Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Chemically-driven "molecular logic circuit" based on osmium chromophores with resettable multiple readout

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Material and Methods: Most of the metal salts and were purchased from BDH chemicals Ltd. and used as received. 4, 5-imidazoledicarboxylic acid, *o*-phenylenediamine and *ortho*-phosphoric acid were purchased from Alfa Aesar and Spectrochem, respectively and used as received. $(NH_4)_2OsCl_6$ was purchased from Sigma Adrich and stored in N_2 atmosphere. Tetra butyl-ammonium salt of each anion was purchased from Sigma Aldrich and stored in freezer. Methanol, dichloromethane (DCM) and acetonitrile (HPLC grade) were purchased from Merck and distilled using reported methods.[S1] Water used for the experiment was double distilled. UV-vis spectra were recorded using JASCO UV-vis-NIR spectrometer (670D) with a quartz cuvette (path length, 1cm). Fluorescence spectra were recorded on Varian Cary eclipse instrument. Mass spectra were recorded on THERMO finnigan LCQ advantage max ion trap mass spectrometer (MSAIF, CDRI, Lucknow, India). All ^1H NMR spectra were recorded on Jeol JNMECX 400p spectrometer at room temperature using DMSO-d_6. All chemical shifts (δ) were recorded in ppm with reference to TMS and coupling constant (J) in Hz. X-ray diffraction data for **1** was collected on the Oxford Diffractometer at low temperature equipped with a CCD detector using graphite-monochromated Mo-Kα radiation (λ=0.71073Å). The ligand 4-(1H-benzo[d]imidazol-2-yl)-1H-imidazole-5-carboxylic acid was synthesized by reported synthetic method[S2]. The precursor complex $[Os(bpy)_2Cl_2]$ was prepared according to the reported procedure[S3].

Synthesis of osmium complex of 4-(1H-benzo[*d*]imidazol-2-yl)-1H-imidazole-5-carboxylic acid(1). A mixture of cis-$[Os(bpy)_2Cl_2]$ (0.57g, 1.0 mmol) and 4-(1H-benzo[d]imidazol-2-yl)-1H-imidazole-5-carboxylic acid (0.23g, 1.0 mmol, ligand) was stirred in ethanol-water mixture (1:1, 100 mL) for 15 min in N_2 atmosphere. Then, triethylamine (0.1g, 1.0 mmol) was added and resulting solution was refluxed with continuous stirring for 72 h in pressure tube. The solution was filtered and maintained at low temperature over ice. An aqueous solution (5 mL) of

$NaClO_4.H_2O$ (0.5g) was added to the reaction mixture. After stirring for 10 min, the dark shiny microcrystalline compound deposited was filtered. The product was recrystallized twice from methanol-water (10:1) containing a few drops of 10^{-4} M $HClO_4$. (Yield = 0.37 g, 46%). Solubility: Soluble in DMF, DMSO, CH_3CN, less solubility in ethanol, methanol, and no solubility in alkanes, water and diethyl ether. Melting Point: 318.5°C. ^{1}H-NMR (400MHz, DMSO-d_6, 25°C, TMS); δ/ppm: 14.47 (s, 1H, NH), 8.76-8.55 (m, 6H), 8.51 (d, 1H, J = 7.73Hz), 7.84 (d, 1H, J = 7.03Hz), 7.73 (d, 1H, J = 8.0Hz), 7.68-7.57 (m, 4H), 7.56-7.36 (m, 6H), 7.16-7.0 (m, 4H), 6.95 (td, 1H, J = 6.77Hz, J = 6.6Hz, J = 1.23Hz), 6.41 (s, 1H). LC-MS: *m/z* (%): 629 (10) [M - $C_7H_5N_2$ + H_2O], 242 (100) [M – $C_{20}H_{16}N_4Os$ + H_2O]. Elemental Analysis (%): C (49.97), H (3.07), N (14.88), Calc (%): C (50.88), H (3.44) N (15.31). UV-vis (λ; nm, ε; M^{-1} cm^{-1}, CH_3CN): 294 (87,303), 519 (15,116), 720 (4,305), CV (*vs.* Ag/AgCl): $E_{1/2}$ = 0.35 V ($Os^{2+/3+}$), ΔE = 75 mV at 300 mVs^{-1}.

