Supporting Information

Two novel fluorescent "turn on" probes based on pyrazolone and thiosemicarbazide for selectivity recognition of In^{3+}

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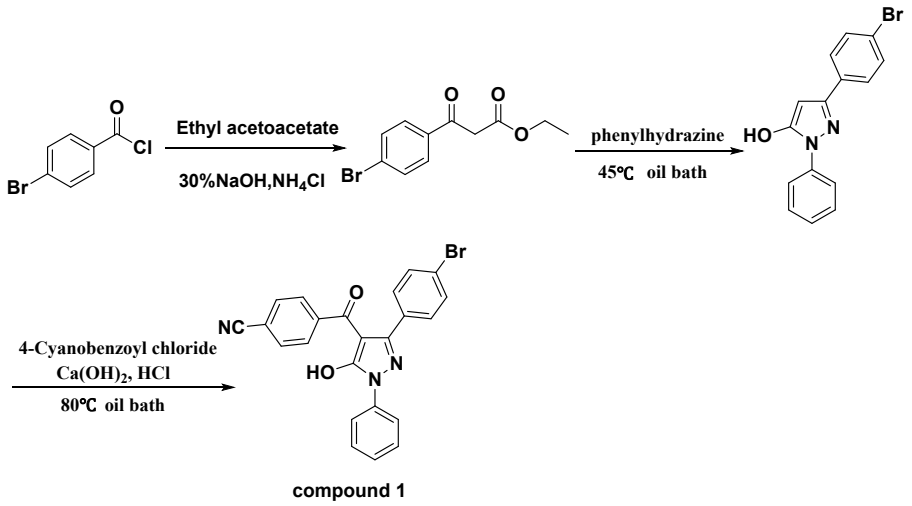
1. Experimental

Starting material 1-phenyl-3-(4-bromobenzoyl)-4-(4-cyanobenzoyl)-5-pyrazolone (compound 1) was synthesized following the previously published procedure reported in literature [1, 2]. The synthetic route was shown as Scheme S1.



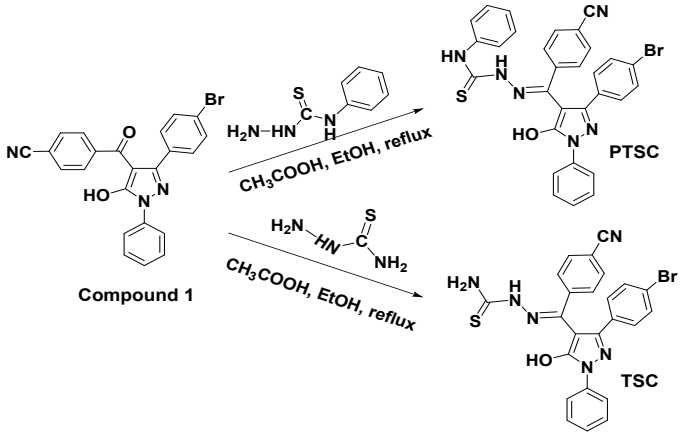
Scheme S1 Synthetic route of compound 1

To a dry 250 ml three-necked flask petroleum ether (25 mL), distilled water (100 mL), ethyl acetoacetate (20 mL, 0.16 mol) were added and placed in an ice bath with stirring. 30% NaOH solution (6 mL) was slowly added to the system (adjusting the pH to about 10-11). Then *p*-bromobenzoyl chloride (25 g, 0.12 mol), 30% NaOH (30 mL) were slowly added dropwise. Raise to room temperature and stir for 1 hour and leave to stratify. Add NH_4Cl (2 g, 0.037 mol) to the aqueous layer and react for about 6 hours, then leave to stratify, take the oil layer and wash with water for 3-5 times and dried to the *p*-bromobenzoyl ethyl acetate 18.3 g without further purification.

Phenylhydrazine (7.57 g, 0.07 mol) and ethyl *p*-bromobenzoylacetate (19 g, 0.07 mol) were placed in a 250 mL flask, stirred and heated to 45°C for 0.5 hour. Then the reaction system was cold to room temperature. The precipitate was filtered and recrystallized with ethanol to give 1-phenyl-3-p-bromophenyl-5-pyrazolone 10.6 g without further purification.

To a three-necked flash,1-phenyl-3-p-bromophenyl-5-pyrazolone (5 g, 0.02 mol), 1,4-dioxane (25 ml) and the temperature was raised to 80℃, followed by the addition of anhydrous $Ca(OH)_2$ (4 g, 0.05 mol). The oil bath was removed and *p*-cyanobenzoyl

chloride was added immediately, the reaction was stirred for 5-6 min at room temperature, the temperature was raised to 80℃ again, and stirred for 8 h. The oil bath was removed and 20 ml HCl (3 M) was added quickly, and the stirring was continued with the addition of an appropriate amount of water. When the system precipitated a brown powder, it was filtered to obtain the brown solid product and recrystallized with ethanol, compound 1 was obtained 6.51 g, yield 70%.



