Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

Design and application of a fluorogenic receptor for selective sensing of cations, small neutral molecules, and anions†

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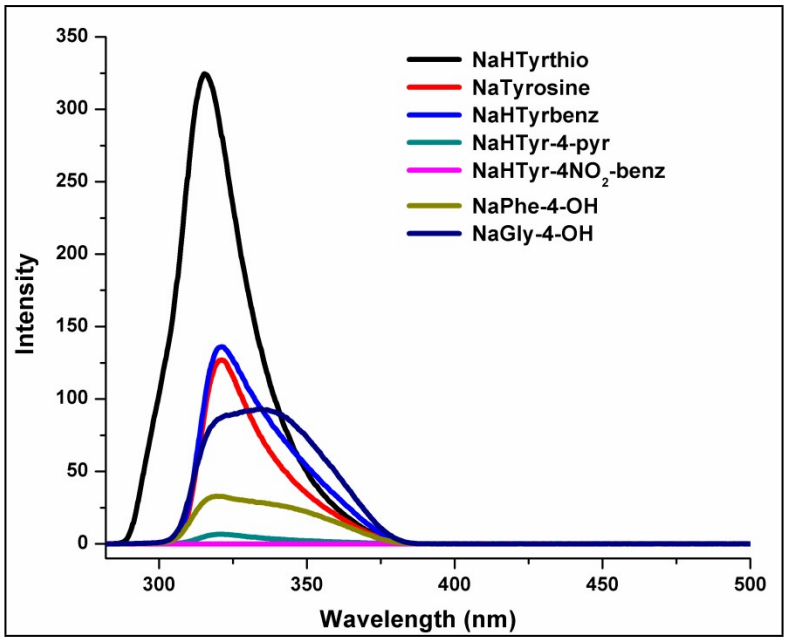


Fig. S1 Comparison of photoluminescence ability of various amino acid based sensors using excitation wavelength = 270 nm.

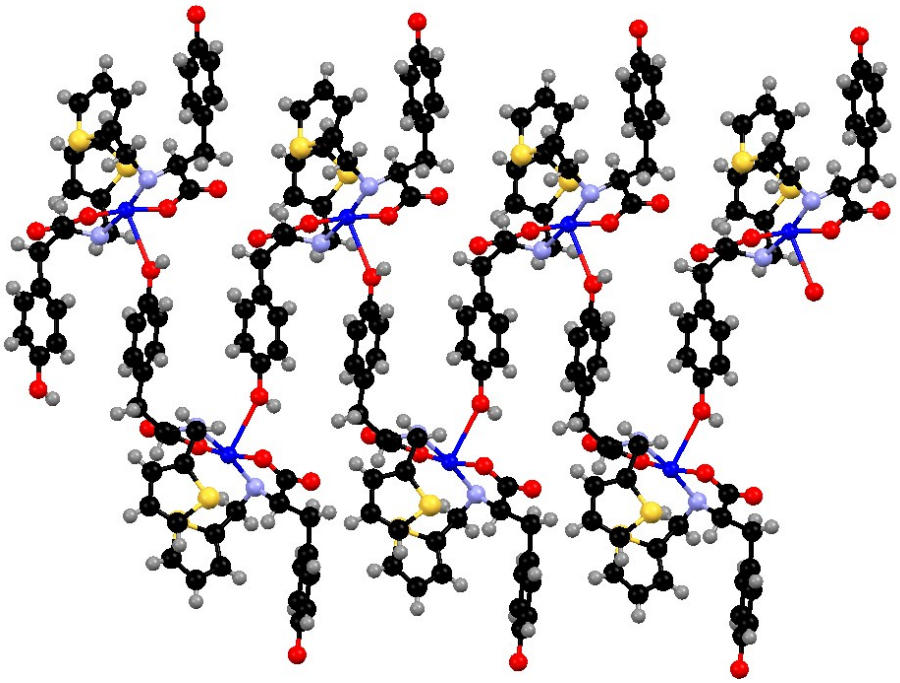


Fig. S2 1D coordination polymer of $\{[Cu(HTyrthio)_2]\cdot H_2O\}_n$ as reported in Reference 35.

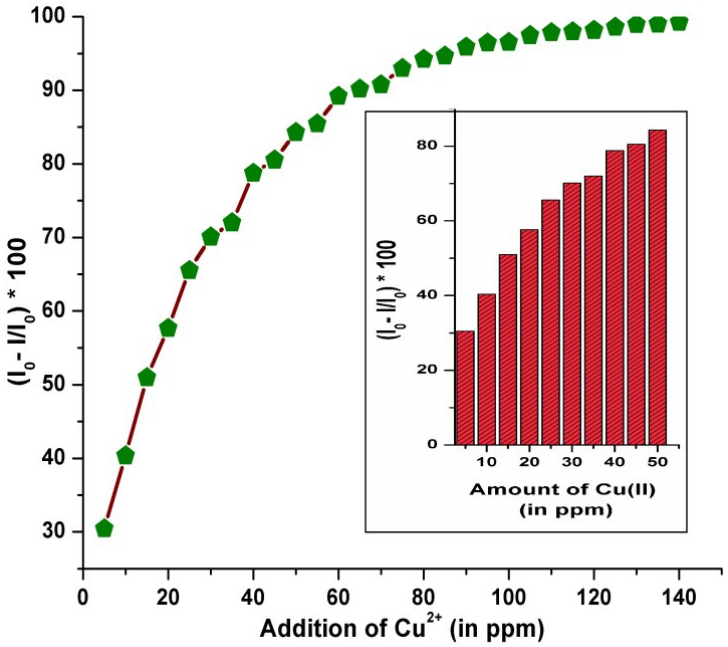


Fig. S3 Quenching (%) in the fluorescence intensity of NaHTyrthio on addition of Cu(II) in ppm level.

