

Electronic Supporting Information

Near-Infrared (NIR) Organic Probe for Rapid Naked-Eye Detection of Fluoride Ion in Aqueous Medium

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General Experimental Information

The starting materials (Malononitrile and 3,4-dihydroxy benzaldehyde) were purchased commercially and used without further purification. Malononitrile dimer was synthesized, followed by a literature report^[1]. Distilled water was used to carry out spectral and colorimetric measurements. F^- , Cl^- , Br^- , I^- , SO_4^{2-} , HSO_4^- , NO_3^- , NO_2^- , and AcO^- were prepared by dissolving their respective sodium salts in deionized water. The stock solution was prepared by dissolving the probe in DMSO for complete dissolution at 10^{-3} M concentration. For colorimetric and spectral measurements, the stock solution was diluted with deionized water to a concentration of 10^{-5} to 10^{-7} M.

Electronic absorption spectra were recorded on UV–Vis JASCO V-750 spectrophotometer at room temperature at 10^{-5} to 10^{-7} M. The FTIR spectra were investigated using the Thermoscientific Nicolet spectrophotometer. 1H (500 MHz) and ^{13}C NMR (101 MHz) spectra were obtained from different NMR spectrophotometers (Bruker). Chemical shifts (δ) are given in parts per million (ppm) using the residual solvent peaks as a reference relative to TMS. ' J ' values are given in Hz. The mass spectra were recorded by Agilent QTOF G6545XT spectrometer at 50000 resolution using ESI mode.

Buffer solution preparation

The NH_4OH/NH_4Cl (pH 9) buffer solution, known as the ammoniacal buffer, has been prepared by dissolving 2.7 g ammonium chloride (NH_4Cl) in 17.8 mL concentrated ammonia (NH_3) and diluting to 100 mL with distilled water.

Sample preparation for real sample analysis

Analysis of NaF in Toothpaste

5 mg of commercially available toothpaste was dissolved in 10 mL of distilled water and filtered using filter paper. The filtrate was then added to the probe **TCP-34Hy** ($10\ \mu M$) in the aqueous solvent having Ca^{2+} ion (4 mg/mL) with NH_4OH/NH_4Cl buffer solution (pH~9) and its colour and spectral changes were observed.

Analysis of NaF in soil samples

Red soil, clay soil and sand soil were collected from nearby places and 10 mg of NaF was added to 1 g of soil samples each, ground well using mortar and pestle. 5 mg of the pretreated soil samples were added to the probe **TCP-34Hy** ($10\ \mu M$) in the aqueous solvent having

Ca²⁺ion (4 mg/mL) with NH₄OH/NH₄Cl buffer solution (pH~9) and its colour, as well as spectral changes, were observed.

Analysis of NaF in different water samples

The water samples from different water sources such as river, pond, tap, and sewage were collected. The collected water samples were filtered and spiked with known concentrations of NaF (0.41 ppm and 0.62 ppm). The spiked samples were added to the probe **TCP-34Hy** (10 μM) in the aqueous solvent with Ca²⁺ion (4 mg/mL) with NH₄OH/NH₄Cl buffer solution (pH~9) and corresponding absorbance spectra were noted. The results obtained from the spiked samples were correlated with the linear absorbance plot calculated with respect to the UV-vis titration and corresponding recovery percentages were calculated.

Synthesis and Characterization of TCP-34Hy

An ethanolic solution (10 mL) of ethyl pyruvate (**1**, 1.007 mg, 8.68 mmol) and malononitrile dimer (**2**, 716 mg, 5.42 mmol) was refluxed under argon atmosphere for 1.5 h. After completion of the reaction (checked by TLC), 3,4-dihydroxy benzaldehyde (**4**, 300 mg, 2.17 mmol) was added to the reaction mixture and refluxed under an argon atmosphere for 3 h more. Then the reaction mixture was cooled to room temperature, filtered using cold ethanol and dried under a high vacuum to obtain the pure product (**5**, **TCP-34Hy**). The compound was characterized by ¹H NMR, ¹³C NMR and mass spectrometry.

Characterization of TCP-34Hy: Dark blue solid (413 mg yield: 62%), mp: 220–222 °C, FT-IR (KBr, cm⁻¹): $\nu = 3506$ (-OH), 3212 (-NH), 2220 (-CN), 1732 (-C=O), 1570 (-C=C); ¹H NMR (500 MHz, DMSO-*d*₆): δ 9.51 (s, 1H), 8.24 (d, *J* = 16 Hz, 1H), 7.24 (s, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 16 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆): δ 167.2, 157.8, 151.7, 148.4, 146.4, 127.0, 124.8, 116.5, 114.6, 113.00, 112.1, 111.5, 111.3, 102.2, 60.1. HRMS *m/z*: [M+H]⁺ calcd for C₁₆H₈N₄O₃, 305.0669; found 305.0667.

