Electronic Supplementary Information

Colorimetric and fluorimetric response of Schiff base molecules towards fluoride anion, solution test kit fabrication, logical interpretations and DFT-D3 study

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1. Experimental

Materials and general methods

Most of the starting materials (reagents, solvents) were commercially available and all reagents and solvents purchased were of analytical grade and used without further purification. All anions tetrabutyl ammonium fluoride, chloride, nitrate, acetate, phosphate monobasic were purchased from Sigma Aldrich company; meanwhile, tetrabutyl ammonium bromide, iodide, hydrogen sulphate were purchased from Alfa Aesar company. Solvents like Methanol, DMSO, Acetonitrile, water were of spectroscopic grade and purchased from Merck India Pvt. Ltd. and used without any further purification. A Perkin Elmer 2400C elemental analyser was used to collect the microanalytical (C, H, N) data. UV-Vis spectroscopy was done on an ALS SEC2000 and Varian Cary-60 spectrophotometer. ESI-MS mass spectra were recorded on an Advion make compact mass spectrometer (serial no. 3013-0140). Fluorescence measurement was done with a Perkin Elmer LS45 spectrofluorimeter. Luminescence lifetime measurements were carried out using a time-correlated single photon counting set up from Horiba Jobin-Yvon. The luminescence decay data were collected on a Hamamatsu MCP photomultiplier (R3809) and were analyzed using the IBH DAS6 software. ^{1}H NMR experiments were carried out on a Bruker made 300 MHz NMR spectrometer.

The average lifetimes (τ_{av}) of **P1**, **P2** and corresponding adducts with fluoride were calculated using following equation:

$$\tau_{av} = a_1\tau_1 + a_2\tau_2$$

τ_1 and τ_2 are the first and second lifetime components respectively which were monitored at the emission maxima of the fluorophore, and a_1 & a_2 are respective amplitudes of the components.

P1: T1 = 1.158984E-09 sec, S. Dev = 1.917736E-11 sec
T2 = 7.28772E-09 sec, S. Dev = 8.853577E-11 sec
B1 = 6.783012E-02, S. Dev = 4.902115E-04
B2 = 7.732297E-03, S. Dev = 5.824619E-05
CHISQ = 1.136105

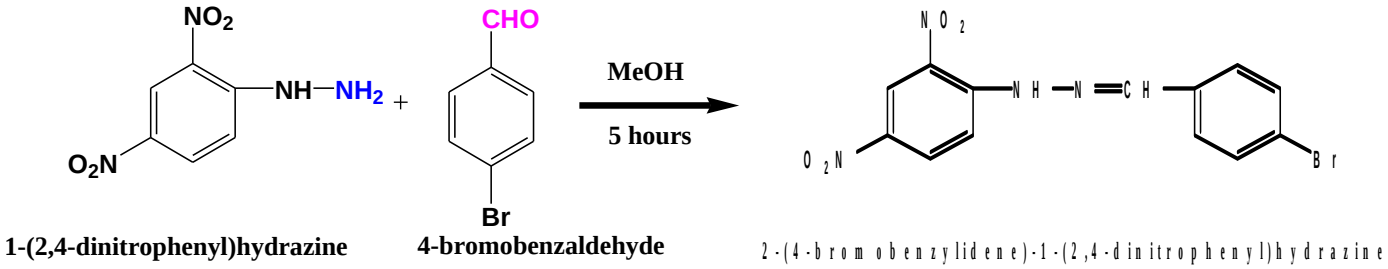
P1●●●F-: T1 = 5.580478E-10 sec, S. Dev = 1.433873E-11 sec
T2 = 4.212882E-09 sec, S. Dev = 5.852167E-11 sec
B1 = 9.989107E-02, S. Dev = 9.091623E-04
B2 = 7.515633E-03, S. Dev = 6.978125E-05
CHISQ = 1.096266

P2: T1 = 2.100857E-10 sec, S. Dev = 5.176959E-12 sec
T2 = 2.111048E-09 sec, S. Dev = 1.095779E-10 sec
B1 = 0.3277334, S. Dev = 2.567874E-03
B2 = 2.97201E-03, S. Dev = 9.100714E-05
CHISQ = 1.047032

P2●●●F$^-$: T1 = 1.068916E-09 sec, S. Dev = 2.352487E-11 sec
T2 = 3.949161E-09 sec, S. Dev = 1.132728E-10 sec
B1 = 2.908506, S. Dev = 2.402942E-02
B2 = 0.444755, S. Dev = 6.113427E-03
CHISQ = 1.025635

Preparation of P1

To the stirring solution of 4-bromo benzaldehyde (185mg, 1 mmol) in MeOH (20 mL) 2, 4-dinitro phenyl hydrazine (198mg, 1 mmol) in 1:1 ratio was added and continues stirring for 5 hours (Scheme S1). After completion of the reaction, excess solvent was removed under reduced pressure and a solid orange colored product was obtained. Yield ~92%. Formation was confirmed by solid state study like elemental analysis and solution state study like ESI-MS and ^{1}H-NMR study. Elemental analysis calculated for $C_{13}H_9BrN_4O_4$: C: 42.76%; H: 2.48%; N: 15.34%, Found: C: 42.74%; H: 2.46%; N:15.35%. ESI-MS (**P1**-H^+): m/z =364, found 363.1 (Fig. S1). ^{1}H-NMR spectra taken in DMSO-d_6 is shown in Fig. S2.



1-(2,4-dinitrophenyl)hydrazine **4-bromobenzaldehyde** 2-(4-bromobenzylidene)-1-(2,4-dinitrophenyl)hydrazine

Scheme S1 Synthesis of **P1.**

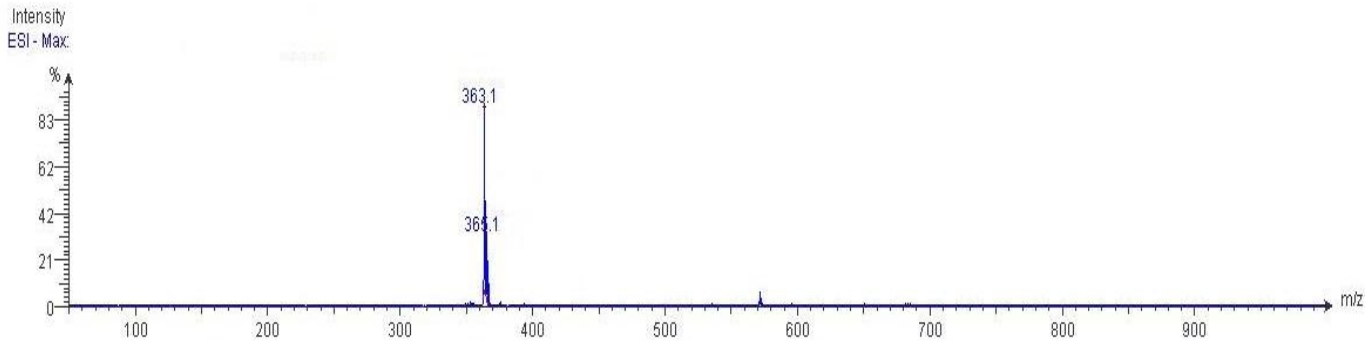


Fig. S1 ESI-MS data of **P1** in MeOH.

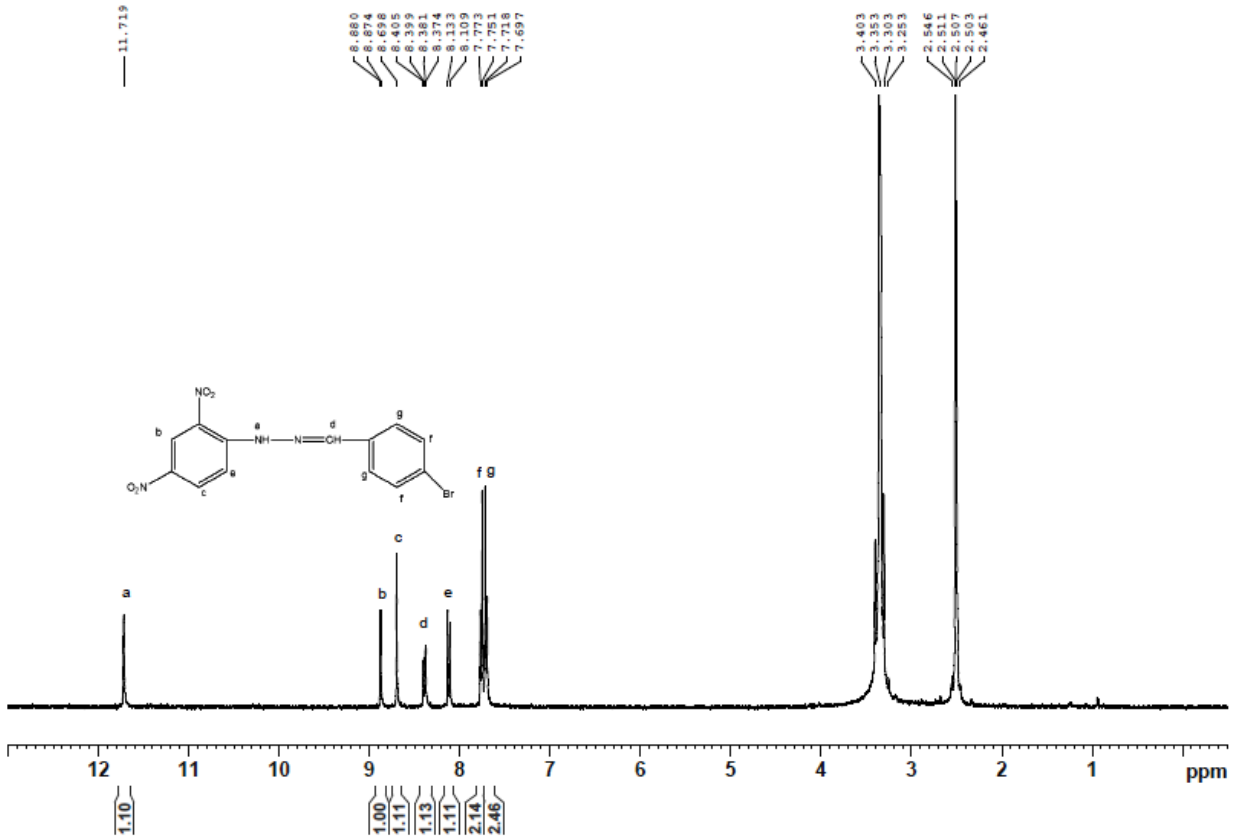
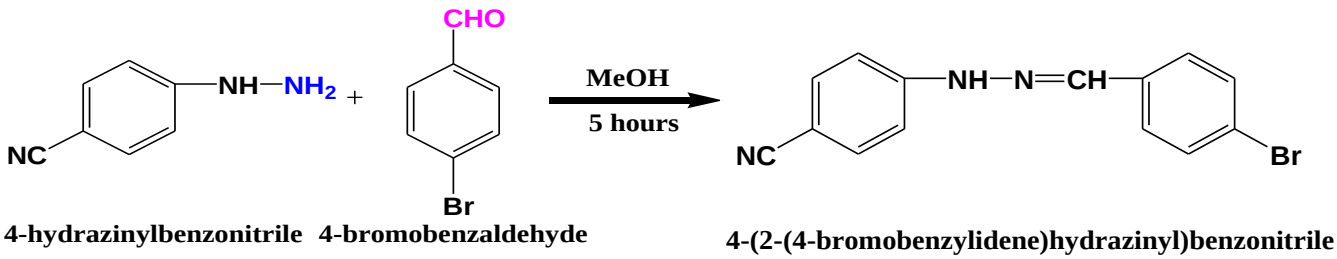


Fig. S2 ^{1}H-NMR data of **P1** in DMSO-d_6.

Preparation of P2

To the stirring solution of 4-bromo benzaldehyde (185mg, 1 mmol) in MeOH (20 mL) 4-cyano phenyl hydrazine (170mg, 1 mmol) in 1:1 ratio was added and continue stirring for 5 hours (Scheme S2). After completion of the reaction, excess solvent was removed under reduced pressure and a solid pale yellow colored product was obtained. The crude product was recrystallized repeatedly from dichloromethane (dcm) and finally layering of dcm solution of **P2** with hexane in 1:1 ratio produced single crystals suitable for x-ray study after 3 days. Formation was confirmed by solid state study like elemental analysis, Single crystal X-Ray analysis and solution state study like ESI-MS and ^{1}H-NMR study. Crystallographic data, bond ditances and bond angles are shown in Table S1-S3. Yield ~93%. Elemental analysis calculated for $C_{14}H_{10}BrN_3$: C, 56.02; H, 3.36; N, 14.00, Found: C: 55.98%; H: 3.32%; N: 13.96%. ORETP and atom numbering picture is shown Fig. 1b. ESI-MS(**P2**-H^+): m/z =299, found 298.29 (Fig. S3). ^{1}H-NMR spectra taken in DMSO-d_6 is shown in Fig. S4.



4-hydrazinylbenzonitrile **4-bromobenzaldehyde** **4-(2-(4-bromobenzylidene)hydrazinyl)benzonitrile**

Scheme S2 Synthesis of **P2.**

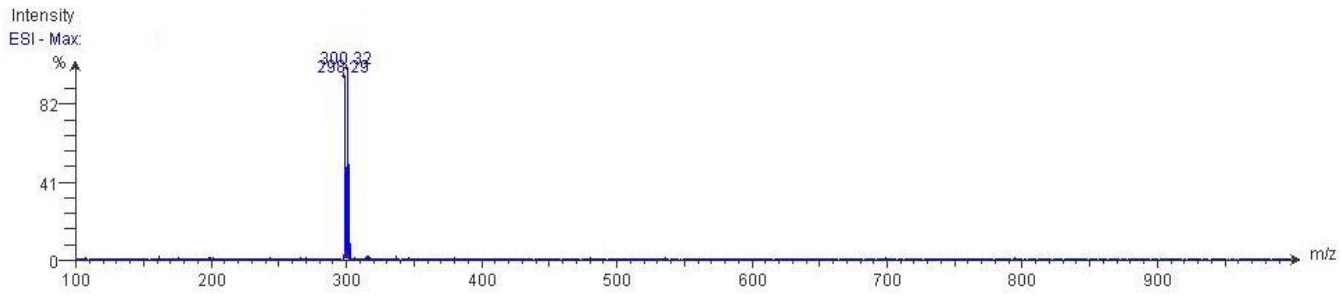


Fig. S3 ESI-MS data of **P2** in MeOH.

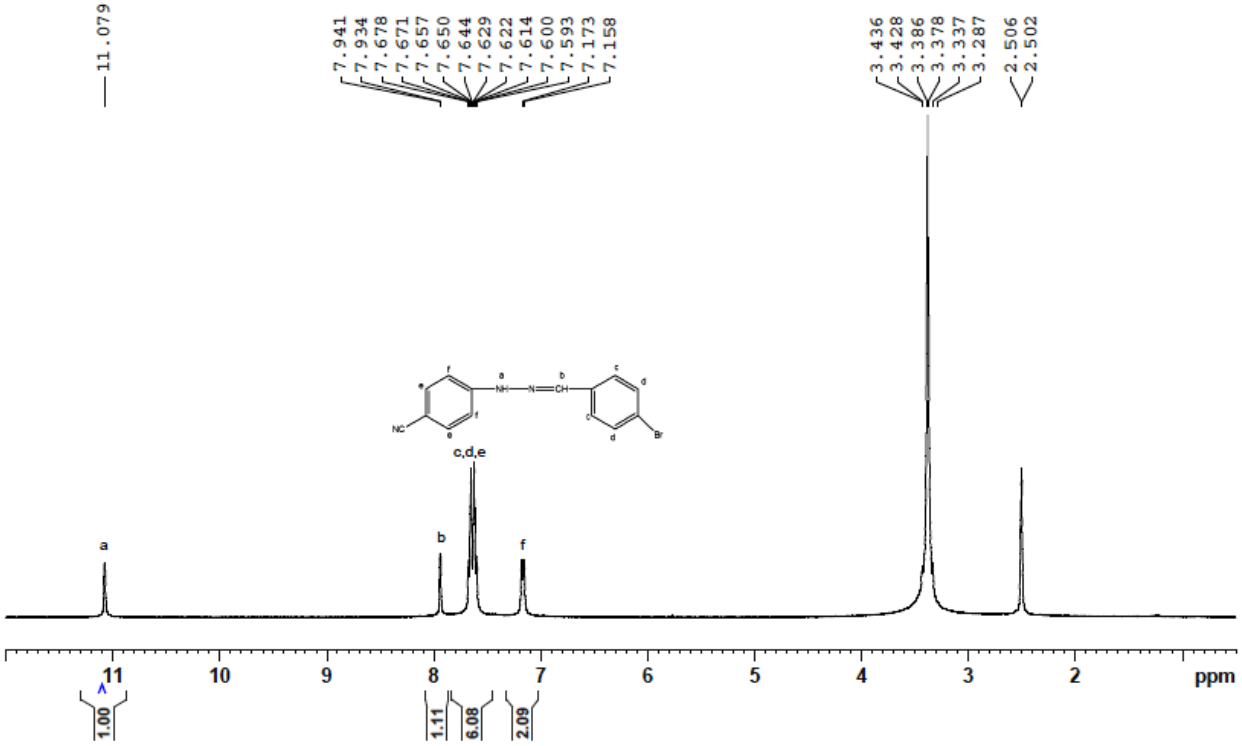


Fig. S4 ^{1}H-NMR data of **P2** in DMSO-d_6.