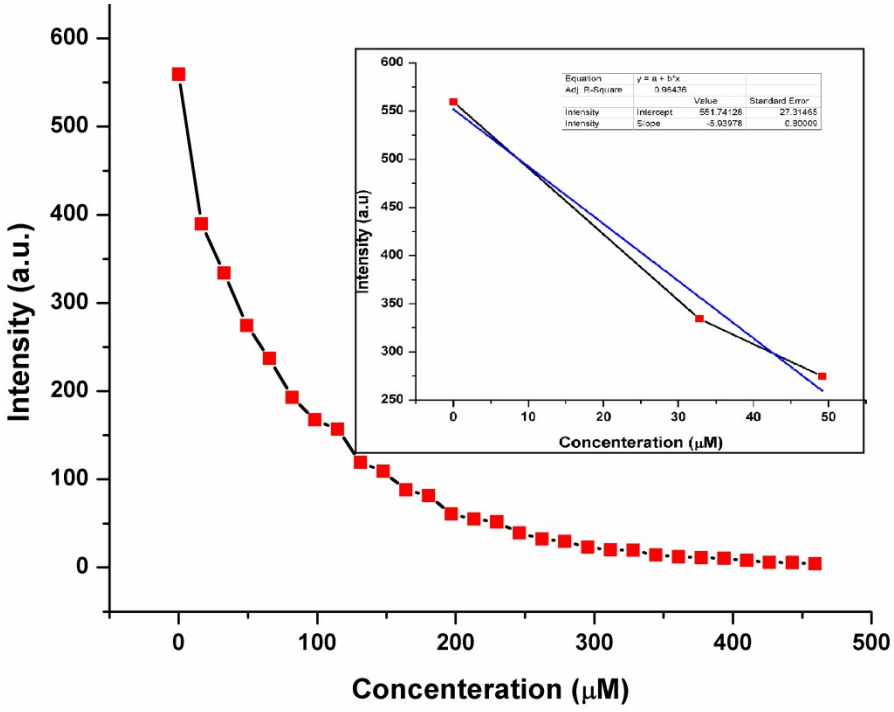


Fig. S4 Plot of fluorescence intensity of NaHTyrthio vs increasing concentration of Cu^{2+}, Inset: Negative slope (m) of graph was found to be 5.9398 (R^2 = 0.96435).

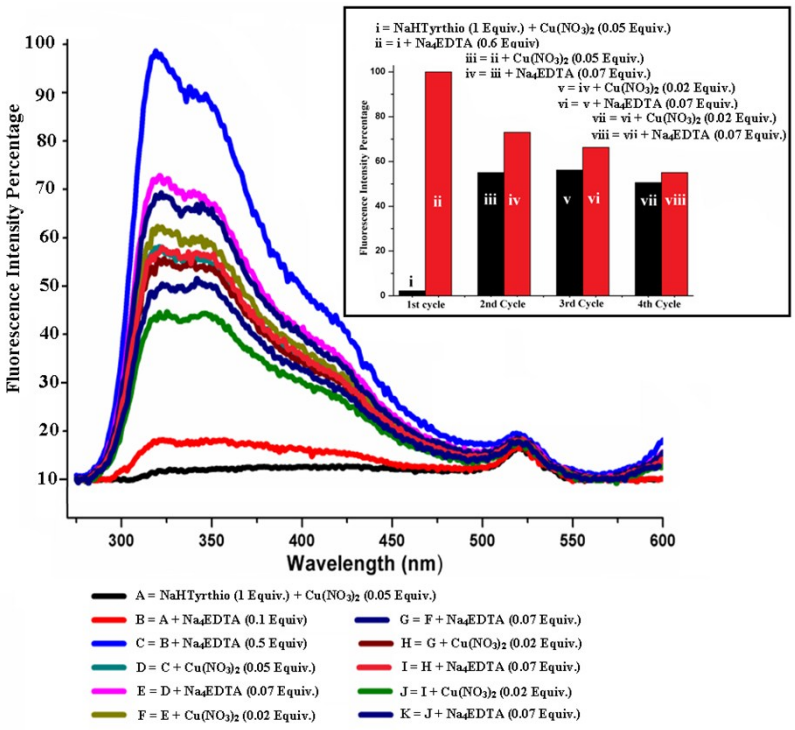


Fig. S5 Emission spectra showing NaHTyrthio as an ON-OFF sensor for Cu(II). Inset: Quenching of fluorescence by Cu^{+2} (black histogram) and redeeming the fluorescence by EDTA solution (red histogram) in subsequent cycles.

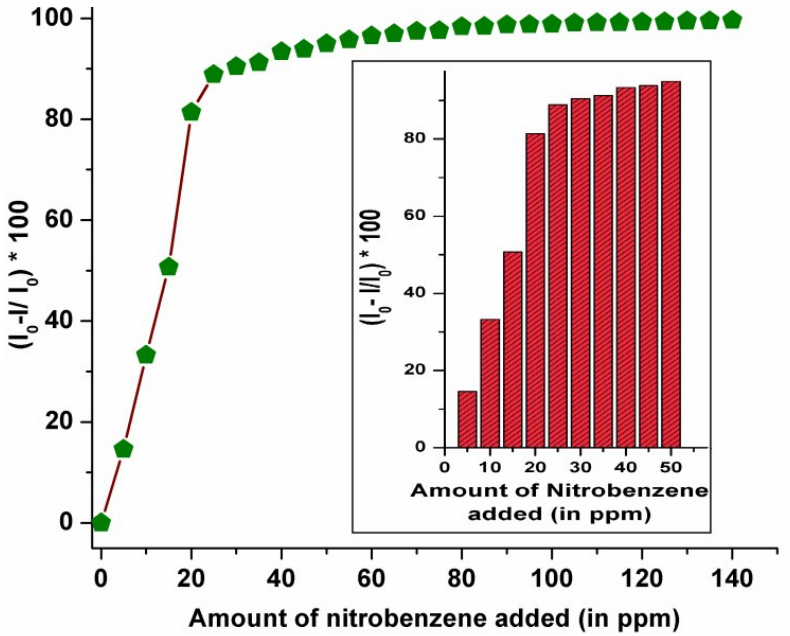


Fig. S6 Quenching (%) in the fluorescence intensity of NaHTyrthio on addition of nitrobenzene in ppm level.