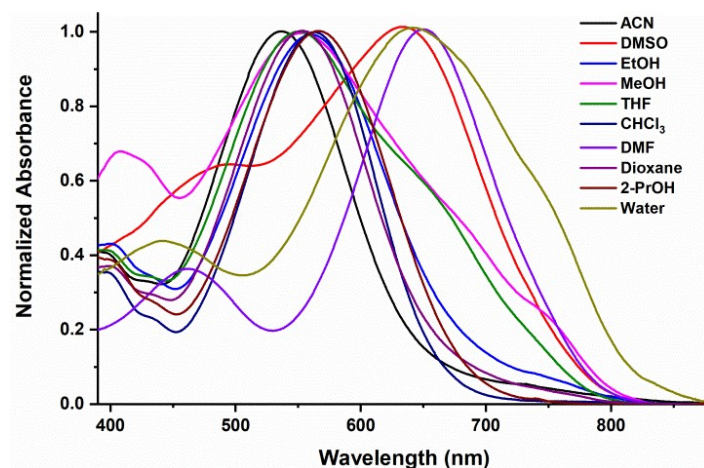


Fig S1. UV- Vis spectra of TCP-34Hy (1×10^{-5} M) in different solvents

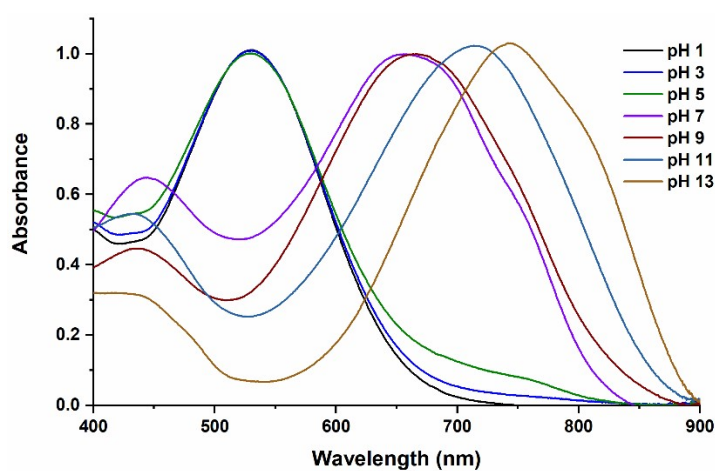


Fig S2. Normalized UV – Vis spectra of TCP-34Hy in aqueous solvent at different pH condition.

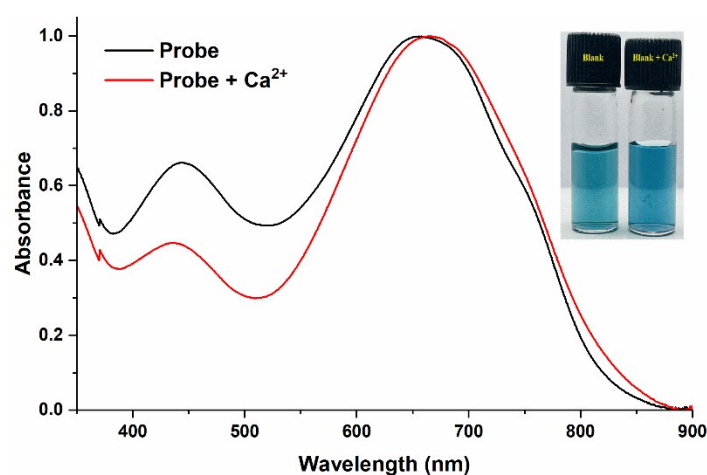


Fig S3. Normalized UV- Vis spectra of TCP-34Hy in the aqueous solvent before and after the addition of Ca^{2+} ion (inset: naked eye colour change before and after the addition of Ca^{2+} ion)