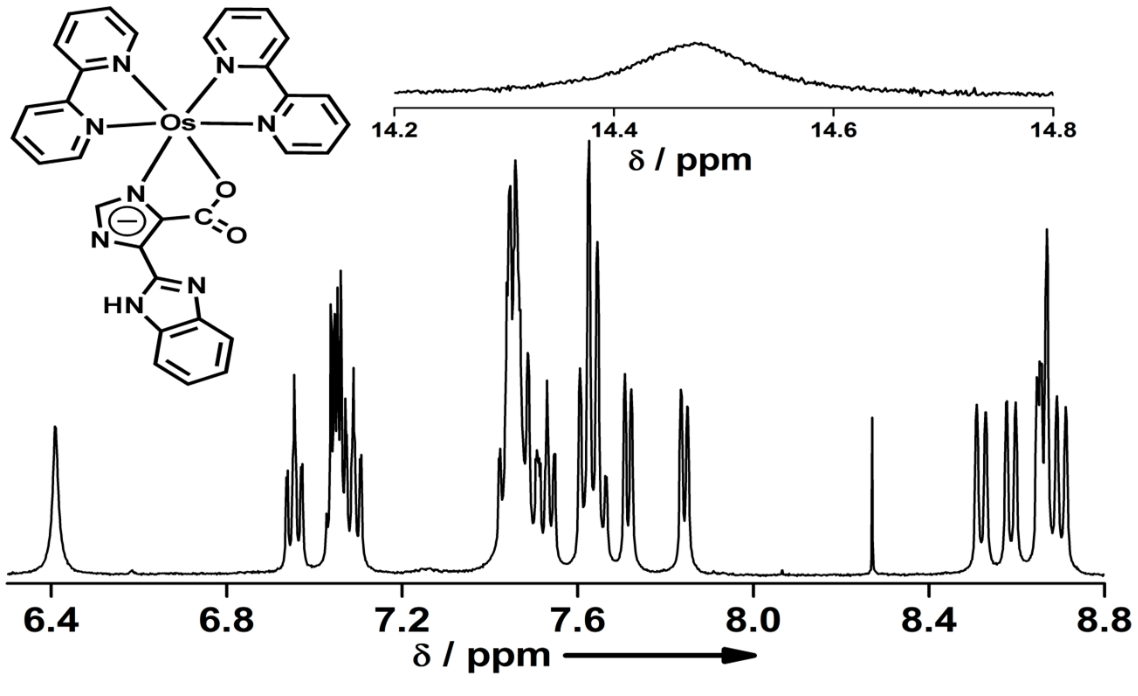

Figure S1: ^{1}H-NMR of **1** in DMSO-d_6 at room temperature, inset highlights the peak due to hydrogen atom of the NH group.