Compound 1 (4.0 mmol, 0.69 g), and glacial acetic acid (1 mL) in ethanol (20 mL) were added to a round bottle and refluxed for about 1h with magnetic stirring, until a large quantity of white precipitate appeared. The precipitate was filtered and recrystallized from ethanol to yield target compound (E)-2-((3-(4-bromophenyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)(4-cyanophenyl)methylene)-N-phenylhydrazine-1-carbothioamide (PTSC) as pale yellow powders 1.97 g, yield 83.4%.

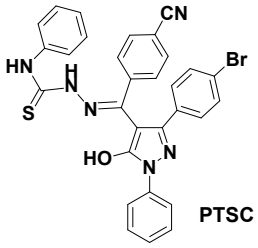
Compound 1 (4.0 mmol, 0.364 g), and glacial acetic acid (1 mL) in ethanol (20 mL) were added to a round bottle and refluxed for about 1h with magnetic stirring, until a large quantity of white precipitate appeared. The precipitate was filtered and recrystallized from ethanol to yield target compound (E)-N'-((3-(4-bromophenyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)(4-cyanophenyl)methylene)hydrazinecarbothiohydrazide (TSC) as grey powders 1.79 g,

yield 86.9%.

Reference

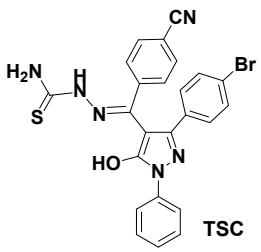
1. J. Y. Li, X. Y. Wang and Q. H. Zhao, Synthesis of 1, 3-diphenyl-4-acyl-5-pyrazolones as chelating agents, *Chin. J. Chem. Reagent*, 1997, **19**, 112.
2. B. S. Jensen and A. Chem, The synthesis of 1-phenyl-3-methyl-4-acyl-pyrazolones-5, *Scand*, 1959, **13**, 1668-1670.

2. Analytical data for the PTSC and TSC



PTSC

(E)-2-((3-(4-bromophenyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)(4-cyanophenyl)methylene)-N-phenylhydrazine-1-carbothioamide (PTSC): Yellow solid, yield 84.4%; m.p. 105 – 107 ℃; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.61 (s, 1H), 10.34 (s, 1H), 8.05 – 8.03 (d, J = 8.0 Hz, 2H), 7.94 – 7.92 (d, J = 8.0 Hz, 2H), 7.79 – 7.77 (d, J = 8.0 Hz, 2H), 7.60 – 7.46 (m, 7H), 7.43 – 7.38 (m, 3H), 7.38 – 7.31 (m, 2H), 7.25 (d, J = 8.0 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 177.26, 146.98, 141.79, 141.24, 139.50, 138.73, 132.65, 132.23, 132.02, 129.45, 128.68, 128.48, 126.86, 126.55, 126.14, 122.17, 119.26, 111.83; **FT-IR** (KBr): 3301.66, 3064.81, 2227.48, 1632.78, 1593.59, 1541.94, 1495.94, 1307.68, 1162.75, 754.76, 694.68 cm^{-1}; **HRMS** (ESI) calcd. for $C_{30}H_{21}BrN_6OS^+$ $[M+H]^+$ 593.0754, found 593.0742.



TSC

(E)-2-((3-(4-bromophenyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)(4-cyanophenyl)methylene)hydrazine-1-carbothioamide (TSC): Gray solid, yield 86.9%; m.p. 133 – 135 ℃ ; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.02 (s, 1H), 8.54 (s, 1H), 8.35 (s, 1H), 8.0 – 7.97 (d, J = 12.0 Hz, 2H), 7.92 – 7.90 (d, J = 8.0 Hz, 2H), 7.78 – 7.75 (d, J = 12.0 Hz, 2H), 7.55 – 7.49 (m, 5H), 7.39 – 7.34 (m, 3H).; **^{13}C NMR** (101 MHz, DMSO-d_6) δ 179.14, 146.72, 141.88, 140.24, 138.74, 132.68, 132.27, 132.03, 129.42, 128.45, 128.25, 126.87, 122.23, 122.11, 119.26, 111.70; **FT-IR** (KBr): 3423.52, 3316.28, 3269.09, 3166.77, 2229.71, 1603.74, 1462.92, 1405.99, 1368.90, 1295.33, 1076.33, 833.08 cm^{-1}; **HRMS** (ESI) calcd. for $C_{24}H_{18}BrN_7OS^+$ $[M+H]^+$ 517.0441 found 517.0456.

