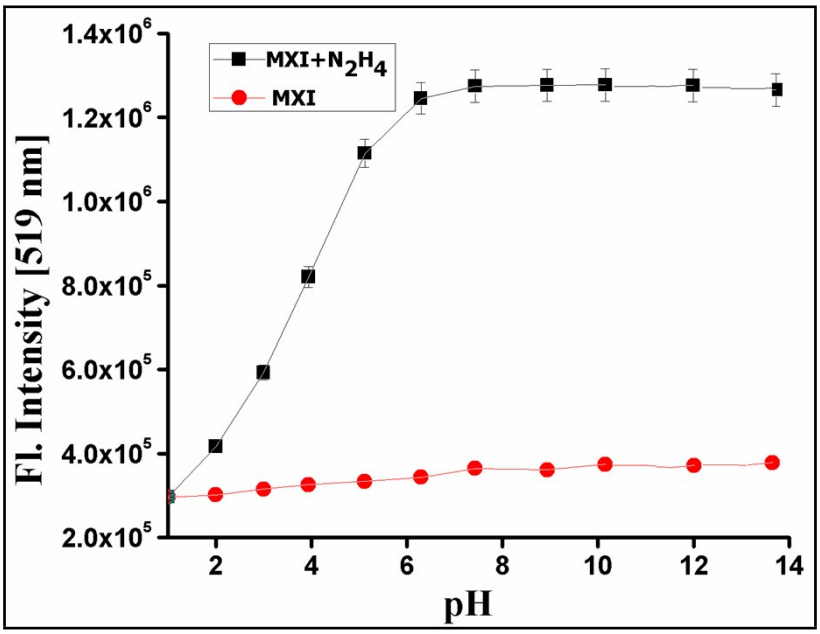

Figure S13. The pH-dependent fluorescence response of probe **MXI** (1.0 mM) towards N_2H_4 (2.5 mM) in DMSO–H_2O HEPES buffer solution (pH 7.4).

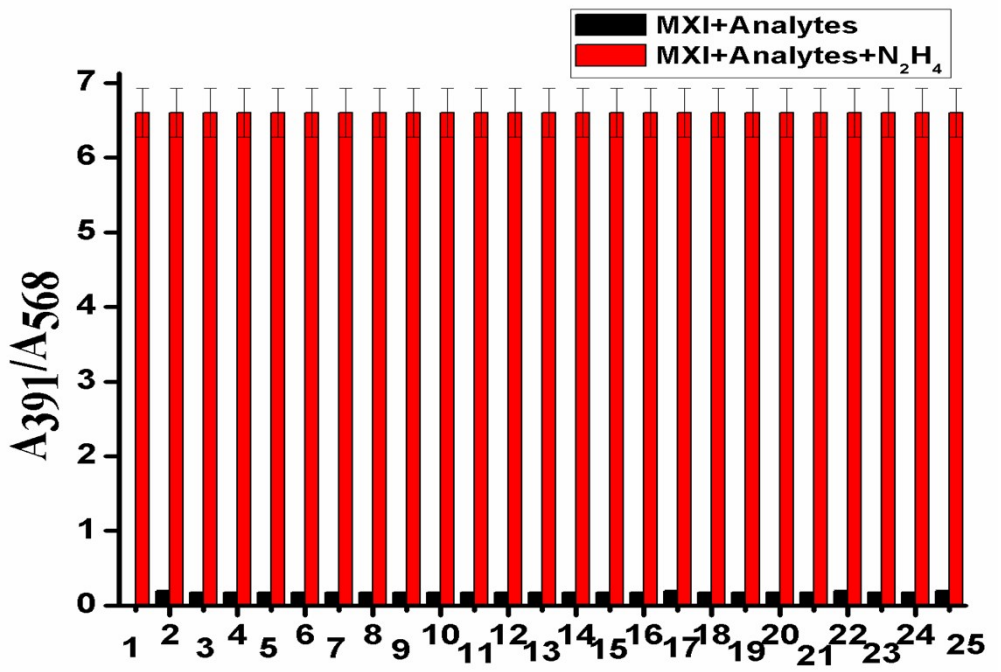

Figure S14 Selectivity profile diagram (Absorption) in bar representation including error bars (error amount, 5%; Y error bar for both [±] deviations). Black bar represents **MXI**+Analytes, red bars: **MXI**+Analytes+ N_2H_4 [1. N_2H_4, 2. SO_4^{2-}, 3. HPO_4^{2-}, 4. AcO^-, 5. NO_3^-, 6. N_3^-, 7. I^-, 8. DIPEA, 9. phenol, 10. TEA, 11. urea, 12. PhSH, 13. CO_3^{2-}, 14. $PhNH_2$, 15. Thiourea, 16. Br^-, 17. Cl^-, 18. Cys, 19. Lys, 20. GSH, 21. His, 22. Zn^{2+}, 23. Cr^{3+}, 24. Na^+, 25. Cu^{2+}] (10.0 equiv. of each)] in DMSO–H_2O (10 mM HEPES buffer, 3 : 7 v/v, pH 7.4, at 25 °C).

