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Perylene diimide–based near-IR ratiometric sensor for detection of Cu^{2+} ions: Ensemble for discrimination of CN^- and S^{2-} ions

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Experimental section

Materials and characterization: Chemicals and solvents were of reagent grade and used without further purification. All reactions were performed under nitrogen atmosphere. DMF, DMSO and CH_3CN solvents were of HPLC grade. Deionized water was obtained from ULTRA UV/UF Rions Lab Water System Ultra 370 series devices. Chromatographic purification was done with silica gel 60–120 mesh. TLC was performed on aluminum sheets coated with silica gel 60 F254 (Merck, Darmstadt). ^1H NMR and ^{13}C NMR spectra were recorded at 400/500 MHz for ^1H; 100/125 MHz for ^{13}C (JEOL 400 and Bruker Ascend 500 spectrometer) using $CDCl_3$ or DMSO-d_6 or CH_3CN-d_3 as solvents. The peak values were obtained as ppm (δ) and referenced to the TMS as reference in ^1H NMR and deuterated solvent in ^{13}C NMR spectra. Chemical shift values are reported in ppm, coupling constant (*J*) in Hz and abbreviations used for splitting patterns are s = singlet, bs = broad singlet, t = triplet, q = quartet, m = multiplet. The absorption spectra were recorded using quartz

cells on UV-Visible Agilent spectrophotometer, (Agilent Technologies, U.S.) equipped with Peltier system as temperature controller. The fluorescence titrations were performed on Shimadzu RF-6000 spectroflurophotometer using slit width (excitation = 10 nm, emission = 10 nm) with excitation at 450 nm, unless otherwise stated. PDI **1** was synthesized according to previously reported literature procedure.

UV-Visible and Fluorescence Studies

Stock solutions for various measurements of **TBP-PDI** were prepared in CH_3CN and dilutions of these stock solutions were used for the photo physical measurements. The solutions were diluted with CH_3CN and HEPES buffer (10^{-2} M, pH 7.2) before taking the readings in quartz cells. All absorption and fluorescence scans were processed in Excel™ to produce all graphs shown.

Method for detection of metal ions:

Stock solutions (10^{-2} M) of metal ions were prepared in deionized Millipore water and were diluted as required. **TBP-PDI** was added in various 10 mL volumetric flask and subsequently different concentrations of metal ions were added. The solutions were diluted with HEPES buffer-CH_3CN (4:6 v/v, pH 7.2) up to the 10 mL mark.

Detection limit: The detection limit was calculated based on the absorbance or fluorescence titrations. To determine the S/N ratio, the absorbance and emission intensity of **TBP -PDI** (10 μM) without Cu^{2+} was measured by 3 times and the standard deviation of blank solution (without addition of analyte) measurements was determined. The detection limit was then calculated with the equation**;** Detection limit = 3σbi/m**.** Where, σbi is the standard deviation of blank solution (without addition of analyte) measurements; m is the slope between intensity versus sample concentration.

Sample preparation for DLS measurements

The stock solutions of **TBP-PDI** (1 mM, CH_3CN) and water were filtered through Millipore membrane filter (Acrodisc syringe filter, 0.2 μm Supor membrane) before measurements to remove suspended impurities. Solutions (10 μM concentration) of **TBP-PDI** and **TBP-PDI**$\cap Cu^{2+}$ in HEPES buffer-CH_3CN (4:6 v/v, pH 7.2) were prepared. 2 mL of each of these solutions was taken in glass cuvette to record the DLS spectrum.

Electrochemical measurements

Electrochemical studies were carried out at room temperature with an electrochemical workstation (Model Metrohm AutolabPGSTAT302N). Three-electrode cell system containing a Pt working electrode, Pt wire as counter electrode and Ag/Ag^+ (0.1 M $AgNO_3$ in CH_3CN) as reference electrode have been used. cyclic voltammogram (CV) was recoded at a scan rate of 50 mVs^{-1} and differential pulse voltammetry (DPV) measurements were carried out at pulse modulation amplitude of 0.05 V, pulse width of 0.05 s and pulse period of 0.5 s in the potential range of −0.5 to 2.5 V vs Ag/Ag^+. The CH_3CN was used as organic solvent and 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte for all the voltammetry measurements. The NOVA software was used to collect, plot and analyze the raw data of CV and DPV measurements.