3. Characterization for PTSC and PTSC + In^{3+}

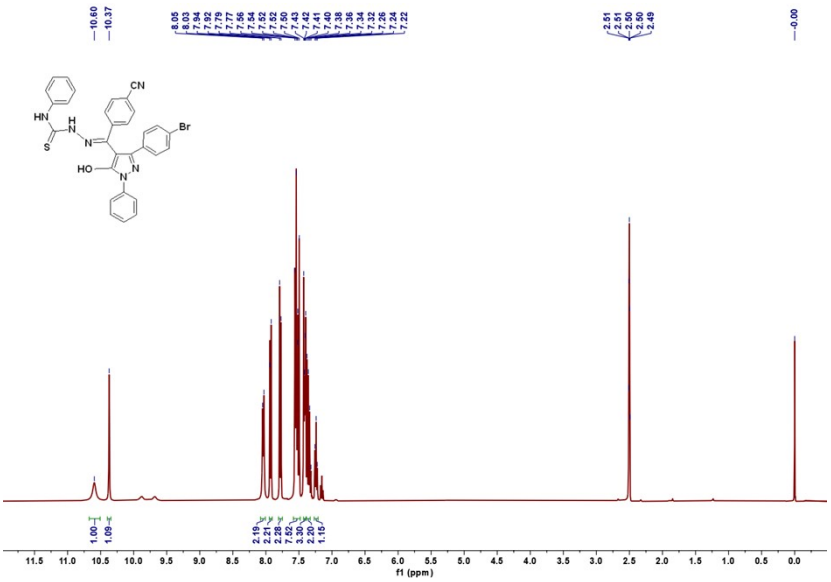


Fig. S1 ^{1}H NMR of PTSC (400 MHz, DMSO-d_6)

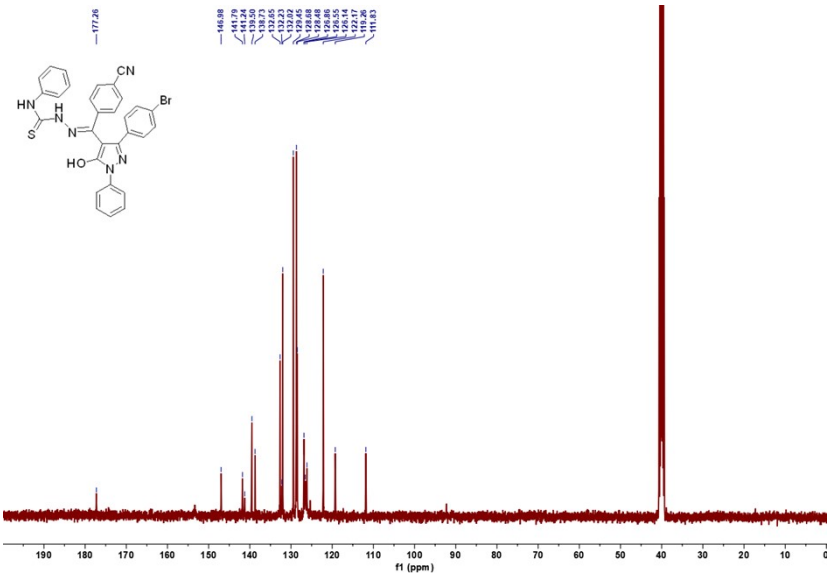


Fig. S2 ^{13}C NMR of PTSC (101 MHz, DMSO-d_6)

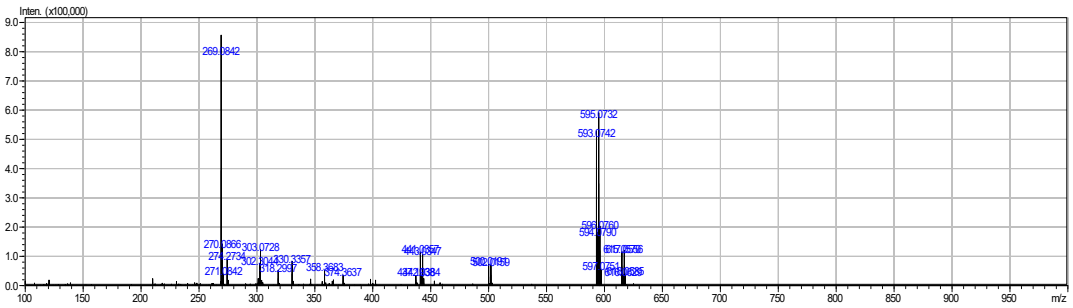


Fig. S3 HRMS spectra of PTSC

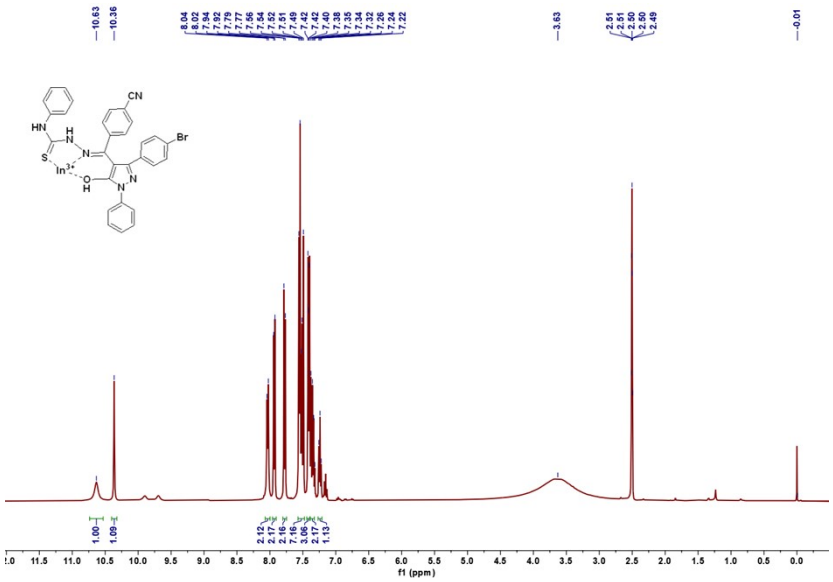


Fig. S4 ^{1}H NMR of PTSC + 0.5 equiv. In^{3+} (400 MHz, DMSO-d_6)

