Supporting Information

A simple and dual responsive efficient new Schiff base chemoreceptor for selective sensing of F^- and Hg^{2+}: application to bioimaging in living cells and mimicking of molecular logic gates†

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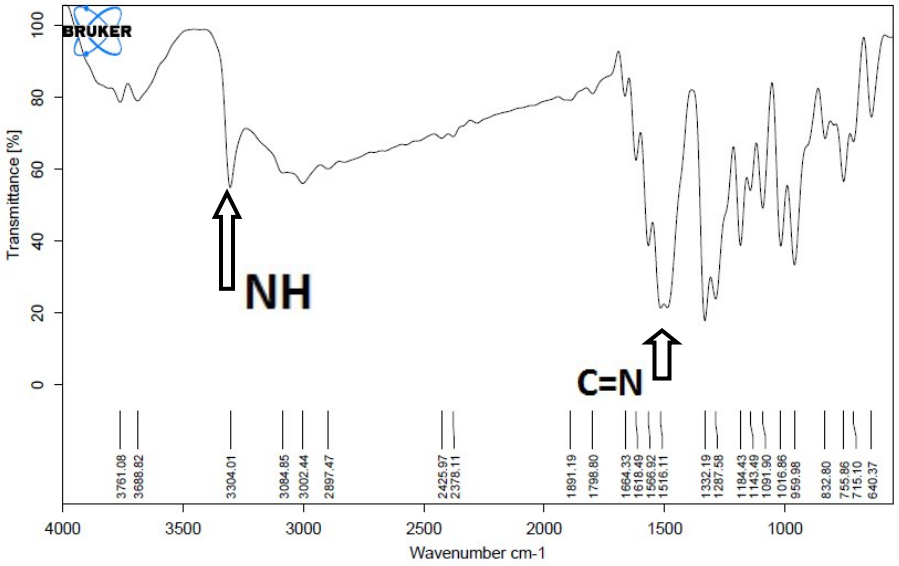


Fig. S1 IR data of **NPMP**.

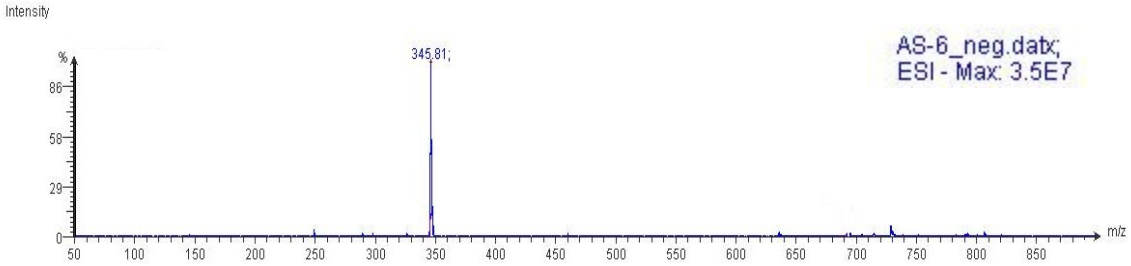


Fig. S2 ESI-Mass data of **NPMP**.