Table S1 Crystal Data and Details of the Structure Determination for **P2**

Crystal Data

Formula	$C_{14}H_{10}BrN_3$	Formula Weight	300.15
Crystal System	Monoclinic	Space group	P21/c (No. 14)
a, b, c [Angstrom]	7.7832(10) 9.8765(13) 16.564(2)	alpha, beta, gamma [deg]	90 91.056(3) 90
V [Ang**3]	1273.1(3)	Z	4
D(calc) [g/cm**3]	1.566	Mu(MoKa) [/mm]	3.213
F(000)	600		
Crystal Size [mm]	0.18 x 0.20 x 0.22		

Data Collection

Temperature (K)	150	Radiation [Angstrom]	MoKa 0.71073
Theta Min-Max [Deg]	2.4, 25.0	Dataset	-9: 9 ; -11: 11 ; -19: 19
Tot., Uniq. Data, R(int)	11727, 2236, 0.054	Observed Data [I > 2.0 sigma(I)]	1922

Refinement

Nref, Npar	2236, 163	R, wR2, S	0.0312, 0.0772, 1.05
w = 1/[\s^2^(Fo^2^)+(0.0356P)^2^+0.6490P] where P=(Fo^2^+2Fc^2^)/3			
Max. and Av. Shift/Error	0.00, 0.00		
Min. and Max. Resd. Dens. [e/Ang^3]	-0.41, 0.56		

Table S2 Bond Distances (Angstrom) for **P2**

Br1	-C12	1.901(3)	C9	-C10	1.395(4)	N1	-C1	1.143(4)	C10	-C11	1.380(4)
N2	-N3	1.360(3)	C11	-C12	1.380(4)	N2	-C5	1.377(3)	C12	-C13	1.388(4)
N3	-C8	1.278(3)	C13	-C14	1.364(4)	N2	-H2	0.8600	C3	-H3	0.9300
C1	-C2	1.434(4)	C4	-H4	0.9300	C2	-C7	1.394(4)	C6	-H6	0.9300
C2	-C3	1.396(4)	C7	-H7	0.9300	C3	-C4	1.368(4)	C8	-H8	0.9300
C4	-C5	1.395(4)	C10	-H10	0.9300	C5	-C6	1.401(4)	C11	-H11	0.9300
C6	-C7	1.382(4)	C13	-H13	0.9300	C8	-C9	1.460(4)	C14	-H14	0.9300
C9	-C14	1.401(4)									

Table S3 Bond Angles (Degrees) for **P2**

N3	-N2	-C5	120.8(2)	Br1	-C12	-C11	120.0(2)	N2	-N3	-C8	116.7(2)
C11	-C12	-C13	120.9(3)	N3	-N2	-H2	120.00	C12	-C13	-C14	119.8(3)
C5	-N2	-H2	120.00	C9	-C14	-C13	121.0(2)	N1	-C1	-C2	177.3(3)
C2	-C3	-H3	120.00	C1	-C2	-C7	121.4(2)	C4	-C3	-H3	120.00
C3	-C2	-C7	119.5(2)	C3	-C4	-H4	120.00	C1	-C2	-C3	119.2(2)
C5	-C4	-H4	120.00	C2	-C3	-C4	120.5(2)	C5	-C6	-H6	120.00
C3	-C4	-C5	120.4(2)	C7	-C6	-H6	120.00	N2	-C5	-C4	117.8(2)
C2	-C7	-H7	120.00	C4	-C5	-C6	119.5(2)	C6	-C7	-H7	120.00
N2	-C5	-C6	122.7(2)	N3	-C8	-H8	119.00	C5	-C6	-C7	119.9(2)
C9	-C8	-H8	119.00	C2	-C7	-C6	120.2(2)	C9	-C10	-H10	119.00
N3	-C8	-C9	121.4(2)	C11	-C10	-H10	119.00	C10	-C9	-C14	118.1(2)
C10	-C11	-H11	121.00	C8	-C9	-C10	120.1(2)	C12	-C11	-H11	121.00
C8	-C9	-C14	121.9(2)	C12	-C13	-H13	120.00	C9	-C10	-C11	121.4(3)
C14	-C13	-H13	120.00	C10	-C11	-C12	119.0(2)	C9	-C14	-H14	120.00
Br1	-C12	-C13	119.1(2)	C13	-C14	-H14	120.00				

2. Benesi-Hildebrand Equation and Plot

The association constant of a complex formed in between the sensors and the incoming fluoride anions 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:

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

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, chemo sensor and the complexation between anion and concerned chemo sensor, respectively. A_o, A and A_1 indicates the optical density or absorbance at a particular wavelength of **P1** (Fig. S5a) and **P2** (Fig. S5b) without adding F^- anion, absorbance after adding fluoride at every successive steps and excess amount of fluoride 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 (B-H) plot of optical density. As shown in the Fig. S5, the Benesi-Hildebrand (B-H) plot of $1/[A-A_0]$ *vs* $1/[F^-]$ for the titration of sensor **P1** and **P2** and TBA^+F^- provides a straight line (best fitted), indicating a 1:1 type complex formation with association constant K = 6.6 x 10^3 M^{-1} for **P1** and 3 x 10^3 M^{-1} for **P2.**

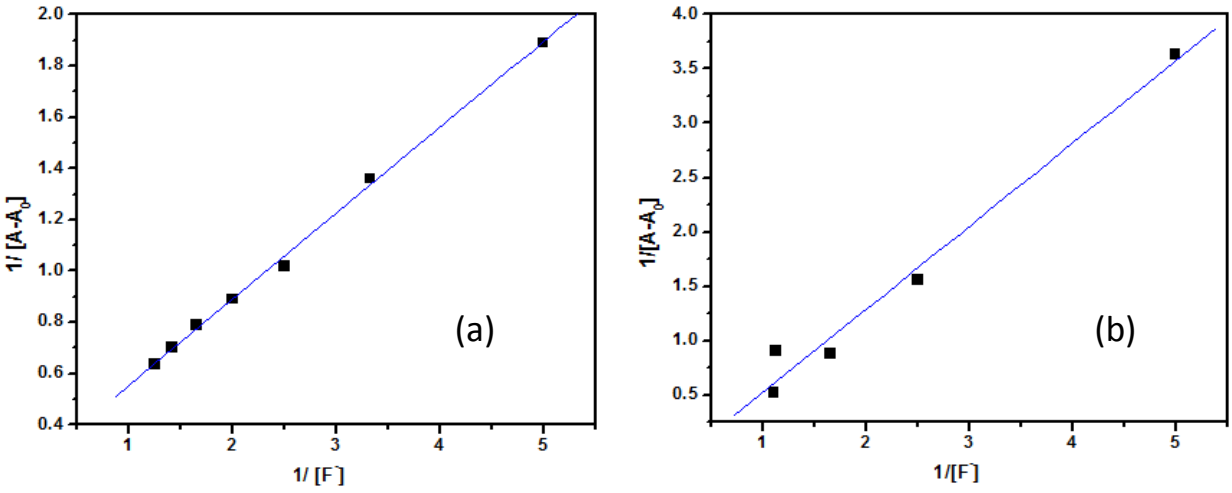


Fig. S5 B-H plot of sensor (a) **P1** and (b) **P2** *vs.* TBA^+F^-.

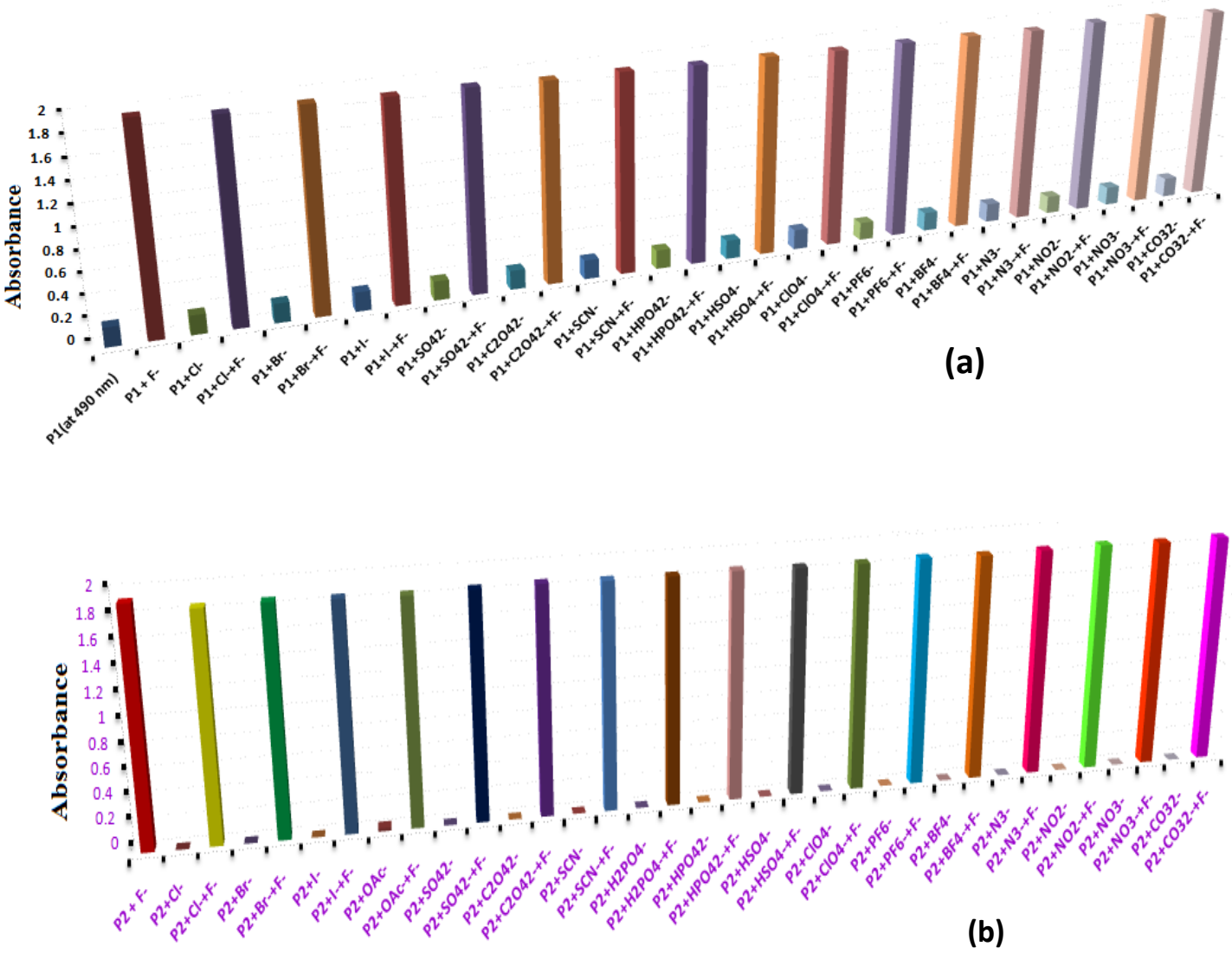
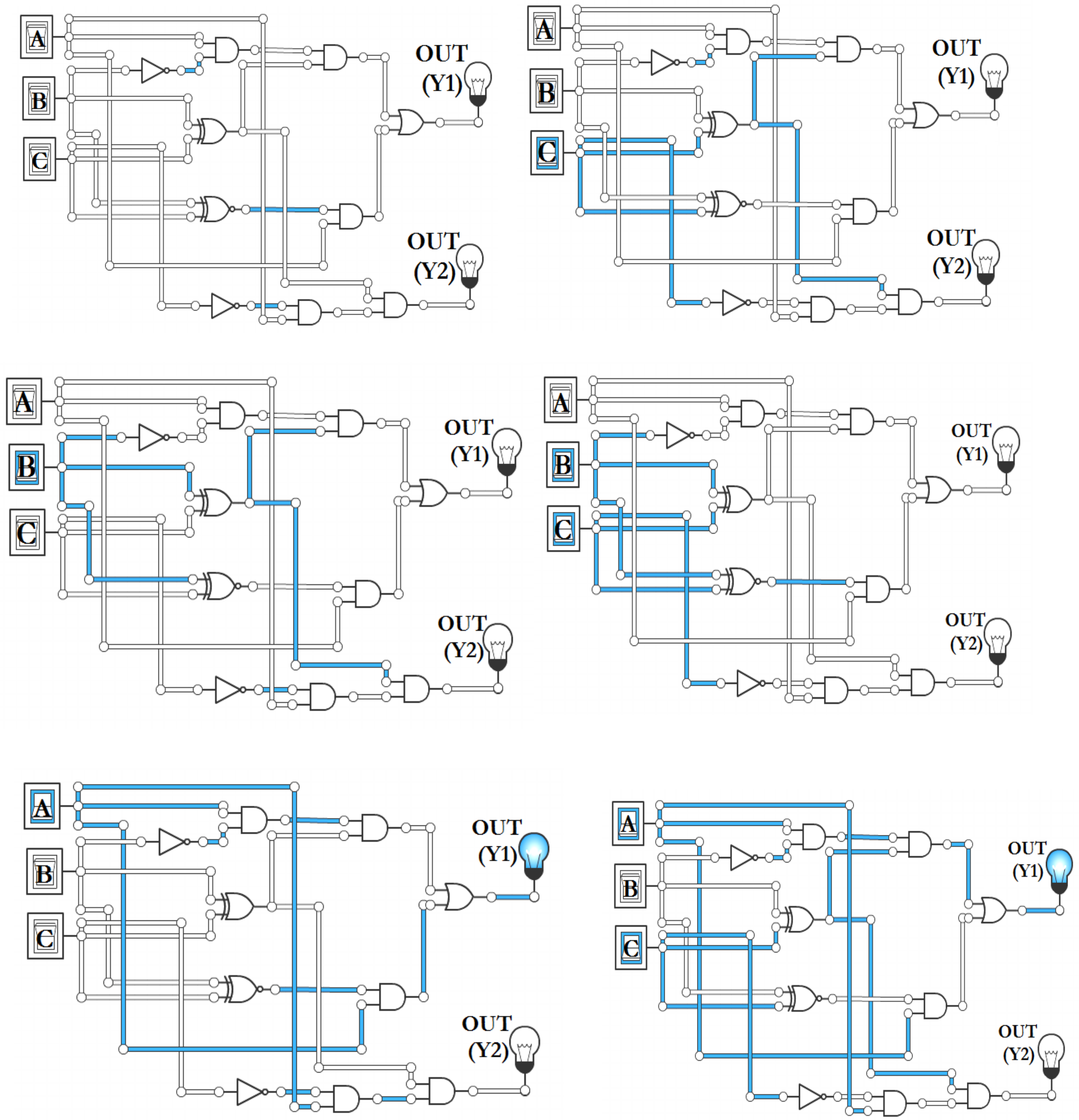


Fig. S6 Interference study of (a) **P1** and (b) **P2** with F^- in presence of other anions.