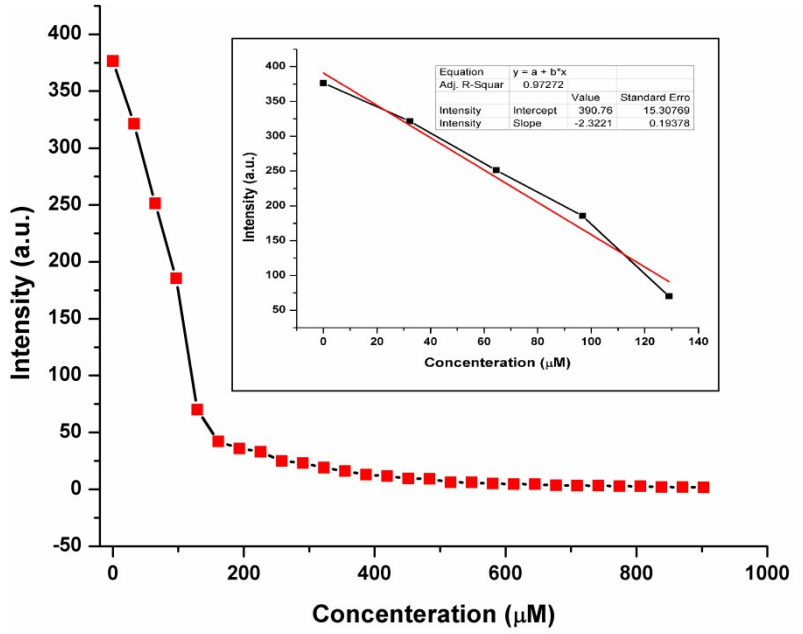


Fig. S7 Fluorescence intensity of NaHTyrthio vs increasing concentration of nitrobenzene, Inset: Negative slope (m) of graph was found to be 2.3221 (R^2 = 0.97272).

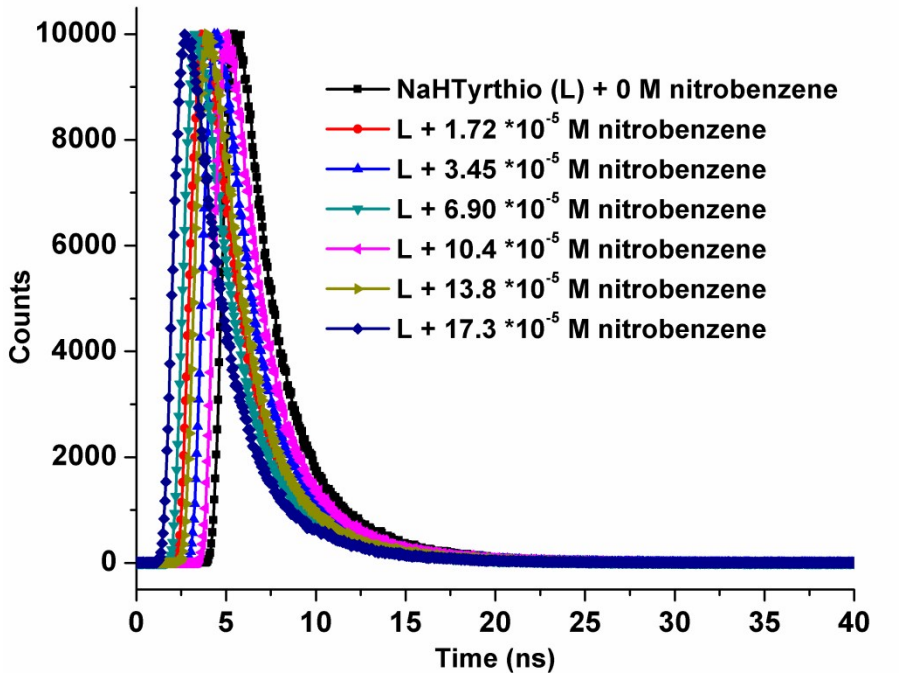


Fig. S8 Lifetime decay profiles of NaHTyrthio (3 mL, 0.72 mM/methanol) in presence of various concentrations of nitrobenzene (λ_{exc} = 280 nm, monitored at 315 nm).

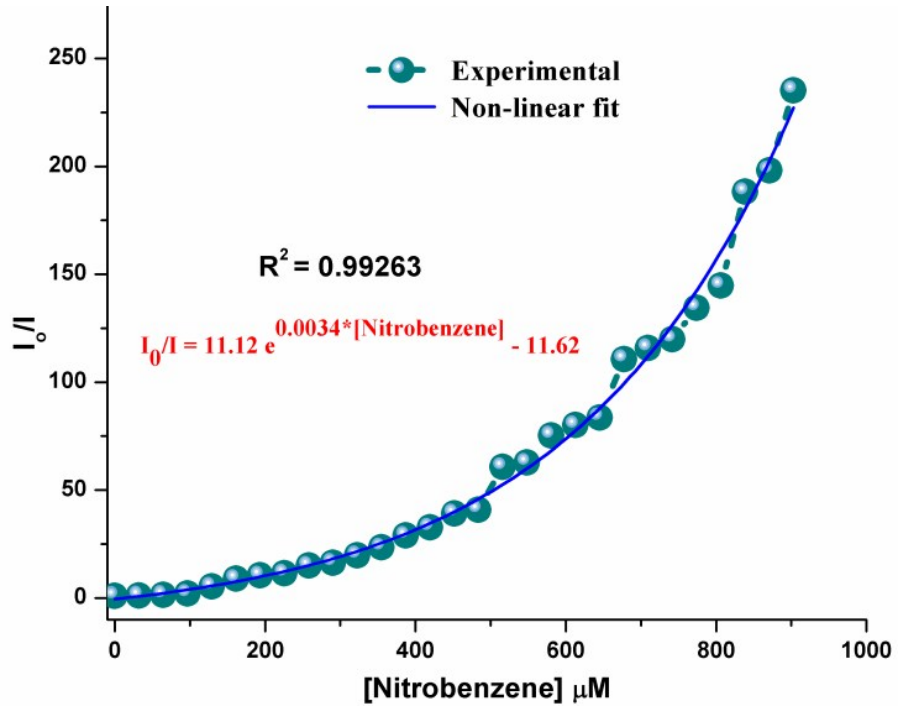


Fig. S9 Stern–Volmer plot I_0 /I versus [Nitrobenzene] in methanol.