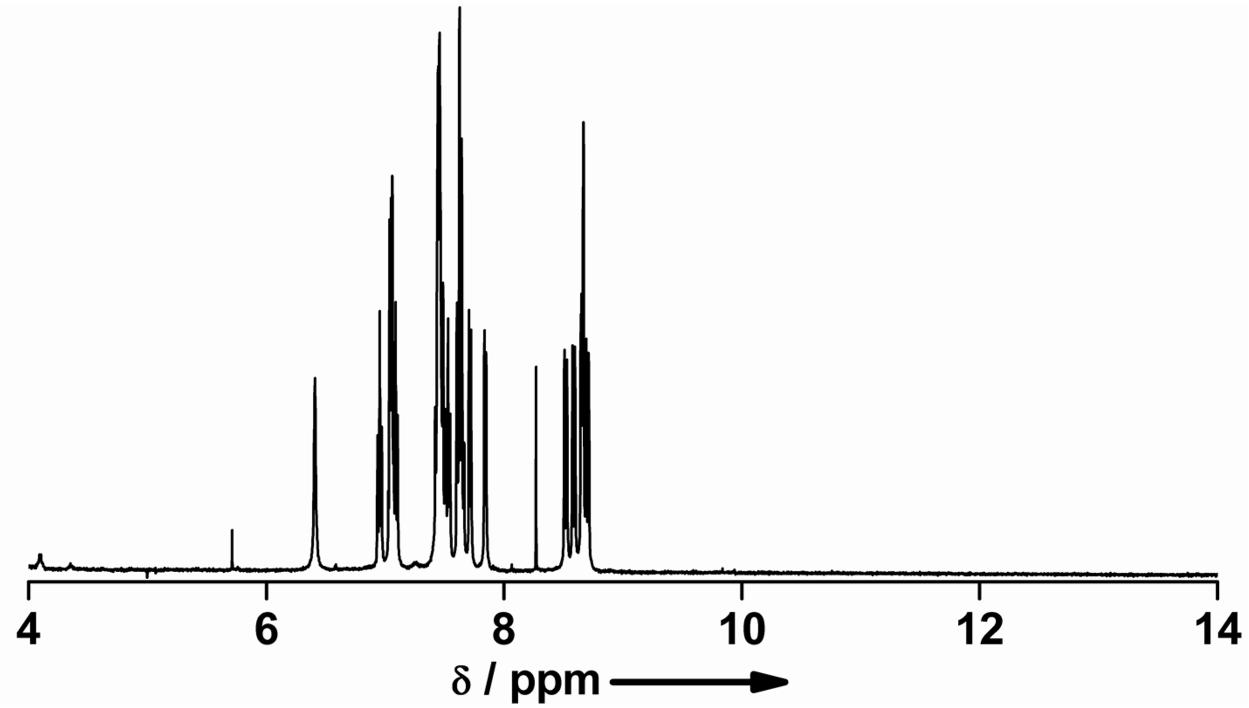

Figure S2: Full range ^{1}H-NMR spectra of **1** in DMSO-d_6 at room temperature.

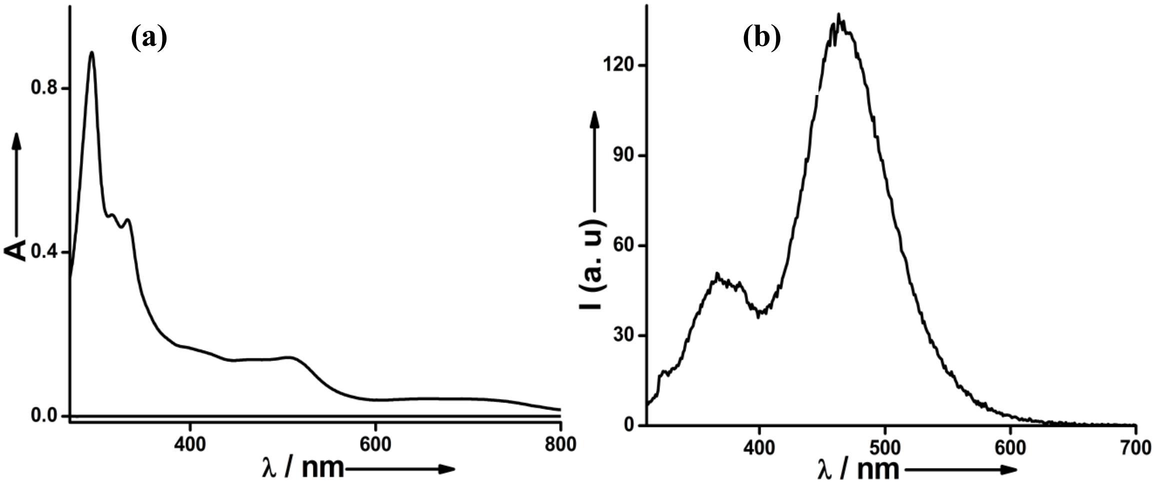

Figure S3: UV-vis spectra (a) Emission spectra (b) of **1** (0.98 x 10^{-5} M) in acetonitrile at room temperature.

