Supplementary Information

Ratiometric sensing of fluoride and acetate anions based on a BODIPY-azaindole platform and its application to living cell imaging

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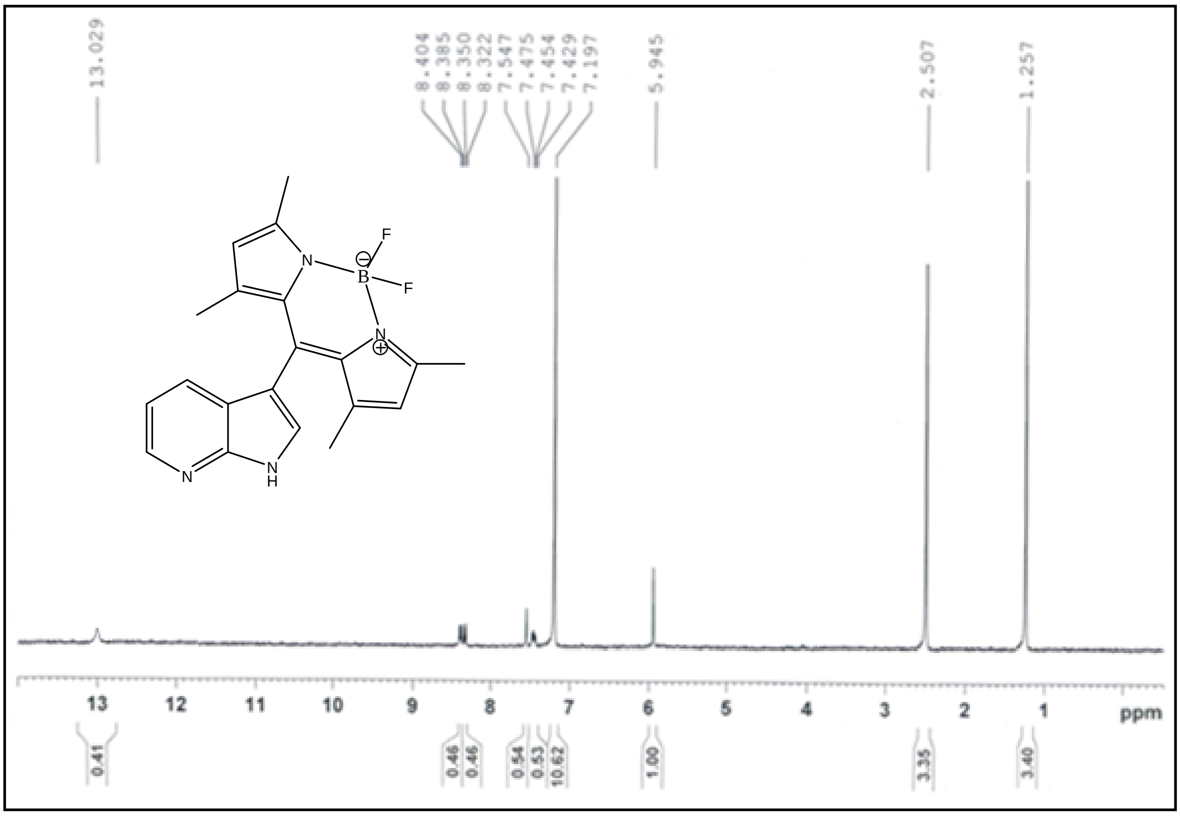


Fig. S1. ^{1}H NMR of sensor **1** ($CDCl_3$, 300 MHz).

