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Electronic supplementary information

Functionalized Schiff-base Containing Phenothiazine and Cholic Acid as a Paper-based Fluorescence Turn-off Sensor for Sn(II) Ion-detection and Its Application

Dipakkumar Bariya, Satyendra Mishra*

Department of Biotechnology and Bioengineering, Institute of Advanced Research, Gujarat, 382426, India

*Author for Correspondence: satyendramishra1@gmail.com; satyendra.mishra@iar.ac.in

Content:

Fig. S16: (a) Fluorescence spectra of ChHSB-PTZ ($1 \times 10^{-6} M$) in THF in the presence of different anions ($1 \times 10^{-5} M$) (b) Fluorescent intensity of ChHSB-PTZ ($1 \times 10^{-6} M$) towards different metal ions (c) Fluorescent intensity of ChHSB-PTZ ($1 \times 10^{-6} M$)towards Sn(II) metal ion ($1 \times 10^{-5} M$) in the presence of different interfering anions.

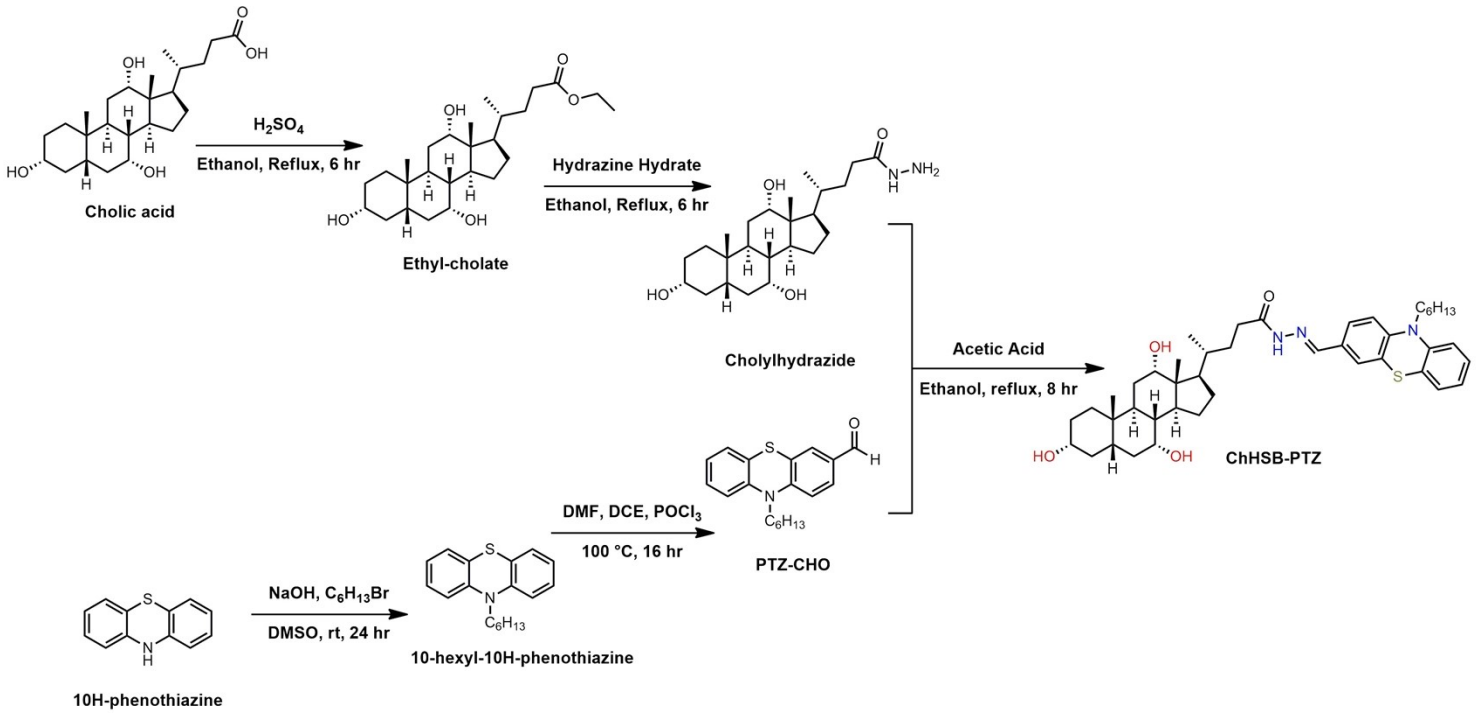
Experimental Section

General Information

All anhydrous reactions were carried out by standard procedures under nitrogen atmosphere to avoid moisture. The solvents were dried by distillation over appropriate drying agents. Reactions were monitored by TLC plates and column chromatography was generally performed on silica gel. ^{1}H and ^{13}C NMR were recorded on a 400 MHz spectrometer. Photophysical properties, including absorption and emission spectra, were recorded using a SHIMADZU (UV-1900i) spectrophotometer and Hitachi F-2700 spectrofluorometer, respectively. Chemicals, reagents and solvents used in this study were obtained from local vendors and employed in their received condition without any additional purification steps. Particularly, starting materials such as cholic acid, hydrazine, 1-bromohexane and phenothiazine were acquired from Sigma Aldrich. DMSO, $POCl_3$, THF, NaOH and other chemical reagents were obtained from SRL Chemicals. The metal ion recognition property of ChHSB-PTZ was explored by spectrofluorometer upon the addition of analytical grade metal salts $Cu(OAc)_2$, $CuCl_2$, $Cu(ClO_4)_2$, $CuSO_4.5H_2O$, $Cu(NO_3)_2.3H_2O$, $Ni(NO_3)_2.6H_2O$, $Pb(NO_3)_2$, $Co(NO_3)_2.6H_2O$, $Hg(NO_3)_2.H_2O$, $Fe(NO_3)_2.9H_2O$, $Zn(NO_3)_2.6H_2O$, $Fe(NO_3)_3.9H_2O$, $AgNO_3$, $Ca(NO_3)_2.4H_2O$, $Mg(NO_3)_2.6H_2O$, $SnCl_2.2H_2O$ for cation and sodium salt NaCl, NaF, NaSCN, $Na_2Cr_2O_7.2H_2O$, Na_2CrO_4, Na_3PO_4, Na_2HPO_4, NaH_2PO_4, NaBr, NaI, $NaNO_3$ used as anion from local vendors. Deionized water used in all spectroscopic investigations was obtained from a Milli-Q reference water purification system by Thermo-Scientific, which

ensures precise resistivity. A stock solution of ChHSB-PTZ (10^{-3} M) was prepared in THF. Similarly, stock solutions for cations and anions (10^{-4} M) were carefully prepared in deionized water, specifically for evaluation of optical properties.