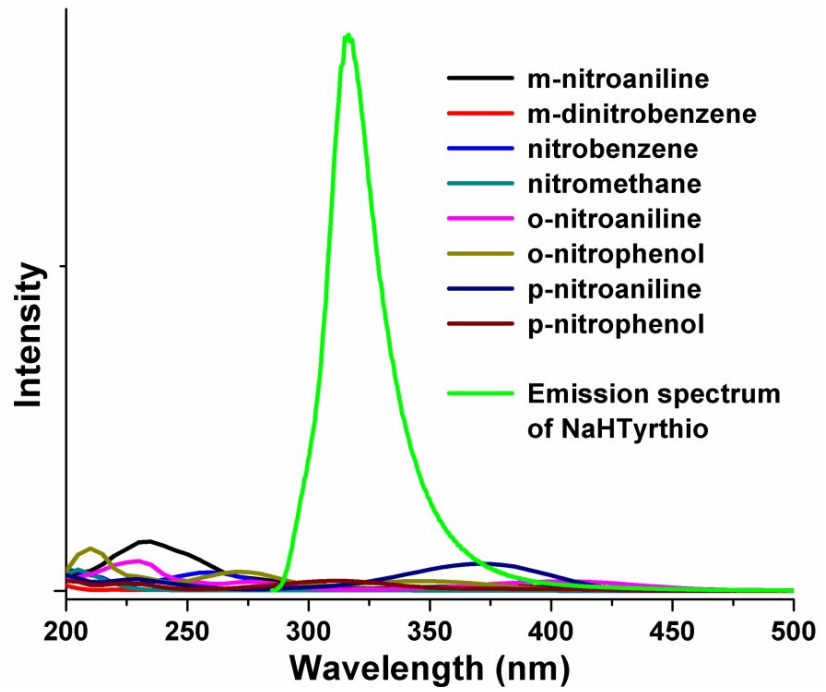


Fig. S10 Overlap between the absorption spectra of various analytes and the emission spectrum of NaHTyrthio in methanol.

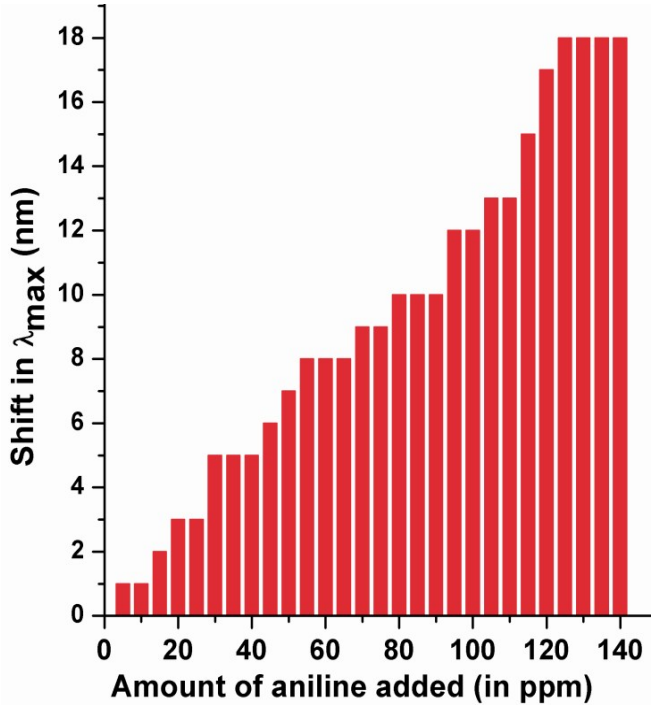


Fig. S11 Shift in λ_{emi} of NaHTyrthio on addition of aniline in ppm level.

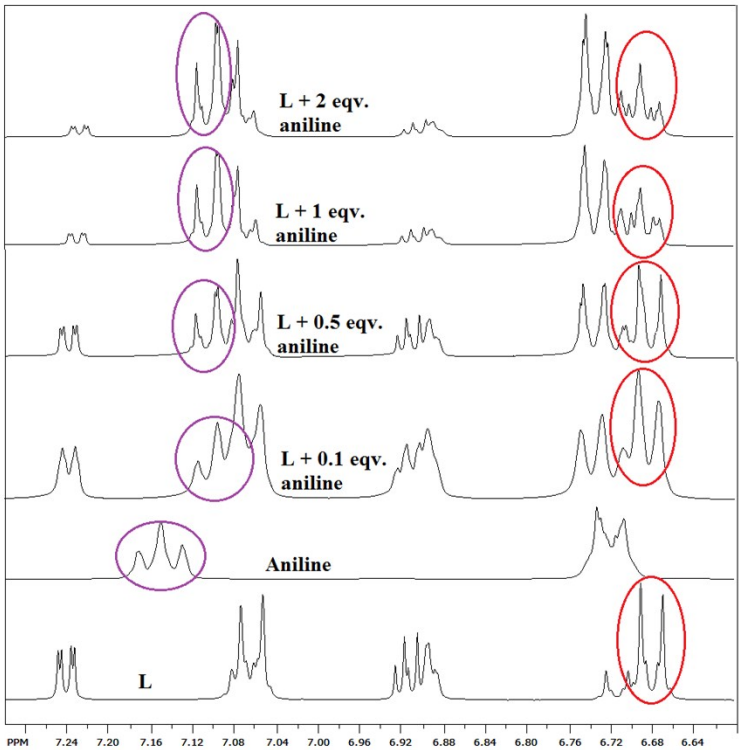


Fig. S12 ^{1}H NMR titrimetry of NaHTyrthio (L) with aniline as an analyte. (distortion in peaks of sensor (red) and analyte (violet)).