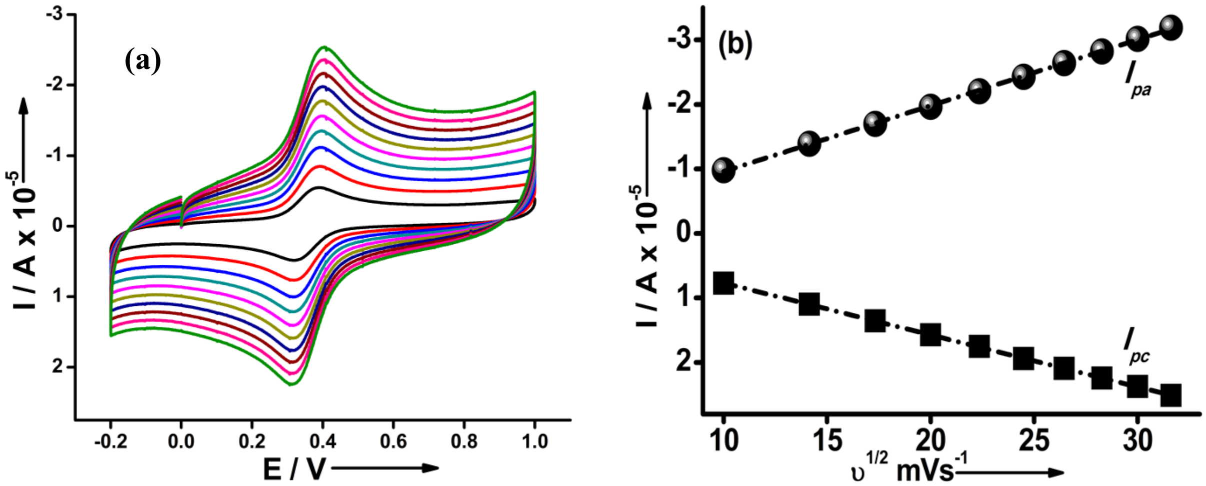

Figure S4: (a) Cyclic voltammogram of **1** (0.97×10^{-3} M) in acetonitrile containing 1.0 M Bu_4NClO_4 at scan rate from 100 to 1000 mVs^{-1}. The glassy carbon was used as the working electrode, platinum wire was used as the counter electrode, and Ag/AgCl in 1.0 M KCl (*aq*) was used as the reference electrode (b) Plot of current density as a function of square root of scan rate ($R^2 = 0.99$).

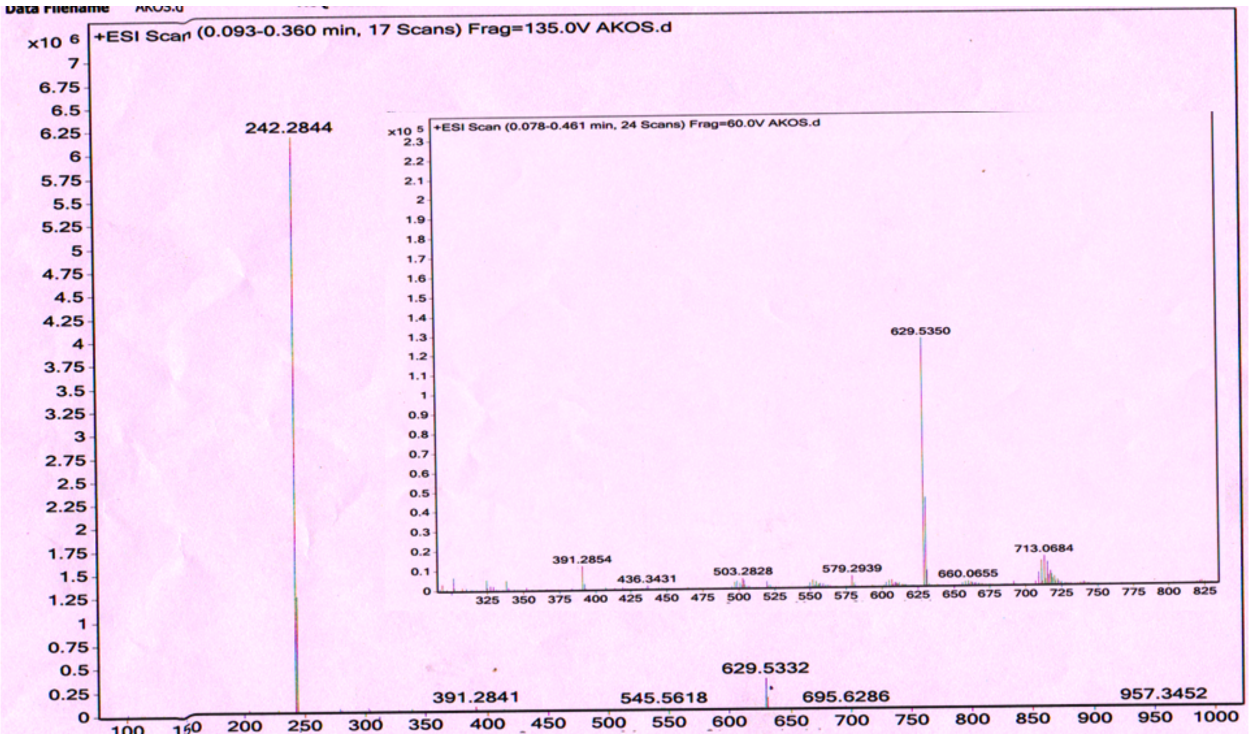

Figure S5: LC-MS spectra of **1** in acetonitrile.