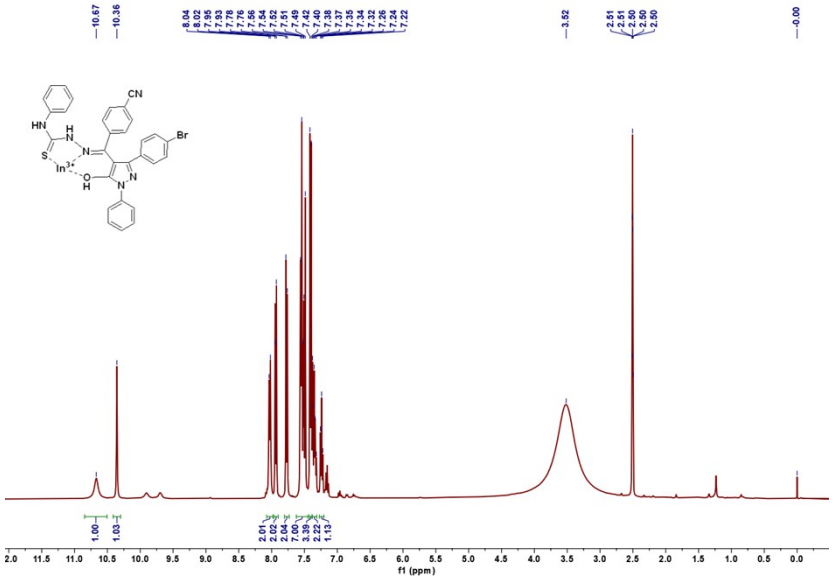


Fig. S5 ^{1}H NMR of PTSC + 1.0 equiv. In^{3+} (400 MHz, DMSO-d_6)

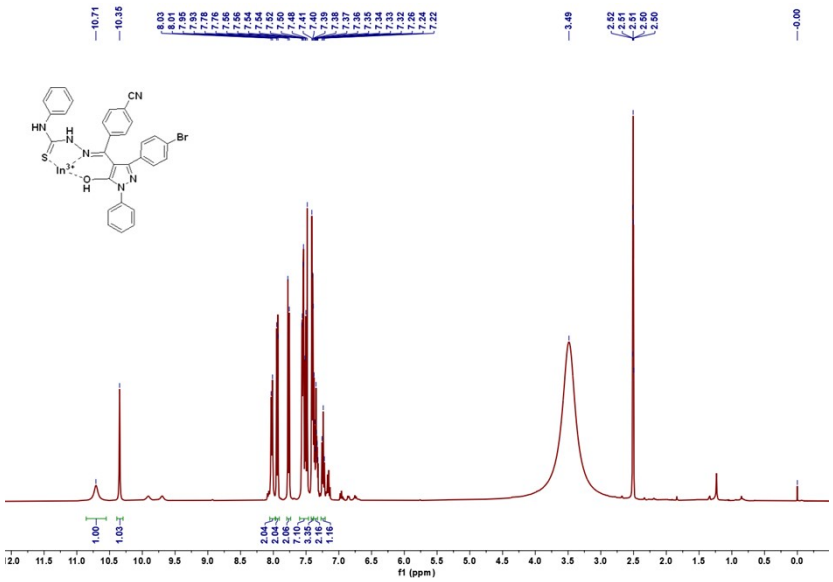


Fig. S6 ^{1}H NMR of PTSC + 1.5 equiv. In^{3+} (400 MHz, DMSO-d_6)