Synthesis of Phenothiazine Carbaldehyde (PTZ-CHO):



Scheme S1: Synthesis of ChHSB-PTZ

[1-2] ***Synthesis of PTZ-CHO***: To a combination of phenothiazine (2.5 g, 12.5 mmol) and $C_6H_{13}Br$ (1.93 ml, 13.9 mmol) in 50 mL DMSO, NaOH (0.85 g, 21.32 mmol) was added under cooling condition. Then, the resultant blend was stirred at RT for 24 hours after which 200 mL of H_2O was mixed. The resultant mix was extracted using $CHCl_3$ (3x50 mL) and water. Then, the organic layer was washed with a saturated brine solution and then dried using anhydrous Na_2SO_4 to remove any

trace of moisture. After evaporating the solvent, the mixture was purified via column chromatography, in which n-hexane was used as the solvent on silica gel. Finally, white oily liquid (Compound 1, yield 86 %) was obtained. After obtaining a 10-hexyl-10H-phenothiazine which is the alkylated form of phenothiazine, PTZ-CHO was synthesized. For the synthesis of PTZ-CHO, $POCl_3$ (2.64 mL, 28.2 mmol) was added dropwise to an ice cooled RB flask comprising DMF (12 mL). The combination was stirred at 0 ˚C for 1 hour and then, compound 1 (1.78 gm, 6.2 mmol) was added to it. Finally, the reaction mix was exposed to a temperature of 80 ˚C for 16 h. After that, the crude product was poured into ice-water. Then, saturated aqueous K_2CO_3 was added to the mixture and extracted with chloroform (4x30 mL). Eventually, moisture was removed using $MgSO_4$. Finally, the solvent was removed using rotatory evaporator, and the crude product was purified using column chromatography [Hexane/EtOAc (8:2) as eluent]. Thus, a pale-yellow solid is obtained (yield 94%).

The fluorescence quantum yields: The fluorescence quantum yields for the ChHSB-PTZ were calculated using Fluorescein as the standard by using the steady-state comparative method:

$$\Phi_f = \Phi_{ST} * \frac{S_U}{S_{ST}} * \frac{A_{ST}}{A_U} * \frac{\eta_{Du}^2}{\eta_{ST}^2}$$

Equation S1: Quantum yield formula

Where, Φ_f is the emission quantum yield of the sample, Φ_{ST} is the emission quantum yield of the standard, and A_{ST} and A_U represent the absorbance of the standard and the sample at the excitation wavelength, respectively. S_{ST} and S_U are the integrated emission band areas of the standard and

the sample, respectively and η_{ST} and η_{Du} are the solvent refractive indices of the standard and the sample.

Optical Band Gap:

$$E_g = \frac{1240}{\lambda_{onset}}$$

Equation S2: Optical Band Gap formula

Spectroscopic analysis of synthesized compounds

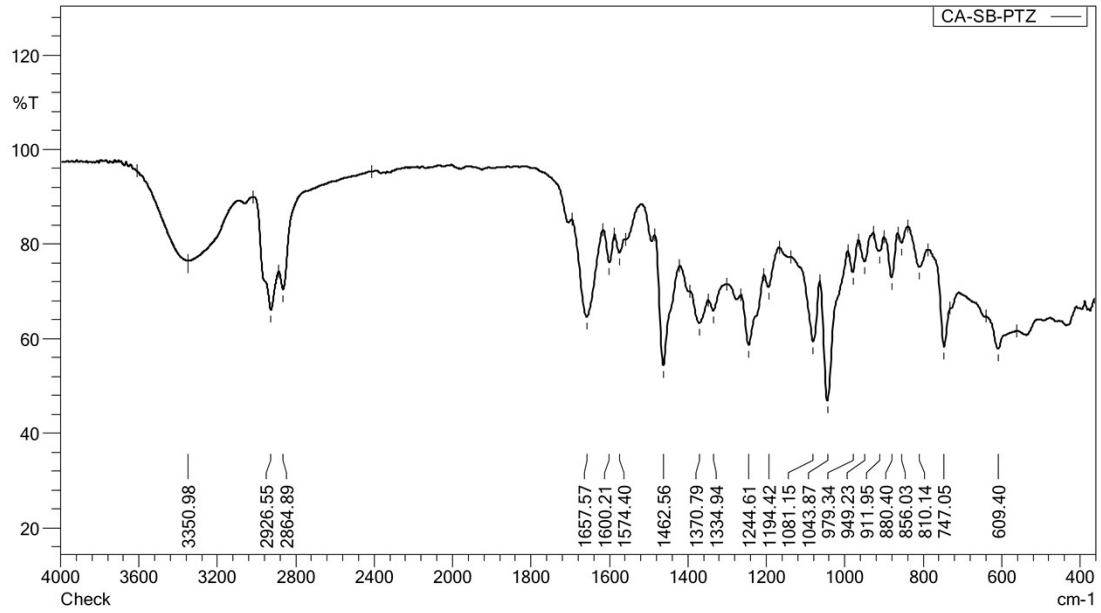


Fig. S1: FT-IR Spectrum of ChHSB-PTZ

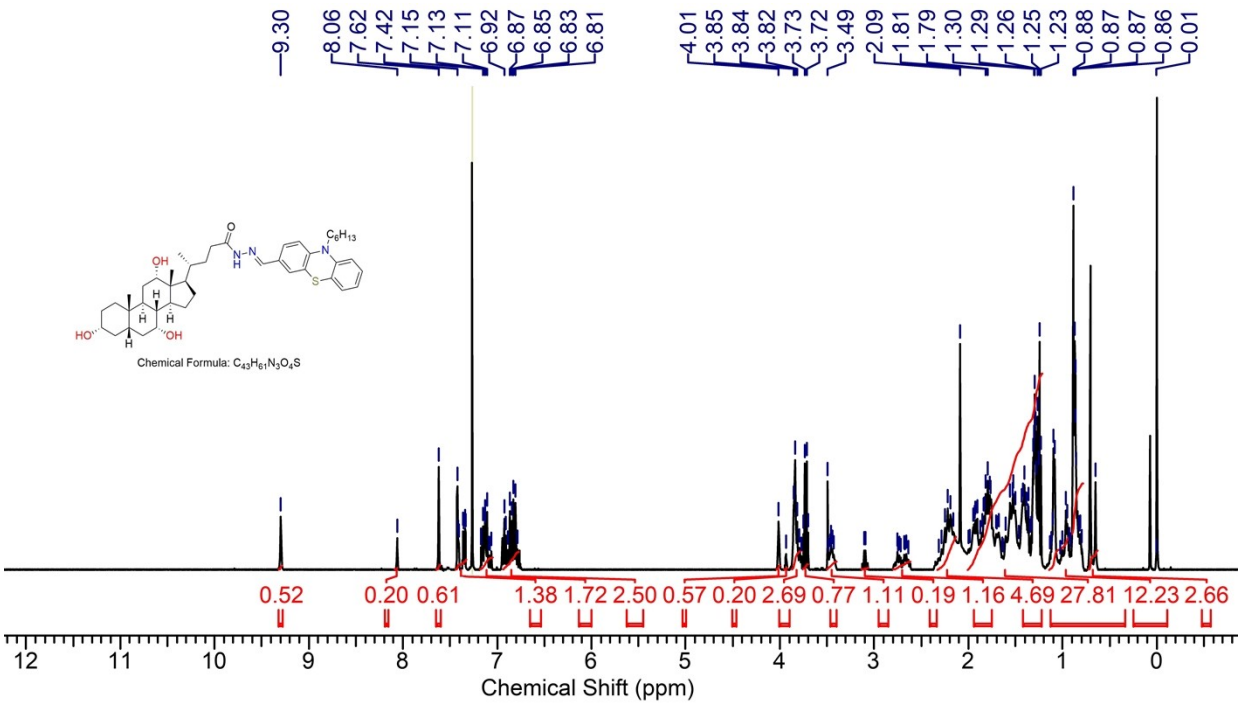


Fig. S2: ^{1}H NMR Spectrum of ChHSB-PTZ in $CDCl_3$

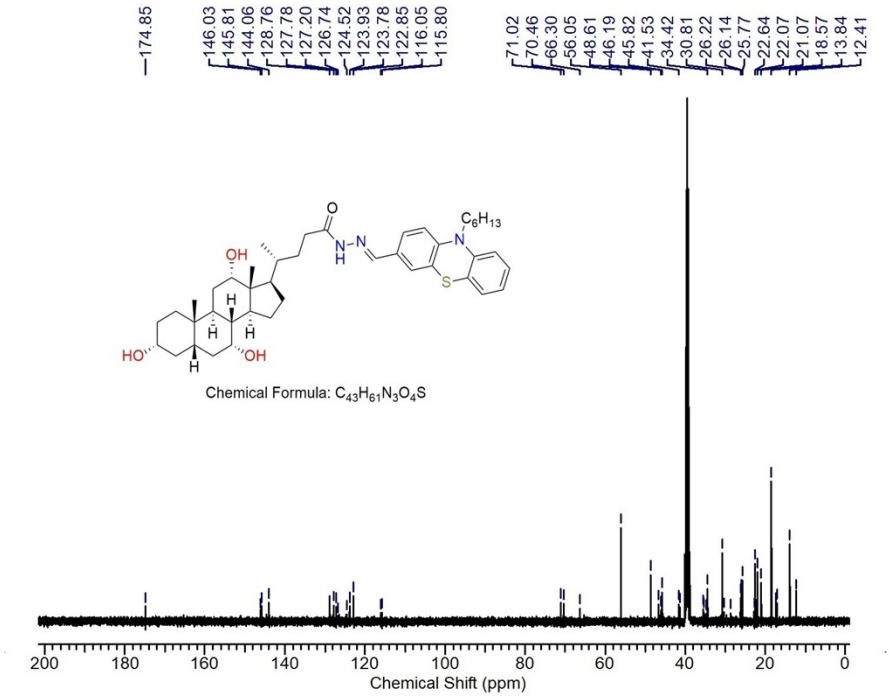


Fig. S3: ^{13}C NMR Spectrum of ChHSB-PTZ in DMSO-d_6

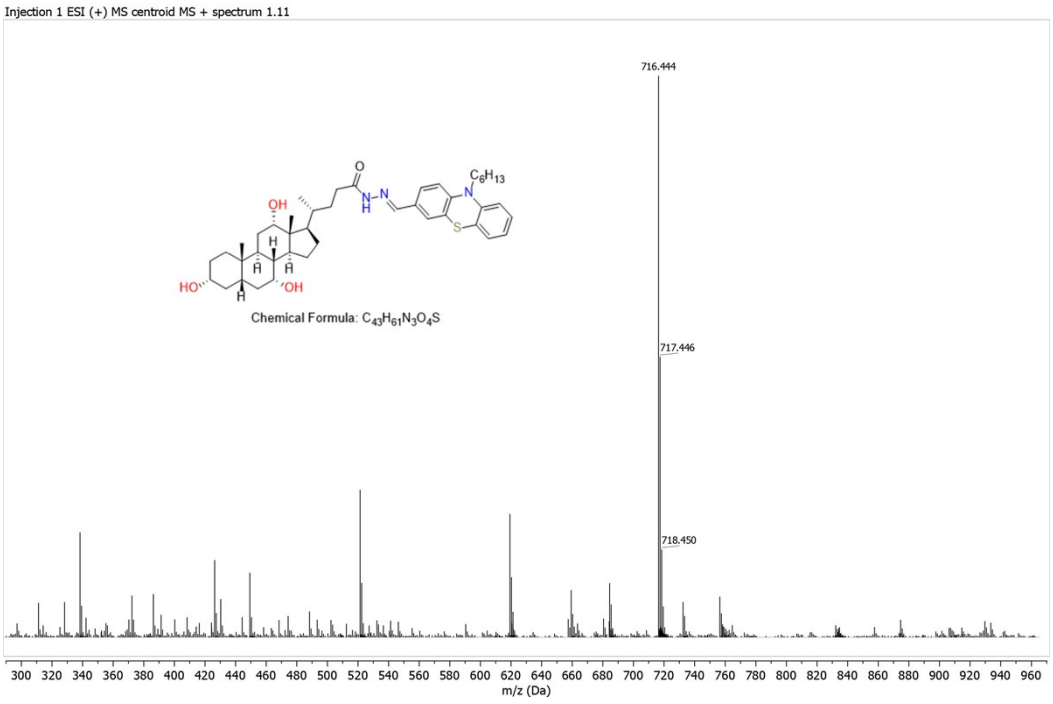


Fig. S4: ESI-Mass Spectrum of ChHSB-PTZ