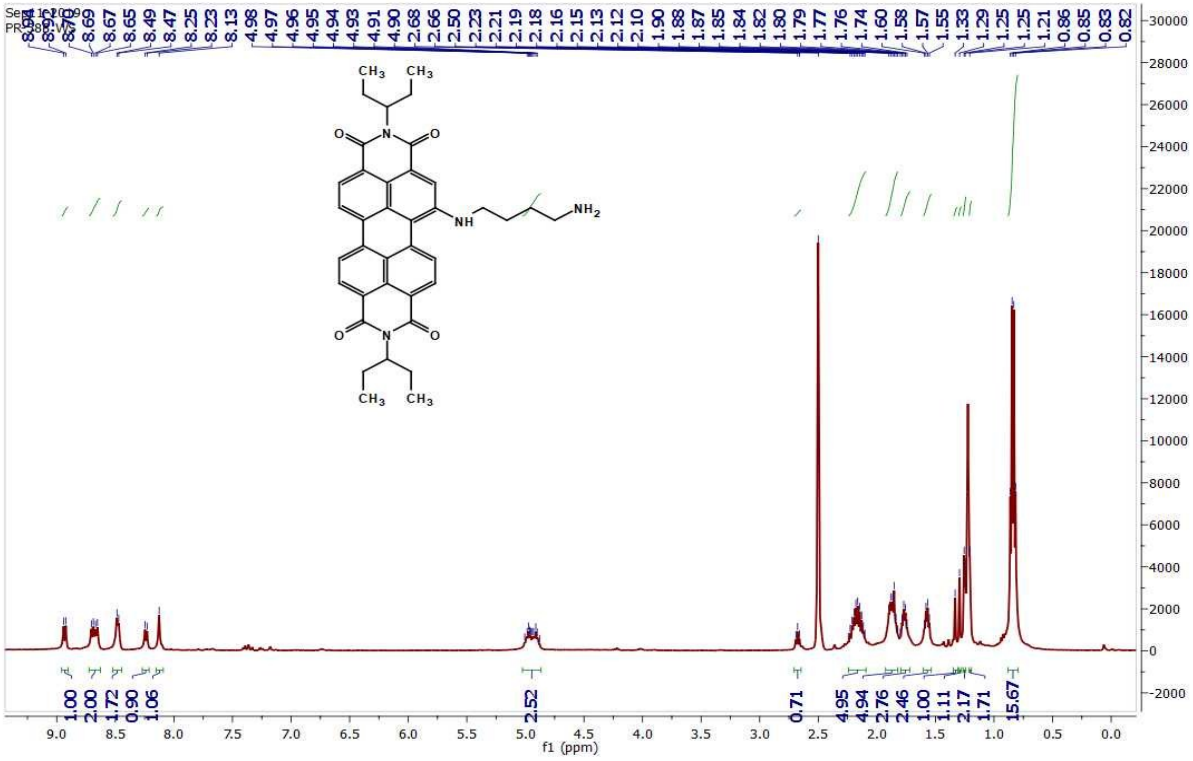

Figure S1a: ^1H NMR Data of PDI **2**.