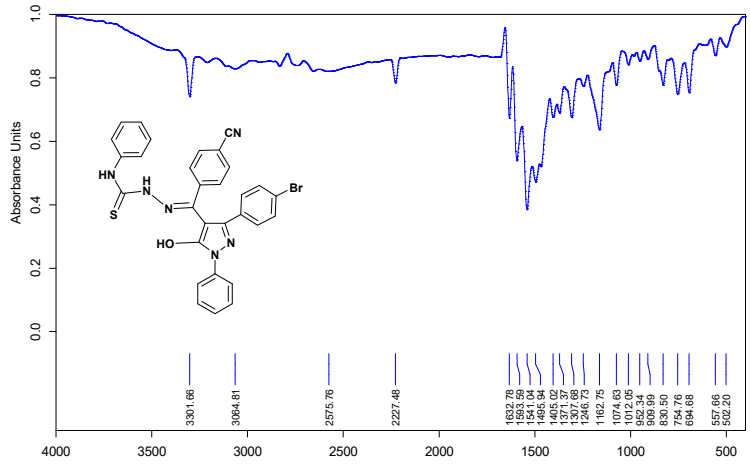


Fig. S7 FT-IR spectra of PTSC

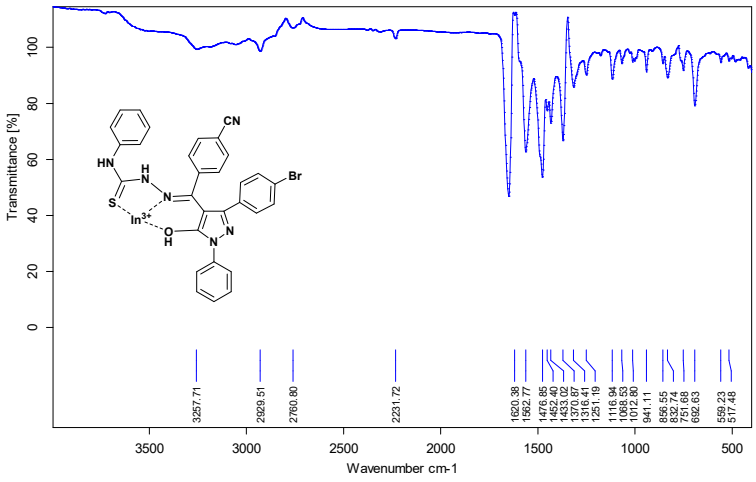


Fig. S8 FT-IR spectra of PTSC + 1.0 equiv. In^{3+}

4. Characterization for TSC and TSC + In^{3+}

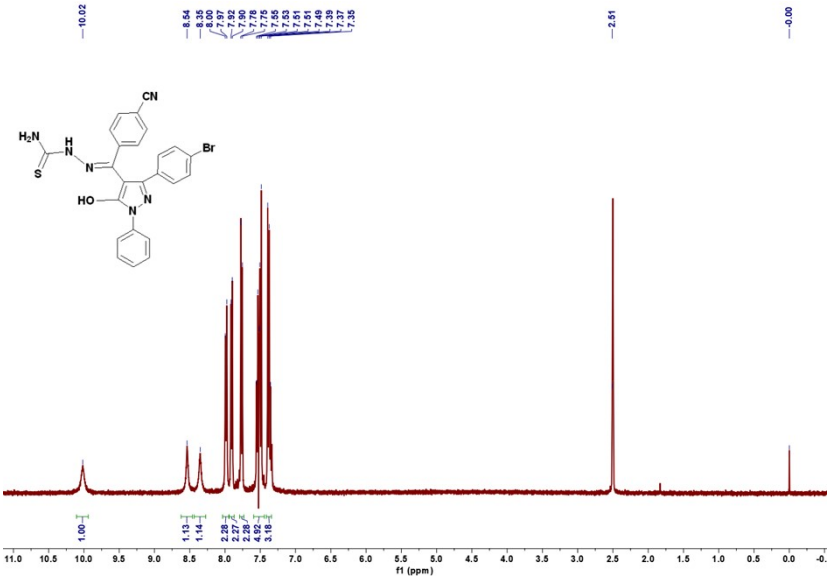


Fig. S9 ^{1}H NMR of TSC (400 MHz, DMSO-d_6)

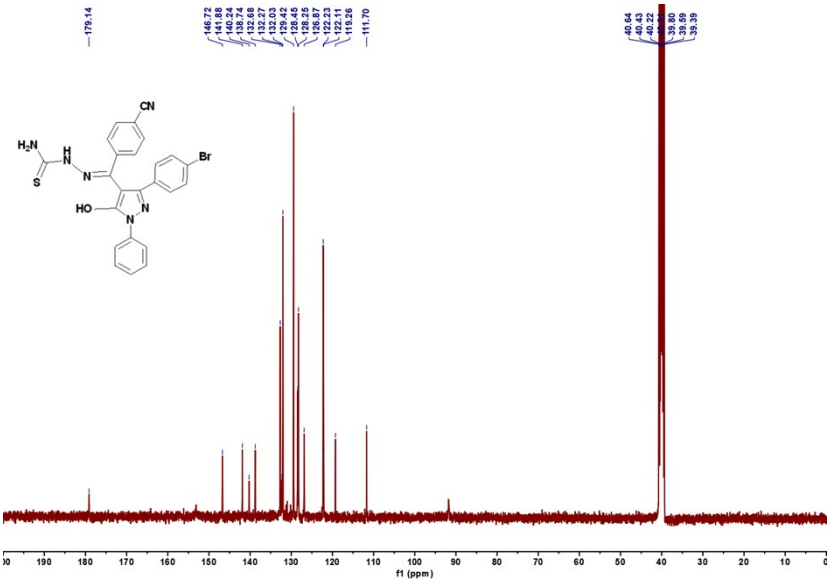


Fig. S10 ^{13}C NMR of TSC (400 MHz, DMSO-d_6)