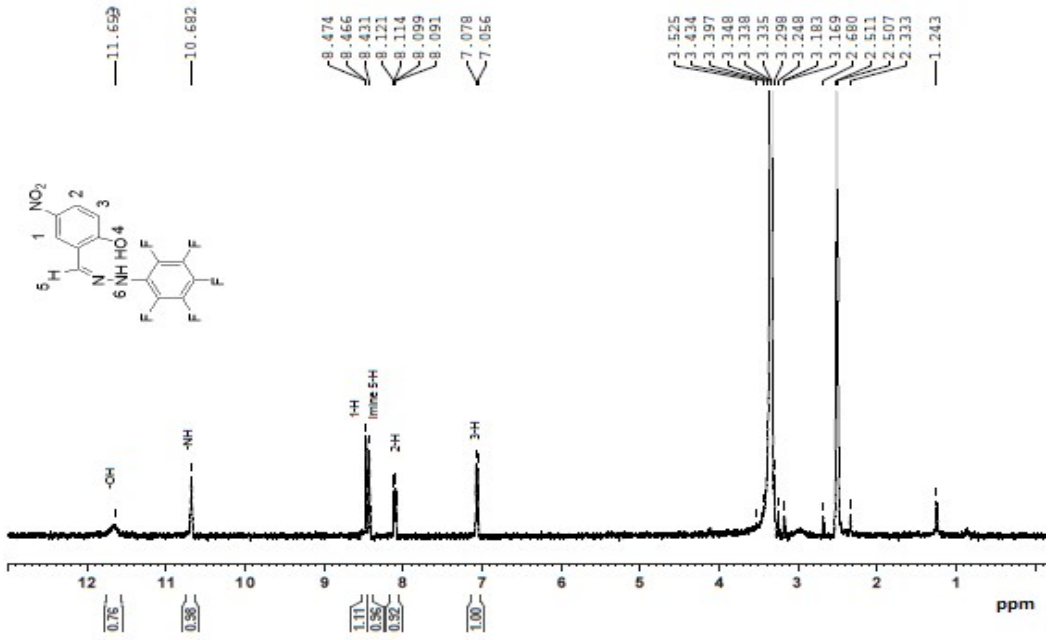


Fig. S3 ^{1}H NMR data of **NPMP** in DMSO-d_6.

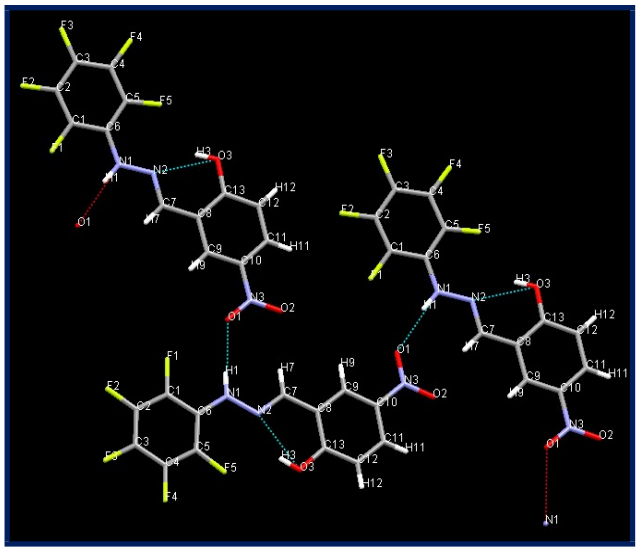


Fig. S4 Wireframe network showing intra & intermolecular hydrogen bonding in **NPMP**.

Table S1 Crystallographic data of **NPMP**

Crystal Data	
Formula	C13 H6 F5 N3 O3
Formula Weight	347.21
Crystal System	Monoclinic
Space group	P21/c (No. 14)
a, b, c [Angstrom]	8.404(2) 13.281(3) 11.867(3)
alpha, beta, gamma [deg]	90 102.612(5) 90
V [Ang**3]	1292.6(5)
Z	4
D(calc) [g/cm**3]	1.784
Mu(MoKa) [/mm]	0.175
F(000)	696
Crystal Size [mm]	0.16 x 0.18 x 0.24

Data Collection	
Temperature (K)	293
Radiation [Angstrom]	MoKa 0.71073
Theta Min-Max [Deg]	2.3, 25.0
Dataset	-9: 9 ; -15: 15 ; -14: 14
Tot., Uniq. Data, R(int)	9515, 2166, 0.087
Observed data [I > 2.0 sigma(I)]	1867
Refinement	
Nref, Npar	2166, 219
R, wR2, S	0.0751, 0.2322, 1.22
w = 1/[\s^2^(Fo^2^)+(0.1675P)^2^]	where P=(Fo^2^+2Fc^2^)/3
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Ang^3]	-0.63, 0.59

Table S2 Selected bond distances (angstrom) of **NPMP**

F1	-C1	1.357(3)	C2	-C3	1.374(3)
F2	-C2	1.344(3)	C3	-C4	1.378(4)
F3	-C3	1.352(3)	C4	-C5	1.395(4)
F4	-C4	1.340(3)	C5	-C6	1.397(3)
F5	-C5	1.345(3)	C7	-C8	1.447(4)
O1	-N3	1.230(3)	C8	-C13	1.434(4)
O2	-N3	1.241(3)	C8	-C9	1.405(4)
O3	-C13	1.346(3)	C9	-C10	1.375(4)
O3	-H3	0.8200	C10	-C11	1.404(4)
N1	-N2	1.371(3)	C11	-C12	1.379(4)
N1	-C6	1.382(3)	C12	-C13	1.393(4)
N2	-C7	1.288(3)	C7	-H7	0.9300
N3	-C10	1.452(4)	C9	-H9	0.9300
N1	-H1	0.8600	C11	-H11	0.9300
C1	-C6	1.395(4)	C12	-H12	0.9300
C1	-C2	1.380(4)			