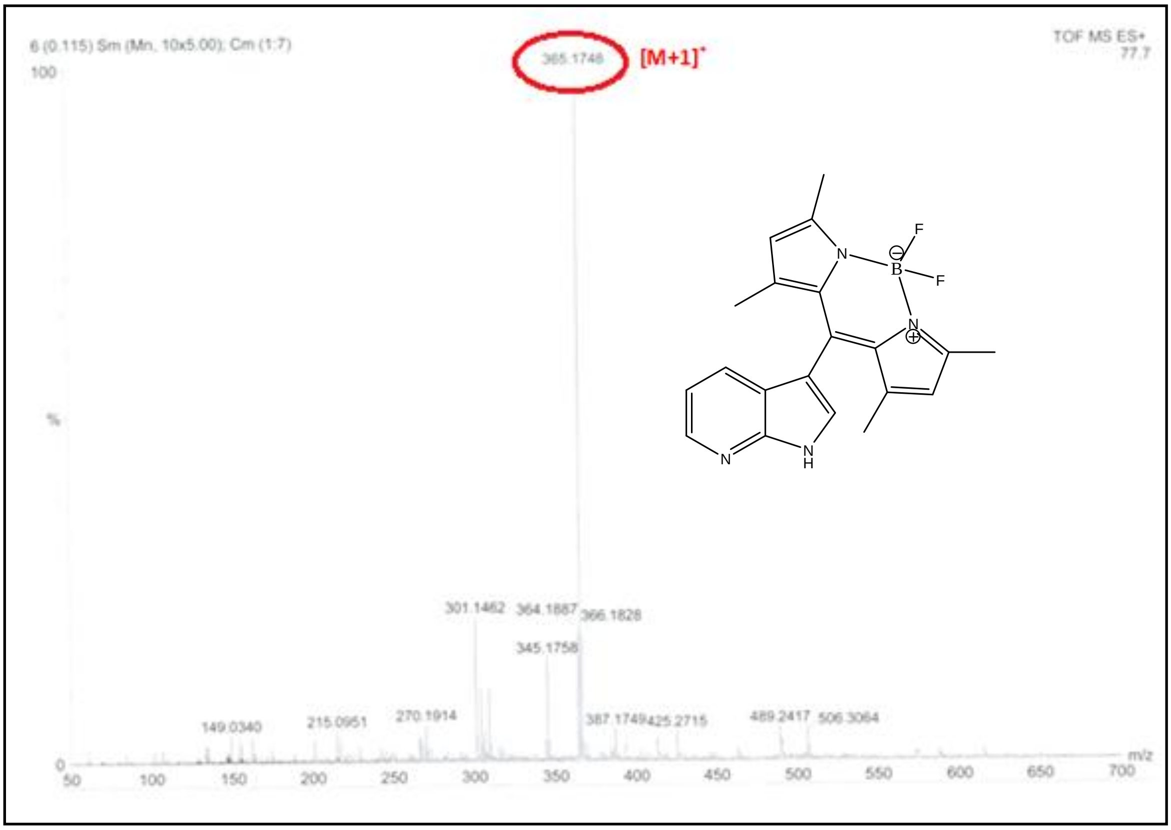


Fig. S2. TOF MS ES+ mass spectrum of sensor **1.**

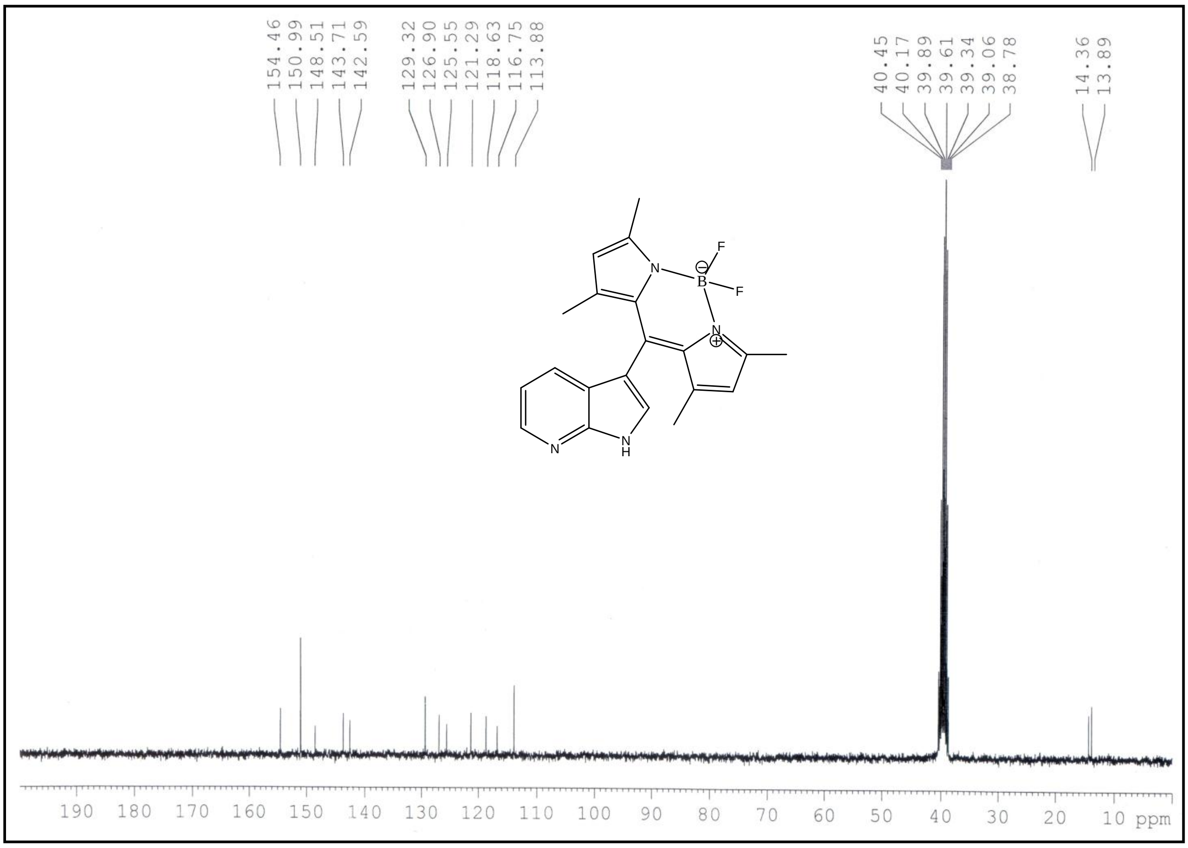


Fig. S3. ^{13}C NMR of sensor **1** ($CDCl_3$, 75 MHz).