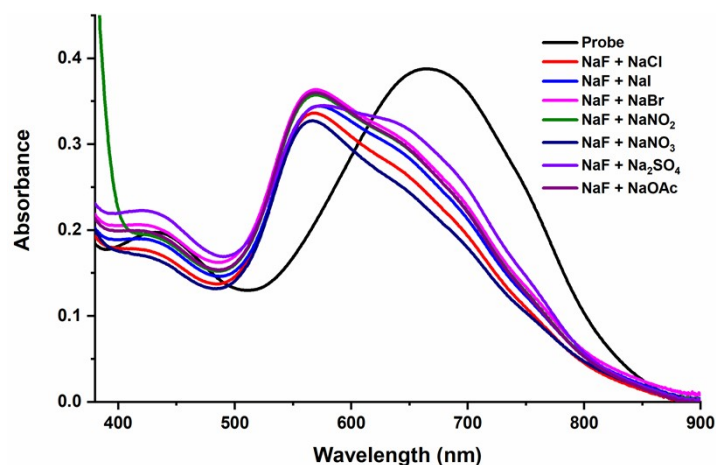


Fig S4. The UV-Vis spectrum of anion-interfering study of activated probe **TCP-34Hy** in aqueous buffer solution.

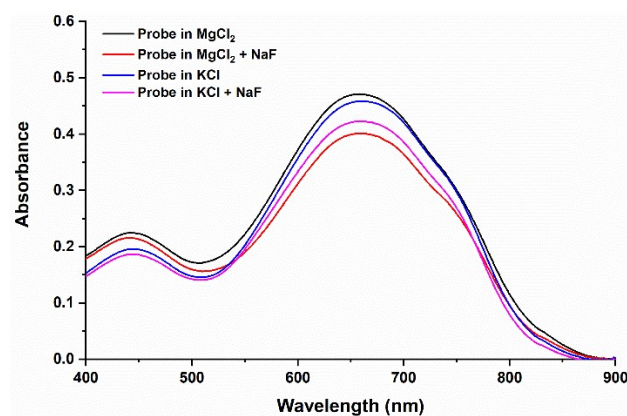


Fig S5. UV- Vis spectra of **TCP-34Hy** towards fluoride ion in the presence of Mg^{2+} and K^{+} ions in aqueous solvent

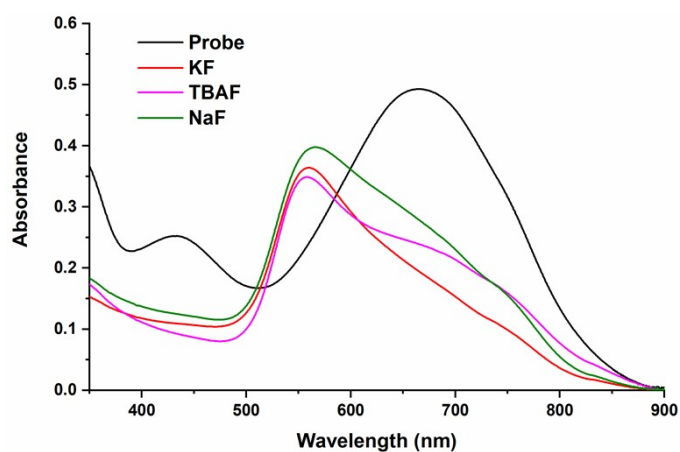


Fig S6. UV-Vis spectroscopic study of probe **TCP-34Hy** in the presence of different fluoride sources (KF and TBAF) in an aqueous buffer solvent having Ca^{2+} ion (4mg/mL)

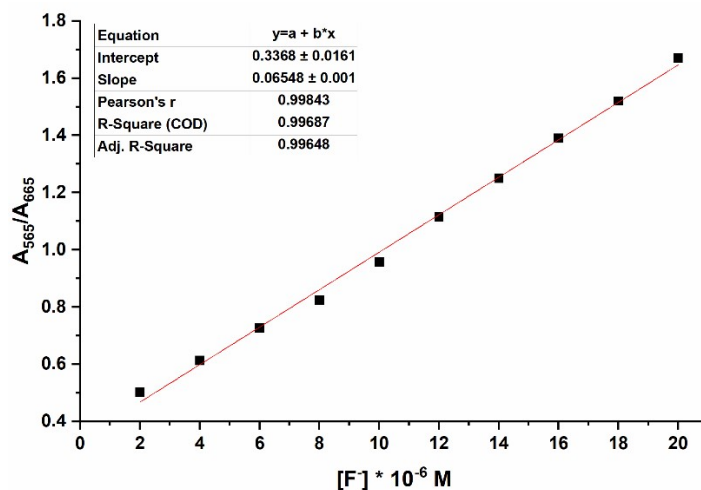


Fig S7. Linear plot of probe **TCP-34Hy** against fluoride ion concentration at pH=9 ($\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ Buffer solution)