A
B
C
OUT
(Y1)
OUT
(Y2)
A
B
C
OUT
(Y1)
OUT
(Y2)
A
B
C
OUT
(Y1)
OUT
(Y2)
A
B
C
OUT
(Y1)
OUT
(Y2)
A
B
C
OUT
(Y1)
OUT
(Y2)
A
B
C
OUT
(Y1)
OUT
(Y2)

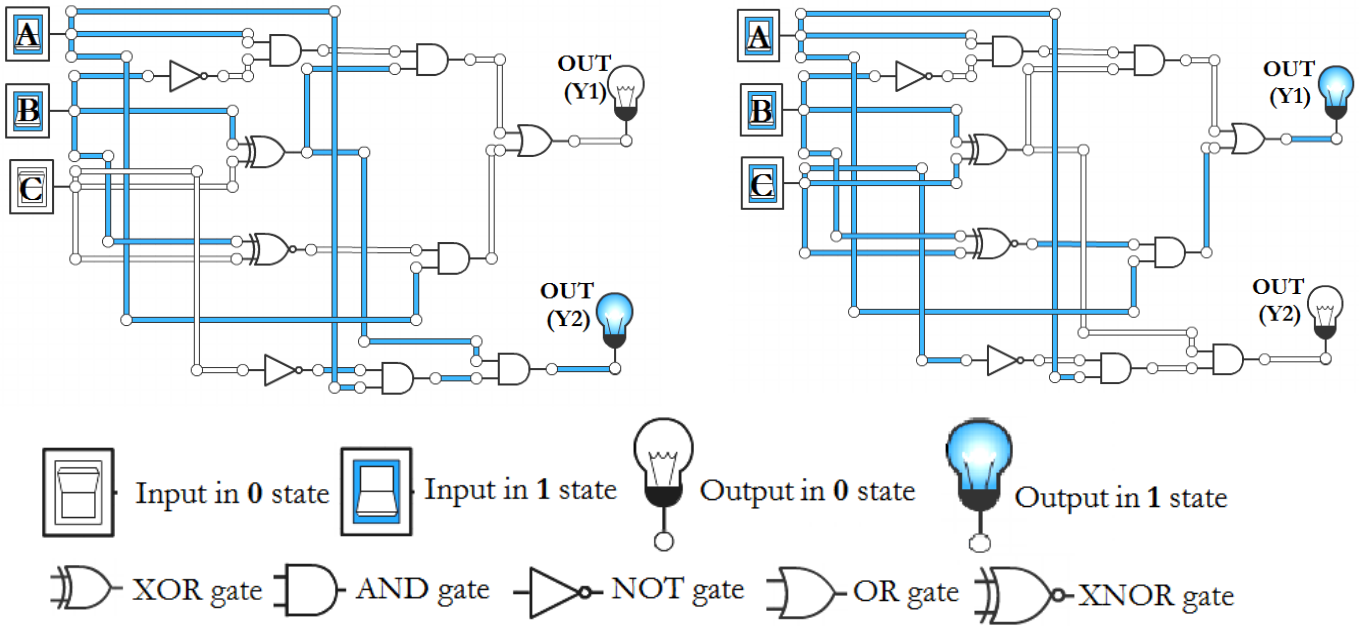
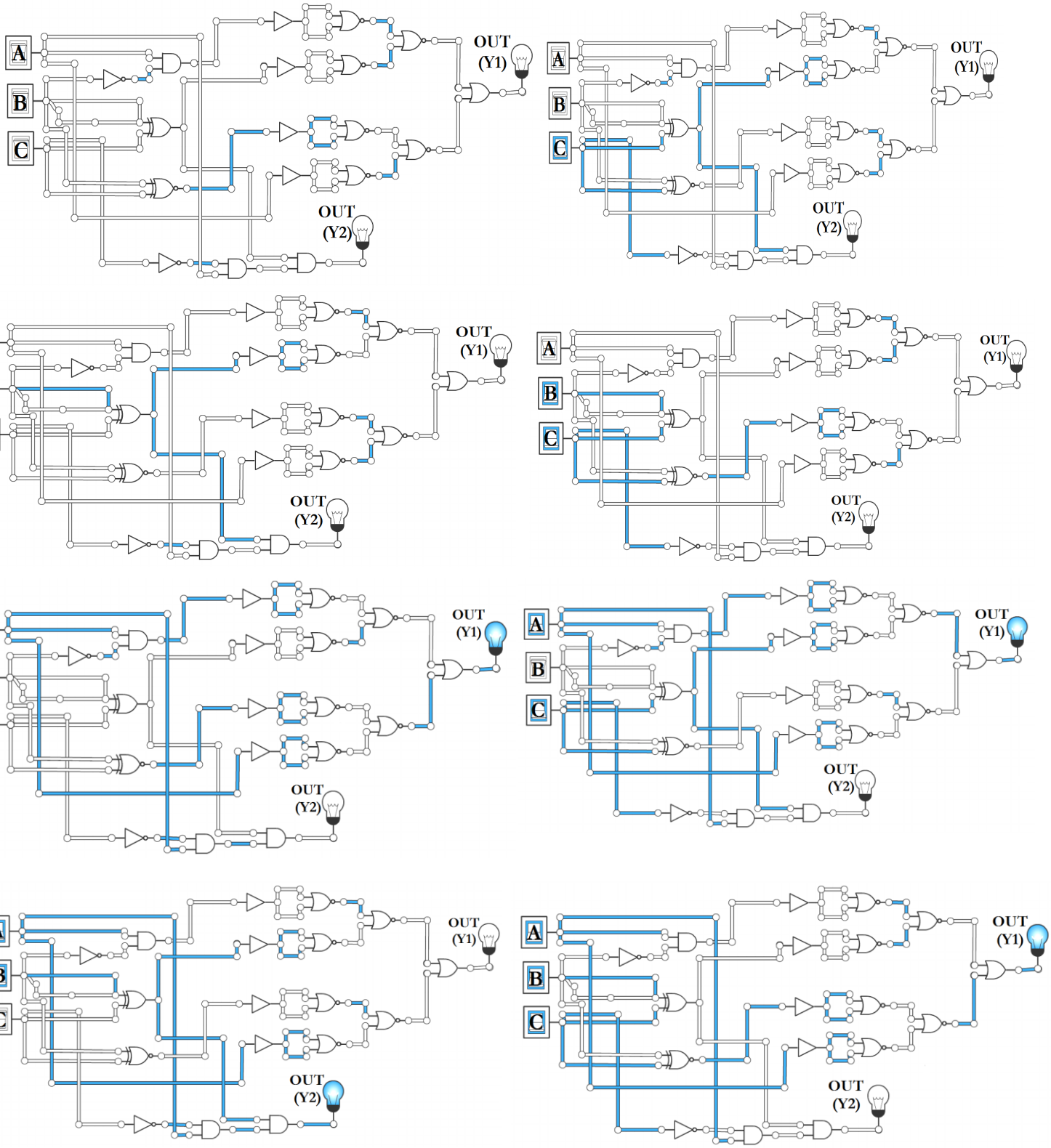


Fig. S7 Verification of the output (Y1 and Y2) with different inputs for AND-NOT-XOR-OR-XNOR logic functions as per truth Table 1.


A
B
C
OUT
(Y1)
OUT
(Y2)

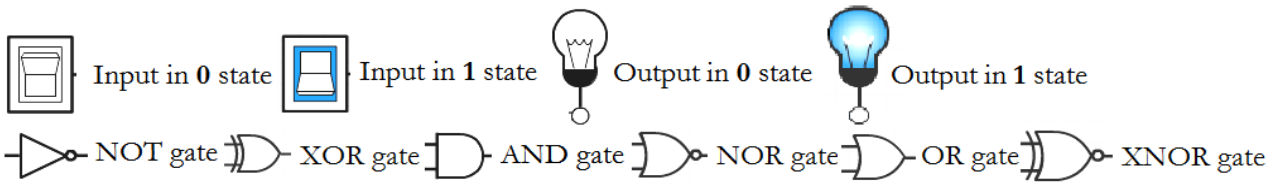
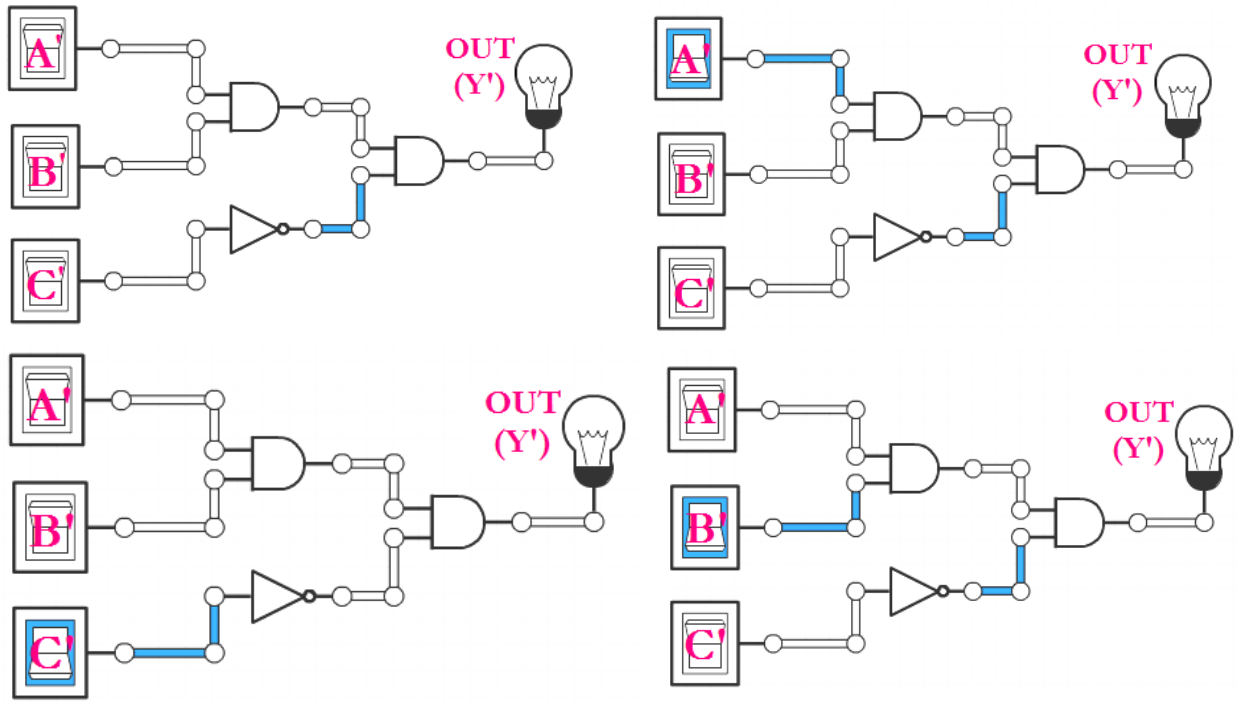


Fig. S8 Verification of the output (Y1 and Y2) with different inputs for AND-NOT-NOR-XOR-OR-XNOR logic functions as per truth Table 1.

Table S4 Truth table for **P2** with F^- and H^+			
Inputs			Output
A'(**P2**)	B' (F^-)	C' (H^+)	Y' (λ_{max} 485 nm)
0	0	0	0
1	0	0	0
0	1	0	0
0	0	1	0
1	1	0	1
1	1	1	0
0	1	1	0
1	0	1	0



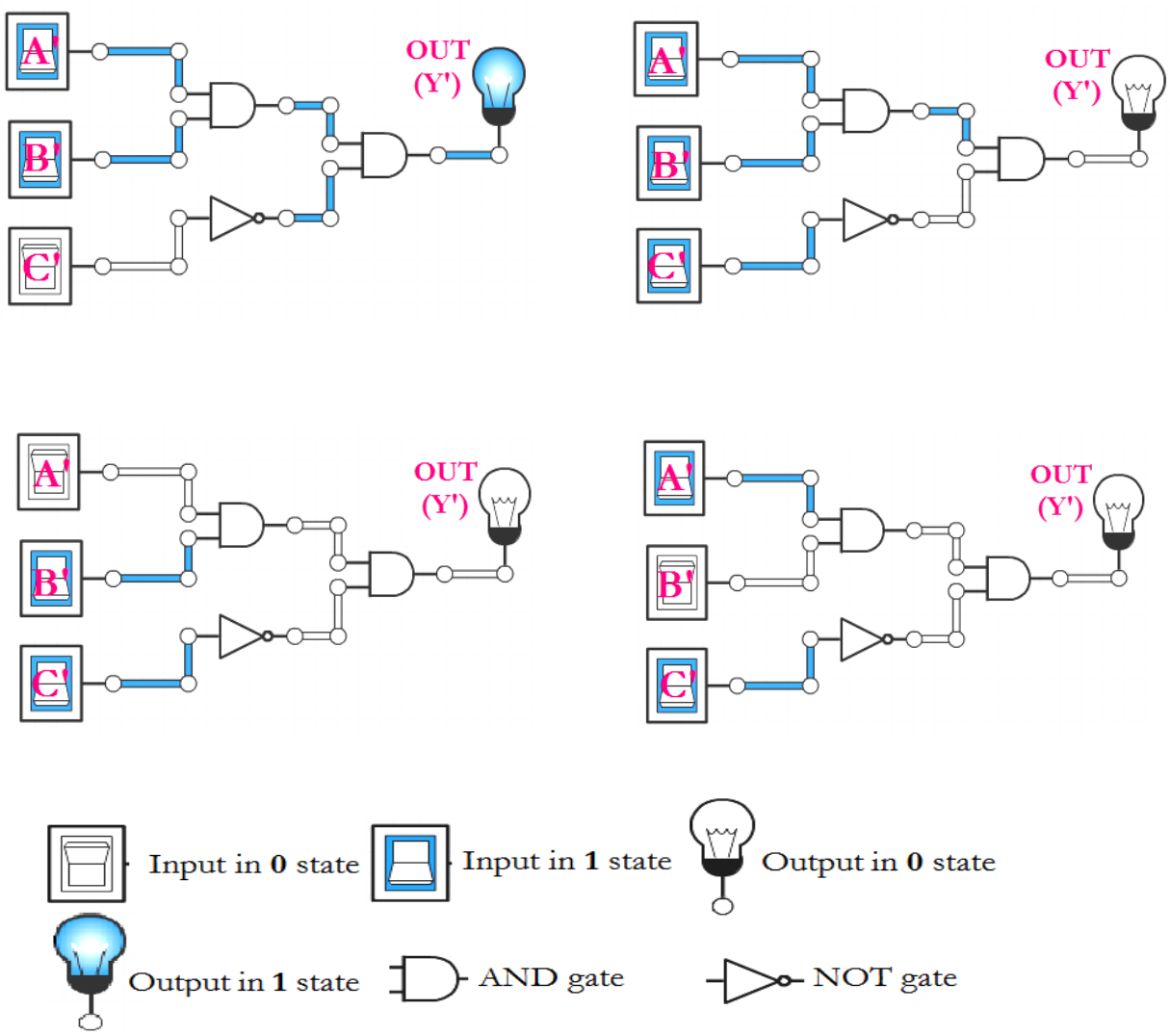
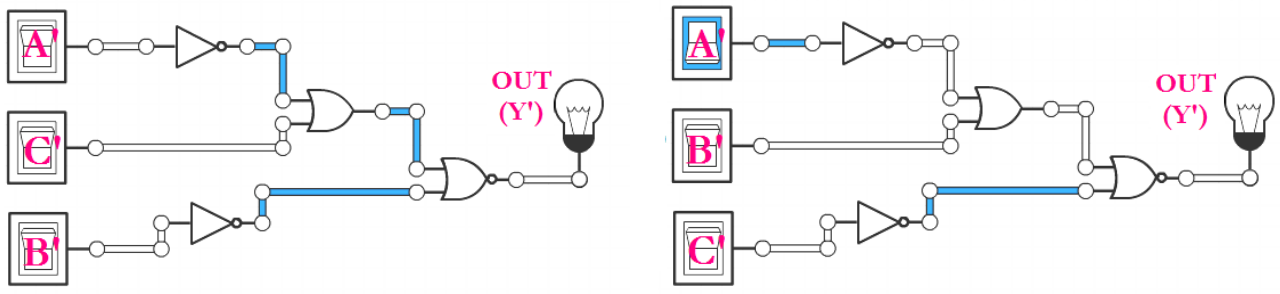


Fig. S9 Verification of the output (Y') with different inputs for INHIBIT logic function as per truth Table S4.