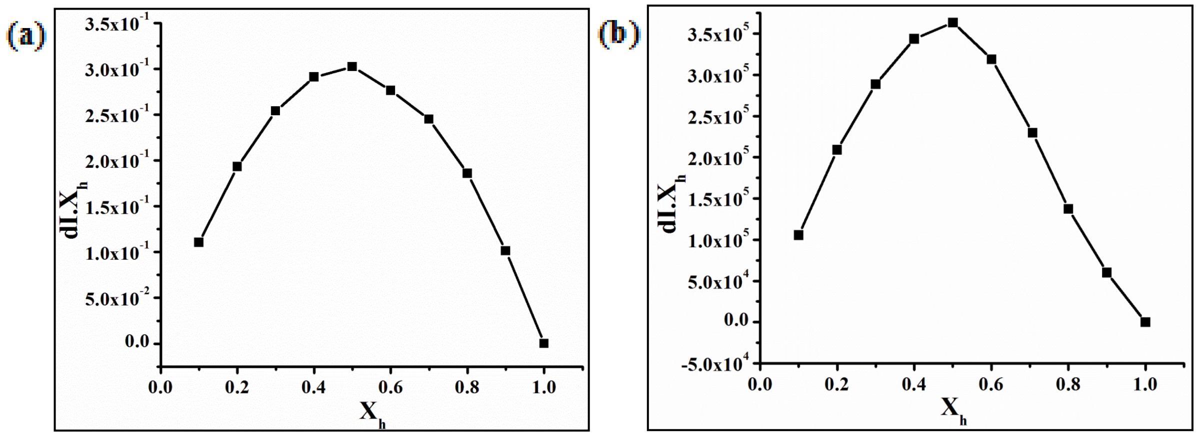


Fig. S4. Job's plot for determining the stoichiometry of sensor **1** and F^- ion by (a) UV-vis method, (b) fluorescence method.

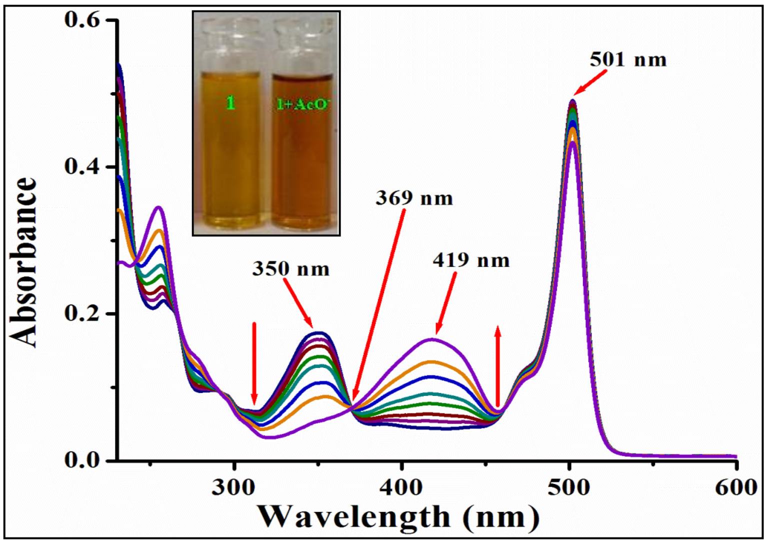


Fig. S5. Changes in the UV/vis absorption spectra of sensor **1** (4.5 μM) in 7:3 CH_3CN : H_2O solution (0.02M HEPES buffer, pH 7.2) in the presence of $[Bu_4N]^+AcO^-$ anions (0 – 200 equiv).