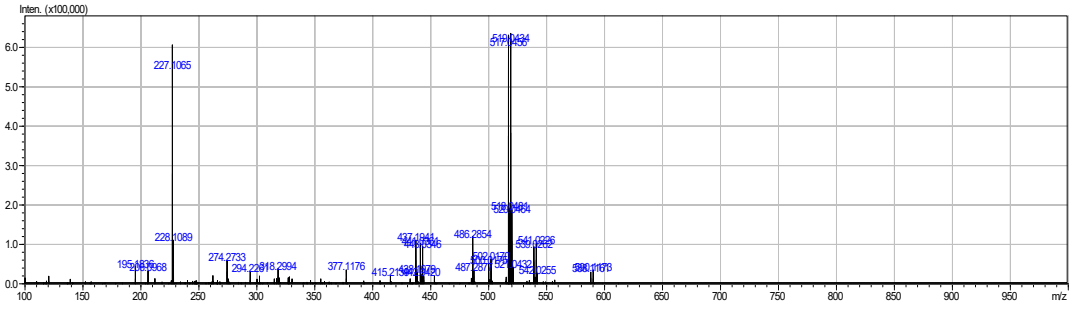


Fig. S11 HRMS spectra of PTSC

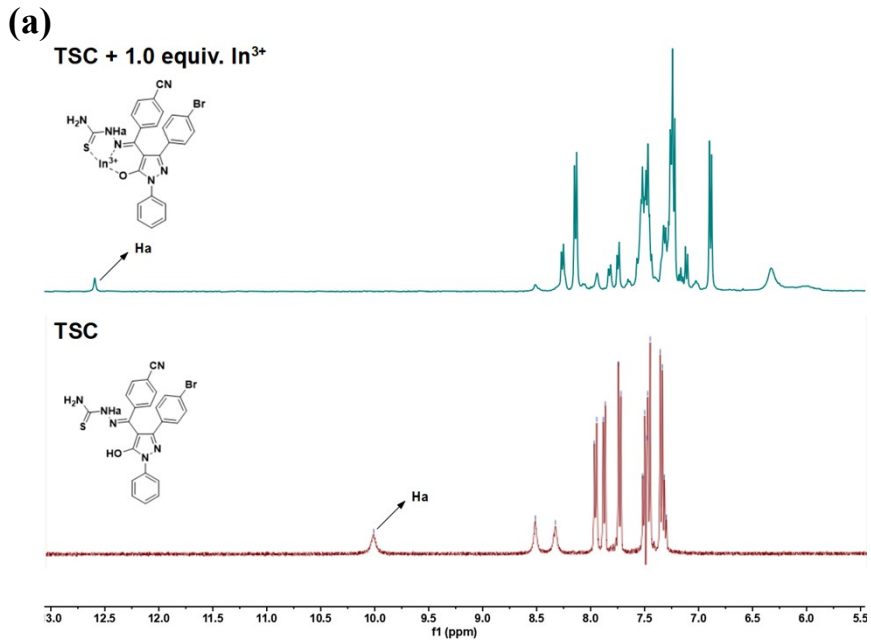


Fig. S12 (a) ^{1}H NMR spectra of TSC (400 MHz, DMSO-d_6) in the absence & presence of In^{3+}