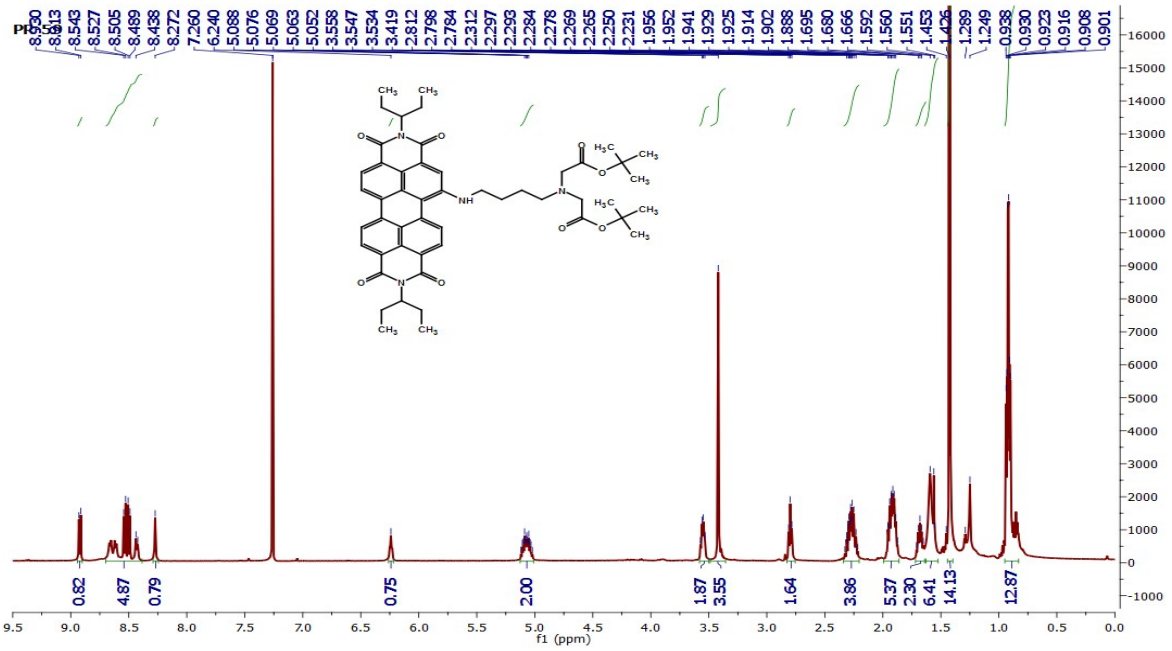

Figure S2a: ^{1}H NMR Data of **TBP-PDI**.

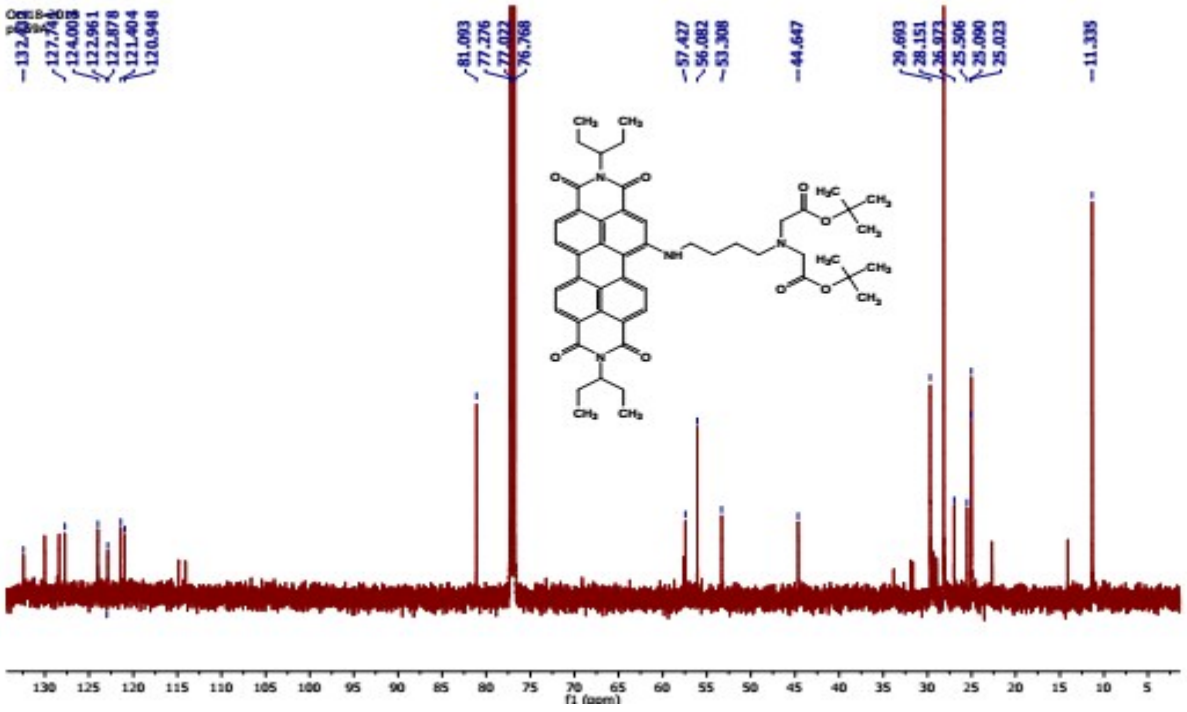

Figure S2b: ^{13}C NMR Data of **TBP-PDI**.