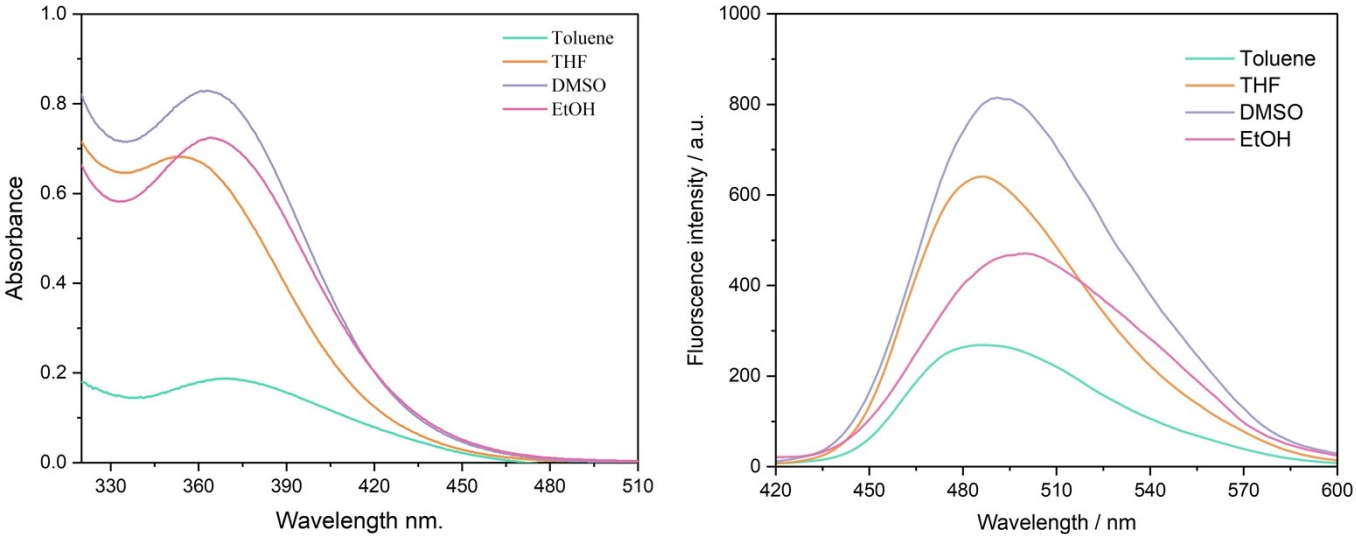


Fig. S5: Absorption spectra (left) and fluorescent spectra (right) of the ICT studies for ChHSB-PTZ ($1 \times 10^{-6} M$) performed for four different solvents**.**

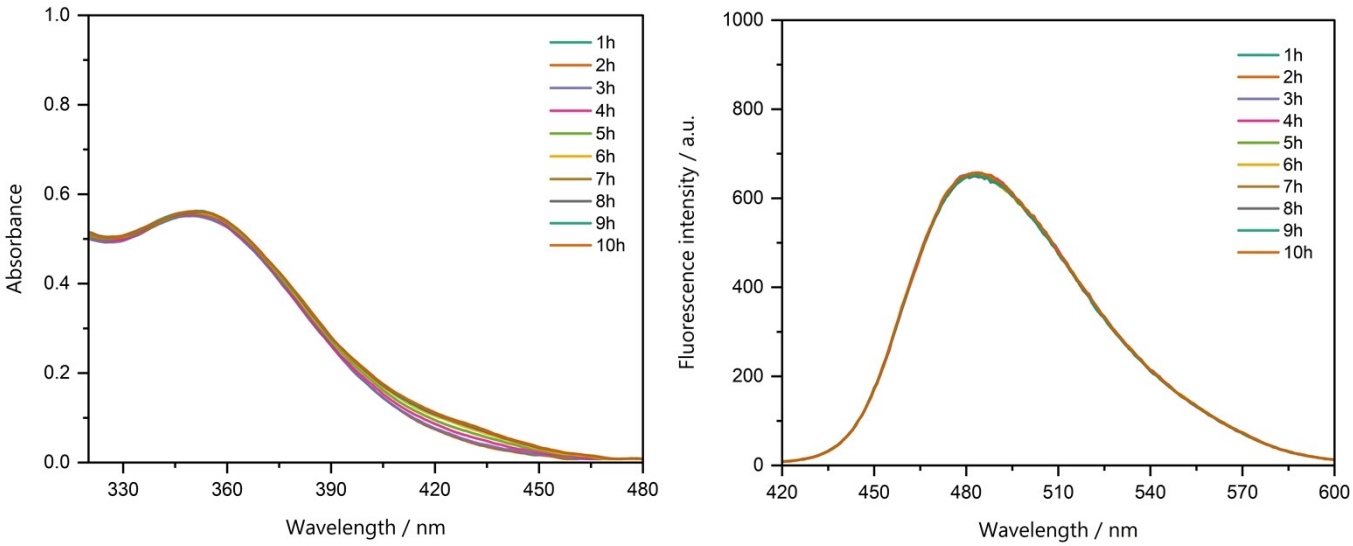


Fig. S6: Time-dependent absorption spectra (left) and fluorescence emission spectra (right) spectra of ChHSB-PTZ ($1 \times 10^{-6} M$) in THF. The spectra were obtained every 1 hour (0–10 hours).