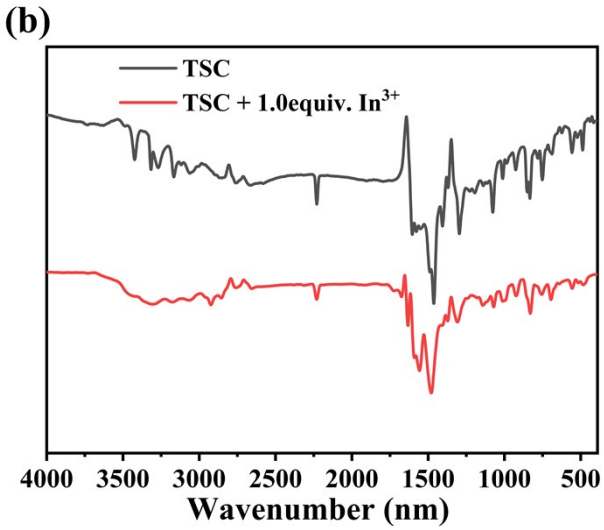


Fig. S12 (b) FTIR spectra of TSC and TSC + In^{3+}

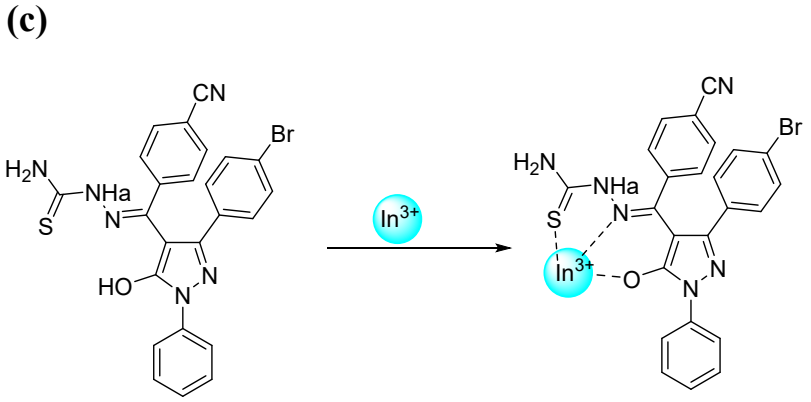


Fig. S12 (c) Binding mode of TSC and In^{3+}

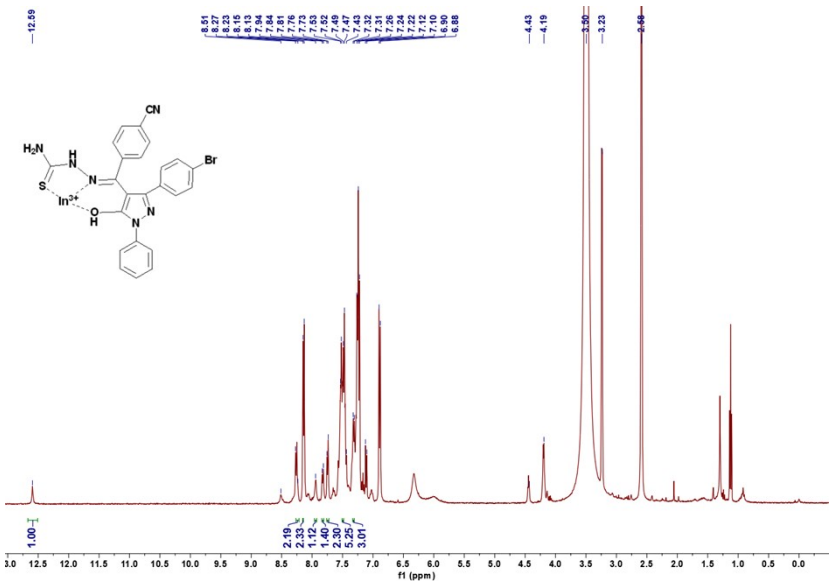


Fig. S13 ^{1}H NMR of TSC + 1.0 equiv. In^{3+} (400 MHz, DMSO-d_6)