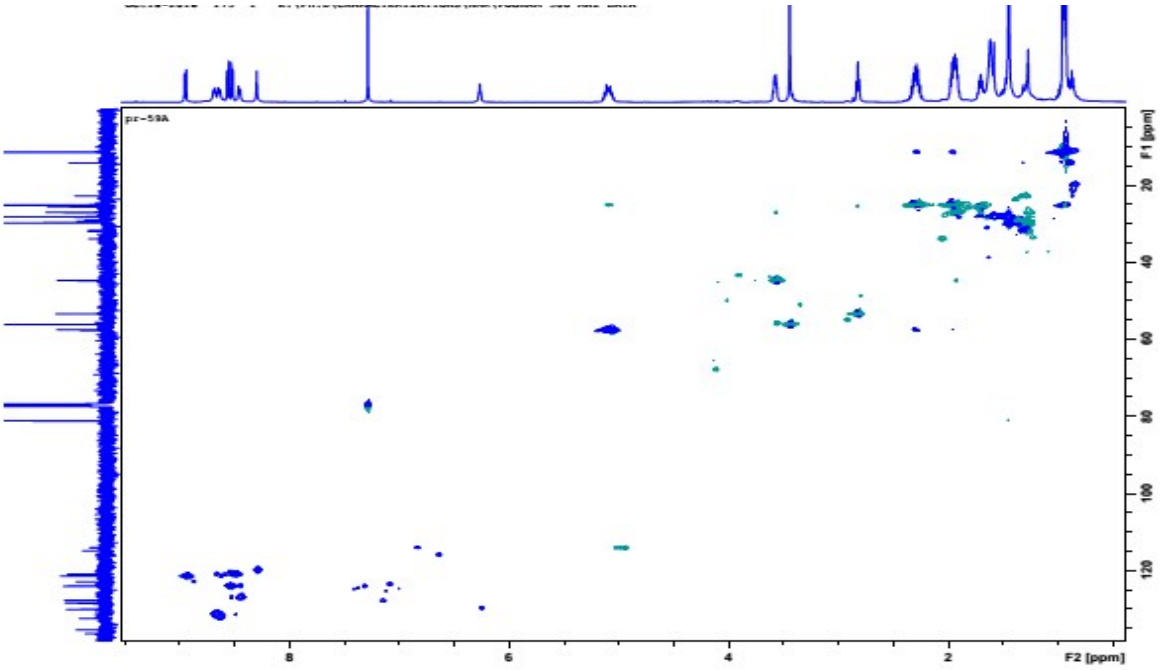

Figure S2c: HSQC Data of **TBP-PDI**.