Table S3 Selected bond angles (degree) of **NPMP**

C13	-O3	-H3	110.00	C1	-C6	-C5	116.0(2)
N2	-N1	-C6	121.1(2)	N1	-C6	-C5	126.4(2)
N1	-N2	-C7	116.8(2)	N2	-C7	-C8	120.7(2)
O1	-N3	-C10	118.4(2)	C7	-C8	-C13	122.8(2)
O2	-N3	-C10	118.5(2)	C7	-C8	-C9	119.5(2)
O1	-N3	-O2	123.1(2)	C9	-C8	-C13	117.7(2)
N2	-N1	-H1	119.00	C8	-C9	-C10	120.2(2)
C6	-N1	-H1	119.00	N3	-C10	-C9	118.9(2)
C2	-C1	-C6	123.0(2)	N3	-C10	-C11	119.1(2)
F1	-C1	-C6	118.5(2)	C9	-C10	-C11	122.1(2)
F1	-C1	-C2	118.5(2)	C10	-C11	-C12	118.9(2)
C1	-C2	-C3	119.8(2)	C11	-C12	-C13	120.5(2)
F2	-C2	-C3	120.6(2)	O3	-C13	-C8	121.4(2)
F2	-C2	-C1	119.6(2)	O3	-C13	-C12	117.9(2)
F3	-C3	-C2	120.3(2)	C8	-C13	-C12	120.7(2)
F3	-C3	-C4	120.3(2)	N2	-C7	-H7	120.00
C2	-C3	-C4	119.4(2)	C8	-C7	-H7	120.00
C3	-C4	-C5	120.5(2)	C8	-C9	-H9	120.00
F4	-C4	-C3	120.9(2)	C10	-C9	-H9	120.00
F4	-C4	-C5	118.6(2)	C10	-C11	-H11	121.00
F5	-C5	-C4	116.7(2)	C12	-C11	-H11	121.00
F5	-C5	-C6	122.0(2)	C11	-C12	-H12	120.00
C4	-C5	-C6	121.4(2)	C13	-C12	-H12	120.00
N1	-C6	-C1	117.6(2)				

Table S4 Hydrogen bonding in **NPMP**

N1 -- H1 .. F1	0.8600	2.3400	2.682(3)	104.00	.
N1 -- H1 .. O1	0.8600	2.2200	3.065(3)	168.00	2_746
O3 -- H3 .. F5	0.8200	2.3800	3.029(3)	136.00	.
O3 -- H3 .. N2	0.8200	1.9200	2.643(3)	147.00	.
C7 -- H7 .. O2	0.9300	2.4600	3.365(4)	165.00	2_746

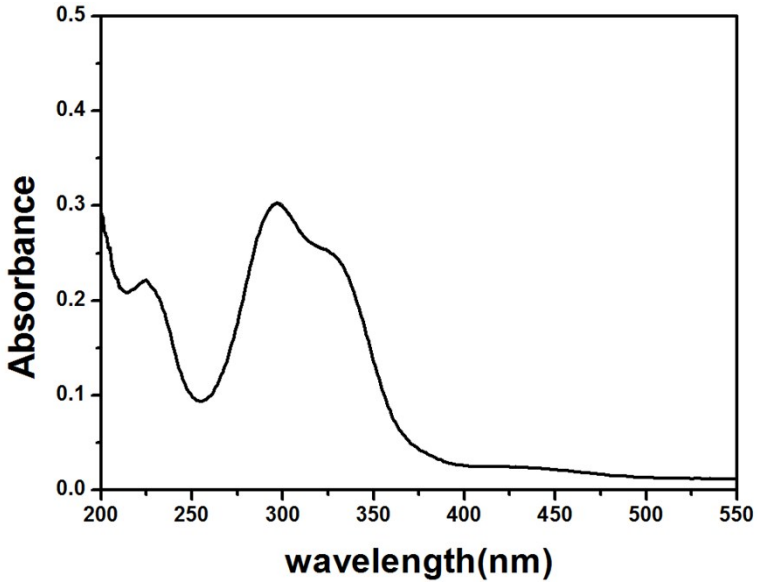


Fig. S5 UV-Vis spectrum of **NPMP** in DMSO.