Table S1- F^- detection in actual water samples

Sample	Added F^- (ppm)	Detected (ppm)	Recovery %
Tap Water	0.41	0.430	104.8
	0.62	0.631	101.7
Pond Water	0.41	0.421	102.6
	0.62	0.625	100.8
River Water	0.41	0.407	99.5
	0.62	0.616	99.3
Sewage Water	0.41	0.396	96.5
	0.62	0.589	95.0

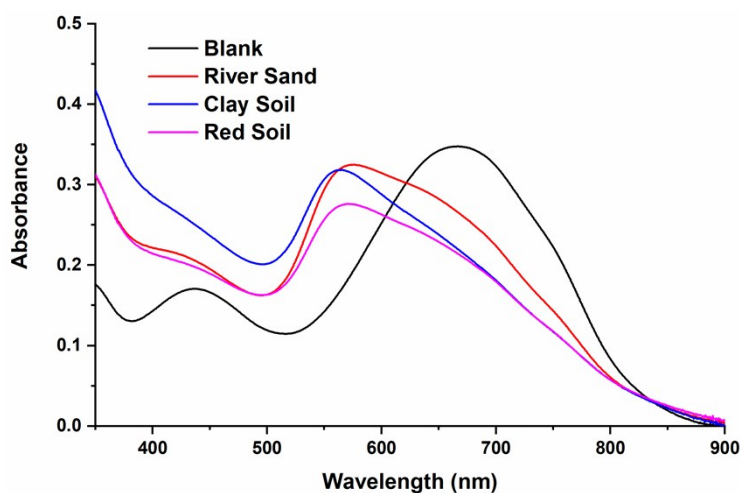


Fig S8. UV-Vis spectroscopic study of probe **TCP-34Hy** in the presence NaF treated soil samples in an aqueous buffer solvent having Ca^{2+} ion (4mg/mL)