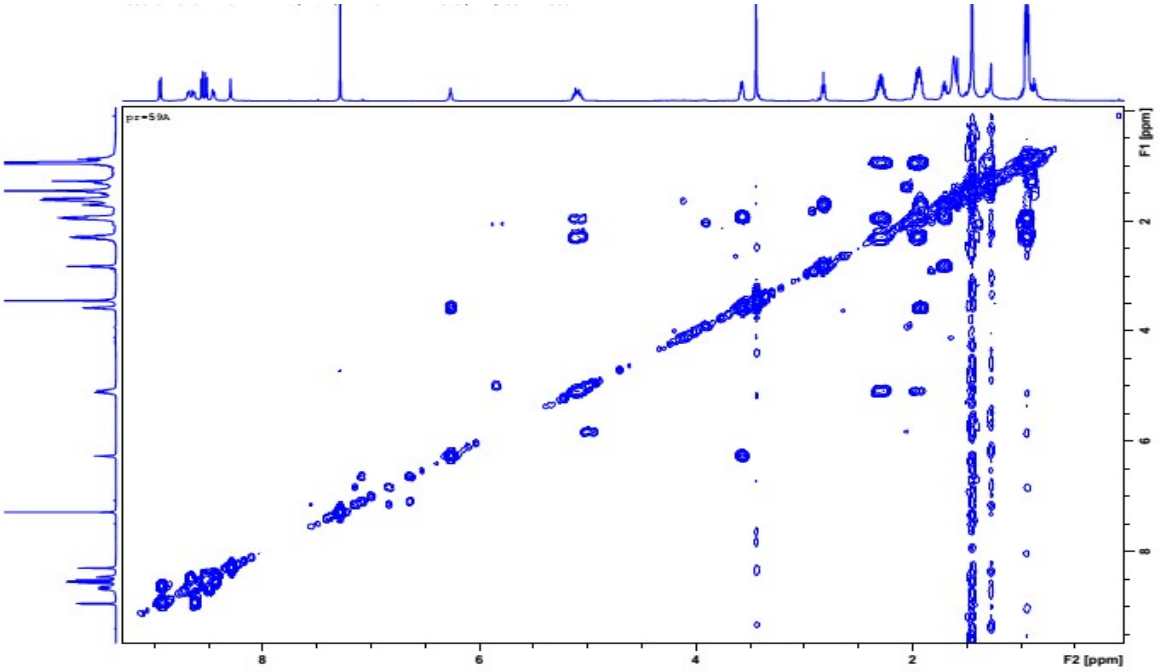

Figure S2d: COSY Data of **TBP-PDI**.

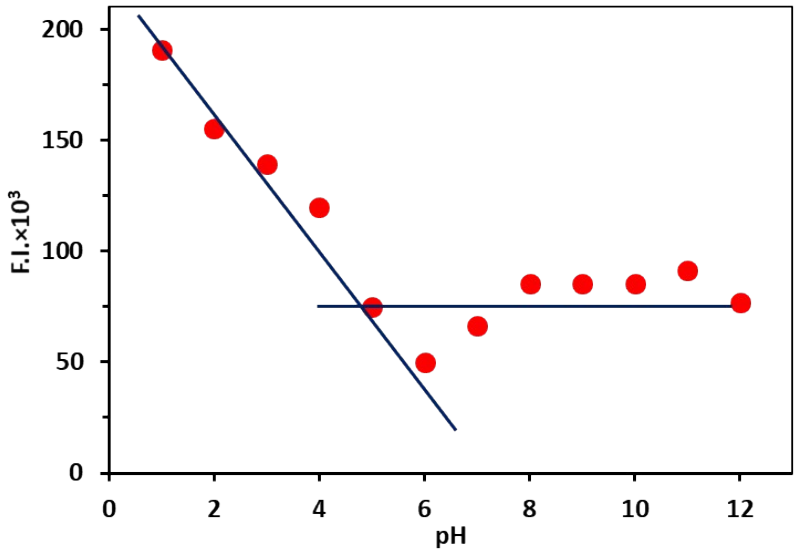

Figure S3a: pH titration of the **TBP-PDI** with variation of pH of the solution.