Benesi-Hildebrand Equation and Plot:

The association constant of a complex formed in between **NPMP** and F^- has been determined from the following complex equilibrium.

$$L + mX^{n-} \longleftrightarrow (X_mL)^{mn-}$$

$$K = \frac{[(X_mL)]^{mn-}}{[L][X^{n-}]m}$$

For 1:1 type complex formation with m=1 following the Benesi-Hildebrand relation, can be expressed in terms of optical density (A) as follows:

$$\frac{A_o + A_1 K[X^{n-}]}{1 + K[X^{n-}]}$$

A =

Or, $$\frac{1}{A - A_0} = \frac{1}{(A_1 - A_0)} + \frac{1}{(A_1 - A_0)K[X^{n-}]}$$

Where $[X^{n-}]$, [L] and $[(X_mL)^{mn-}]$ are the concentration of the added anion, receptor and the complexation between anions and receptors, respectively. A_o, A and A_1 indicates the optical density or absorbance at a particular wavelength of **NPMP** without adding any anion, absorbance after adding anion at every successive step and excess amount of added anion, respectively. The binding constant or association constant K (M^{-1} or M^{-2}) is determined from the ratio of intercept and slope of Benesi-Hildebrand plot of optical density.

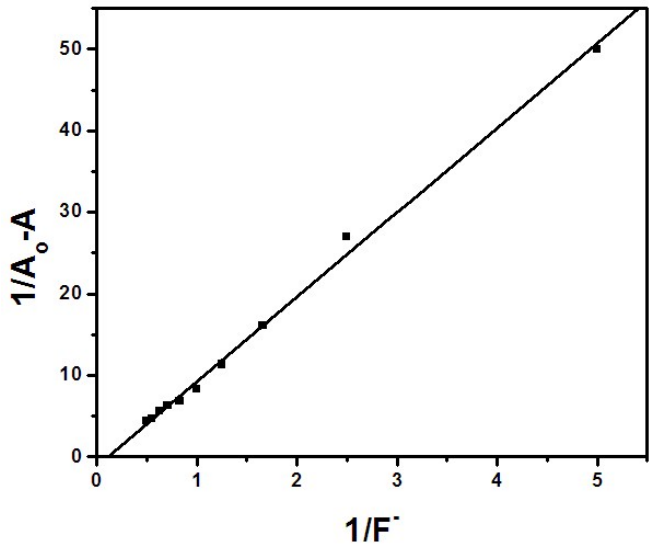
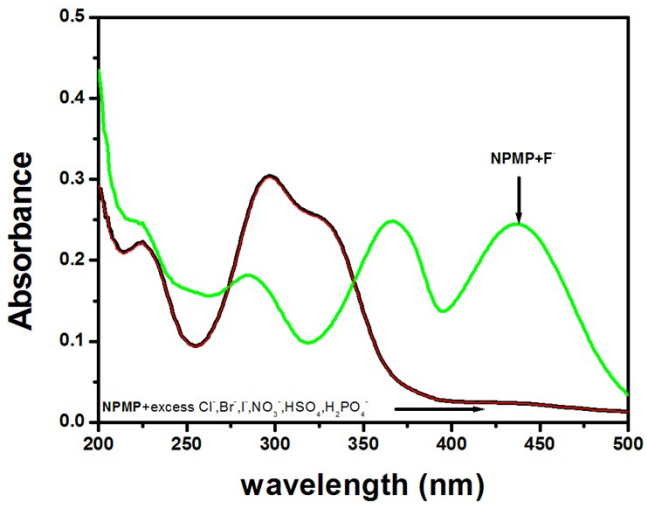
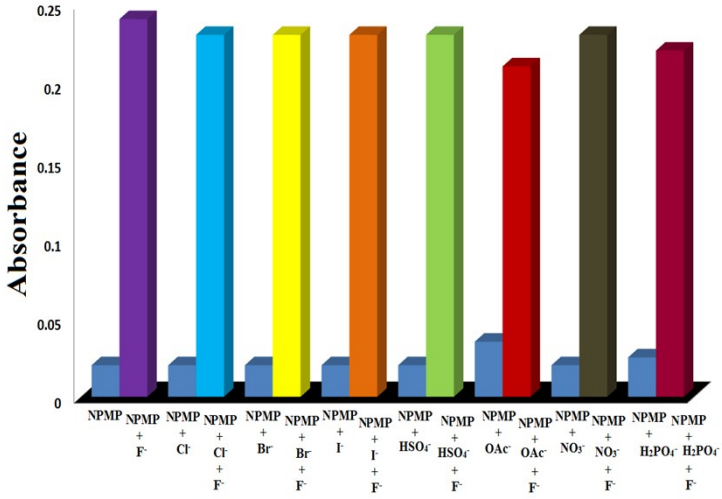