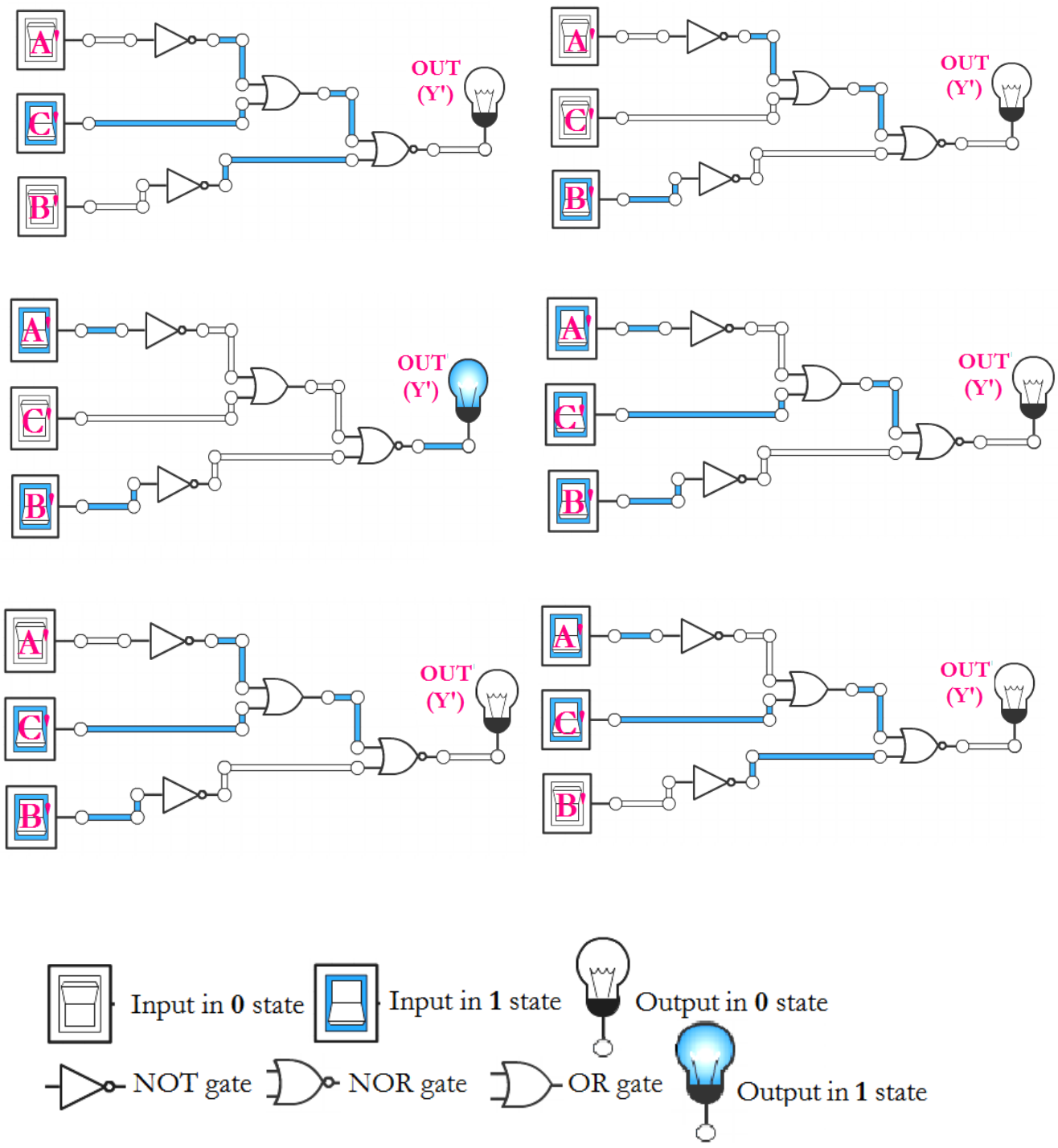
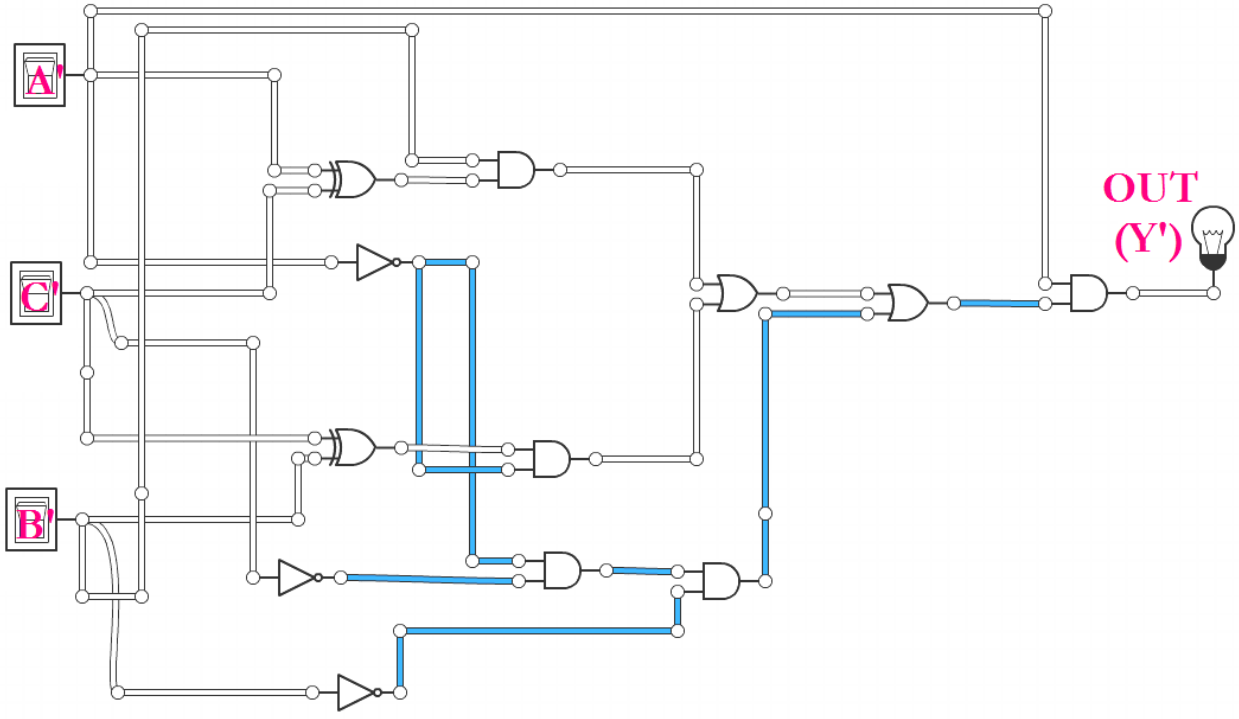
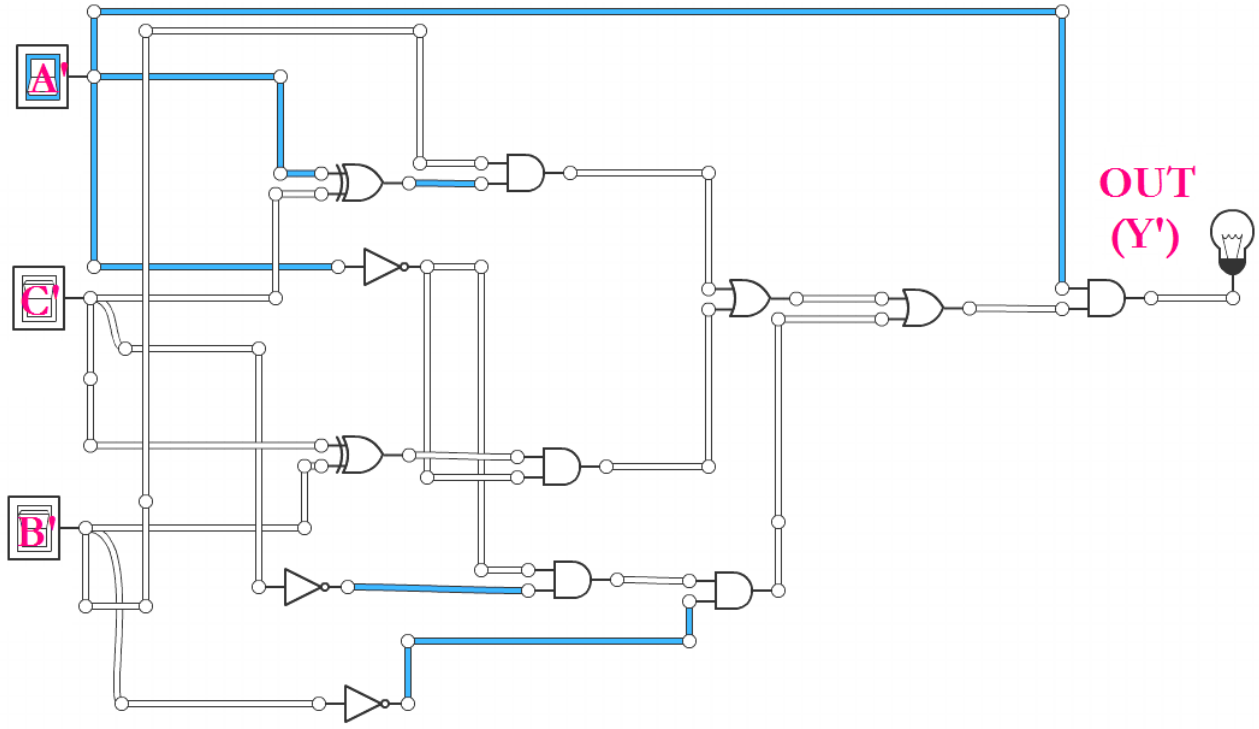
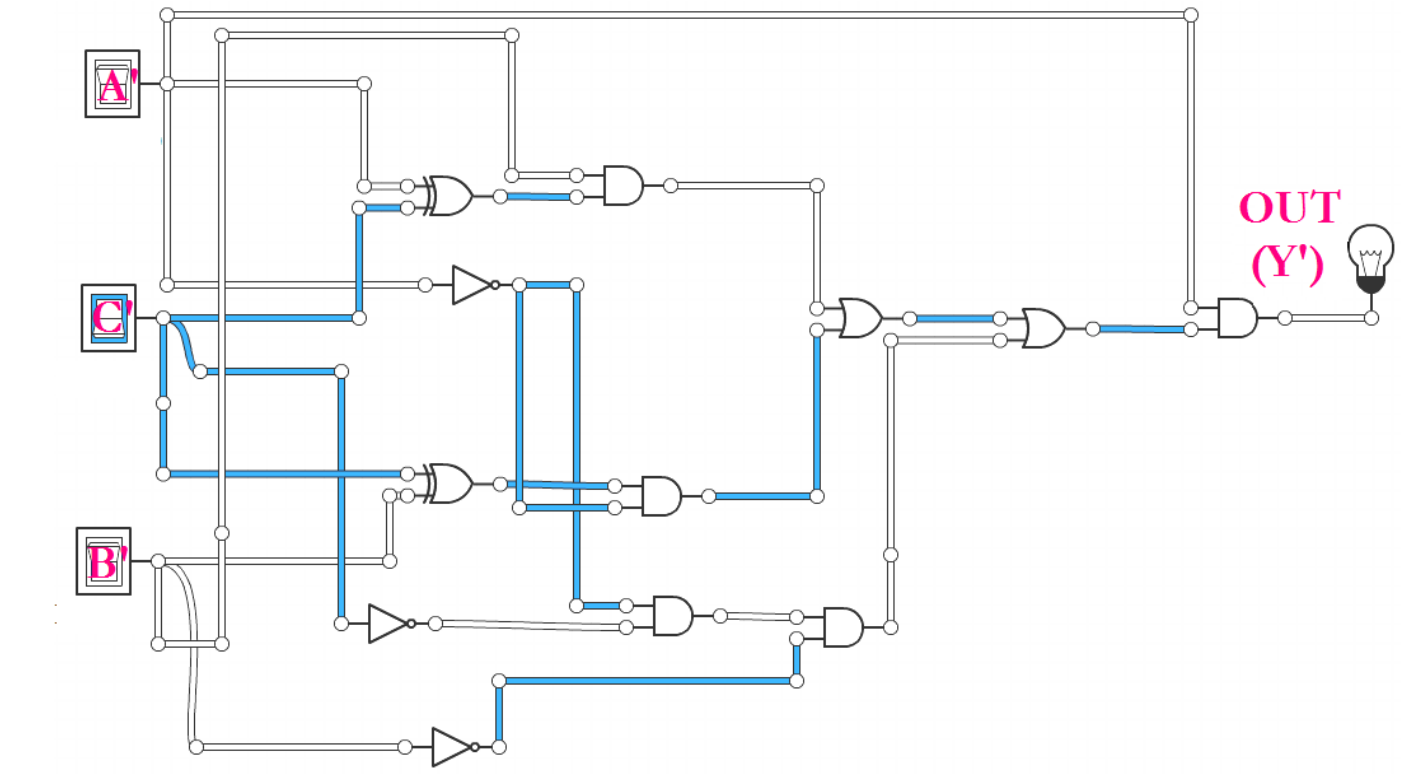
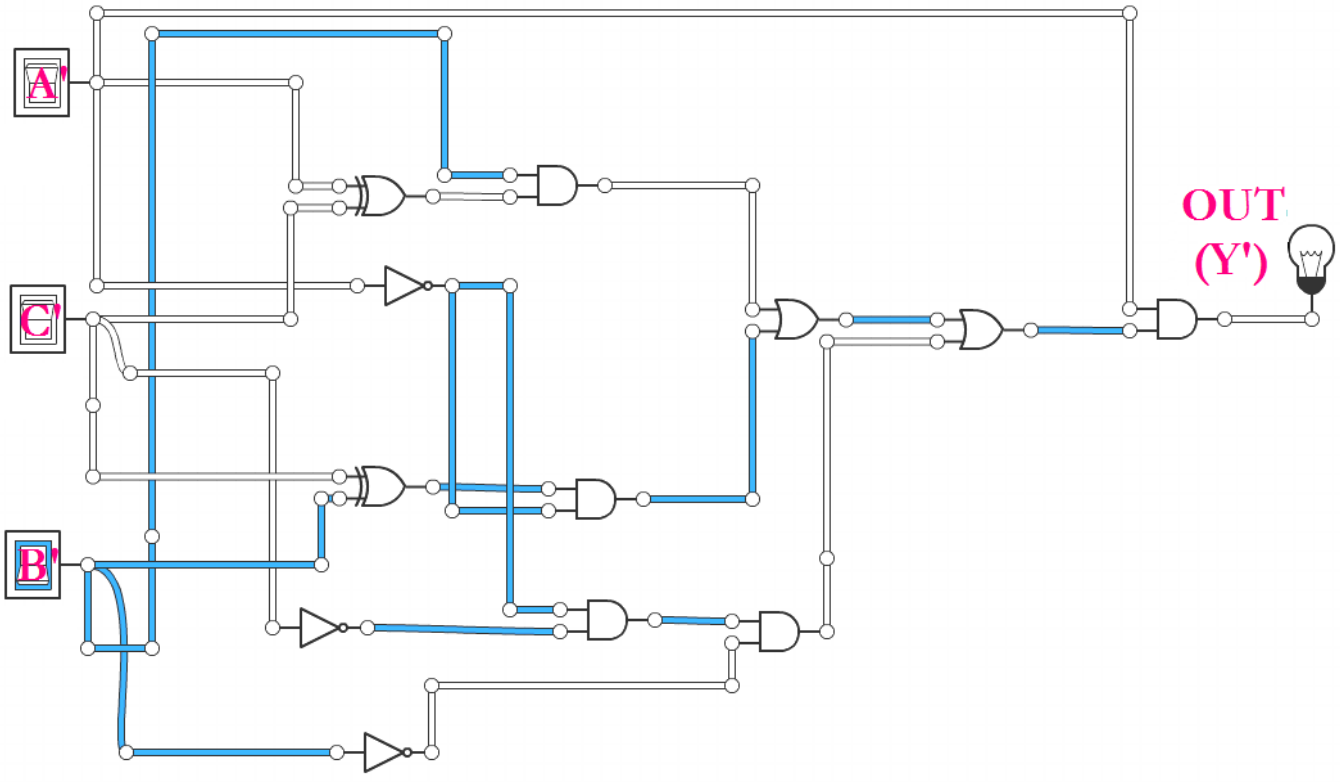


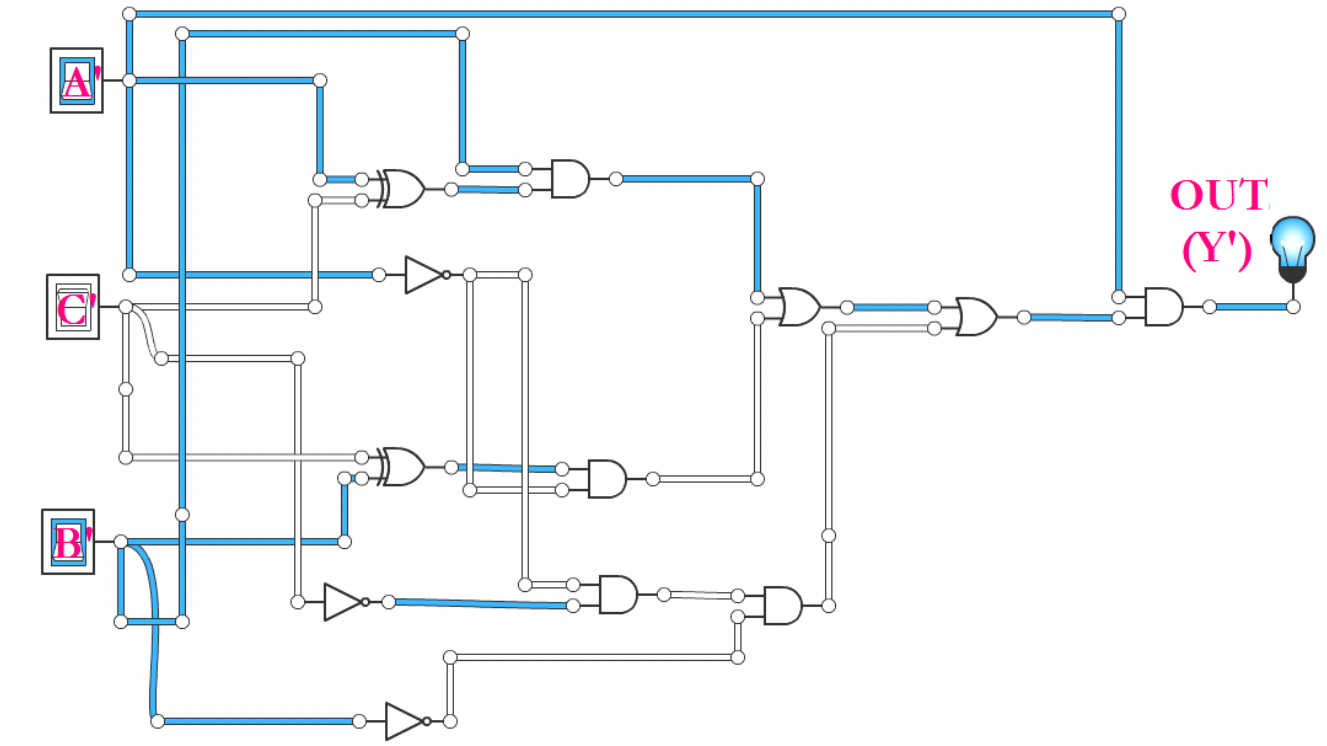
Fig. S10 Verification of the output (Y') with different inputs for NOT-NOR-OR gate circuit as per truth Table S4.