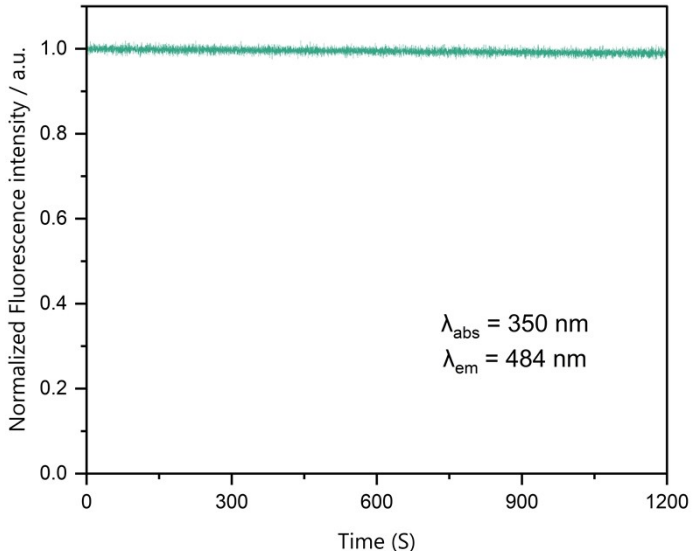


Fig. S7 Time-resolved photoluminescence spectrum for photostability of ChHSB-PTZ ($1 \times 10^{-6} M$) in THF. The remaining fluorescence emission intensities of ChHSB-PTZ as a function of irradiation time. Irradiated at 350 nm. Fluorescence intensity was measured at 484 nm.

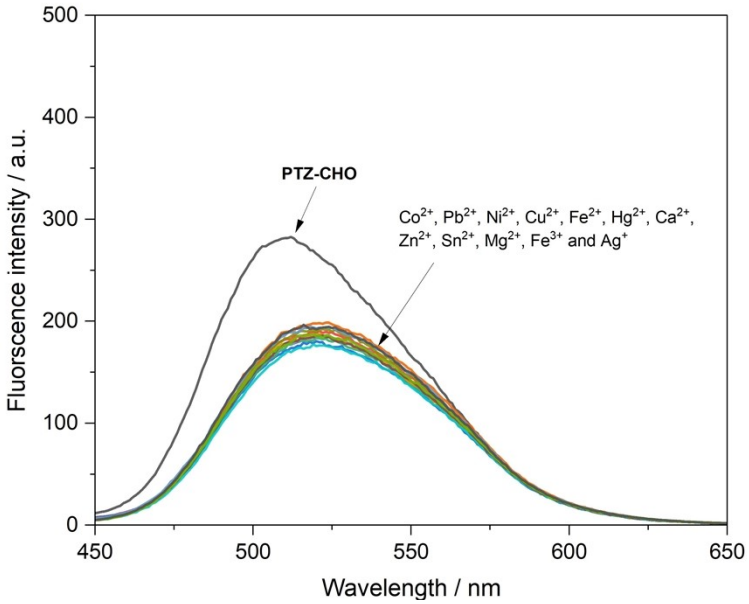


Fig. S8: Fluorescence spectra of PTZ-CHO ($1 \times 10^{-6}\,M$, THF) in THF in the presence of different metal ions ($1 \times 10^{-5}\,M$).

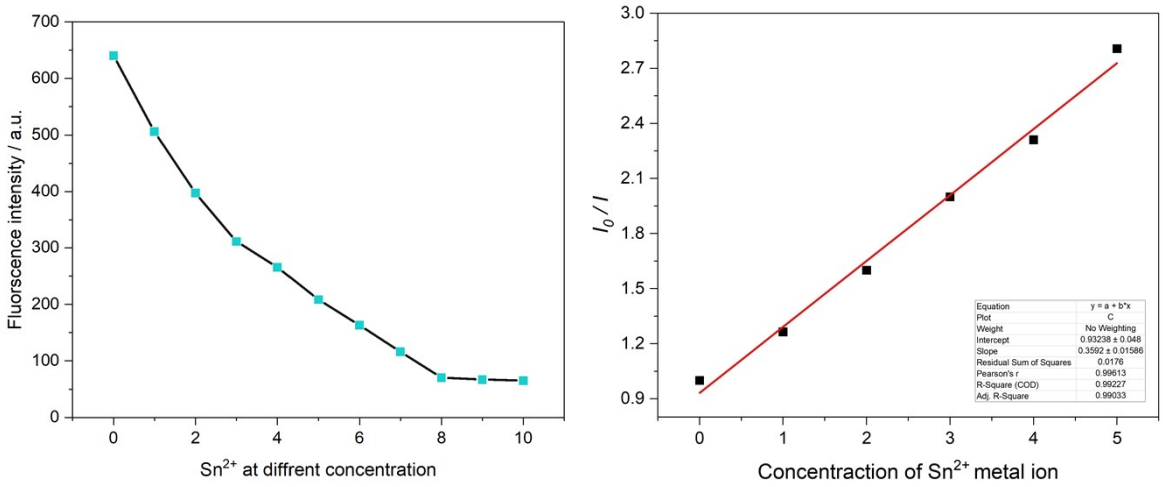


Fig. S9: (a) Relative fluorescence intensity changes of ChHSB-PTZ ($1 \times 10^{-6}\,M$) as a function of tin ($1 \times 10^{-5}\,M$) concentration (b) Stern-Volmer graph of ChHSB-PTZ ($1 \times 10^{-6}\,M$) upon addition of Sn^{2+} metal ion ($1 \times 10^{-5}\,M$).