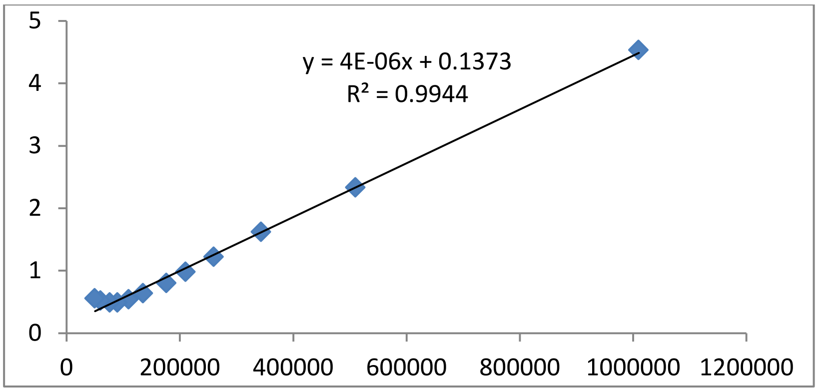


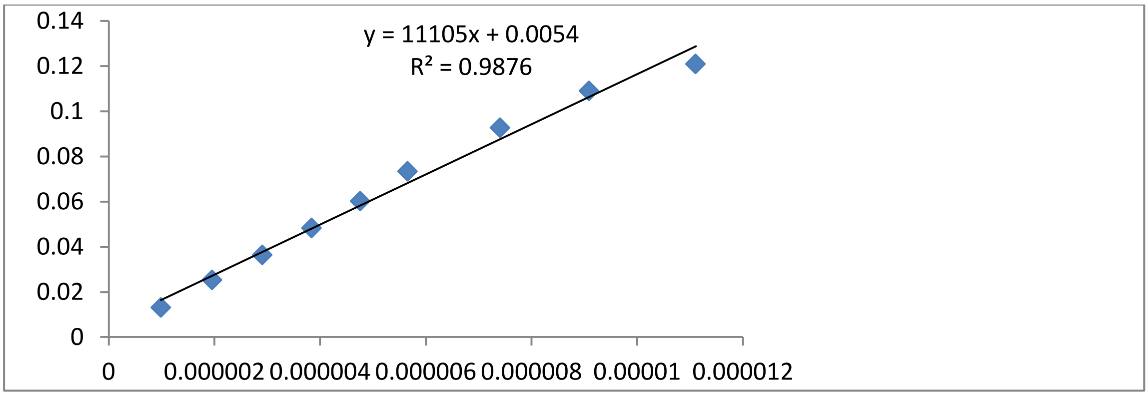
Fig. S6. Association constant curve of sensor **1** with F^- determined by UV -vis method.

Calculations for detection limit:

The detection limit (DL) of **1** for F^- were determined from the following equation[1]:

DL = K* Sb1/S

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



From the graph we get slope = 11105, and Sb1 value is 0.004472.

Thus using the formula we get the Detection Limit = 1.21 μM.

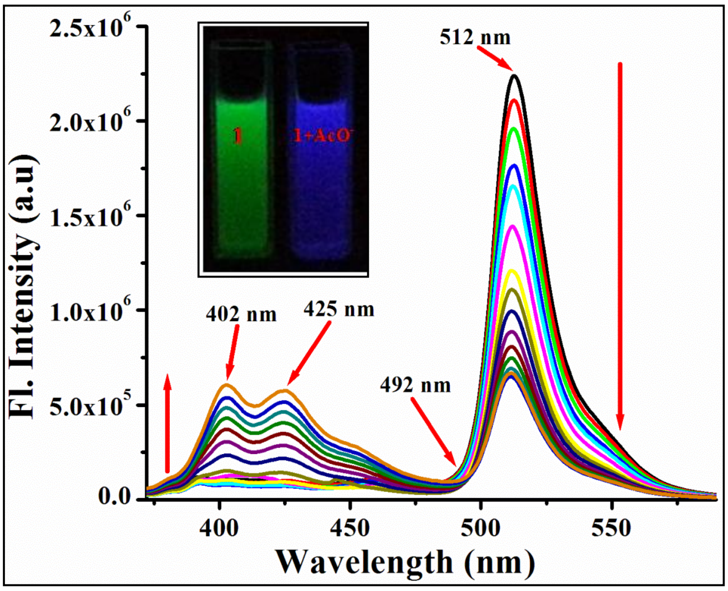


Fig. S7. Fluorescence spectra (excitation at 350 nm) of sensor **1** (4.5 μM) in 7:3 CH_3CN : H_2O solution (0.02M HEPES buffer, pH 7.2) in the presence of 0–200 equiv. of $[Bu_4N]^+AcO^-$.