Fig. S6 B-H plot of **NPMP** *vs.*TBAF.



(a)



(b)

Fig. S7 (a) UV-Vis spectral changes of **NPMP** ($2x10^{-5}$M) with other **TBA** salts of in 9:1 *v/v* DMSO-HEPES buffer at pH 7.4 (0-2eq), (b) 2D plot showing interference of F^- in presence of other anions.

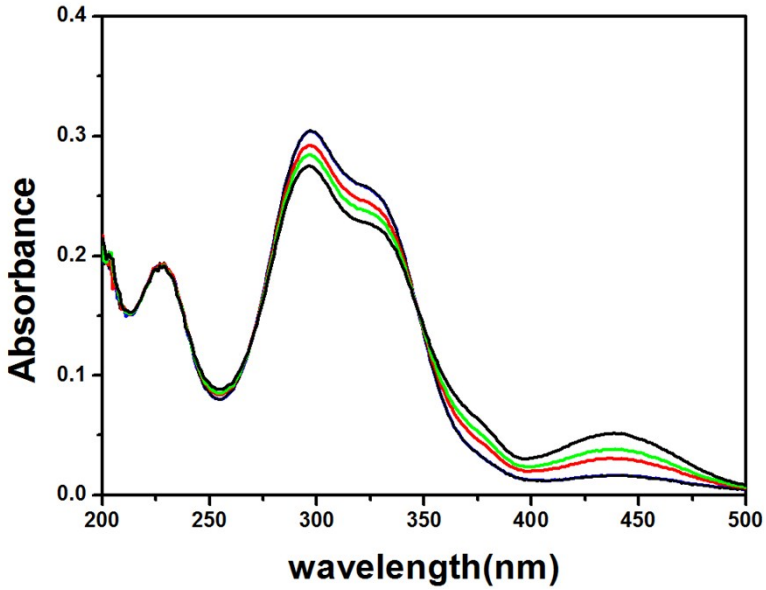


Fig. S8 UV-Vis spectral changes of **NPMP** ($2x10^{-5}$M) with **TBA** salts of OAc^- in 9:1 *v/v* DMSO-HEPES buffer at pH 7.4 (0-2eq).