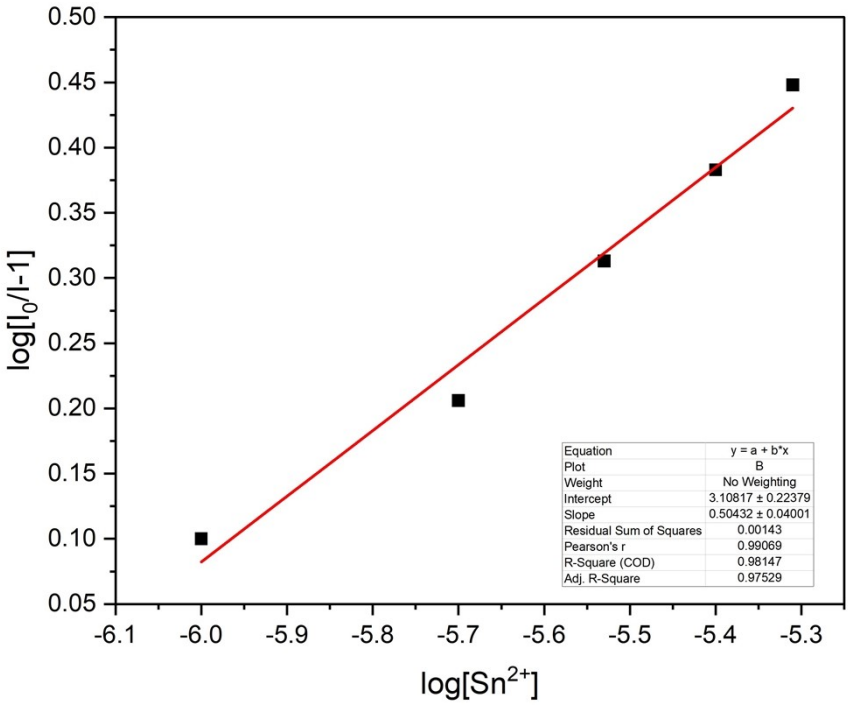


Fig. S10: Modified Stern-Volmer plot for fluorescence quenching of ChHSB-PTZ ($1 \times 10^{-6} M$) by Sn(II) metal ion ($1 \times 10^{-5} M$).

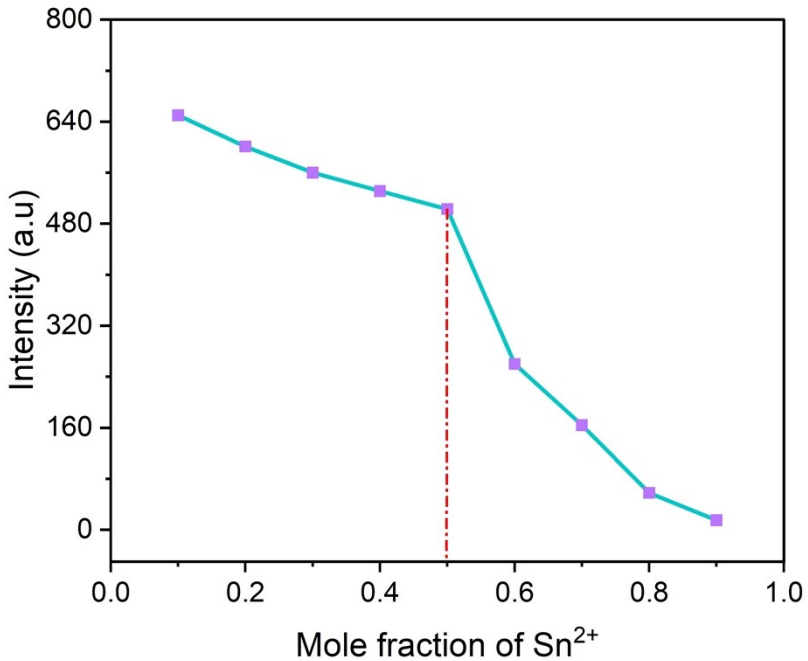


Fig. S11: Job's plot for the realization of the stoichiometry of ChHSB-PTZ and Sn(II) metal ion.

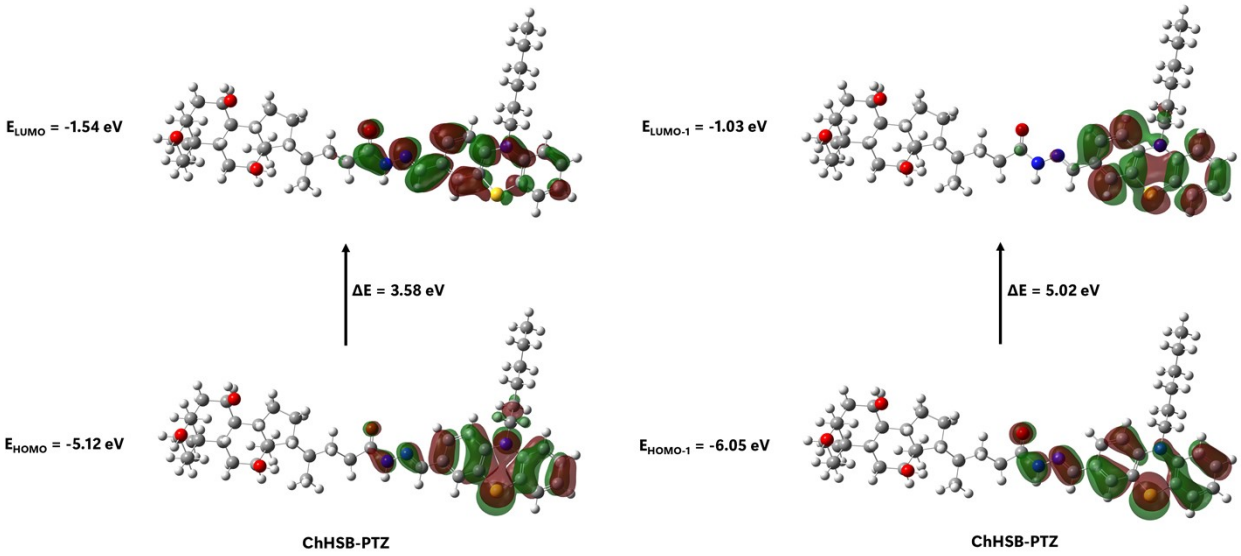


Fig. S12: Contour plots for the HOMO, HOMO – 1, LUMO, and LUMO + 1 orbitals were generated for the ChHSB-PTZ.