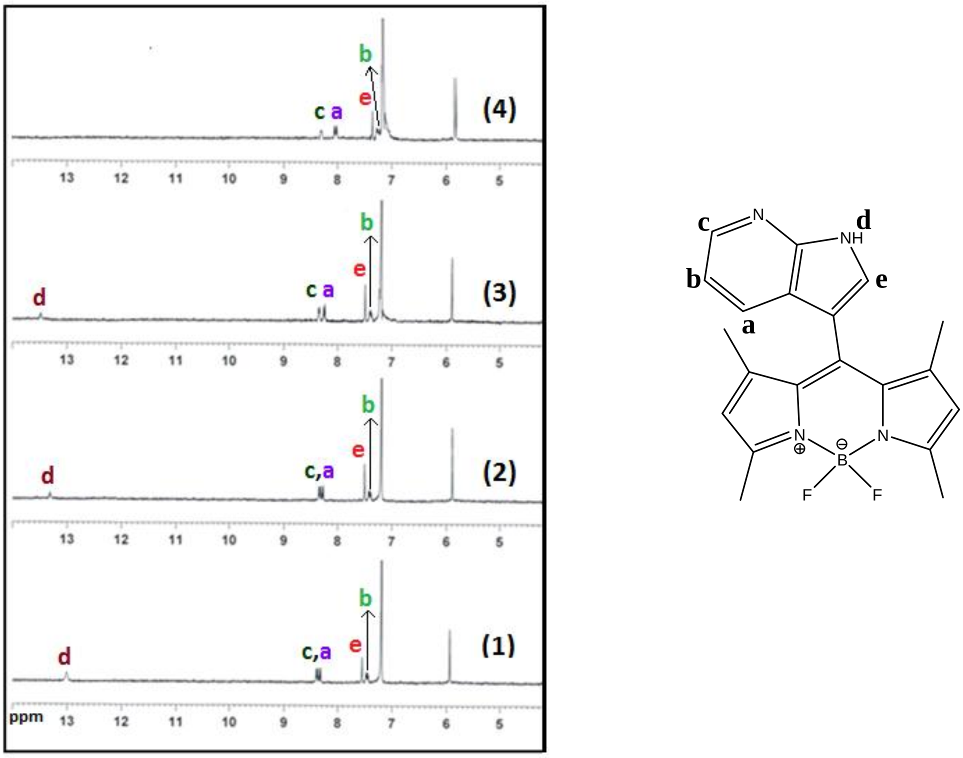


Fig. S8. Change in partial ^1H NMR spectra of **1** upon addition of $[Bu_4N]^+AcO^-$ in $CDCl_3$ solvent: (1) 0, (2) 0.5, (3) 1.0, and (4) 2.0 equiv. $[Bu_4N]^+AcO^-$.

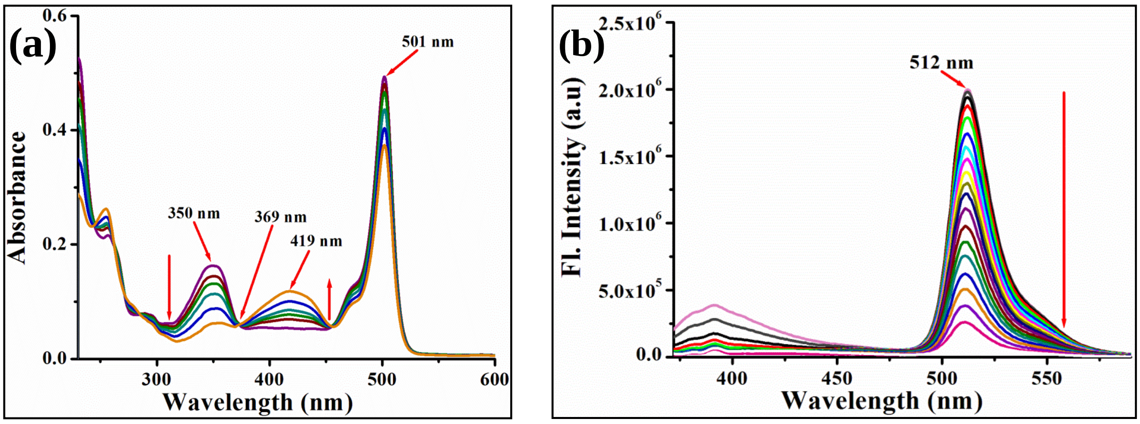


Fig. S9. (a) UV-vis spectral change of sensor **1**(4.5 μM) in 7:3 CH$_3$CN : H$_2$O solution (0.02M HEPES buffer, pH 7.2) in the presence of $[Bu_4N]^+OH^-$ anions (0 – 20 equiv), (b) Fluorescence spectra (excitation at 350 nm) of sensor **1** (4.5 μM) in 7:3 CH$_3$CN : H$_2$O solution (0.02M HEPES buffer, pH 7.2) in the presence of 0–300 equiv. of $[Bu_4N]^+OH^-$.