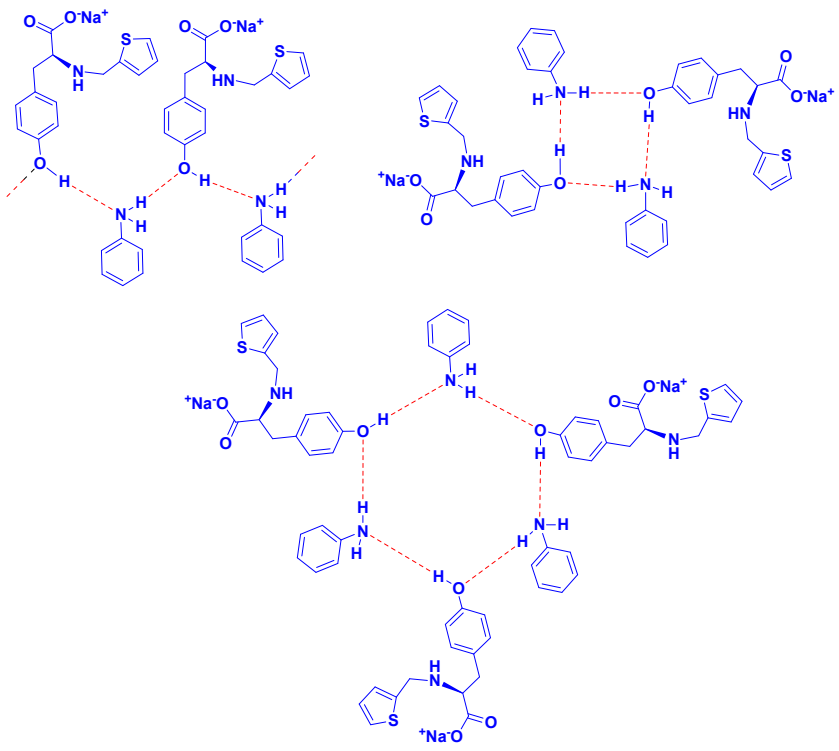


Fig. S13 Probable hydrogen bonding patterns between NaHTyrthio and aniline.

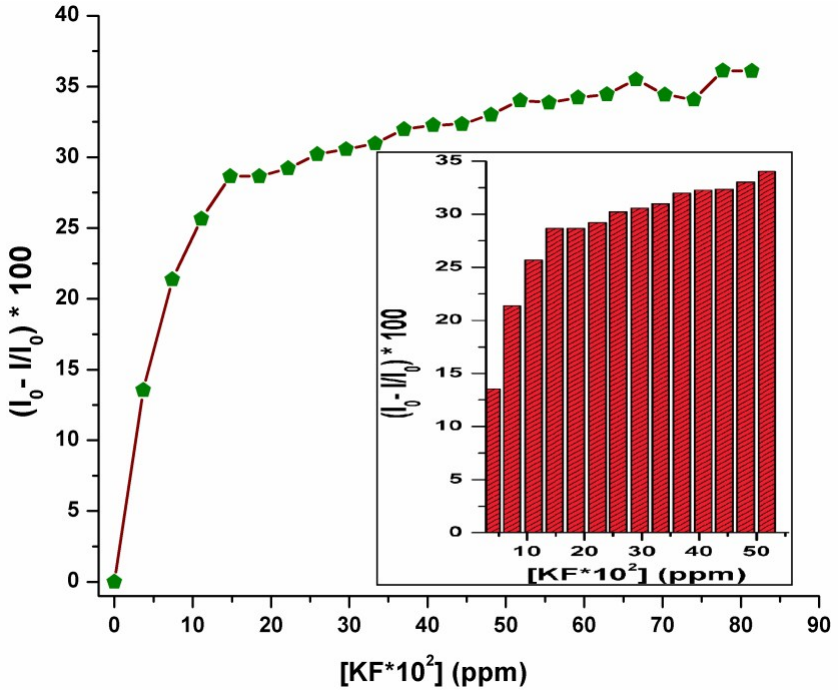


Fig. S14 Quenching (%) in the fluorescence intensity of NaHTyrthio on addition of KF in ppm level.

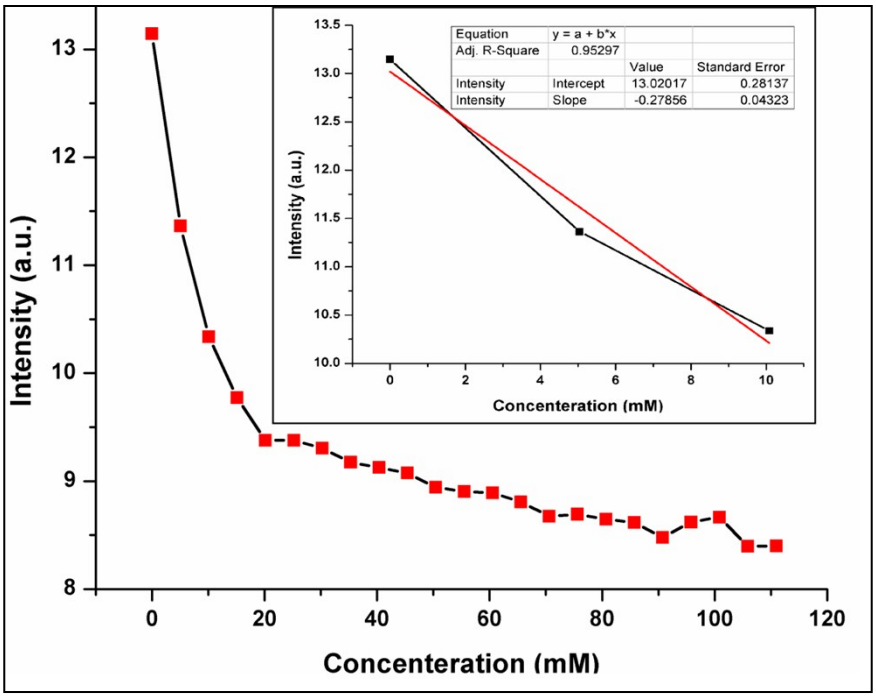


Fig. S15 Fluorescence intensity of NaHTyrthio vs increasing concentration of KF (in methanol), Inset: Negative slope (m) of graph was found to be 0.27856 (R^2 = 0.95297).