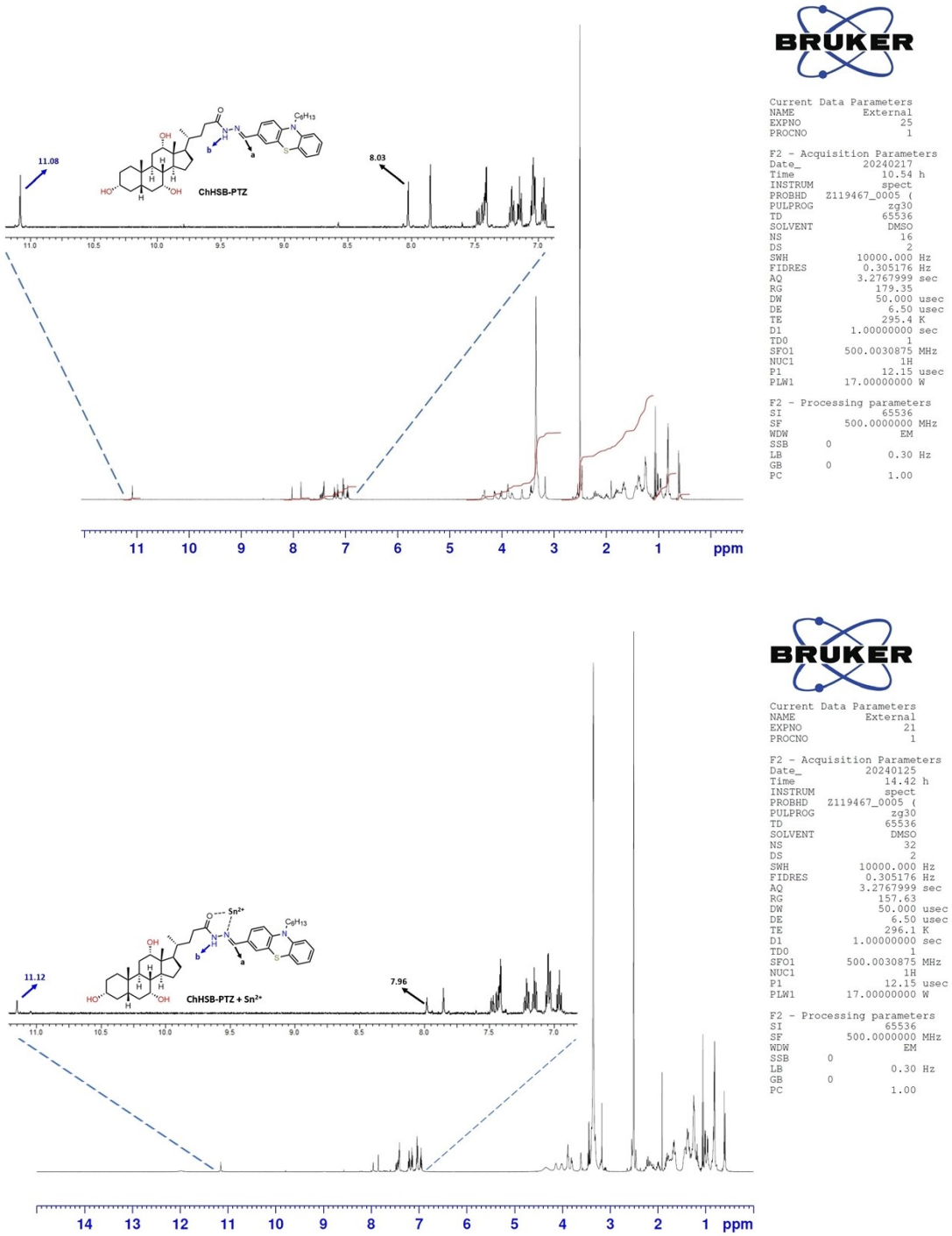


Fig. S13: ^{1}H NMR spectra of ChHSB-PTZ and ChHSB-PTZ (1 equivalent) in presence of Sn(II) metal ion (1 equivalent) in $DMSO - d_6$ solvent (500 MHz).

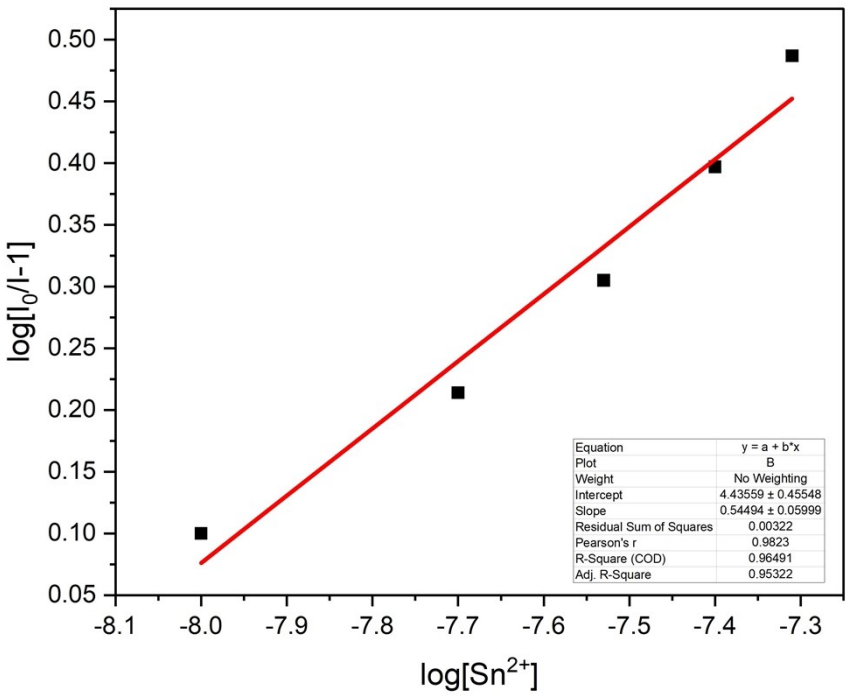


Fig. S14: Modified Stern-Volmer plot of paper sensor in presence of Sn(II) metal ions.