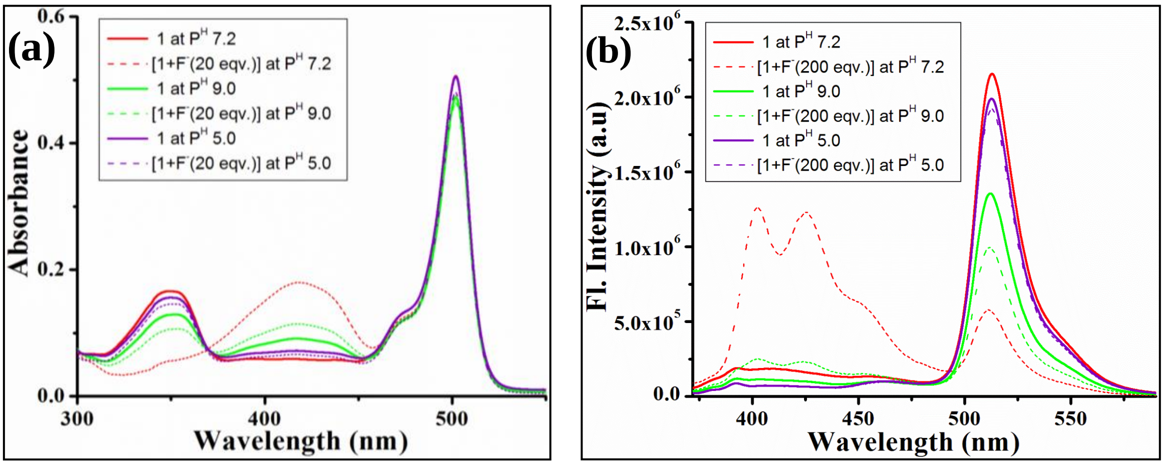
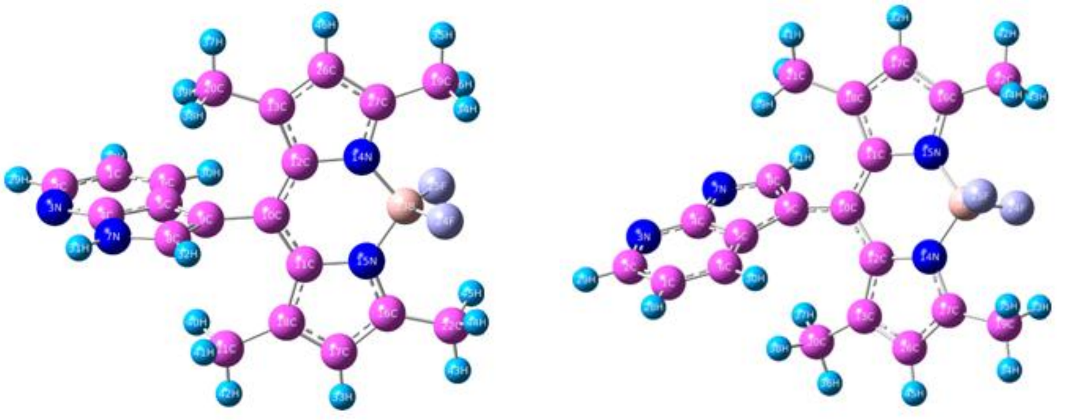


Fig. S10. (a) UV/vis absorption spectra and (b) fluorescence spectra of solutions of sensor **1** (4.5 μM) at various pH values (Green: pH 9.0; red: pH 7.2; violet: pH 5.0) in absence of F^- ion (solid lines) and in the presence of F^- ion (dotted lines). The spectra were recorded at RT in the presence of 0.02M HEPES buffer.

Theoretical Methods. All the calculations on sensor **1** and the deprotonated species were carried out with the Gaussian 03 program package [2] by using density functional theory (DFT) and time-dependent DFT (TD-DFT): Becke's three-parameter functional [3] combined with Lee, Yang, and Parr's correlation functional [4] (B3LYP), along with the 6-31G(d) basis set, were used. All the geometries and electronic properties were calculated by assuming sensor **1** and the deprotonated species to be the isolated molecules.



Sensor 1

Deprotonated species

Dihedral angle between 12C- 10C-9C-5C = 89.5°

11C- 10C- 9C- 8C = 90.5°

Dihedral angle between 11C-10C-9C-8C = 51.9°

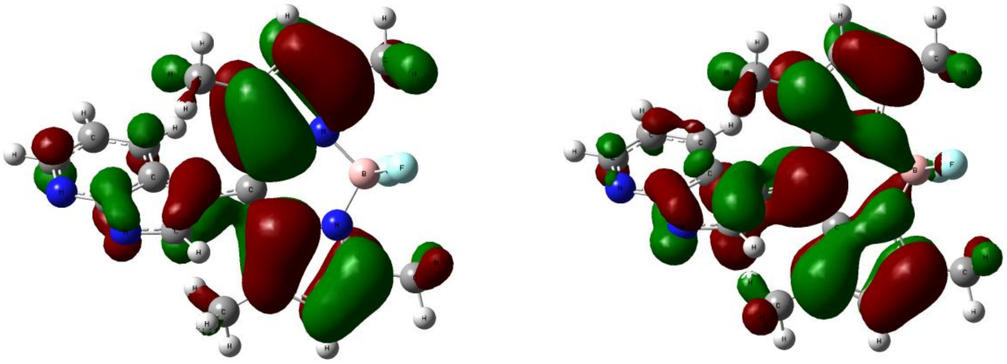
12C-10C-9C-5C = 53.3°

Fig. S11. Optimized ground-state geometries of sensor **1** and the deprotonated species.