X-ray Crystal structure determination: Crystal suitable for structure determination was obtained by diffusion of diethyl ether over saturated solution of **1** in acetonitrile for two/three week at room temperature. The structure was solved using direct and Fourier methods and refined by full-matrix least squares based on F^2 using WINGX software, which operated SHELX-97 software. The non-H atoms were refined anisotopically. The final least-squares refinement [I >2σ (I)] converged to reasonably good R values, $R_1 = 0.0298$, $wR_2 = 0.0697$ for **1**.The goodness of fit for 0.981 and the maximum and minimum peaks on the final difference Fourier map corresponding to 1.212 and -1.420eÅ^{-3} respectively. Complex **1** crystallized in the monoclinic form with space group P 21/c.

Summary of crystal data:

Empirical formula	$C_{31} H_{22} N_8 O_7 Os$	
Formula weight	808.77	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 9.5534(2) Å	α = 90°.
	b = 25.7853(5) Å	β = 93.470(2)°.
	c = 12.6272(3) Å	γ = 90°.
Volume	3104.85(12) Å^3	
Z	4	
Density (calculated)	1.730 Mg/m^3	
Absorption coefficient	4.168 mm^{-1}	
F(000)	1584	
Crystal size	0.19 x 0.17 x 0.14 mm^3	
Theta range for data collection	2.87 to 25.00°.	
Index ranges	-11<=h<=11, -30<=k<=30, -15<=l<=15	
Reflections collected	40852	
Independent reflections	5464 [R(int) = 0.0264]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5930 and 0.5048	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	5464 / 0 / 439
Goodness-of-fit on F^2	0.981
Final R indices [I>2sigma(I)]	$R_1 = 0.0298$, $wR_2 = 0.0692$
R indices (all data)	$R_1 = 0.0306$, $wR_2 = 0.0697$
Largest diff. peak and hole	1.212 and -1.420 e.Å^{-3}

Selected Bond Angles and Bond lengths:

Selected Bond Angles (°)		Selected Bond Lengths (Å)	
N(6)-Os(1)-N(5)	78.64(15)	N(1)-Os(1)	2.064(4)
N(6)-Os(1)-N(8)	89.21(15)	N(5)-Os(1)	2.045(4)
N(5)-Os(1)-N(8)	96.11(15)	N(6)-Os(1)	2.021(4)
N(6)-Os(1)-N(7)	97.65(15)	N(7)-Os(1)	2.046(4)
N(5)-Os(1)-N(7)	173.55(14)	N(8)-Os(1)	2.048(4)
N(8)-Os(1)-N(7)	78.47(15)	O(1)-Os(1)	2.117(3)
N(6)-Os(1)-N(1)	95.92(15)		
N(5)-Os(1)-N(1)	89.13(14)		
N(8)-Os(1)-N(1)	173.31(15)		
N(7)-Os(1)-N(1)	96.55(14)		
N(6)-Os(1)-O(1)	171.69(14)		
N(5)-Os(1)-O(1)	96.02(14)		
N(8)-Os(1)-O(1)	97.75(14)		
N(7)-Os(1)-O(1)	88.23(14)		
N(1)-Os(1)-O(1)	77.49(13)		

Preparation of ppm/ppb-level solution of metal salts and anions. A stock solution of 1000 ppm (*m/v*) of various metal salts of $Zn(NO_3)_2.6H_2O$,$Pb(NO_3)_2$, $Ni(NO_3)_2.6H_2O$, $NaNO_2$, $MnCl_2.4H_2O$, $MgSO_4.7H_2O$, KNO_3,$FeCl_3$, $Co(NO_3)_2.6H_2O$, $Cd(NO_3)_2.4H_2O$, LiCl, $CaCl_2$, $Hg(NO_3)_2.H_2O$, and $FeSO_4.7H_2O$ in dry acetonitrile/DMF/DCM/water were made by dissolving 10 mg of each metal salts in 10 ml of mixture of solvent. Further, the stock solution was diluted to 1.0 ppm by taking 5 µl volume of stock solution (1000 ppm) and making up it in acetonitrile solution of **1** upto 5 ml. The solution was used for ppm-level analyses. The 5 µl volume of final stock solution (1.0 ppm) was diluted to 5 ml acetonitrile solution of **1** for 1.0 ppb concentration. The solution was used for ppb-level analyses.