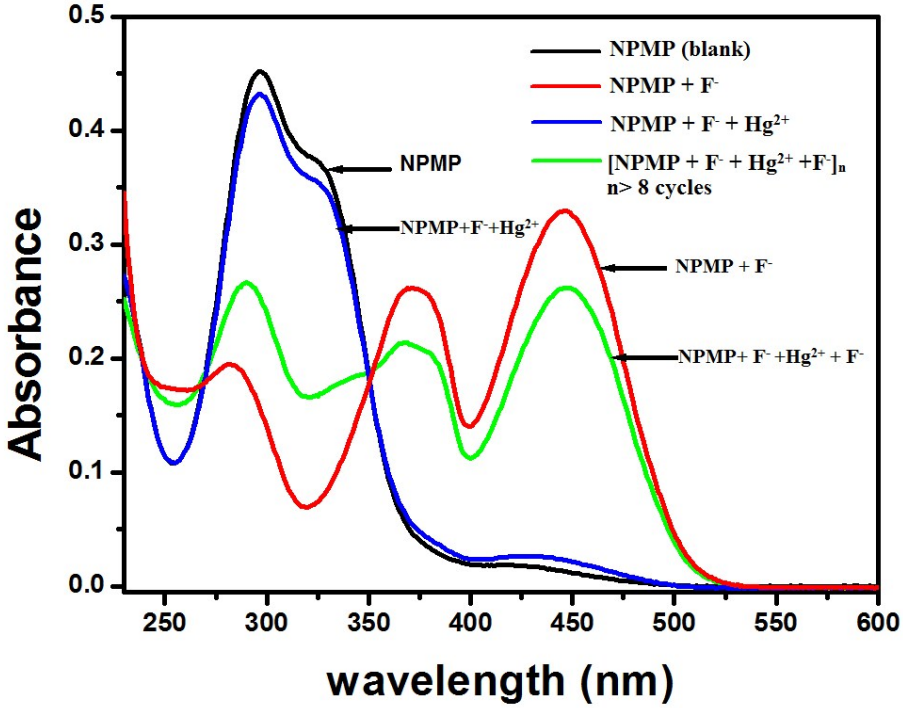


Fig. S9 UV-Vis spectral changes of **NPMP** ($2x10^{-5}$M) with F^- ($2 x10^{-4}$M) followed by Hg^{2+} (10^{-4}M) and further addition of F^- in 9:1 *v/v* DMSO- HEPES buffer at pH 7.4 in same repetitive manner.

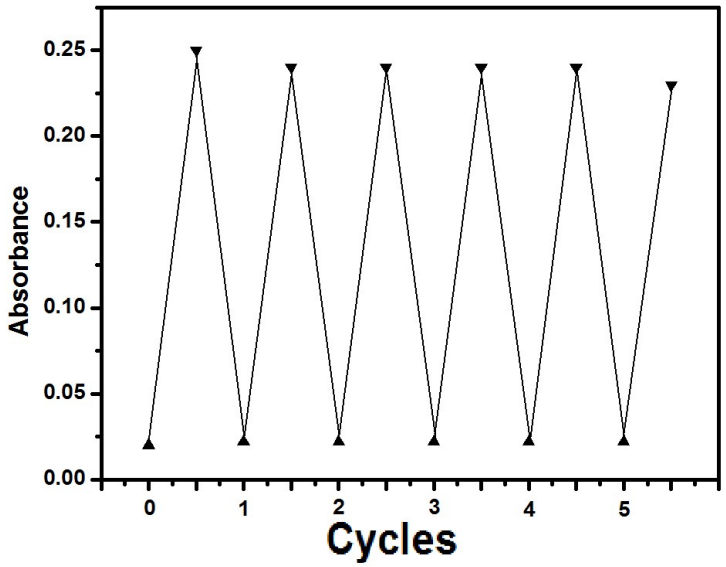


Fig. S10 Repeatability experimentation of **NPMP** in presence of F^- and Hg^{2+}.