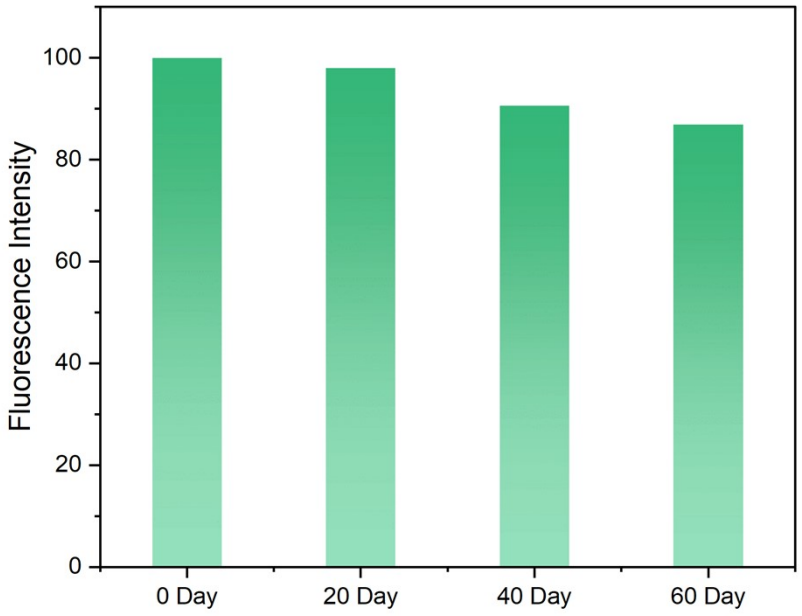


Fig. S15: Stability of ChHSB-PTZ Paper Sensor after two months.

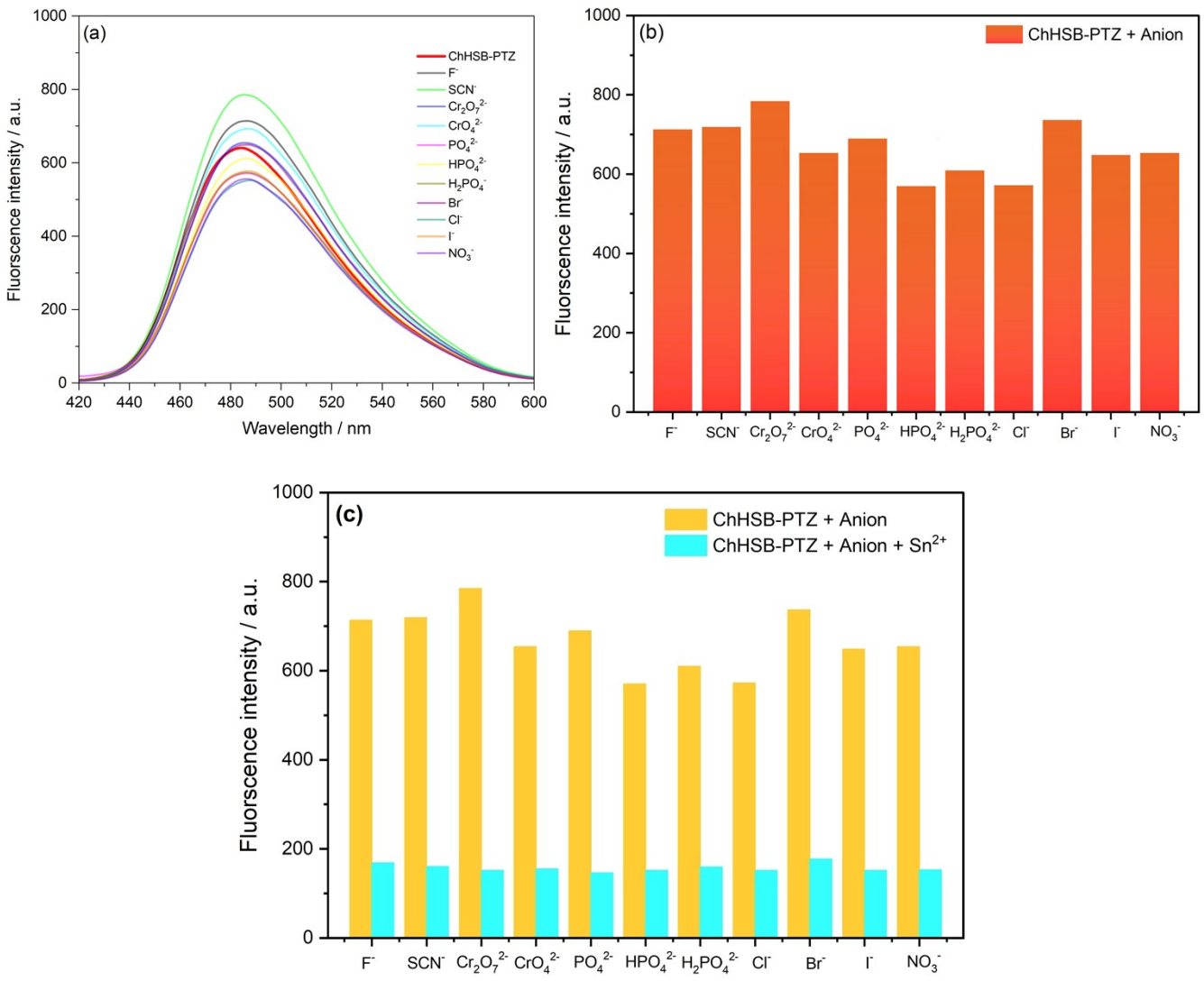


Fig. S16: (a) Fluorescence spectra of ChHSB-PTZ ($1 \times 10^{-6} M$) in THF in the presence of different anions ($1 \times 10^{-5} M$) (b) Fluorescent intensity of ChHSB-PTZ ($1 \times 10^{-6} M$) towards different metal ions (c) Fluorescent intensity of ChHSB-PTZ ($1 \times 10^{-6} M$) towards Sn(II) metal ion ($1 \times 10^{-5} M$) in the presence of different interfering anions.

Reference:

1. Y. B. Barot, V. Anand and R. Mishra, *New J. Chem.*, 2022, **46**, 15666–15677.

2. Y. B. Barot, V. Anand and R. Mishra, J. Photochem. Photobiol. A Chem., 2023, 434, 114224.