Supplementary information

Hydrogen sulfate ion sensing in aqueous media based on fused pyrimido benzothiazole derivative

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Experimental Section.

General Material and Methods:

2-aminobenzothiazole, dimethylformamide (DMF) and tetrabutyl ammonium slats were purchasedfrom Sigma Aldrich (Bangalore, Karnataka, India) and areused without further purification, unless otherwise specified. UV-vis absorption spectra were recorded by UVvis-1800 schimadzu spectrophotometer. Fluorescence emission spectra were obtained on FluoroMax-4spectrofluorometer.

Synthesis of SVK-1¹



2-Amino benzothiazole 1, (500 mg, 3mmol) and bis(methylthio)methylene malonitrile 2 (566 mg, 3 mmol) was dissolved in 10 mL anhydrous N-N dimethylformamide and stirred the reaction mixture for half an hour. Then the pinch of K_2CO_3 was added and the reaction

mixture was refluxed for 5 h. The reaction mixture was cooled to room temperature and then poured dropwise in crushed ice with continuous stirring. The obtained yellow precipitate was filtered, washed with water and recrystallised from solid DMF:EtOH to yield pure product **SVK-1**.

FT-IR (KBr, $v \text{ cm}^{-1}$): 757, 902, 1041, 1185, 1262, 1487, 1616, 1622, 2201, 2926, 3115, 3307, 3431. ¹H NMR (CDCl₃, 400 MHz) δ : 2.61 (s, 3H, -SCH₃) 7.47 (t, J = 6.6 Hz, 1H) 7.55 (m, 2H) 7.68 (d, J = 7.8 Hz, 1H) 9.50 (d, J = 8.4 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ : 13.3(-SCH₃), 87.6, 114.8 (-C=N), 121.5, 121.6, 123.4, 126.8 (-C=NH), 127.5, 136.6, 153.7, 167.7; ESI-MS (m/z %): 273 (100) [M+H]⁺.

UV-vis spectrophotometric titrations

The probe **SVK-1** was dissolved in acetonitrile: water (2.5:7.5; v/v) with c $\approx 1.0 \times 10^{-5}$ M corresponding to the maximum of absorbance in the range ≈ 0.3 to 0.5 for the UV experiments. The solution of the probe was placed in a quartz cuvette (l=1 cm, $V_0 = 3 \text{ mL}$), and the various anion solutions (c $\approx 1.0 \times 10^{-3}$ M) were added. Upon each addition, UV-vis spectrum was recorded. The titrations were performed at room temperature.

Fluorescence titrations

The anion solutions were added to a solution of 1.0 x 10⁻⁵ M of probe **SVK-1** in acetonitrile: water (2.5:7.5; v/v. Upon each addition, emission spectrum was recorded with excitation wavelength of ($\lambda_{ex} = 350$ nm). The titrations were performed at room temperature.

Naked-eye experiment

The anion solutions were added to a solution of 1.0×10^{-5} M of probe SVK-1 in acetonitrile: water (1:1; v/v). Upon addition of anion solutions (100 equiv.) image was recorded with well resolved camera at room temperature.

Computational methods^{2,3,4}

The ground state calculations were performed in the frame of density functional theory using Gaussian 09 ab initio/DFT quantum chemical simulation package and were optimized at B3LYP/6-311++G (d,p) level of theory. To investigate the effect of solvent (water) on geometries. The polarisable continuum model (PCM) is used.



Fig. S1 FT-IR of SVK-1



Fig. S2 ¹H NMRof **SVK-1**; **"*"** = indicates solvent peaks



Fig. S3 ¹³C NMR of SVK-1



Fig. S4 ESI-MS of SVK-1



Fig. S5 Absorbance responses of SVK-1 at 378 nm upon addition of various anions (30 equiv.) in ACN: H_2O (2.5:7.5; *v:v*).



Fig. S6 Absorbance responses of **SVK-1** at 356 nm upon addition of various anions (30 equiv.) in ACN: $H_2O(2.5:7.5; v:v)$.



Fig.S7 Benesi–Hilderbrand plot of receptor SVK-1 for HSO₄⁻ ion.



Fig. S8 Competitive selectivity of receptor **SVK-1** (1×10^{-5} M) towards HSO₄⁻ in the presence of other anions (30 equiv.) in ACN: H₂O (2.5:7.5, v:v) .



Fig. S9Fluorescence emission spectra ($\lambda_{ex} = 350 \text{ nm}$) of **SVK-1** (1 x 10⁻⁵ M) in ACN:H₂O (2.5:7.5; *v:v*) upon addition of 30 equiv. of various anions.



Fig.S10Frontier molecular orbitals of HSO₄⁻ anion.



Fig. S11Optimized structures of the molecules (HSO_4^- , **SVK-1** and complex **YMN-1**) obtained at B3LYP/6-311++G (d,p) level of theory and few bond length in Å.





SVK-1-72- (LUMO+1) SVK-1-73- (LUMO+2) SVK-1-74- (LUMO+4)



Fig.S12a Frontier molecular orbitals of SVK-1in water.



Fig.S12b Frontier molecular orbitals of YMN-1in water.



Fig. S13 Calibration plot for successive addition of HSO_4^- ion to SVK-1 solution in $ACN:H_2O$ (2.5:7.5; v:v).

Molecules	Excitation Energy(eV)	Excitation Wavelength(nm)	Oscillator Strength(f)	Excitations
SVK-1	3.4424	360	0.2473	70 -> 71
	3.9379	315	0.3206	69 → 71
	4.8271	257	0.1336	68 → 71
				68 → 72
				70 - 72
				70 - 73
	5.1541	241	0.2025	64 -> 71
				67 → 71
				69 → 72
				69 - 73
				70 -> 75
	5.3335	232	0.1092	67 -> 71
				69 → 72
				69 → 73
				70 - 75
YMN-1	3.4040	364	0.2607	95 -> 96
	3.9207	316	0.3219	94 ->96
	4.8283	257	0.1300	92 -> 97
				95 -> 97
				95 -> 98
	5.1833	239	0.1757	86 -> 96
				89 -> 96
				94 ->97
				94 -> 98
				95 -> 98
				95 → 101

 Table S1: Calculated TDDFT excitation properties of SVK-1 and YMN-1

References

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