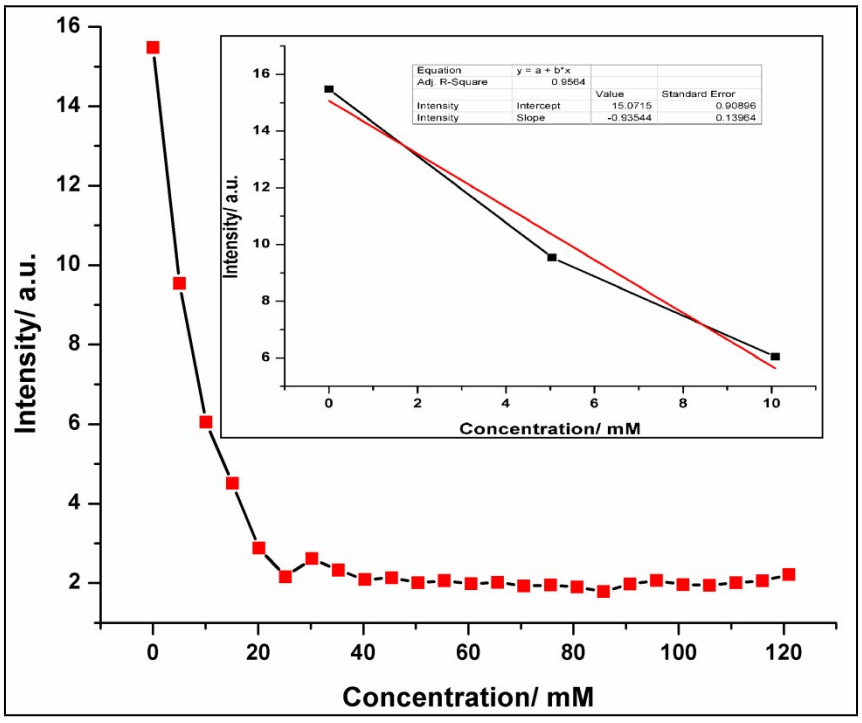


Fig. S16 Fluorescence intensity of NaHTyrthio vs increasing concentration of NaF (in DMSO) Inset: Negative slope (m) of graph was found to be 0.93544 (R^2 = 0.9564).

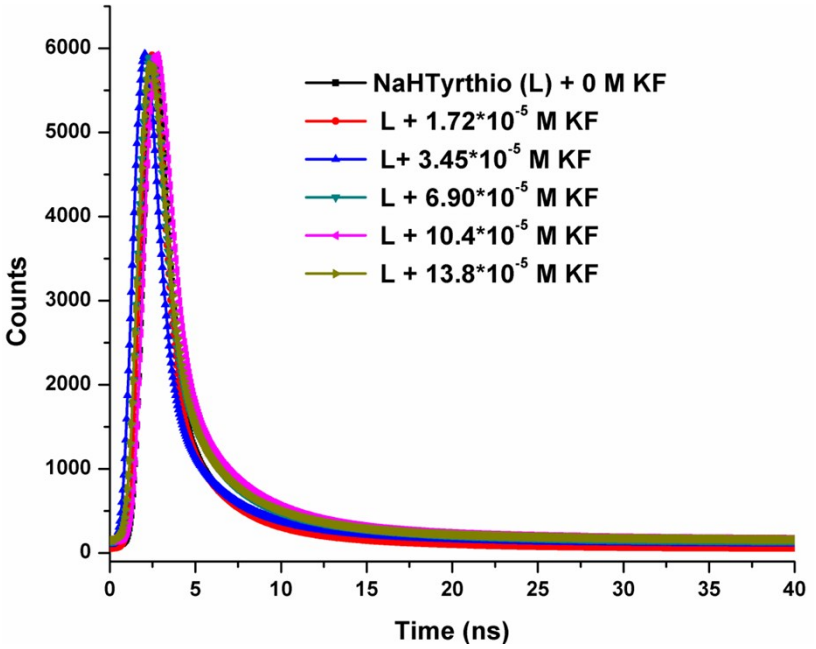


Fig. S17 Lifetime decay profiles of NaHTyrthio (3 mL, 0.72 mM/methanol) in presence of various concentrations of F^- (λ_{exc} = 370 nm, monitored at 465 nm).

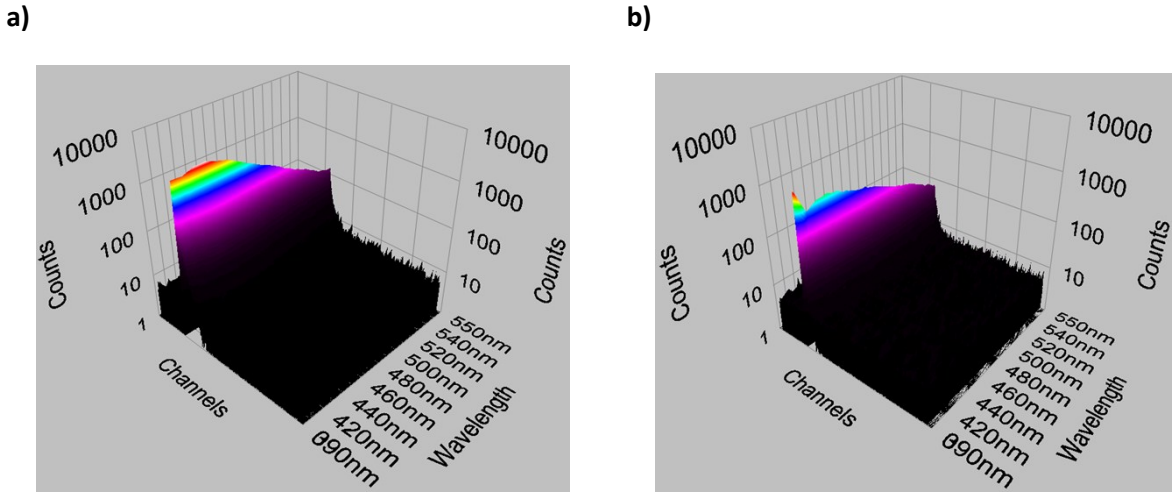


Fig. S18 Time resolved spectra of NaHTyrthio in a) absence of F^- and b) presence of F^- (λ_{exc} = 370 nm).