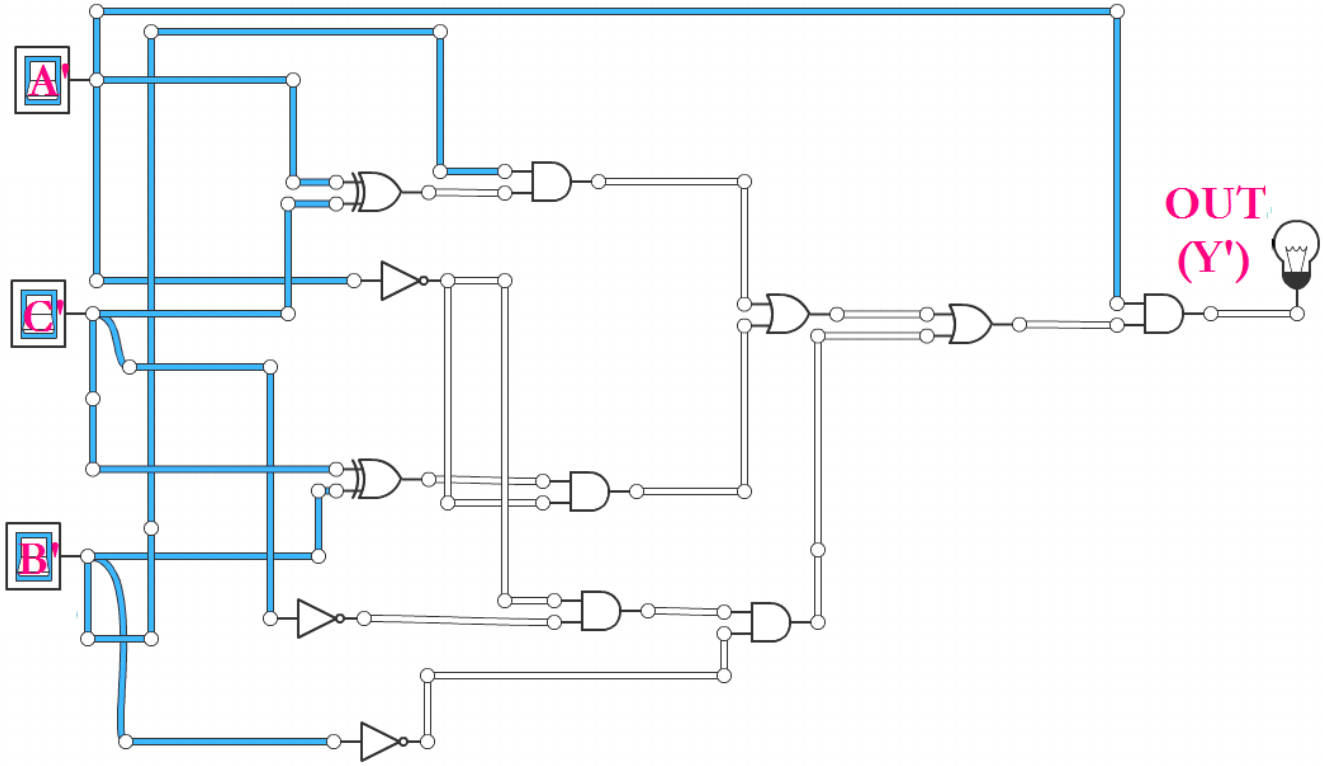

A'
C'
B'
OUT
(Y')

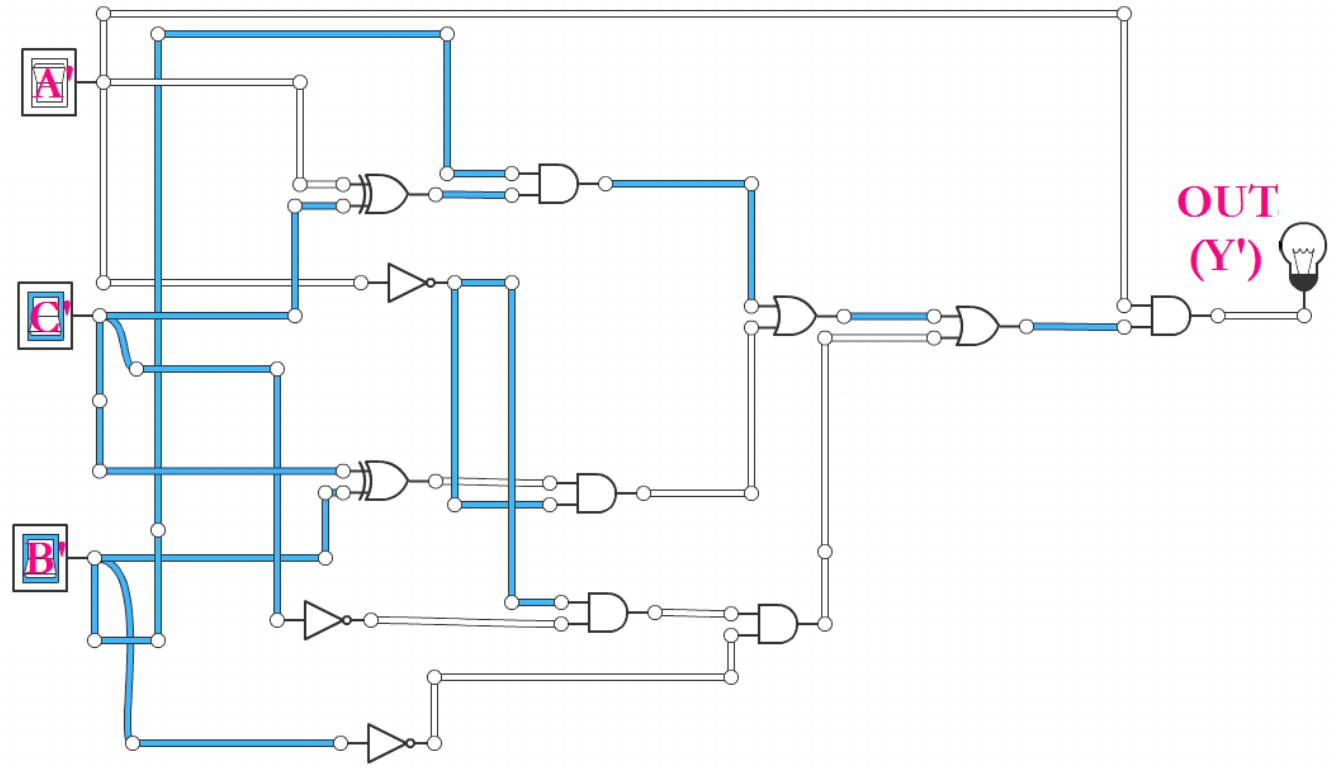

A'
C'
B'
OUT
(Y')

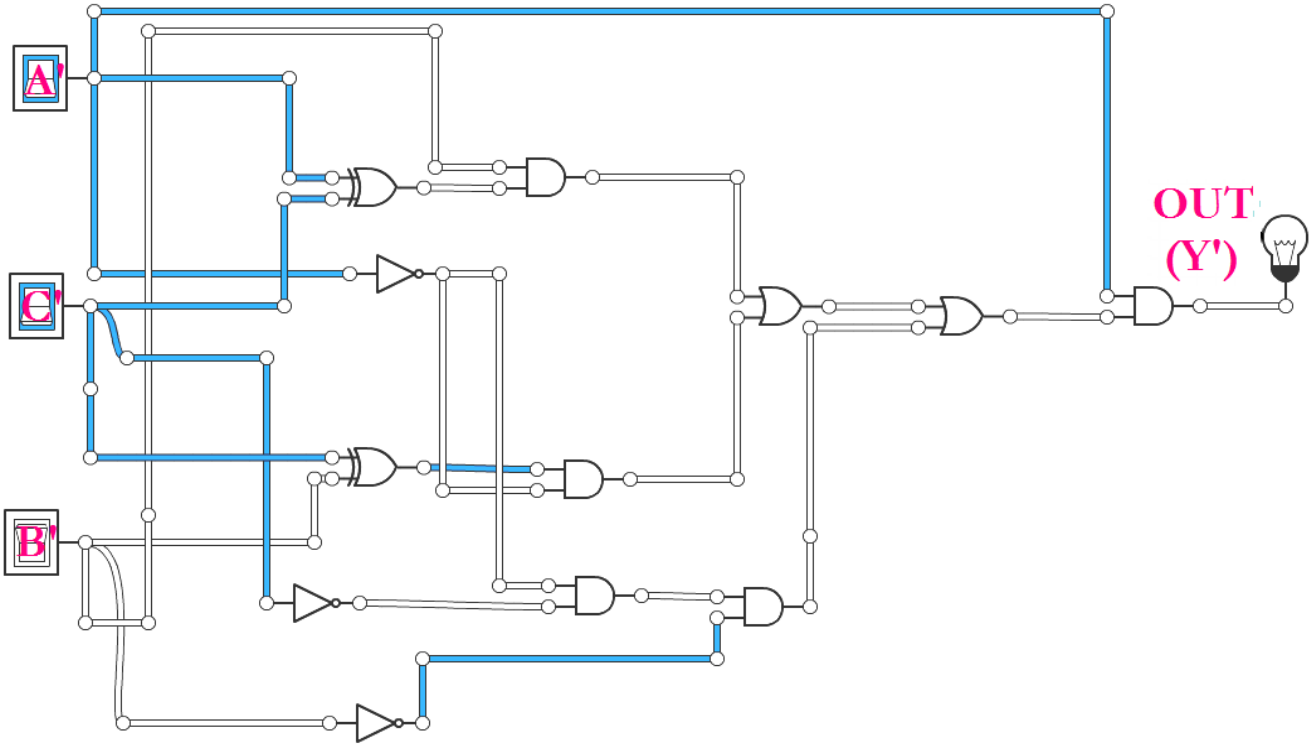

A'
C'
B'
OUT
(Y')


A'
C'
B'
OUT
(Y')


A'
C'
B'
OUT
(Y')


A'
C'
B'
OUT
(Y')


A'
C'
B'
OUT
(Y')


A'
C'
B'
OUT
(Y')

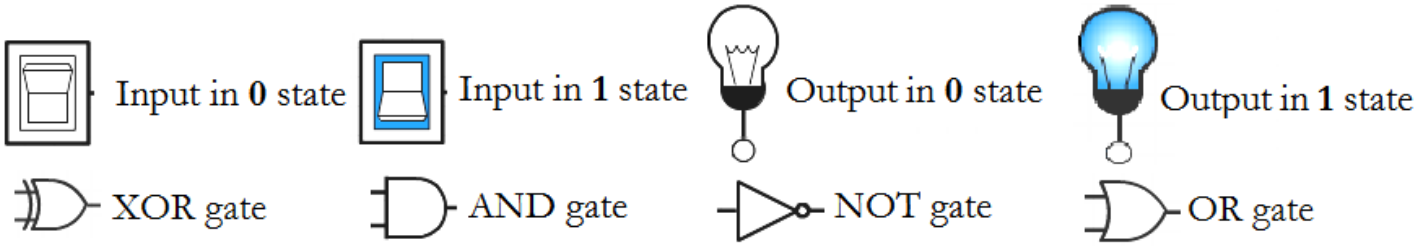
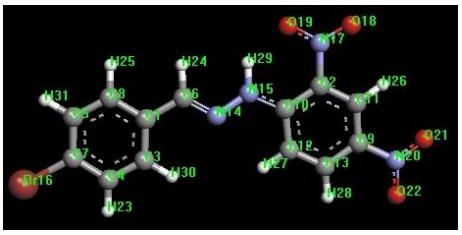
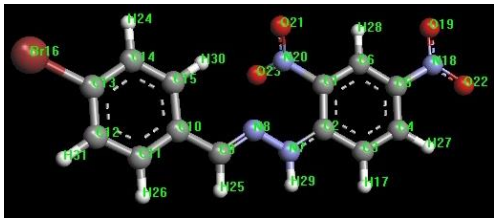
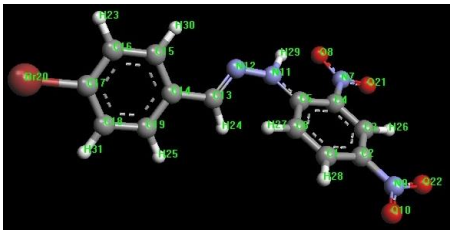
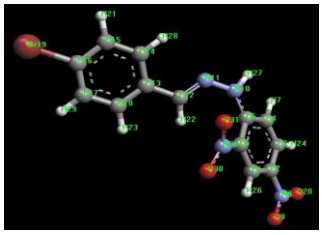


Fig. S11 Verification of the output (Y') with different inputs for AND-NOT-XOR-OR gate circuit as per truth Table S4.

3. Theoretical Calculations

All computational calculations were performed for **P1** and **P2** in its different states (from unbound to conjugated state) with the ORCA software package (version 3.0.0).[1] Optimization of the ground state geometries was done in implicit solvation model COSMO[2] (the conductor-like screening model) using the DFT method B3LYP[3] with resolution of the identity approximation along with chain of spheres exchange method (RIJCOSX).[4,5] Here DMSO (ε = 46.68) was taken as implicit solvent, as it is used during the experiment. The def2-SVP[6] basis set and the corresponding auxiliary basis set were used in the optimization technique. Restricted formalism was considered for all closed shell structure during the computational analysis. For the consideration of the different non-covalent interactions, Grimme's dispersion (D3)[7] correction with Becke-Johnson (BJ)[8] damping parameter was included during computational calculation. The nature of all the energy minimized structures (stationary points) further confirmed by the frequency analysis. In all cases, no imaginary mode was observed.