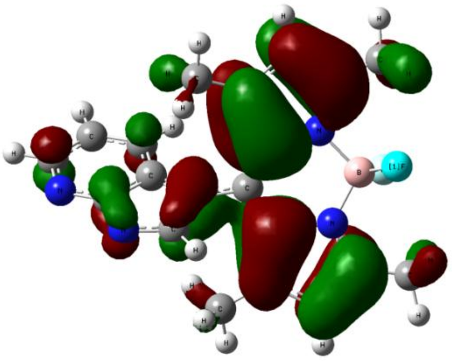
Table S1. Selected electronic excitation energies (eV), oscillator strengths (f), main configurations, and CI Coefficients of the low-lying excited states of probe and the deprotonated product. The data were calculated by TDDFT//B3LYP/6-31+G(*d*,*p*) based on the optimized ground state geometries.

Molecules	Electronic Transition	Excitation Energy[a]	f^b	Composition[c]	CI[d]
Probe					
	$S_0 \rightarrow S_1$	2.94 eV(421 nm)	0.4025	H → L	0.64867
	$S_0 \rightarrow S_{28}$	5.84 eV(211 nm)	0.5019	H-1 → L+3	0.50791
Deprotonated species					
	$S_0 \rightarrow S_1$	2.38 eV(521 nm)	0.2637	H → L	0.69903
	$S_0 \rightarrow S_3$	3.05 eV(406 nm)	0.3794	H-1 → L	0.67407

[a] Only selected excited states were considered. The numbers in parentheses are the excitation energy in wavelength. [b] Oscillator strength (only the f > 0.2 was considered). [c] H stands for HOMO and L stands for LUMO. [d] The CI coefficients are in absolute values.



HOMO **LUMO**



HOMO-1

Fig. S12. Plots of the frontier orbitals of deprotonated species.

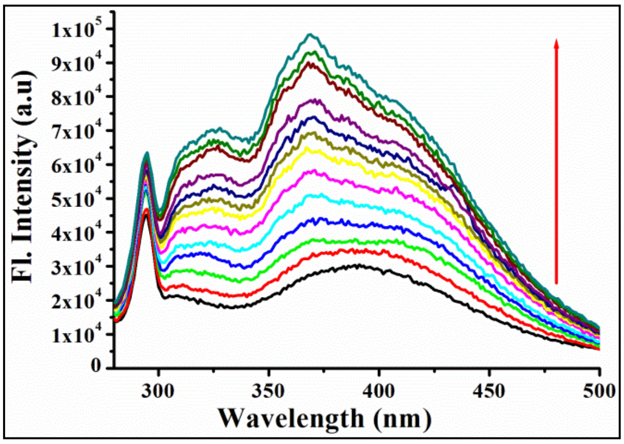
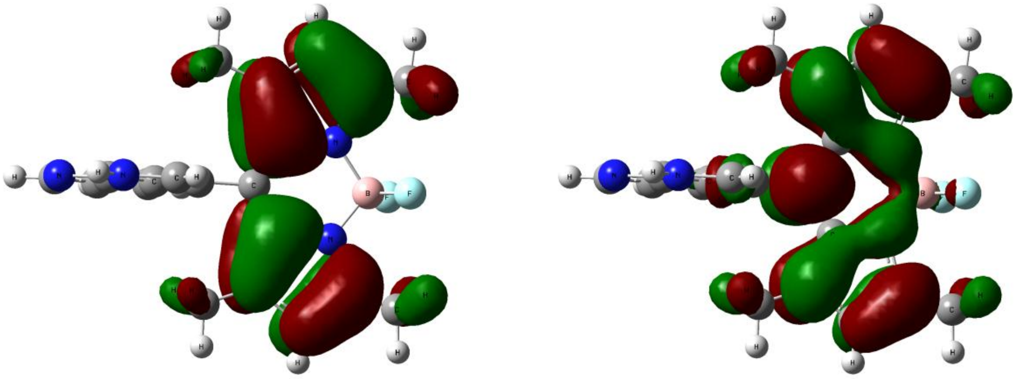
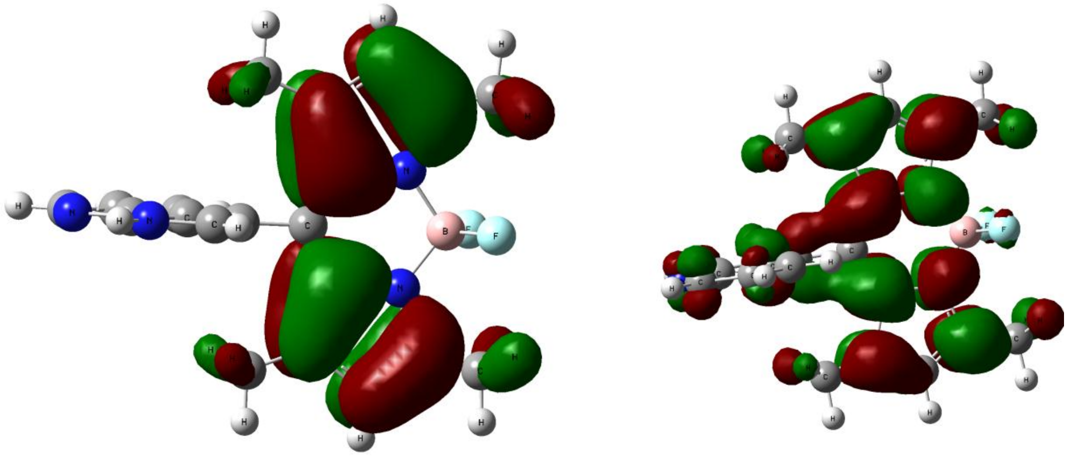


Fig. S13. Fluorescence spectra (excitation at 270 nm) of 7-Azaindole-3-carboxaldehyde (4.5 μM) in CH_3CN (0.02M HEPES buffer, pH 7.2) in the presence of 0–200 equiv. of $[Bu_4N]^+$ F^-.