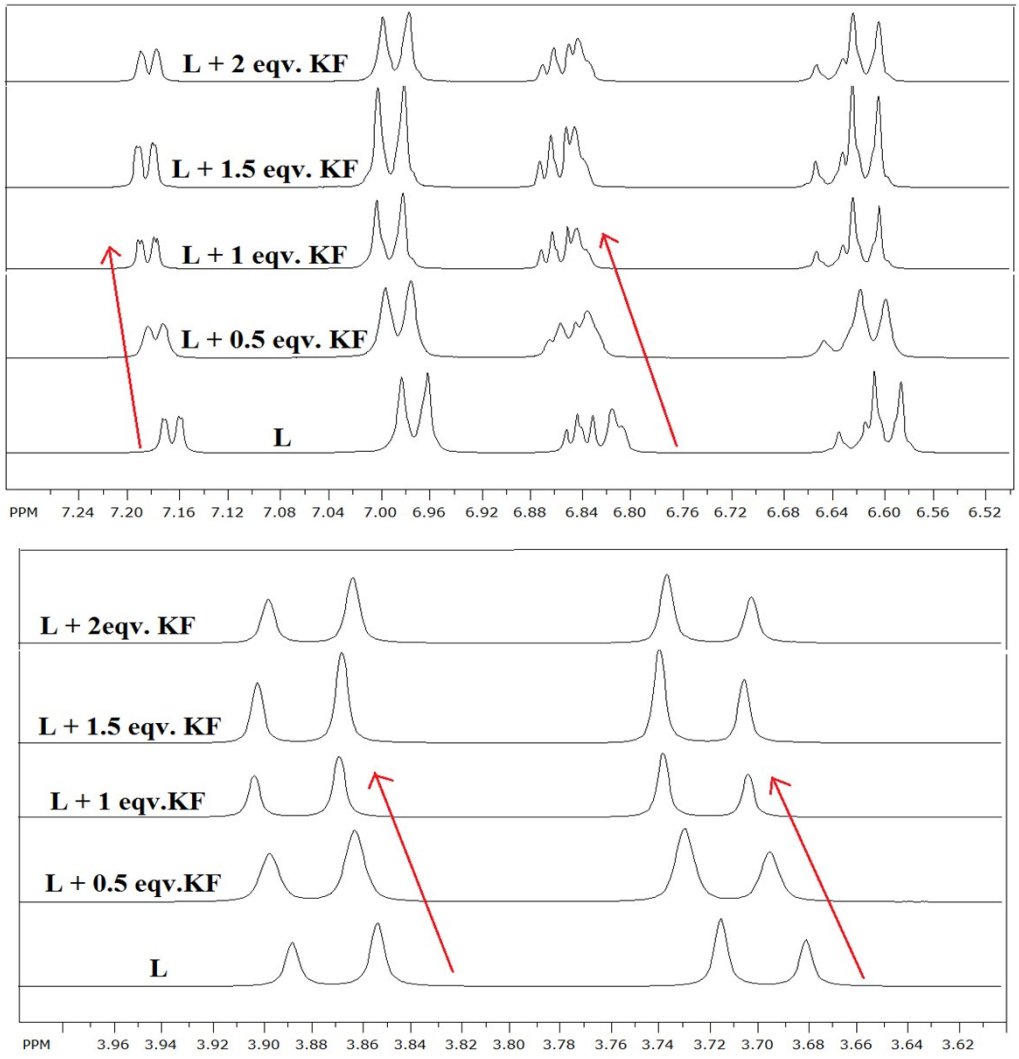
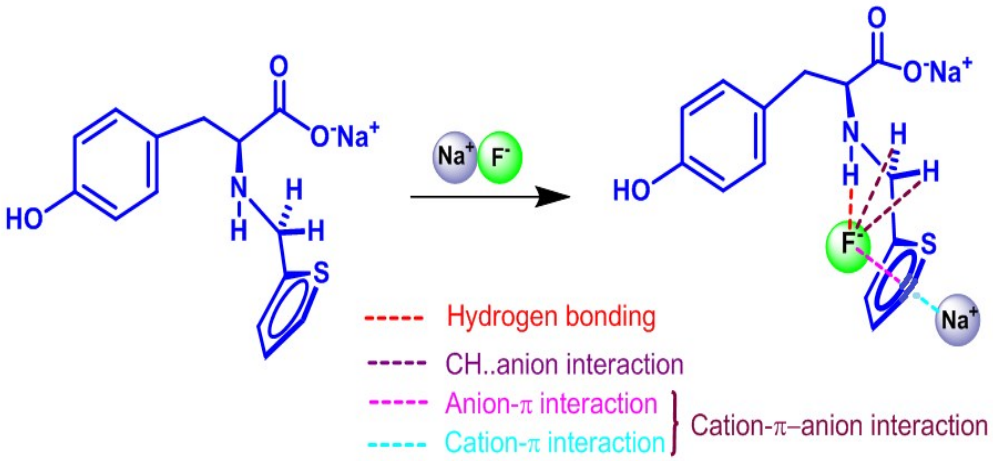


Fig. S19 ^{1}H NMR titrimetry of NaHTyrthio (L) with KF as an analyte: (a) effect on the thiophene protons (top) and (b) effect on the diastereomeric methylene protons (bottom).



Scheme S1. Schematic representation of various interactions between sensor [NaHTyrthio (L)] and analyte [NaF].