Table S5 Possible conformers for **P1** with energy

 Conformer 1 Energy: -3593.019382918 Hartree	 Conformer 2 Energy: -3593.008613341 Hartree
 Conformer 3 Energy: -3593.005586626 Hartree	 Conformer 4 Energy: -3592.998132593 Hartree

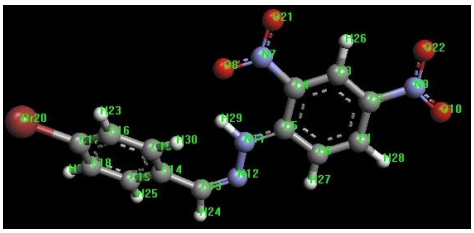
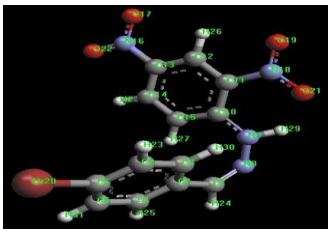
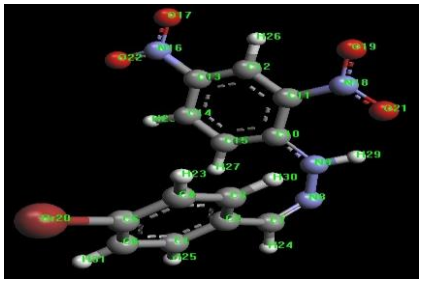
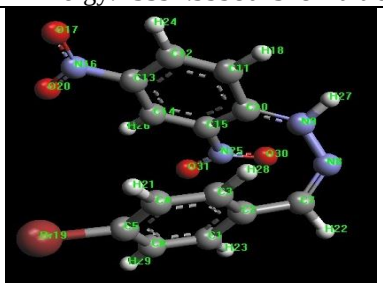
 Conformer 5 Energy: -3593.012731530 Hartree	 Conformer 6 Energy: -3592.999804348 Hartree
 Conformer 7 Energy: -3593.001918732 Hartree	 Conformer 8 Energy: -3592.993044555 Hartree

Table S6 Cartesian coordinates and Loewdin atomic charges of **P1**

The cartesian coordinates of B3LYP(RIJCOSX, D3BJ)/def2-SVP optimized geometries of **P1**			Loewdin atomic charges of **P1**	
C	1.21400665956310	2.31516492183630	12.08474379443846	0 C : -0.050341
C	5.90187286322157	-1.49072102962566	12.31156047056295	1 C : -0.051205
C	0.54844100140285	2.15246784760048	13.31644280472215	2 C : 0.008373
C	-0.53708259710817	2.95938422757898	13.64661406366024	3 C : -0.028733
C	-0.32669867185561	4.11585653760911	11.50798845339545	4 C : -0.032185
C	2.37039896370600	1.50791632090525	11.70971776459322	5 C : 0.029923
C	-0.96571599807487	3.93680000042408	12.73758658176370	6 C : -0.108762
C	0.75962821332640	3.30085828378913	11.18870448353690	7 C : 0.003956
C	6.27881708234252	-2.50662186532649	14.45336322912584	8 C : -0.050859
C	4.72200471927517	-0.83613466299939	12.79828064448143	9 C : 0.060447
C	6.66835073378027	-2.31167782010567	13.14043217406360	10 C : 0.040304
C	4.35661716104961	-1.08291199212032	14.15366240372300	11 C : -0.027114
C	5.11454110321047	-1.89737491519103	14.96428229458015	12 C : 0.036348
N	2.90995475831913	0.65464480537187	12.50843109153890	13 N : -0.041594
N	3.98121364987456	-0.00849353185417	12.02388277810535	14 N : 0.112275
Br	-2.44819744608311	5.05169628719752	13.18586893805791	15 Br: 0.082516
N	6.38168215809089	-1.32154073119133	10.95424466584563	16 N : 0.297217
O	7.42307883257529	-1.87145471135146	10.62661467990679	17 O : -0.231245
O	5.72130208613221	-0.62806431786973	10.17297388331216	18 O : -0.240866
N	7.09923995445989	-3.34105840947666	15.31696820851805	19 N : 0.292474
O	8.08087920347274	-3.89172161828414	14.83146079564843	20 O : -0.248092
O	6.76967108336115	-3.44882527210904	16.49276800031263	21 O : -0.246054
H	-1.04776773475927	2.83062885847943	14.60205661828741	22 H : 0.041171
H	2.78363043668179	1.67453501913246	10.70076670171904	23 H : 0.024612
H	1.26681874250409	3.43702694920798	10.23007082006236	24 H : 0.041613
H	7.56270978580430	-2.78624020894241	12.74583603932405	25 H : 0.047683
H	3.45901000936386	-0.60027510619121	14.53452841522224	26 H : 0.042306
H	4.82145402153665	-2.08187629956299	15.99723761320757	27 H : 0.049946
H	4.30794725918552	0.13709171260875	11.06294988588931	28 H : 0.066137
H	0.89007688412988	1.38779426913047	14.01662479670308	29 H : 0.038027
H	-0.67012990948888	4.87806145432990	10.80689495269198	30 H : 0.041722

Table S7 Cartesian coordinates and Loewdin atomic charges of **P1-F**

The cartesian coordinates of B3LYP(RIJCOSX, D3BJ)/def2-SVP optimized geometries of **P1-F**			Loewdin atomic charges of **P1-F**
C	-1.72534799423368	2.53166557991820 -3.59090711810547	0 C : -0.008252
C	-1.33831522778921	1.18436201937159 -3.47137469462179	1 C : -0.049537
C	-1.40814445123356	0.35980883614374 -4.61369012875336	2 C : -0.001194
C	-1.84889592027679	0.86215689924091 -5.83425742718239	3 C : -0.036393
C	-2.22969254085756	2.20722989828206 -5.92258259449029	4 C : -0.119002
C	-2.17200604339360	3.04877276374774 -4.80876420674321	5 C : -0.037523
C	-0.85766245439144	0.68446837930244 -2.18396196884157	6 C : 0.002317
N	-0.53228084110546	-0.55459750210688 -2.03462326810294	7 N : -0.055082
N	-0.08806175486026	-0.92485686874699 -0.80970286325730	8 N : 0.069043
C	0.46625034055925	-2.14921976622594 -0.68780943692343	9 C : 0.040423
C	0.98036683117023	-2.64182252870245 0.55868043884739	10 C : -0.058043
C	1.71610458750554	-3.81847015729935 0.64116117125481	11 C : 0.028552
C	1.90171672026987	-4.58957421587744 -0.50106543689772	12 C : -0.065566
C	1.33992071308988	-4.19152569292147 -1.73260498562372	13 C : 0.019168
C	0.64374550833545	-3.00800992053266 -1.81889086092411	14 C : -0.039354
N	2.66633114631793	-5.81126137010784 -0.41449983662969	15 N : 0.287936
O	3.15044271931453	-6.12494237985977 0.67126784378622	16 O : -0.262774
N	0.69355364700092	-1.97559783748757 1.82180907505008	17 N : 0.289085
O	1.52268186782071	-2.05904889869400 2.72427923302854	18 O : -0.240052
Br	-2.84119410908217	2.89601740696290 -7.59593224119361	19 Br: 0.078470
O	-0.38190732011358	-1.40456318632809 1.93818547231483	20 O : -0.211096
O	2.80531071199327	-6.48463921220060 -1.43361015097331	21 O : -0.259775
F	0.25127706248912	1.07250937692957 0.61026545705257	22 F : -0.485689
C	0.44928275521649	3.23157314330071 2.88208530477935	23 C : 0.058780
N	0.07200310584824	2.03000096451002 3.69691513494822	24 N : 0.126632
C	1.15442914135357	1.00183030604874 3.53751778612372	25 C : 0.056928
C	-1.21564889740827	1.47013419275173 3.15935647065897	26 C : 0.055207
C	-0.08627878202421	2.40036795982807 5.13476818129021	27 C : 0.061726
H	-1.89428967427289	0.21780497685389 -6.71403110901435	28 H : 0.041806
H	-0.74424062869012	1.39058816283662 -1.34727332918857	29 H : 0.004883
H	-1.67682268938939	3.18547750398835 -2.71615219768677	30 H : 0.041306
H	2.12029607640183	-4.14081977446075 1.59798441205050	31 H : 0.048362
H	0.23324262697174	-2.67487140755089 -2.76949184601319	32 H : 0.038640
H	1.48096884282972	-4.82029487471112 -2.61160870406320	33 H : 0.047825
H	0.04407843156840	-0.10397436434232 -0.05519617703550	34 H : 0.026128
H	-1.09707985597224	-0.68307419215585 -4.53438647182523	35 H : 0.036802
H	-2.47648918986241	4.09353759636284 -4.88748246081376	36 H : 0.042265
H	2.08516706160714	1.41151704627510 3.94873874884156	37 H : 0.037166
H	0.86556993896772	0.08966155959195 4.06897158058510	38 H : 0.028324
H	1.23180655263614	0.80167315094027 2.46204461735020	39 H : 0.021577
H	1.40269115090506	3.62317557429765 3.25813172099585	40 H : 0.040520
H	0.53768019264243	2.88946934855222 1.84283480011739	41 H : 0.028411
H	-0.33502922104955	3.99135444151577 2.98676481512838	42 H : 0.041249
H	0.86524501587565	2.79819969784424 5.50838354480750	43 H : 0.044613
H	-0.87117356493667	3.16168605790705 5.22273437884028	44 H : 0.045077
H	-0.36895876431818	1.50355378324779 5.69953479829739	45 H : 0.045040
H	-1.99478902270227	2.23463773487283 3.26899551012268	46 H : 0.036314
H	-1.02179955829734	1.21056555617447 2.10865946140191	47 H : 0.024273
H	-1.47405424242999	0.57736413271256 3.73982985723085	48 H : 0.034484

Table S8 Cartesian coordinates and Loewdin atomic charges of **P1-2F**

The cartesian coordinates of B3LYP(RIJCOSX, D3BJ)/def2-SVP optimized geometries of **P1-2F**			Loewdin atomic charges of **P1-2F**
C	0.98579908058983	-0.27988855536097	4.01802989897006	0 C : 0.005681
C	2.19148449711546	-0.97627782222236	3.72135522105215	1 C : -0.081681
C	2.21386316458390	-1.92322716052202	2.70272267809890	2 C : 0.020004
C	1.06009446799308	-2.20810070815812	1.98430337893150	3 C : -0.066455
C	-0.18105356344498	-1.46373280463104	2.17434734390861	4 C : 0.009228
C	-0.12866790660497	-0.48879673894727	3.25667981453448	5 C : -0.052491
N	1.18109641104776	-3.19565074482617	0.95301319555814	6 N : 0.287243
O	0.17775743959199	-3.82844537463339	0.62832581655907	7 O : -0.222828
N	3.38193055325375	-0.71506955474125	4.46533550976268	8 N : 0.284576
O	3.31251889365768	0.03859849564471	5.44031727475086	9 O : -0.281450
N	-1.23128429998418	-1.59875697648251	1.39124735502911	10 N : -0.084180
N	-2.21556011014657	-0.61829678150811	1.50164826030545	11 N : -0.069355
C	-2.03234687644056	0.37261717440607	0.70539037420651	12 C : -0.009292
C	-2.94816111942711	1.51111336267732	0.59856924710114	13 C : -0.050129
C	-4.11448752650833	1.64063783415143	1.37464886301402	14 C : -0.007031
C	-4.93363741814016	2.75903928167632	1.23392868551266	15 C : -0.041222
C	-4.57776056810278	3.75026290429927	0.30848415036478	16 C : -0.122418
C	-3.42629628517812	3.64145953904426	-0.47738234951133	17 C : -0.045062
C	-2.61123911978540	2.51656524729194	-0.32889573437657	18 C : -0.012173
Br	-5.69673689693781	5.28937069679386	0.12246661125321	19 Br: 0.068986
O	2.28501319387686	-3.37306866389086	0.42293811776208	20 O : -0.257208
O	4.44101010712598	-1.24448103636534	4.10592147004077	21 O : -0.284289
H	-5.83888679653292	2.86293191565238	1.83393671588448	22 H : 0.039013
H	-1.15221533290543	0.42636175459925	0.03991902182486	23 H : 0.008100
H	-1.69572429819216	2.38247760378708	-0.91945728595733	24 H : 0.020751
H	3.13166940832913	-2.45933536889437	2.47330796684367	25 H : 0.044076
H	-1.03817809040578	0.07145395535787	3.46767812165695	26 H : 0.032134
H	0.97507728923699	0.43327905492374	4.84229102667070	27 H : 0.042027
H	-1.86933706153859	-2.70257065158044	0.45914693295015	28 H : 0.009935
H	-4.37385923606019	0.85616209518526	2.08912181817862	29 H : 0.032772
H	-3.16706444764491	4.42565234102901	-1.19138934301114	30 H : 0.037797
F	-2.44479957546120	-3.21751537312857	-0.16782243378460	31 F : -0.220905
F	0.01110873861286	1.14413603001893	-1.47446052305603	32 F : -0.582034
N	2.95391005732569	1.31406651295253	0.00002030224581	33 N : 0.125457
N	-1.15345828180862	-1.55289648346594	-3.04882726706043	34 N : 0.127752
C	1.80064613811596	1.45492478524092	0.95132495825589	35 C : 0.057723
C	4.25122241536157	1.29588359055079	0.73843169052639	36 C : 0.062298
C	2.77868865373120	0.04063206593238	-0.77465416254679	37 C : 0.060013
C	2.90637006780738	2.46698283403466	-0.95861581631838	38 C : 0.054684
C	-0.16389703664155	-1.89467301278358	-1.97389337306556	39 C : 0.045715
C	-0.51102038220220	-0.58504832474331	-3.99646828169286	40 C : 0.058084
C	-1.58449224809222	-2.79864371909291	-3.75151923539423	41 C : 0.061528
C	-2.34178648568854	-0.88691024788201	-2.41454450463214	42 C : 0.048648
H	3.70491371453755	2.34549461265392	-1.70057461746309	43 H : 0.037385
H	1.91557916214207	2.43724890105574	-1.43235493343694	44 H : 0.023636
H	3.05392969284600	3.39622648868289	-0.39405111868769	45 H : 0.037878
H	5.06897547461060	1.19137457967103	0.01414082258852	46 H : 0.045362
H	4.35767134900201	2.23487813541205	1.29552165540238	47 H : 0.044710
H	4.25589536514706	0.44416618271028	1.43077034579125	48 H : 0.046014
H	1.89929467143150	2.40879217664596	1.48448475113364	49 H : 0.040822

H	0.88857177949707	1.42248673964209	0.33466907781809	50 H : 0.031091
H	1.83598500502489	0.62457599924435	1.66166148817666	51 H : 0.037980
H	3.60710498483835	-0.05605478787253	-1.48655456569254	52 H : 0.038221
H	2.78301532149887	-0.80831259007314	-0.07834644387751	53 H : 0.036884
H	1.81185510144403	0.13785409387735	-1.28639725214507	54 H : 0.035913
H	-2.29248636156491	-2.53509647080832	-4.54619663221250	55 H : 0.042532
H	-0.70020364295329	-3.28771812192590	-4.17818751449848	56 H : 0.042914
H	-2.06470851440600	-3.45616722841884	-3.01698694519953	57 H : 0.042173
H	-3.10193576030687	-0.71930915440438	-3.18688988269585	58 H : 0.033489
H	-2.71782459666625	-1.54352674145443	-1.62178726311813	59 H : 0.022283
H	-1.98456898798970	0.06251591125735	-2.00196954535523	60 H : 0.025250
H	-1.24754332542099	-0.29260975614737	-4.75509646304251	61 H : 0.039975
H	-0.19043333408118	0.27402697749052	-3.38643766354003	62 H : 0.028036
H	0.34444725974494	-1.07966932908660	-4.47350209299428	63 H : 0.040064
H	0.09279799473036	-0.94415710159458	-1.49043979944339	64 H : 0.023030
H	-0.64251280596545	-2.58198643980701	-1.27348815242352	65 H : 0.018537
H	0.71487103937757	-2.35825604813985	-2.43890866643054	66 H : 0.031797

Table S9 Cartesian coordinates and Loewdin atomic charges of **P1-3F**

The cartesian coordinates of B3LYP(RIJCOSX, D3BJ)/def2-SVP optimized geometries of **P1-3F**				Loewdin atomic charges of **P1-3F**
C	-0.59838287962520	0.48403427841981	3.28020606285113	0 C : -0.046409
C	0.45515020447029	0.25105204148802	2.29721009131832	1 C : -0.016778
C	1.04506295258892	-1.08586178456836	2.35356284960926	2 C : -0.060059
C	0.53839539250032	-2.06264778279485	3.19563932798493	3 C : 0.019294
C	-0.53193877990681	-1.79859236958392	4.04633828171971	4 C : -0.097507
C	-1.08591239645791	-0.48549514679429	4.10225292951907	5 C : -0.017711
N	0.81606977752875	1.15809290705400	1.41168198523958	6 N : -0.114177
N	0.25661939597576	2.39088789273185	1.57540880104780	7 N : -0.074357
C	-0.01718738009436	3.01847840653504	0.48106643088536	8 C : -0.019071
C	-0.55329319903208	4.38079857409969	0.47558178346331	9 C : -0.048608
C	-0.93691143226823	4.93664596854238	-0.76299052983418	10 C : -0.014488
C	-1.47285447353988	6.22446184442374	-0.83278105970009	11 C : -0.045803
C	-1.62365843314953	6.96260910917387	0.34550489095176	12 C : -0.126055
C	-1.24160336641201	6.43813458339006	1.58700468993966	13 C : -0.042840
C	-0.71046006193153	5.15086048209022	1.64529683173175	14 C : -0.011473
Br	-2.37147269160632	8.72405966190512	0.26618174693818	15 Br: 0.064121
N	2.14929283098569	-1.49778223727204	1.52880131415087	16 N : 0.291378
O	2.60304489275470	-0.72430535290838	0.68609757677769	17 O : -0.238683
N	-1.09054984306888	-2.84722952324853	4.80915138079926	18 N : 0.275084
O	-2.11506951186505	-2.62463016657526	5.47496786506923	19 O : -0.311389
O	-0.56471566172828	-3.97635840899870	4.78261813700997	20 O : -0.314152
O	2.62771233585466	-2.62753245488818	1.70035740222696	21 O : -0.293796
F	-1.87530822322786	-1.71298735432831	0.96647129198740	22 F : -0.320490
C	-0.73189689122545	-5.18933736272921	1.60509336856523	23 C : 0.051995
N	-2.22492737958845	-5.21016526654803	1.42927452595225	24 N : 0.124727
C	-2.86064256816397	-4.26894122749527	2.41283063697927	25 C : 0.054815
C	-2.57092951538769	-4.76766241036700	0.03713452520292	26 C : 0.058723
C	-2.72917336300452	-6.59894803178260	1.65510930316857	27 C : 0.063931
F	-0.01049807385159	-2.65226272823398	0.05681027860408	28 F : -0.321759
F	0.24061394981825	2.51136438774303	-2.47209819098933	29 F : -0.583949
C	0.80356101085563	-0.45174296773132	-2.02711741675813	30 C : 0.049043