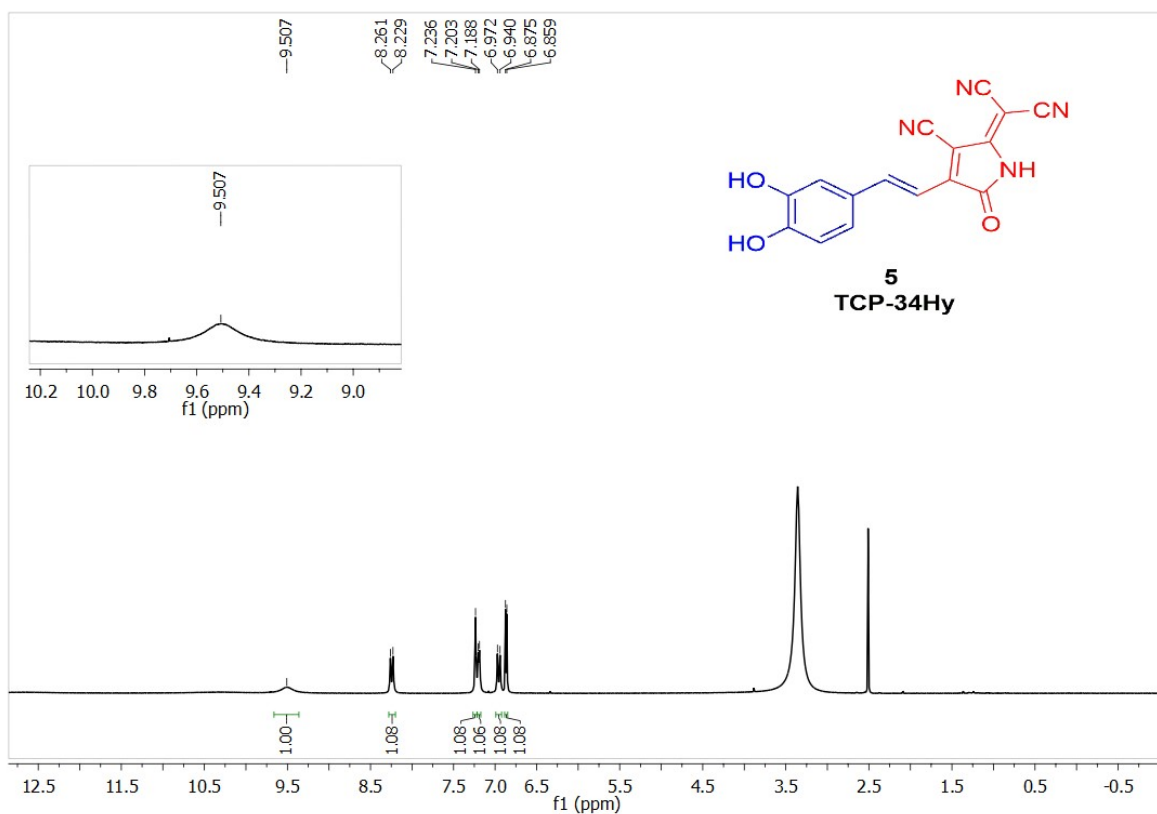


Fig S9. ¹H NMR Spectrum of TCP-34Hy in DMSO-*d*₆

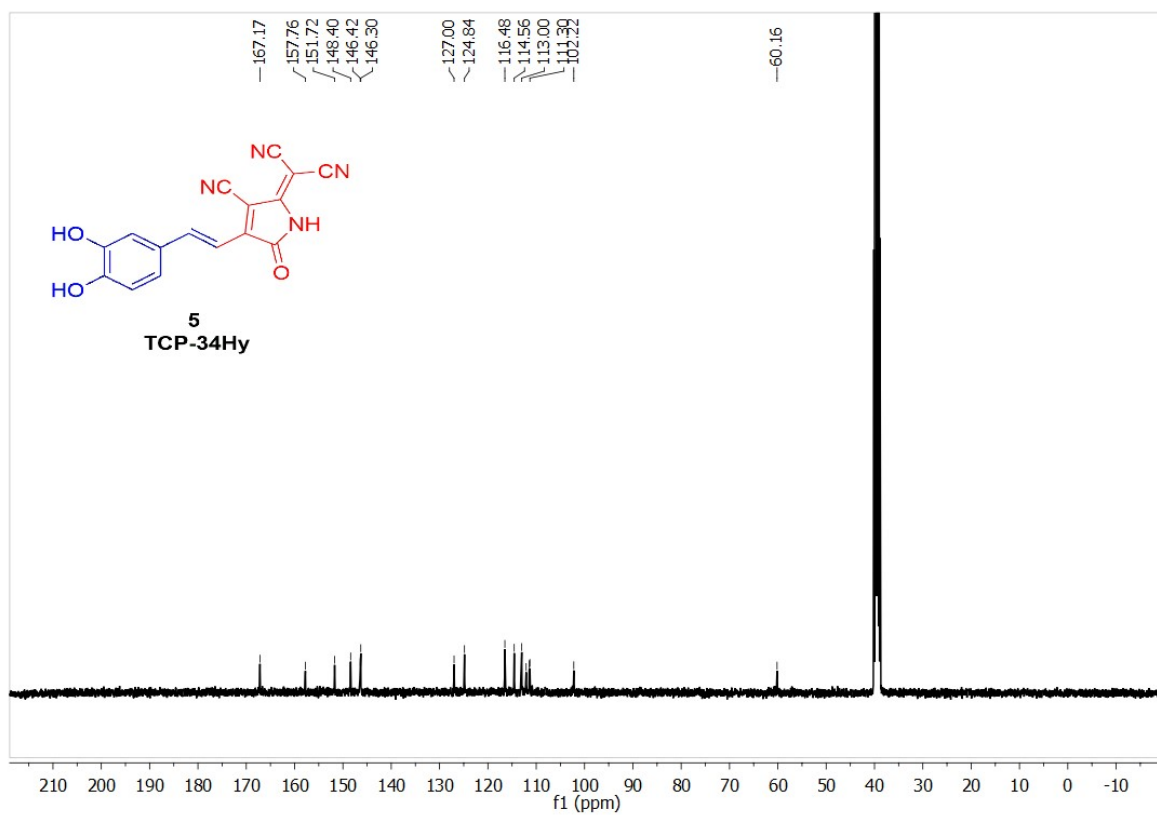


Fig S10. ¹³C NMR Spectrum of TCP-34Hy in DMSO-*d*₆

Limit of detection

The limit of detection was calculated using absorbance titration data with the equation (1) Where 'σ' is the standard deviation of blank measurements and 'm' represents the slope between the concentration of fluoride ion.

$$\text{LOD} = 3.3 \sigma/m \quad \text{-----> (1)}$$

$$\text{TCP-34Hy} = 2.3 \times 10^{-6} \text{ M}$$

Where, SD = 0.046 and slope = 65480

References

1. Singh, S.P., et al., New Triphenylamine-Based Organic Dyes with Different Numbers of Anchoring Groups for Dye-Sensitized Solar Cells. *J. Phys. Chem. C*, **2012**, 9, 116, 5941-5950