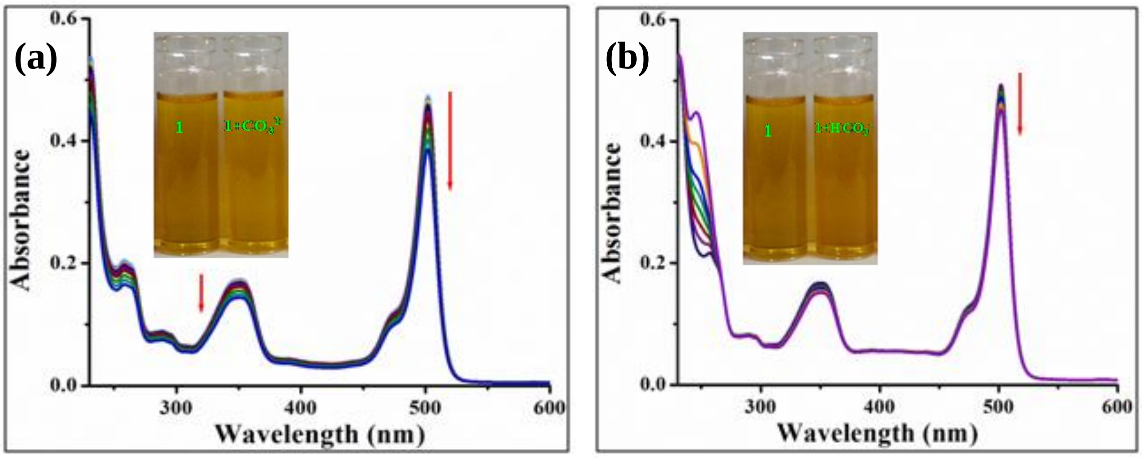


HOMO **LUMO**



HOMO-1 **LUMO+3**

Fig. S14. Plots of the frontier orbitals of sensor **1**.



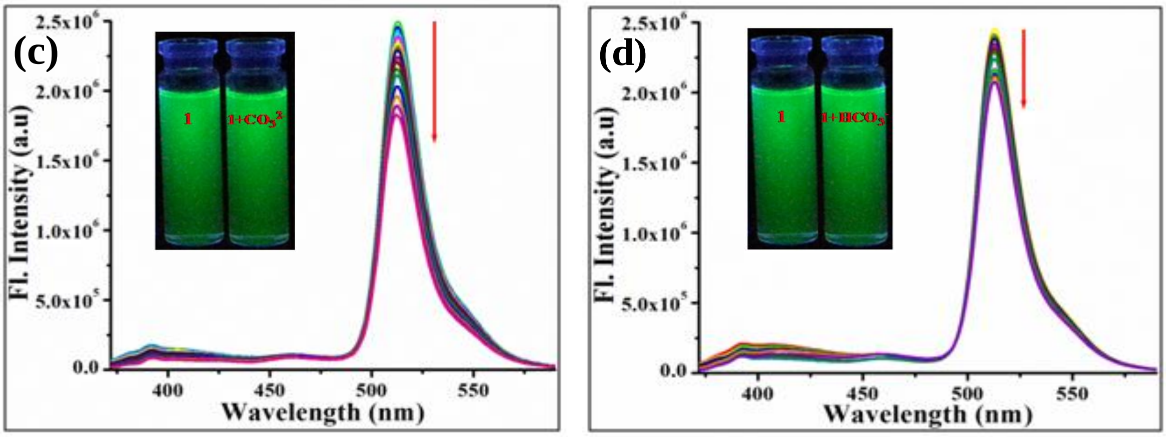


Fig. S15. (a),(b) UV-vis spectral change of sensor **1**(4.5 μM) in 7:3 CH_3CN : H_2O solution (0.02M HEPES buffer, pH 7.2) in the presence of CO_3^{2-} and HCO_3^{-} anions (0 – 20 equiv) respectively. (c),(d) Fluorescence spectra (excitation at 350 nm) of sensor **1** (4.5 μM) in 7:3 CH_3CN : H_2O solution (0.02M HEPES buffer, pH 7.2) in the presence of 0–300 equiv. of CO_3^{2-} and HCO_3^{-} anions respectively.

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