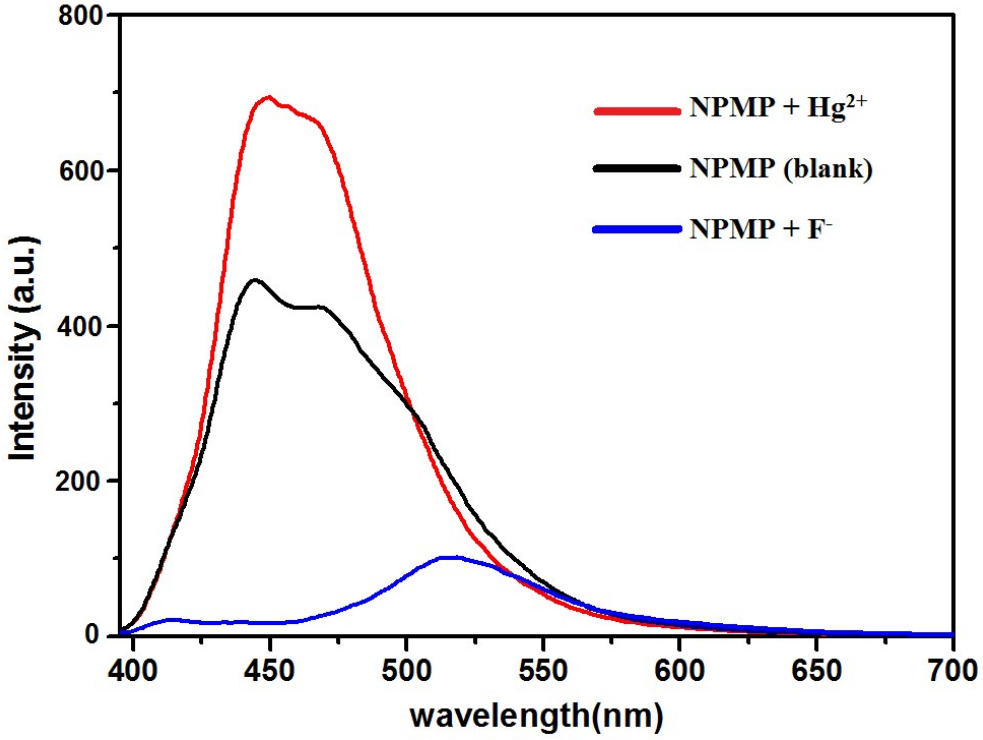


Fig. S11 Intensity changes of **NPMP** ($2x10^{-6}$M) after addition of F^-($2x10^{-5}$M) and Hg^{2+} (10^{-5}M) in 9:1 *v/v* DMSO-HEPES buffer at pH 7.4 (0-2eq).

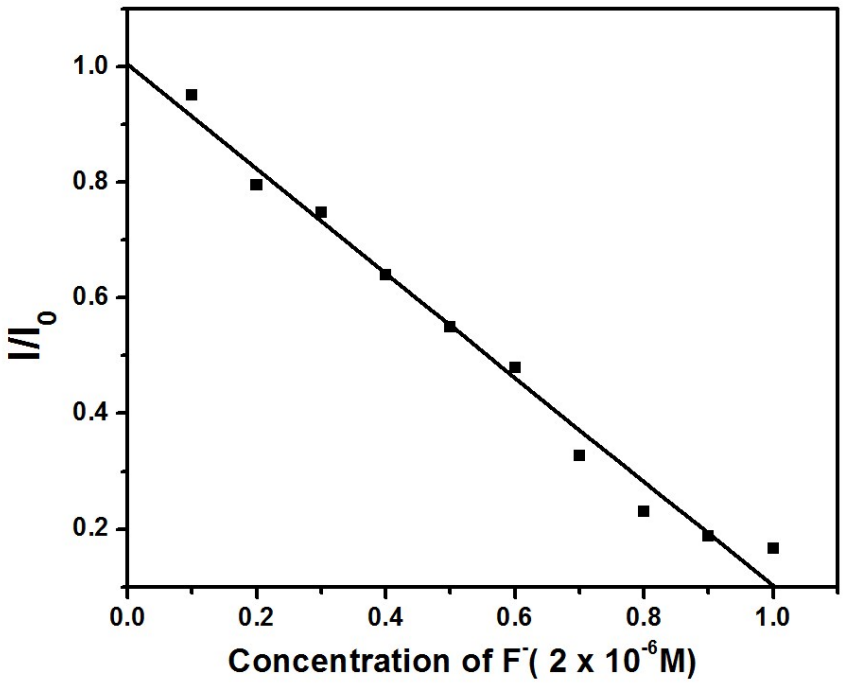


Fig. S12 Plot of ratio of emission intensity *vs* equivalent of F^- for calculation of limit of detection.

Preparation of cells

Candida albicans cells (IMTECH No. 3018) from exponentially growing culture in yeast extract glucose broth medium (pH 6.0 and incubation temperature 37^0C) were washed by suspending them in normal saline and centrifuged at 3000 rpm for 10 minutes. It was washed twice with 0.1 M HEPES buffer (pH 7.4). Then cells were treated with F^- solution (10 μM) for 1hr (Fig. 8a). After incubation, the cells were again washed with HEPES buffer and then incubated with **NPMP** (100 μM) for another 1hr. Cells obtained this way were mounted on a grease free glass slide and observed under a Leica DM 1000 Fluorescence microscope with UV filter (Fig. 8c). Cells treated with F^- were used as control.

Preparation of pollen grains to detect intracellular F^-: Pollen grains of *Techoma stans* (Family: Bignoniaceae) were collected from fresh buds and washed twice with 0.1 M HEPES buffer at pH 7.4. These were then treated with 10 μM F^- for 1hr in 0.1 M HEPES buffer (pH 7.4) containing 0.01% Triton X100 as a permeability enhancing agent(Fig. 8b). After incubation the pollens are washed again with HEPES buffer at pH 7.4 and incubated with **NPMP** (100 μM) for 1hr. **NPMP** treated pollens were washed by centrifugation (3000 rpm for 5 minutes) using HEPES buffer and are mounted on a grease free glass slide and observed under a Leica DM 1000

fluorescence microscope equipped with a UV filter (Fig. 8d). Cells treated with F^- were used as control.