N	-0.54301442749092	-0.65078132545061	-2.66575934029228	31 N :	0.128590
C	-0.79800140495691	-2.10994645041284	-2.86329677154642	32 C :	0.049800
C	-1.58753853728424	-0.05162102473229	-1.76769073088378	33 C :	0.050513
C	-0.56679997078031	0.07569957584106	-3.97703902500414	34 C :	0.050909
C	3.06865994426311	2.31483078480028	-3.35524361411002	35 C :	0.051178
N	3.54289525104099	2.90726001425872	-2.05673586611712	36 N :	0.124911
C	4.99677356443119	3.24166588505122	-2.15301139360925	37 C :	0.061834
C	3.32514411909883	1.92891814832634	-0.93643200994209	38 C :	0.061744
C	2.73661834539204	4.14626146543107	-1.78745244122345	39 C :	0.056299
H	-1.36573348257768	7.02946709013193	2.49637263338470	40 H :	0.037806
H	0.12996335249901	2.56282131083832	-0.51210438074955	41 H :	0.006783
H	-0.78811460821483	4.32704313813718	-1.66113323276264	42 H :	0.019866
H	0.98106278694508	-3.05237091579422	3.17056192030084	43 H :	0.033951
H	-1.01874471533348	1.48837139669245	3.30708389250055	44 H :	0.023621
H	-1.89553967992102	-0.28021875559063	4.80308579135624	45 H :	0.034405
H	-0.93916570058061	-2.13823847787968	0.55600158736833	46 H :	-0.016973
H	-0.40374903720169	4.72410245183656	2.60231736515820	47 H :	0.030584
H	-1.77622856785119	6.65019787630303	-1.79117690681824	48 H :	0.036788
H	3.56415113976399	1.34759782208956	-3.50209102969488	49 H :	0.036607
H	1.97208838966210	2.22256268562395	-3.27682121613261	50 H :	0.024022
H	3.34725322132944	3.00311810868548	-4.16330533258408	51 H :	0.037789
H	5.55719185060683	2.32486280644139	-2.37376317118813	52 H :	0.044989
H	5.13924726766695	3.97069701264527	-2.95991897825756	53 H :	0.043765
H	5.32978616377703	3.66915625417171	-1.19948730492278	54 H :	0.044535
H	2.99101097623803	4.89515664593051	-2.54732974999773	55 H :	0.038496
H	1.67871636587886	3.85359698674603	-1.86578732341926	56 H :	0.029927
H	2.99395761116949	4.52228831078936	-0.78975679224341	57 H :	0.036568
H	3.85600911447408	0.99877725777750	-1.16780856925369	58 H :	0.034443
H	3.72230346949314	2.36551857313383	-0.01297233593239	59 H :	0.037563
H	2.25654295668263	1.73235402990243	-0.81305391180798	60 H :	0.040536
H	-1.82307475707069	-2.24466881531399	-3.23226429738241	61 H :	0.035811
H	-0.08636919457540	-2.48672210417416	-3.60834059136530	62 H :	0.037463
H	-0.64235981038793	-2.60653603850398	-1.89681591420406	63 H :	0.022837
H	-2.55978548313789	-0.14268884060333	-2.26971808852529	64 H :	0.031400
H	-1.60677068738353	-0.58369662763193	-0.80928834785605	65 H :	0.021153
H	-1.32014997354935	1.00481677319168	-1.63651798754508	66 H :	0.026613
H	-1.55198731783932	-0.06659358021285	-4.44068781246599	67 H :	0.035521
H	-0.36367890581306	1.13446692305128	-3.74886909109208	68 H :	0.022201
H	0.21221359917705	-0.35008634231244	-4.62234063779202	69 H :	0.035572
H	0.93586573021823	0.63316760402624	-1.95280282567692	70 H :	0.021887
H	0.80235299138436	-0.94493082519655	-1.05148263903786	71 H :	0.021167
H	1.56107854676233	-0.90443687719643	-2.68069886544777	72 H :	0.028274
H	-2.45482578613847	-6.91012294298195	2.67037792364524	73 H :	0.044574
H	-3.81972838330356	-6.60640637290308	1.53537410105467	74 H :	0.045918
H	-2.26572612236871	-7.26729124936576	0.92022532162967	75 H :	0.046282
H	-0.50698198844974	-5.33111721529525	2.66851840352999	76 H :	0.023373
H	-0.30839490433874	-6.00702340388271	1.00990649186506	77 H :	0.041388
H	-0.34660606141199	-4.22959005964115	1.23608805359006	78 H :	0.026624
H	-2.59178833138059	-4.58979354158875	3.42590619954629	79 H :	0.023809
H	-2.48927240951795	-3.25729567141076	2.19838228825910	80 H :	0.028967
H	-3.94842242325684	-4.31110339392540	2.27543025166556	81 H :	0.042744
H	-3.64686456818713	-4.91627255825726	-0.11600501936497	82 H :	0.042986
H	-2.30227008157374	-3.70976774673551	-0.04799683579896	83 H :	0.025486
H	-2.00133565427466	-5.37445343560951	-0.67529875521801	84 H :	0.042545

Table S10 Cartesian coordinates and Loewdin atomic charges of **P2**

The cartesian coordinates of B3LYP(RIJCOSX, D3BJ)/def2-SVP optimized geometries of **P2**			Loewdin atomic charges of **P2**
C	0.92238921615152	2.52831898884077	12.10514210817074	0 C : -0.046518
C	5.87808251128273	-0.85970731339748	11.84314638871616	1 C : -0.047879
C	0.50295789588157	2.28691351191274	13.42926284489739	2 C : -0.001590
C	-0.64986835243407	2.88074205622560	13.93263445796743	3 C : -0.032362
C	-1.01073043288408	3.98393435961592	11.78936169777702	4 C : -0.035621
C	2.12694620753358	1.90424281868284	11.55879471487565	5 C : -0.003605
C	-1.40415657540558	3.72046390406657	13.10308489539339	6 C : -0.117731
C	0.15259280191495	3.38675202527081	11.29863898545539	7 C : -0.007011
C	6.43184512477406	-2.01738614992336	13.90358650648418	8 C : -0.113601
C	4.73232886160307	-0.30435391372492	12.45625096485589	9 C : 0.035035
C	6.71475763242628	-1.70527203832608	12.55639291066642	10 C : 0.019152
C	4.44333797160495	-0.62088318327915	13.80247582255454	11 C : -0.050424
C	5.28415323815570	-1.46504467464126	14.51231571185604	12 C : 0.021671
N	2.83391453431962	1.09427191505493	12.26615626630522	13 N : -0.036497
N	3.92084512726362	0.53584145081120	11.72527952436005	14 N : 0.082582
Br	-3.00025987555370	4.51197215027841	13.78833600943099	15 Br: 0.073088
C	7.29941515462924	-2.87205291274493	14.65007319767041	16 C : -0.006742
N	8.00165645483288	-3.56526363648837	15.26713746539676	17 N : -0.155074
H	-0.96663007257615	2.68738061040999	14.95875597983740	18 H : 0.039267
H	2.40448950283390	2.15658454871938	10.52107667610593	19 H : 0.018091
H	0.46609880282496	3.59288992770303	10.27183387263116	20 H : 0.038717
H	7.59469150840713	-2.13331773360787	12.07257250882209	21 H : 0.044462
H	3.56196383376506	-0.18976549974351	14.27429329195012	22 H : 0.033305
H	5.05347320315732	-1.70825621507854	15.55152321639358	23 H : 0.044140
H	4.18320766159845	0.75896854962115	10.76310575700972	24 H : 0.089803
H	6.10877863542898	-0.61080356771154	10.80431447857854	25 H : 0.040886
H	1.09469954966101	1.62450428333445	14.06371385678096	26 H : 0.034471
H	-1.60485512119703	4.64182773811922	11.15248988905679	27 H : 0.039985

Table S11 Cartesian coordinates and Loewdin atomic charges of **P2-F**

The cartesian coordinates of B3LYP(RIJCOSX, D3BJ)/def2-SVP optimized geometries of **P2-F**			Loewdin atomic charges of **P2-F**
C	1.25193021132643	-3.27956012935505	3.49459465390375	0 C : 0.010666
C	2.55792429213323	-3.66375437843359	3.11741121700659	1 C : -0.124992
C	3.25980435560555	-2.87929011405991	2.17126643045983	2 C : 0.007887
C	2.67368954761900	-1.75169998611414	1.62381872922535	3 C : -0.056990
C	1.36412380661421	-1.36217390512025	2.00821131022882	4 C : 0.025832
C	0.65811514833729	-2.15064450036847	2.94816819448167	5 C : -0.062492
C	3.16168116065704	-4.82412740184019	3.68661090745933	6 C : -0.008899
N	3.65542351525986	-5.77014220065613	4.15343965564106	7 N : -0.169758
N	0.85396520226381	-0.22992221342595	1.42660242836619	8 N : 0.050470
N	-0.41121361087902	0.13953947601104	1.64872740601479	9 N : -0.047310
C	-0.85101296247782	1.17701972927921	1.01559442451239	10 C : -0.034924
C	-2.22329971968457	1.65398376860290	1.16489998814487	11 C : -0.044459
C	-3.12837180809202	1.07380252415641	2.07936540244018	12 C : -0.009027
C	-4.43033304019286	1.55349399221197	2.20148455580244	13 C : -0.037302
C	-4.84467251701737	2.62391785970377	1.39688320823305	14 C : -0.126583
C	-3.97484873443811	3.21473537582376	0.47770198936863	15 C : -0.037600
C	-2.67048849982263	2.72859864764759	0.37087781899446	16 C : -0.020151
Br	-6.63082778925580	3.28837333151459	1.55564843388218	17 Br: 0.071551
H	-5.12015388997531	1.09867153447566	2.91490600688345	18 H : 0.040700
H	-0.19663883388915	1.73782662341938	0.33011895529912	19 H : 0.008532
H	-1.98668229479877	3.19594362716446	-0.34324291255911	20 H : 0.037469
H	4.26475913308304	-3.17532413136587	1.86332571409798	21 H : 0.042388
H	-0.34888924704048	-1.85753115262251	3.24164688855592	22 H : 0.031163
H	0.70267544684495	-3.88242753090110	4.22164984044930	23 H : 0.042951
H	1.48656660912339	0.25482848743110	0.68055992725799	24 H : 0.021527
H	3.18393449177986	-1.13187210302213	0.88385917248176	25 H : 0.024515
H	-2.79491959748170	0.23894257824916	2.69862660935970	26 H : 0.034365
H	-4.30729619500754	4.04659333588015	-0.14560384196158	27 H : 0.040751
F	2.38992104775383	0.62736893043340	-0.37067538272644	28 F : -0.526723
N	0.71971350653654	0.42697570906949	-3.10498840669043	29 N : 0.125527
C	2.10638127365467	-0.09699176352824	-3.35847549398568	30 C : 0.060505
C	-0.09354352608924	0.38738138785566	-4.35657653732331	31 C : 0.062572
C	0.08290535246553	-0.41491737049271	-2.03660895841541	32 C : 0.058034
C	0.83391419347610	1.83968909787206	-2.60359938389739	33 C : 0.055711
H	2.57558772625814	0.52004806264225	-4.13388292724835	34 H : 0.040991
H	2.64533101192561	-0.02058838294808	-2.40501669712333	35 H : 0.028460
H	2.03131391230727	-1.13667181930706	-3.70056289067174	36 H : 0.040966
H	-1.09068155815318	0.79074793639121	-4.14106258404684	37 H : 0.046337
H	0.40243356353161	0.99890358729276	-5.11988439826461	38 H : 0.045737
H	-0.17213973212893	-0.65189634255079	-4.69724898157163	39 H : 0.045747
H	-0.91356638206715	-0.01325403624933	-1.81660305186337	40 H : 0.038266
H	-0.00021169645556	-1.44507805829675	-2.40239823803137	41 H : 0.041335
H	0.74629454038762	-0.34159206721795	-1.16733126843093	42 H : 0.023686
H	-0.17487560403377	2.22059260906803	-2.40341131433486	43 H : 0.036345
H	1.44313914349608	1.79378821862805	-1.68857606999214	44 H : 0.024525
H	1.31313924654034	2.44769305705216	-3.38025072941226	45 H : 0.041697

Table S12 Cartesian coordinates and Loewdin atomic charges of **P2-2F**

The cartesian coordinates of B3LYP(RIJCOSX, D3BJ)/def2-SVP optimized geometries of **P2-2F**			Loewdin atomic charges of **P2-2F**
C	0.84711583669621	-2.51870170041657	4.91101626508423	0 C : 0.009885
C	2.10519058954186	-3.07353750625025	4.58436513400016	1 C : -0.129808
C	2.66331007707834	-2.80371568746206	3.31077506519470	2 C : 0.004606
C	1.98672626673904	-2.01218915660121	2.40231744250173	3 C : -0.060057
C	0.72041249580662	-1.45527646773052	2.72973535544165	4 C : 0.027260
C	0.16295055279998	-1.72030231703063	4.00590612718121	5 C : -0.067820
C	2.80870368700292	-3.88939713945639	5.51753930633773	6 C : -0.010360
N	3.39525377378740	-4.55859878007592	6.26986222127760	7 N : -0.173832
N	0.10875973965055	-0.68263814056933	1.78329088807855	8 N : 0.053279
N	-1.12988108913100	-0.19498680984596	1.98582716428471	9 N : -0.060459
C	-1.61588672973958	0.57083495063334	1.06502548621319	10 C : -0.027309
C	-2.96649061331646	1.13053289548067	1.15842319135410	11 C : -0.048899
C	-3.86607534381296	0.81877692066055	2.19838101134387	12 C : -0.015124
C	-5.14374977428328	1.37729450058745	2.22703515238687	13 C : -0.045843
C	-5.52787512662846	2.25606542209990	1.20501133570085	14 C : -0.127899
C	-4.65334084040424	2.58575149562415	0.16459037347965	15 C : -0.050667
C	-3.37561791381296	2.02206178332830	0.14254470777442	16 C : -0.021403
Br	-7.28611951008808	3.01796494840636	1.22947826941377	17 Br: 0.060503
H	-5.83867714724985	1.12814505646528	3.03133056701369	18 H : 0.037639
H	-1.05561251347937	0.86679840861257	0.16122592672932	19 H : 0.014862
H	-2.63972568881672	2.25341805238802	-0.64345588774810	20 H : 0.014348
H	3.63340560636620	-3.22991547825535	3.04605387199105	21 H : 0.040948
H	-0.80248315532523	-1.28625729712020	4.26316328196428	22 H : 0.029262
H	0.40902842340034	-2.72479987755098	5.89047032632377	23 H : 0.041575
H	0.63502204779489	-0.57514148735566	0.85323705170536	24 H : 0.034889
H	2.38738038128576	-1.78332057194754	1.41263271137254	25 H : 0.020861
H	-3.55580055302205	0.12883209318849	2.98604292395017	26 H : 0.031258
H	-4.96853839044870	3.27475486864721	-0.62200336286997	27 H : 0.035415
F	1.56795307355608	-0.71403452131595	-0.32644952545747	28 F : -0.519974
F	-0.86792954936409	2.19390950550536	-1.36760861835972	29 F : -0.608298
N	2.18621174180295	2.79820099375871	-1.34161379045392	30 N : 0.127879
N	-0.29948664282528	-2.23475981507389	-2.52859154876348	31 N : 0.123777
C	1.80346294356316	1.73407467704265	-2.33431755051601	32 C : 0.044106
C	3.66392601068748	2.98138341848739	-1.30893164973773	33 C : 0.059505
C	1.50447025474014	4.07527605779976	-1.73450350093315	34 C : 0.053851
C	1.67741663110604	2.37877367549829	0.01369039416593	35 C : 0.045436
C	-0.25204219038016	-2.99269755108631	-1.23295924544362	36 C : 0.059492
C	-1.18029811177453	-2.93742852919902	-3.50815672600998	37 C : 0.062181
C	-0.80644367285637	-0.84285858530270	-2.25979428710328	38 C : 0.055822
C	1.09942610162120	-2.13243507888869	-3.06361598948838	39 C : 0.057583
H	3.91011988852210	3.76648488274398	-0.58352777488179	40 H : 0.041748
H	4.13007582395004	2.03584702080377	-1.00587355614417	41 H : 0.042612
H	4.01306707667720	3.27367823288898	-2.30748178222579	42 H : 0.041268
H	2.19782952779929	0.77876707381316	-1.96916565754520	43 H : 0.020253
H	0.70116147018428	1.70957400581016	-2.30967886045868	44 H : 0.022036
H	2.21367182341234	2.00843145030573	-3.31476210092742	45 H : 0.026144
H	2.02075311058313	3.10961346352513	0.75579957151641	46 H : 0.029396
H	0.58275973085299	2.34893336778454	-0.09902292493361	47 H : 0.024811
H	2.04890094834864	1.36672774787697	0.21653892468077	48 H : 0.023880
H	1.75779786895519	4.85272687778969	-1.00311620242407	49 H : 0.037203
H	1.85698388873808	4.37040539125097	-2.73136491999400	50 H : 0.036437