Similarly, stock solution of 1000 ppm (*v/v* or *m/v* whichever is applicable) of various anions was prepared by dissolving 10mg/10μl of required anion salt into 10 ml acetonitrile. Finally, this solution was diluted to 1.0 ppm by making up 5 μl in to 5 ml of acetonitrile solution of **1**.

Detection procedure of ppb/ppm-levels of Cu^{2+} and F^-: 5 ml solution of **1** (0.98×10^{-5}M) was treated with 5μl stock solution (100 ppm) of Cu^{2+} (1.0 ppb in acetonitrile solution of **1**), mixed thoroughly within seconds. Subsequently, absorbance spectra were recorded at room temperature using quartz cuvette. Further, 5 μl of Cu^{2+} was added to same solution for 2, 3, 4, 5, 6, 7, 8, 9, and 10 ppm. In contrast, the ppm levels of F^- were retained by addition of 5 μl of stock solution (1000 ppm) of F^- in 5 ml of **1** in acetonitrile.

Selectivity test: exclusive and matrix. The ppm-level solutions (5μl) of the various metal salts in mixture of solvents was added to 5ml solution of **1** in acetonitrile. The spectra was run immediately to analyse the change obtained. Moreover, for matrix test of metal ions, a solution of analytes (5μl of Cu^{2+} + 5μl of each metal ion) was added to 5ml of **1** to analyse the selectivity in matrices.

Similarly, the selectivity with various anions were performed in exclusive and matrix detection.

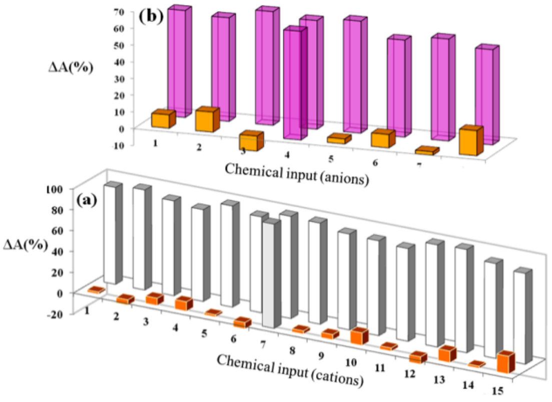

Figure. S6: Representative bar chart showing absorption intensity change for individual and in matrix seletivity as ΔA, % (where ΔA, % = [A_{Final} - $A_{initial}/A_{initial}$] × 100) at (a) λ = 509 nm: front row for various cationic inputs (1-15), back row for matix addition of various metal ions (1-15 cations) with 50 ppb of Cu^{2+}.

(b) chart showing absorption intensity change for individual and in matrix seletivity as ΔA, % (where ΔA, % = [A_{Final} - $A_{initial}/A_{initial}$] × 100) (b) λ = 554 nm: front row for various anionic inputs (1-8), back row for matix addition of various anionic input (1-8 anions) with 30 ppm of F^-. **Cationic inputs** : 1 = Zn^{2+}, 2 = Pb^{2+}, 3 = Ni^{2+}, 4 = Na^+, 5 = Mn^{2+}, 6 = Mg^{2+}, 7 = Cu^{2+}, 8 = K^+, 9 = Fe^{3+}, 10 = Co^{2+}, 11 = Cd^{2+}, 12 = Li^+**,** 13 = Ca^{2+}, 14 = $Hg^{2+}$and 15 = Fe^{2+}: **Anionic inputs**: 1 = I^-, 2 = Br^-,3 = Cl^-, 4 = F^-, 5 = NO_2^-, 6 = ClO_4^-, 7 = AcO^-, 8 = CN^-.

Reversibility test (Experimental details for the Fig. 3): The regenerative sensory asset was judged by successive addition of Cu(II) and H_2O, F^- and H^+ into the solution of **1**. In methodology, 5ml solution of **1** was treated with 5µl of Cu^{2+} (1000 ppm, acetonitrile) and spectra was taken to observe the change. Further, 5µl of double distilled water was added to the same solution to revert the spectral change and spectra was run again to confirm the regeneration (95% reversibility for first cycle while reduce to 87% till 3 cycles at λ = 509 nm). Similarly, 5ml solution of **1** was treated with 50µl of F^- (1000 ppm, acetonitrile) and spectra was taken to observed the spectral change. Further, 5µl of HCl (10^{-4}M, in acetonitrile) was added to the same solution to revert the spectral change and spectra was run again to confirm the regeneration (85% reversibily after 3 cycles at λ = 554 nm). The obtained spectroscopic and colourimetric perturbation on the repetitive-processing of Cu^{2+}/H_2O and F^-/H^+ were representated using absorbance intensity change (ΔA, % = [A_F - A_i/A_i] × 100) at λ = 509 and 554 nm with corresponding colour changes were shown in Fig 3.