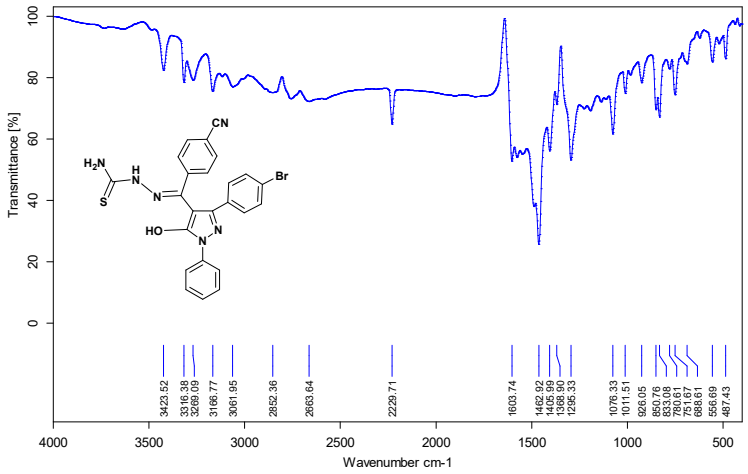


Fig. S14 FT-IR spectra of TSC

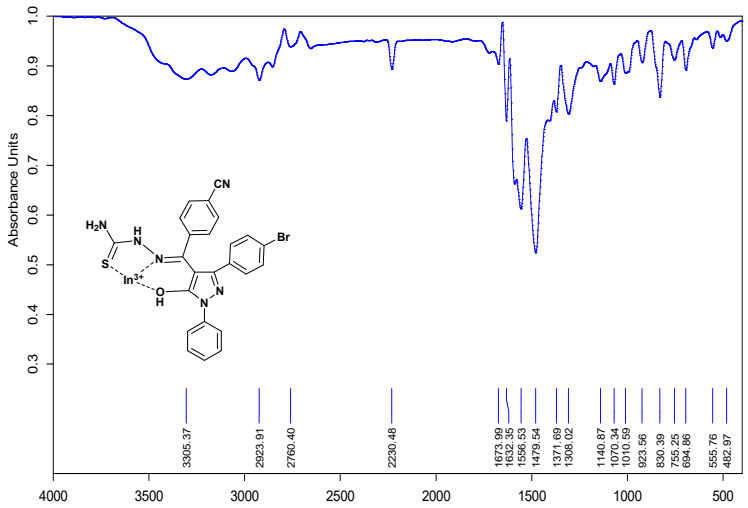


Fig. S15 FT-IR spectra of TSC+ 1.0 equiv. In^{3+}

5. Stokes shifts of PTSC + In^{3+} and TSC + In^{3+}

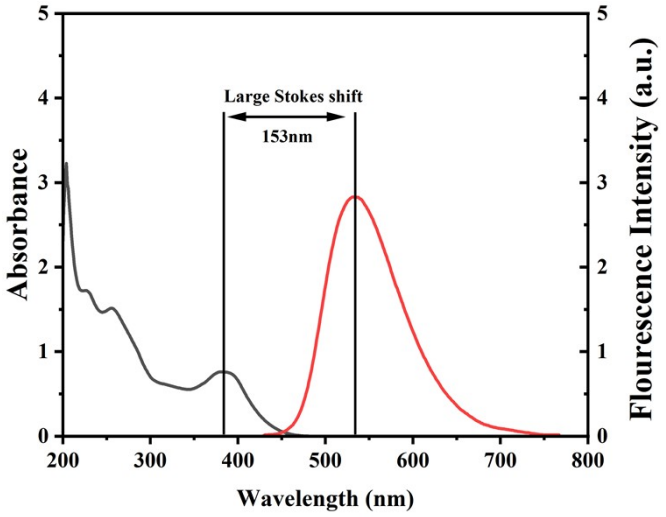


Fig. S16 Stokes shift of PTSC + In^{3+} (λ_{ex} = 400 nm)

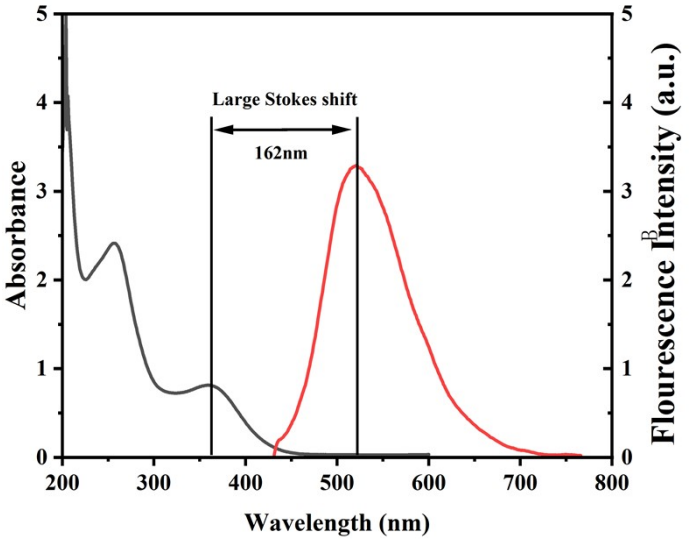


Fig. S17 Stokes shift of TSC + In^{3+} (λ_{ex} = 400 nm)

6. Fluorescence spectra of PTSC and PTSC + In^{3+} with different solvents.

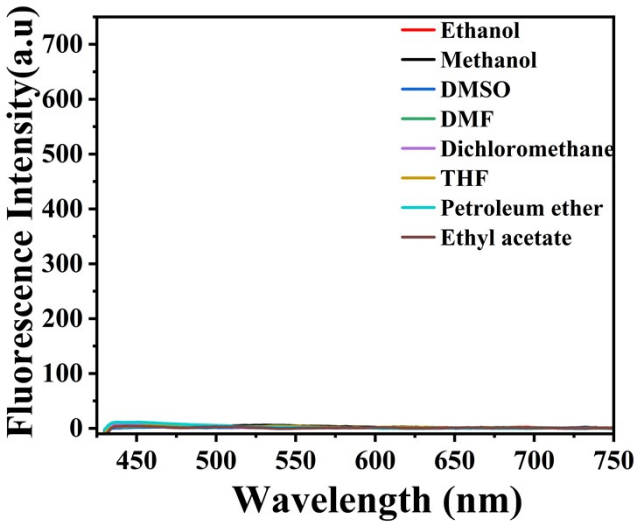


Fig.S18 (a) Fluorescence emission spectra of PTSC with different solvents.

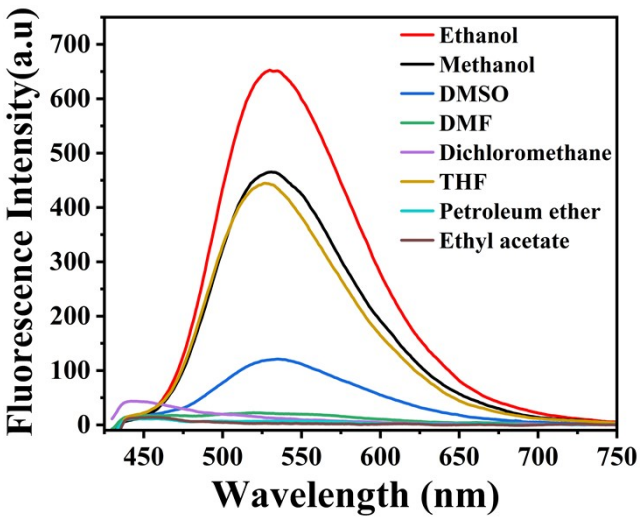


Fig.S18 (b) Fluorescence emission spectra of PTSC + In^{3+} with different solvents.