Table S1. Standard deviation for probe/sensor NaHTyrthio**.**

Blank Reading (Only sensor, NaHTyrthio)	Fluorescence intensity
Reading 1	559.317
Reading 2	560.224
Reading 3	557.213
Standard Deviation (σ)	1.544646

Table S2. Detection limit for NaHTyrthio in case of Cu^{2+} as an analyte.

Slope from graph (m)	-5.9398	μM^{-1}
Detection limit (3σ/m)	0.78	μM
Limit of detection (LOD)	49.54	ppb

Table S3. Thermodynamic parameters for interaction between NaHTyrthio (5 mM) and Cu^{2+} (0.5 mM) in methanol at 25 °C.

Sequential binding Mode (binding Sites per molecule: 3)	K (M^{-1})	ΔH (kcal/mol)	ΔS (cal/mol/deg)	ΔS (kcal/mol/deg)	T (Kelvin)	TΔS (Kcal/mol)	ΔG = ΔH−TΔS (kcal/mol)
1st site	1.59E5	-7.7	-2.11	-0.00211	298	-0.62878	-7.07122
2nd site	3.62E3	98.7	347	0.347	298	103.406	-4.706
3rd site	6.41E4	-109.9	-346	-0.346	298	-103.108	-6.792

Total ΔG = ΔG1 + ΔG2 + ΔG3 = (-7.07122) + (-4.706) + (-6.792) = -18.5692 kcal/mol

Table S4. Standard deviation for probe/sensor NaHTyrthio**.**

Blank Reading (Only sensor, NaHTyrthio)	Fluorescence intensity
Reading 1	376.50
Reading 2	372.23
Reading 3	377.67
Standard Deviation (σ)	2.86343

Table S5. Detection limit for NaHTyrthio in case of nitrobenzene as an analyte.

Slope from graph (m)	-2.3221	μM^{-1}
Detection limit (3σ/m)	3.70	μM
Limit of detection (LOD)	455	ppb

Table S6. Fluorescence decay parameters of the NaHTyrthio in methanol at 315 nm (λ_{exc} = 280 nm) in the presence of different amounts of nitrobenzene[a]

Sr. No.	[NB] * 10^{-5} M	A_1 (%)	A_2 (%)	τ_1 (ns)	τ_2 (ns)	$<\tau>$ (ns)[b]
1	0	77	23	1.37	3.79	1.93
2	1.72	77	23	1.36	3.81	1.93
3	3.45	77	23	1.34	3.80	1.89
4	6.90	79	21	1.30	3.80	1.86
5	10.40	78	22	1.29	3.74	1.86
6	13.80	78	22	1.31	3.74	1.87
7	17.30	78	22	1.31	3.68	1.88

[a]Determined from $I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where A and τ are the fractional amount and fluorescencence lifetime of the shorter (1)- and longer(2)-lived species, respectively; concentration of NaHTyrthio: 0.72 mM. [b]Weighted mean lifetime determined from $<\tau> = (A_1\tau_1 + A_1\tau_1)/(A_1 + A_2)$.

Table S7. Standard deviation for probe/sensor NaHTyrthio**.**

Blank Reading (Only sensor, NaHTyrthio)	Fluorescence intensity
Reading 1	13.146
Reading 2	13.904
Reading 3	12.464
Standard Deviation (σ)	0.720334

Table S8. Detection limit for NaHTyrthio in case of F^- as an analyte(in methanol)

Slope from graph (m)	-0.27856	mM^{-1}
Detection limit (3σ/m)	7.76	mM
Limit of detection (LOD)	148	ppm

Table S9. Effect of solvent and counter cation on the detection limits of ligand for analyte F^-.

Ligand	analyte	solvent	Detection limit	
NaHtyrothio	NaF	DMSO	13.8 ppm	$3.3*10^{-4}$ M
NaHtyrothio	NaF	Methanol	21 ppm	$5.0*10^{-4}$ M
NaHtyrothio	KF	DMSO	17 ppm	$2.9*10^{-4}$ M
NaHtyrothio	KF	Methanol	148 ppm	$2.5*10^{-3}$ M
LiHtyrothio	KF	Methanol	81 ppm	$1.39*10^{-3}$ M
LiHtyrothio	KF	DMSO	41 ppm	$7.07*10^{-4}$ M
KHtyrothio	KF	DMSO	15.3 ppm	$2.62*10^{-4}$ M
H_2tyrothio	KF	DMSO	85 ppm	$1.46*10^{-3}$ M

Table S10. Standard deviation for probe/sensor NaHTyrthio**.**

Blank Reading (Only sensor, NaHTyrthio)	Fluorescence intensity
Reading 1	15.478
Reading 2	15.654
Reading 3	15.205
Standard Deviation (σ)	0.22624

Table S11. Detection limit for NaHTyrthio in case of F^- as an analyte (in DMSO)

Slope from graph (m)	-0.93544	mM^{-1}
Detection limit (3σ/m)	0.725	mM
Limit of detection (LOD)	13.8	ppm

Table S12. Fluorescence decay parameters of the NaHTyrthio in methanol at 465 nm (λ_{exc} = 370 nm) in the presence of different amounts of F^{-a}

Sr. No.	$[F^-] * 10^{-5}$ M	A_1 (%)	A_2 (%)	A_3 (%)	τ_1 (ns)	τ_2 (ns)	τ_3(ns)	$<\tau>$ (ns)[b]
1	0	11	02	87	2.23	7.97	0.34	0.70
2	1.72	11	02	87	2.35	7.77	0.38	0.75
3	3.45	13	02	85	2.53	8.42	0.46	0.77
4	6.90	17	04	79	2.31	7.93	0.50	1.10
5	10.40	17	02	81	3.09	10.15	0.62	1.23
6	13.80	16	02	81	3.31	11.19	0.67	1.30

[a]Determined from $I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where A and τ are the fractional amount and fluorescence lifetime of varied species,; concentration of NaHTyrthio: 0.72 mM. [b]Weighted mean lifetime determined from $<\tau> = (A_1\tau_1 + A_2\tau_2 + A_3\tau_3)/(A_1 + A_2 + A_3)$.