H	0.42819257262782	3.85076007392949	-1.73510115032661	51 H :	0.023398
H	-1.27140427735427	-3.07737337146084	-0.83689888602517	52 H :	0.039444
H	0.16215576371547	-3.98988940688131	-1.42761255309705	53 H :	0.042018
H	0.39562896704960	-2.41183332672778	-0.56264317983674	54 H :	0.028847
H	-1.21045954311411	-2.35690095885813	-4.43777621446824	55 H :	0.044799
H	-0.77066731614361	-3.93673831080054	-3.70090603103089	56 H :	0.044614
H	-2.18731177280476	-3.02001059511597	-3.08170950275389	57 H :	0.045448
H	1.08375675194061	-1.51517917661305	-3.97040051103130	58 H :	0.039165
H	1.70356240630697	-1.66969398311278	-2.27203583678861	59 H :	0.028097
H	1.45812150715291	-3.14055510746388	-3.30447237600481	60 H :	0.039723
H	-0.83591792886585	-0.29429447541514	-3.20754359887739	61 H :	0.035769
H	-1.81365947209375	-0.91222773370809	-1.83312955688459	62 H :	0.034329
H	-0.10917059470810	-0.37710996804436	-1.55508528891746	63 H :	0.030094

Table S13 Cartesian coordinates and Loewdin atomic charges of **P2-3F**

The cartesian coordinates of B3LYP(RIJCOSX, D3BJ)/def2-SVP optimized geometries of **P2-3F**				Loewdin atomic charges of **P2-3F**	
C	-4.31793470468517	2.19938284697776	0.04543350458715	0 C :	-0.022272
C	-3.82712383726678	1.45272187848097	1.13862661154852	1 C :	-0.049208
C	-4.73911135814316	0.93041599188246	2.07842331122571	2 C :	-0.015065
C	-6.10973365062603	1.13732641425059	1.93232285289396	3 C :	-0.045673
C	-6.57432932926786	1.87189808808669	0.83280756489692	4 C :	-0.128109
C	-5.69098730878405	2.40694500091586	-0.10896195622256	5 C :	-0.050558
C	-2.38693028955049	1.19742904427127	1.20371038924387	6 C :	-0.029988
N	-1.86451157006919	0.48989043222239	2.14830900530816	7 N :	-0.057259
N	-0.55750743728762	0.18137046055971	2.05633304181821	8 N :	0.054573
C	0.01664833302416	-0.63088544102812	3.00745822271762	9 C :	0.025916
C	1.28338034303738	-1.19015375018842	2.72122628049969	10 C :	-0.061279
C	1.91840585368198	-2.04133749952309	3.61145615202206	11 C :	0.001368
C	1.29169899057942	-2.34300093325853	4.84374188941546	12 C :	-0.133079
C	0.02953070306153	-1.78089088861247	5.14292383085290	13 C :	0.005419
C	-0.60480654973182	-0.93643161156959	4.24163195128927	14 C :	-0.071389
C	1.92674870870486	-3.21541055924737	5.77806548152466	15 C :	-0.009813
N	2.45110240019610	-3.92551072783412	6.53860739229516	16 N :	-0.179215
Br	-8.45836962513149	2.13424802997981	0.60395773579202	17 Br:	0.060508
F	0.79405390079160	0.03932235165316	-0.19484210857261	18 F :	-0.518619
F	-1.86060916529988	2.81121332882231	-1.50282335973390	19 F :	-0.607184
C	0.90232086310558	2.34736359168470	-2.27295438660382	20 C :	0.040251
N	1.18389693093824	3.51540130914886	-1.36725259381851	21 N :	0.128323
C	0.60214553903922	3.21183507871817	-0.01251970440703	22 C :	0.044972
C	2.65002360855543	3.75636625599422	-1.25995945235010	23 C :	0.060795
C	0.49092059389839	4.72420030338441	-1.92478981361327	24 C :	0.057263
C	-2.08120503309044	-0.10897557788932	-1.80365570370888	25 C :	0.058022
N	-1.70641814509005	-1.56196427748437	-1.78195272136821	26 N :	0.124492
C	-0.37629622256485	-1.70411757017256	-2.45598630961897	27 C :	0.057052
C	-1.56365887411497	-2.01457088277497	-0.35775632389988	28 C :	0.058822
C	-2.74801658108349	-2.37424857890764	-2.47839935275956	29 C :	0.063673

H	-6.81171195538557	0.72171978882998	2.65747996029293	30 H :	0.037702
H	-1.80086829846967	1.60408925734091	0.36753158521055	31 H :	0.013672
H	-3.58446001967697	2.58791530487711	-0.67946909431352	32 H :	0.014494
H	2.87719554052725	-2.48479782758151	3.29286917453399	33 H :	0.014959
H	-1.57828762988662	-0.50455300131829	4.47054935973631	34 H :	0.028113
H	-0.45443561839957	-2.02078103853108	6.09284794289091	35 H :	0.039268
H	-0.03541883546392	0.26720171233545	1.13289235110024	36 H :	0.043014
H	1.73790909868198	-0.95236095178789	1.76208990817565	37 H :	0.027819
H	-4.36151970934596	0.34361542624503	2.91884279596546	38 H :	0.031339
H	-6.07442134364260	2.97467665148068	-0.95952392106059	39 H :	0.035306
H	2.82553641609739	4.58920838601390	-0.56772140315827	40 H :	0.043708
H	3.13007191237765	2.84837550523519	-0.87480612710741	41 H :	0.035671
H	3.04789281040235	4.00314276592223	-2.25227585962431	42 H :	0.042643
H	1.28220047745133	1.44367477392888	-1.77985412992260	43 H :	0.017803
H	-0.19724714896074	2.29621086913733	-2.33262864477779	44 H :	0.021681
H	1.38206569136816	2.53532034868677	-3.24159064529188	45 H :	0.027268
H	0.82811910955732	4.04824034907882	0.65990831367586	46 H :	0.030922
H	-0.47693756474330	3.08508416249029	-0.19354450525325	47 H :	0.024203
H	1.04191316486248	2.27264452049723	0.34167802001202	48 H :	0.023483
H	0.66862813038729	5.57382080799927	-1.25341570245085	49 H :	0.038351
H	0.90253280205333	4.93808577248396	-2.91942608869778	50 H :	0.037979
H	-0.57551776780594	4.46197140923334	-1.97583559566331	51 H :	0.025953
H	-2.51342180815132	-1.84710940997793	0.16387548840418	52 H :	0.040414
H	-1.31327049707981	-3.08235257930025	-0.35245258006753	53 H :	0.042958
H	-0.75712234929061	-1.42230822376361	0.08642964890323	54 H :	0.028724
H	-2.84860489012596	-2.01294665694785	-3.50889745836960	55 H :	0.045484
H	-2.44161898481181	-3.42733908077913	-2.47430201147281	56 H :	0.045643
H	-3.69874826059705	-2.25616042511004	-1.94394746270248	57 H :	0.046305
H	-0.46123775208429	-1.34057253164314	-3.48699667983532	58 H :	0.042378
H	0.32729284303777	-1.09565704604282	-1.87086832080065	59 H :	0.029225
H	-0.09057499197557	-2.76301732365280	-2.45043801400956	60 H :	0.041823
H	-2.18461559724697	0.21279882593180	-2.84519926044542	61 H :	0.037407
H	-3.03286374269429	0.01688445972760	-1.27811308548154	62 H :	0.036392
H	-1.28858698164521	0.45511296043800	-1.30872350760771	63 H :	0.031318
F	4.12115804759261	-2.90269428887126	2.00044590218590	64 F :	-0.638843
N	3.66820772757090	-1.98156612490473	-0.95879134338993	65 N :	0.130871
C	3.85693261868781	-0.79419856387692	-0.05165955360547	66 C :	0.037437
C	3.39203663070880	-1.53506658983679	-2.35277715849591	67 C :	0.055257
C	4.90375639675158	-2.82821493575642	-0.89823310774912	68 C :	0.049900
C	2.51343397164853	-2.78248222929415	-0.41987150881586	69 C :	0.041333
H	4.75975976249721	-3.70981049011326	-1.53527649877538	70 H :	0.034637
H	5.75312529698338	-2.23582344225286	-1.26273981641980	71 H :	0.034121
H	5.01493412484087	-3.10531748843885	0.16223757223505	72 H :	0.017681
H	3.22605042525635	-2.41569505306968	-2.98589869567650	73 H :	0.042774
H	2.49926738755333	-0.89896823170065	-2.34342531306627	74 H :	0.033900
H	4.25213391576111	-0.96454223830252	-2.72445815483643	75 H :	0.041615
H	4.69454947275651	-0.19538477012728	-0.43346757722712	76 H :	0.028255
H	2.91401703703839	-0.22949307215999	-0.05730377570136	77 H :	0.019681
H	4.06770789954856	-1.23361592752226	0.93815697955173	78 H :	0.018615
H	2.34561860554304	-3.64043082188652	-1.08285054118491	79 H :	0.028293
H	2.82985718769256	-3.08047246486371	0.59549938968566	80 H :	0.017889
H	1.64425965542128	-2.11589353704231	-0.38973248075550	81 H :	0.020422

4. Imaging System The imaging system was comprised of an inverted fluorescence microscope (Leica DM 1000 LED), digital compact camera (Leica DFC 420C), and an image processor (Leica Application Suite v3.3.0). The microscope was equipped with a mercury 50 watt lamp.

In both case of cell study (pollens and candida) the experimental fluoride solution in 10^{-6}M concentration was prepared with hand pump water collected from Bankura, West Bengal, India.

Preparation of pollen grains to detect intracellular F^-:

Pollen grains of *Techoma stans* (Family: Bignoniaceae) are collected from fresh buds and washed twice with 0.1 M HEPES buffer at pH 7.4. Then, they are treated with 10 μM F^- for 30 minutes in 0.1 M HEPES buffer (pH 7.4) containing 0.01% Triton X100 as a permeability enhancing agent. After incubation the pollens are washed again with HEPES buffer at pH 7.4 and incubated with **P1** (10^{-4} M) for 30 minutes. **P1** treated pollens are washed by centrifugation (3000 rpm for 5 minutes) using HEPES buffer and are mounted on grease free glass slide and observed under a Leica DM 1000 fluorescence microscope equipped with a UV filter. Pollens treated with F^- only are used as control (Fig. S12a).

Preparation of *Candida* Cell to detect intracellular F^-:

Candida albicans cells (IMTECH No. 3018) from exponentially growing culture in yeast extract glucose broth medium (incubation temperature 37^0C) were washed by suspending them in normal saline and centrifuged at 3000 rpm for 10 minutes washed twice with 0.1 M HEPES buffer (pH 7.4). Then cells were treated with F^- solution (10 μM) for 30 minutes. After incubation, the cells were again washed with HEPES buffer and then incubated with **P1** (10^{-4} M) for another 30 minutes. Cells obtained this way are mounted on grease free glass slide and observed under a Leica DM 1000 Fluorescence microscope with UV filter. Cells treated with F^- only are used as control (Fig. S12b).

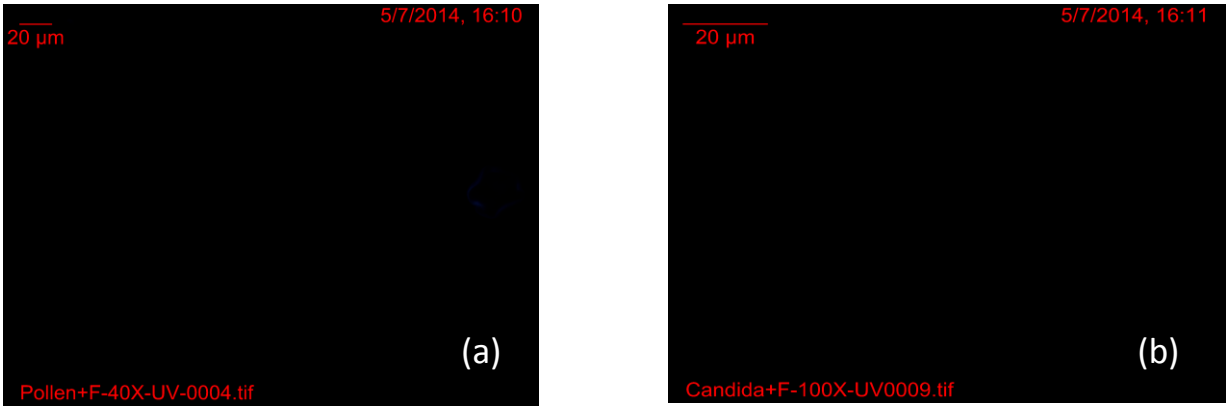


Fig. S12 (a) Pollens treated with F^- only and (b) Candida cells treated with F^- only.

Analytical applications of P1 by in vitro F^- detection:

In addition of developing test kit, on another wing of our research we are interested for *in vitro* detection of F^- for quick and easy identification of non skeletal fluorosis as non skeletal fluorosis affects all the soft tissues and organs of human body. In between two sensors **P1** only have fluorescence enhancement with F^-. Therefore we have performed the *in vitro* F^- detection experiment with **P1** only. **P1** can easily detect intracellular F^- at 10^{-6}(M) concentration, which are confirmed on experimentation with two different types of cells *viz.* pollen grains of *Techoma stans* (Fig. 12) and *Candida albicans* (IMTECH No. 3018) (Fig. S13). **P1** can easily permeate through the cell membrane without causing any harm to the cells. F^- solutions in 10^{-6}M concentration were prepared with ground water sample collected from Bankura, West Bengal (an endemic of fluorosis). Noticeably, after incubation with F^- contaminated water, when **P1** is added to the cells, blue emission is observed which confirms the detection of intracellular F^-.

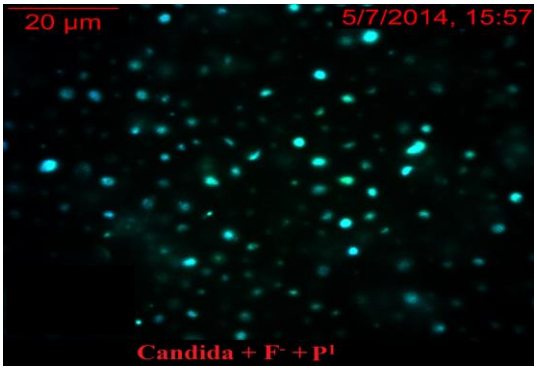


Fig. S13 *In vitro* detection of F^- in ppm level concentration by **P1** in *Candida albicans* cells (IMTECH No. 3018).

Reference:

1 Orca 3.0.0, developed by Prof. Dr. Frank Neese, Max Planck Institute for Bioinorganic Chemistry, Muelheim/Ruhr, Germany.
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