Details of logical additions of various inputs in absorption mode (Experimental details of Fig. 4): The processing of logically matrices for Cu^{2+}/H_2O *viz.* "00" was assumed as absence of all input, "01" as addition of 5µl of H_2O, "10" as addtion of 5µl of Cu^{2+} (1000 ppm, acetonitrile) and "11" as addition of 5µl of H_2O and 5µl of Cu^{2+} simultaneously, in 5ml of same solution of **1**

and spectra was run in no time to observe the corresponding changes at λ = 509 and 293 nm as shown in Fig. S7a, b. Further, the output was converted into binary term depending upon the threshold value (absorbance = 0.1) and obtained circuit was represented in Fig. 4a.

Integration of Logic Gates:

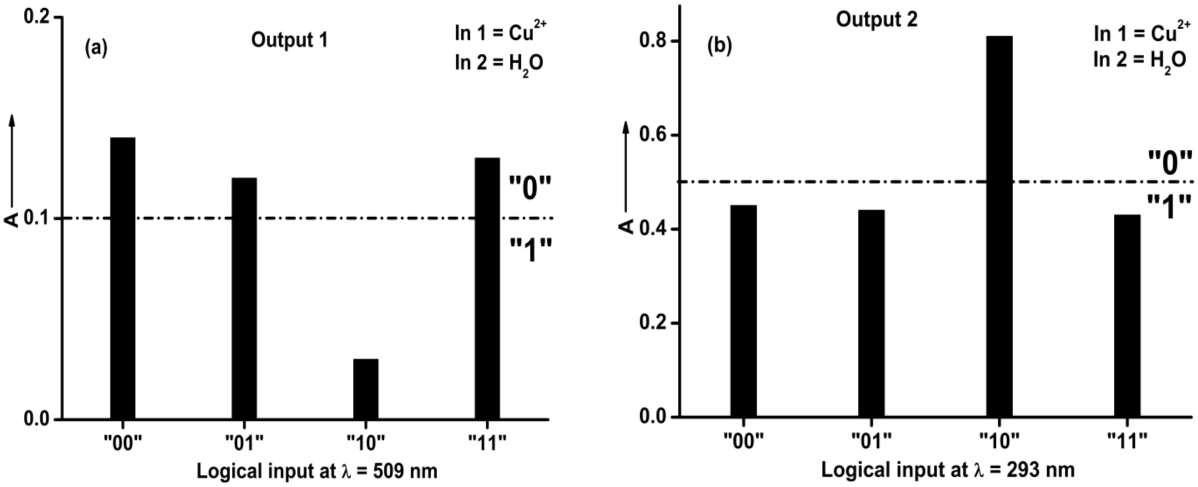

Figure S7: (a) The obtained absorbance at λ = 509 nm and (b) λ = 293 nm as output 1 and output 2 as function of logical input.

Similar methodology was adopted for the designing of logic circuit for the F$^-$/H$^+$ chemical information/stimuli and obtained absorbance and circuit was represented in Fig.S8a, b and 4b.

Integration of Logic Gates:

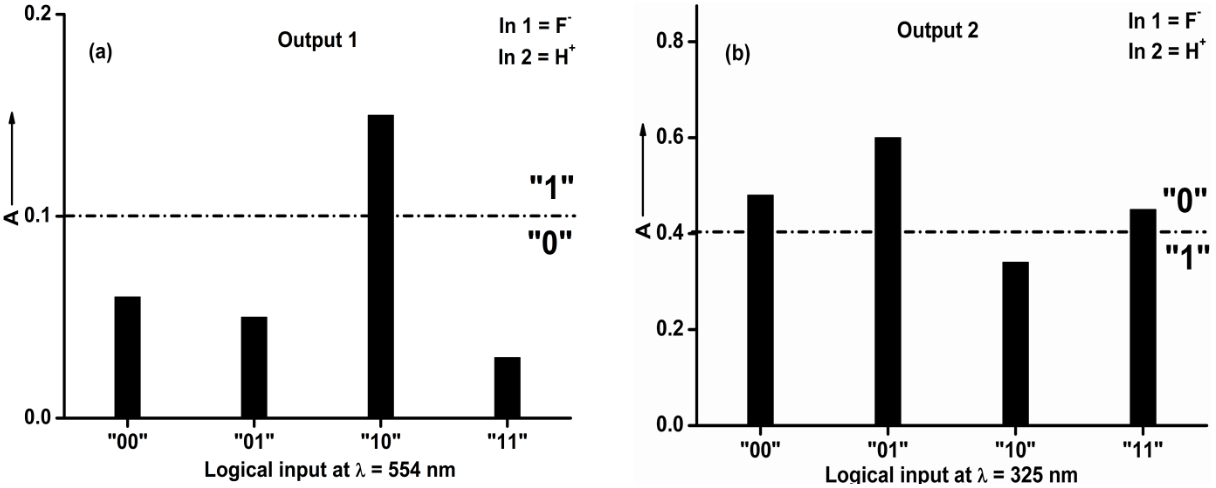

Figure S8: (a) The obtained absorbance at (a) λ = 554 nm and (b) λ = 325 nm as output 1 and output 2 as function of logical input.

Details of logical additions of various inputs in flourogenic mode (Experimental details of Fig. 6): Various responsive chemical inputs such as Cu^{2+} (5µl of Cu^{2+} in acetonitrile), H_2O (5µl of double distilled water), 50µl of F^- (1000 ppm, acetonitrile), 5µl of HCl (10^{-4}M, in acetonitrile) were added in **1** (5 ml in acetonitrile) in the four logic sequence (16 different sets), whereas the obtained fluorescence (Fig. 9) was converted into the logical output depending upon the decided threshold value (Intensity = 50 a.u) and obtained circuit was represented in Fig. 6.

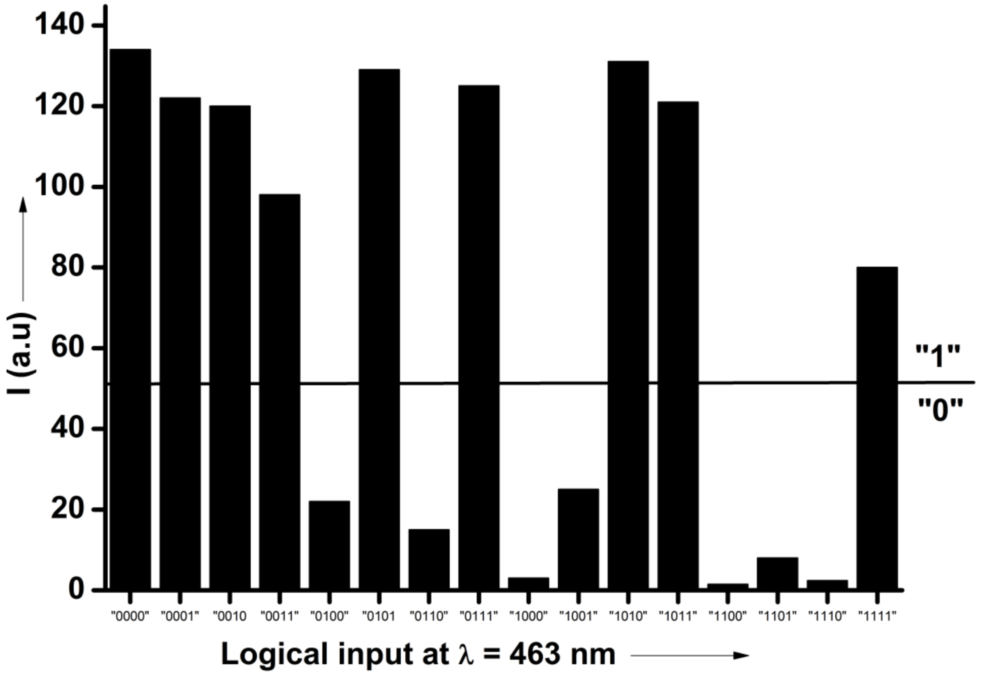

Figure S9: (a) The obtained emission at λ = 463 nm as output as function of logical input.

References:

S1. A. Kumar, A. K. Singh and T. Gupta, *Analyst,* 2013, **138**, 3356-3359.

S2. A. Kumar, M. Chhatwal and T. Gupta, *Tetrahedron Lett.* 2012, **53**, 5691-5694.

S3. T. Gupta, *Inorg. Chem. Commun.*, 2010, **13**, 724-726.