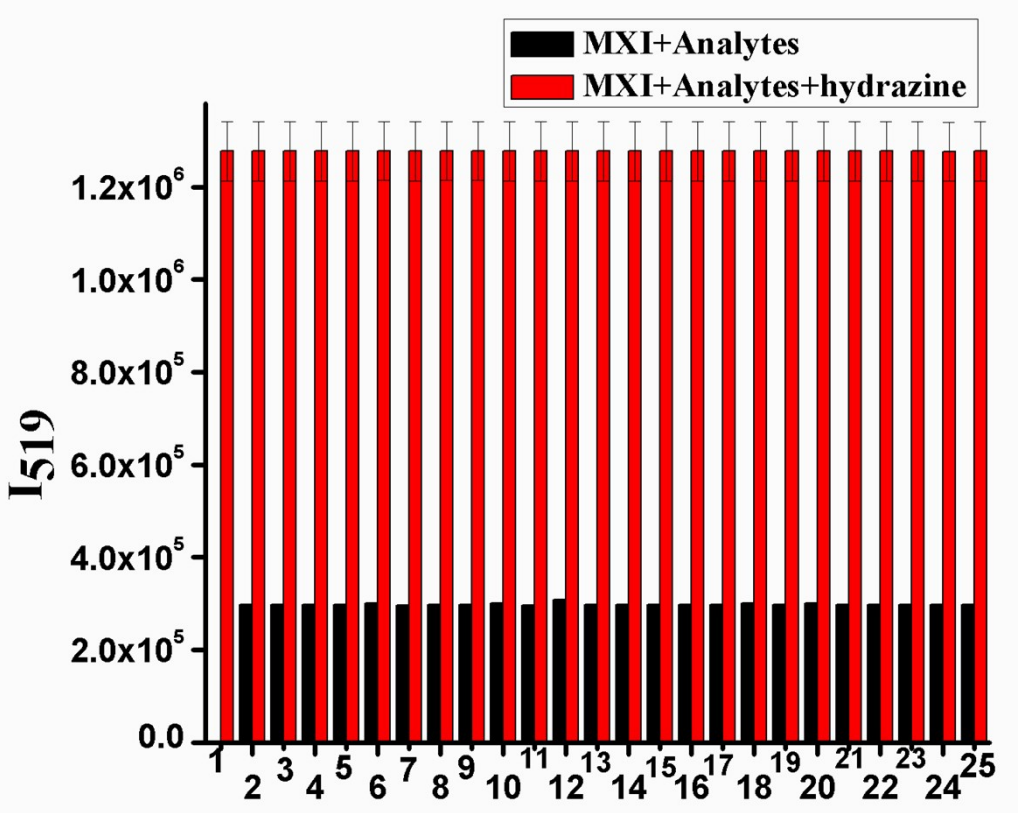

Figure S15 Selectivity profile diagram (fluorescence) in bar representation including error bars (error amount, 5%; Y error bar for both [±] deviations). Black bar represents **MXI**+Analytes, red bars: **MXI**+Analytes+ N_2H_4 [1. N_2H_4, 2. SO_4^{2-}, 3. HPO_4^{2-}, 4. AcO^-, 5. NO_3^-, 6. N_3^-, 7. I^-, 8. DIPEA, 9. phenol, 10. TEA, 11. urea, 12. PhSH, 13. CO_3^{2-}, 14. $PhNH_2$, 15. Thiourea, 16. Br^-, 17. Cl^-, 18. Cys, 19. Lys, 20. GSH, 21. His, 22. Zn^{2+}, 23. Cr^{3+}, 24. Na^+, 25. Cu^{2+}] (10.0 equiv. of each)] in DMSO–H_2O (10 mM HEPES buffer, 3 : 7 v/v, pH 7.4, at 25 °C).

Table S1. Calculated excitation energies (eV), oscillator strengths (f), contributions for **MXI** and **MXH**. The data were calculated by the TDDFT//B3LYP/6-311+G(*d,p*) level of theory based on the optimized ground state geometries.

Species	Electronic Transition	Excitation Energy	f	Contributions[a]
MXI	$S_0 \rightarrow S_1$	2.3655 eV 524.14 nm	1.2242	H → L (100%)
MXH	$S_0 \rightarrow S_1$	3.0412 eV 407.68 nm	0.7029	H → L (98%)

[a] H and L represents HOMO and LUMO respectively.

Table S2. Energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)

Species	E_{HOMO} (a.u)	E_{LUMO}(a.u)	ΔE(a.u)	ΔE(eV)	ΔE(kcal/mol)
MXI	-0.2058	-0.10953	0.09627	2.619660732	60.4
MXH	-0.19085	-0.06724	0.12361	3.363625876	77.6

Computational Details:

The geometries are fully optimized by employing density functional theory (DFT) using Becke's three-parameter hybrid exchange functional and the Lee−Yang−Parr correlation functional (B3LYP)[1-3] with the Pople's spilt-valence triple zeta basis set 6-311+G(d,p) basis set[4]. The frequency calculations have also been carried out to verify exact minima of the complex. The effect of solvent (dimethyl sulfoxide) were considered by using self-consistent reaction field (SCRF) procedure with the integral equation formalism polarized continuum model (IEF-PCM).[5-9] Time dependent DFT calculation were also conducted at the same level of theory.[10-11] All the computations have been carried out in Gaussian 16 program.[12]

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