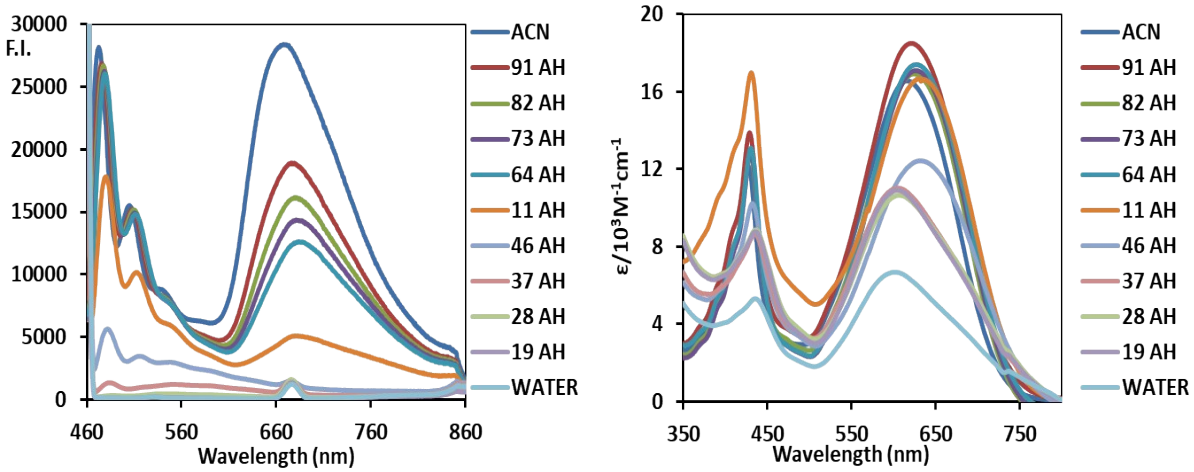

Figure S3b. (a) Absorbance (10 μM) and (b) fluorescence (5 μM) spectra of **TBP-PDI** on addition of 10 vol % H_2O in CH_3CN solvent (λ_{ex} = 450 nm; slit width Ex/Em = 10/10 nm).

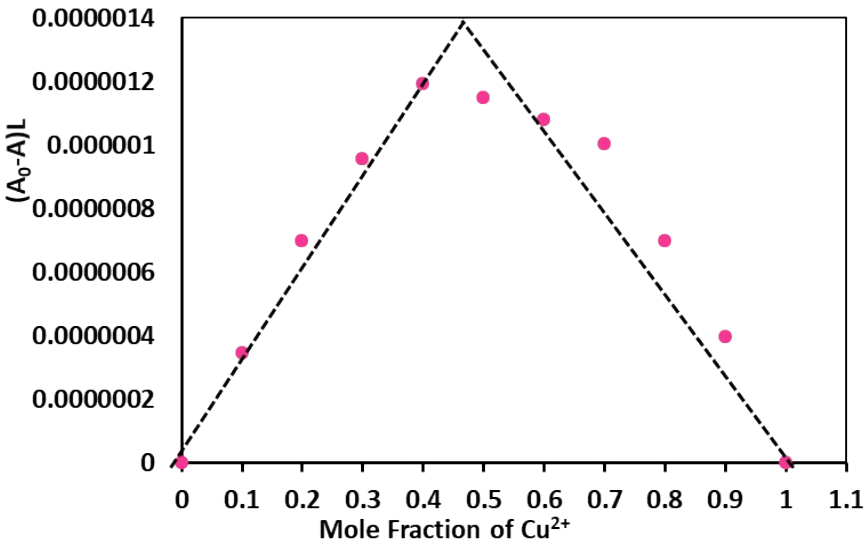

Figure S4: Job Plot (Absorption) of **TBP-PDI** with Cu^{2+} ions

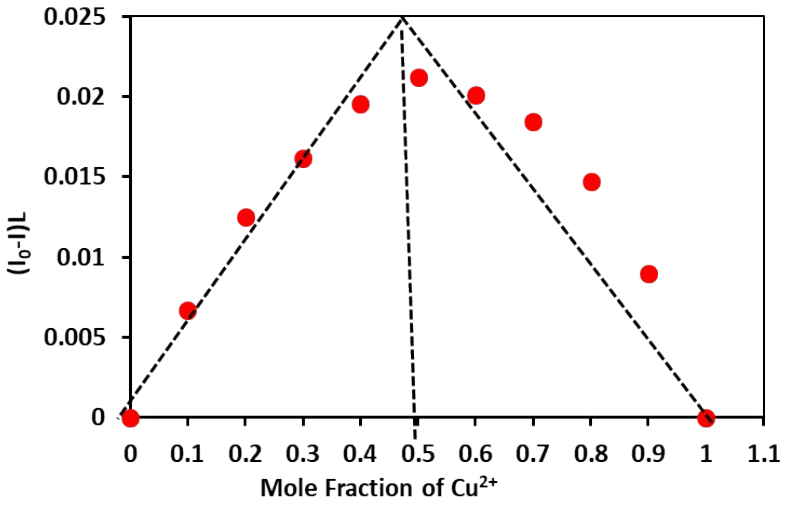

Figure S5: Job Plot (Emission) of **TBP-PDI** with Cu^{2+} ions.

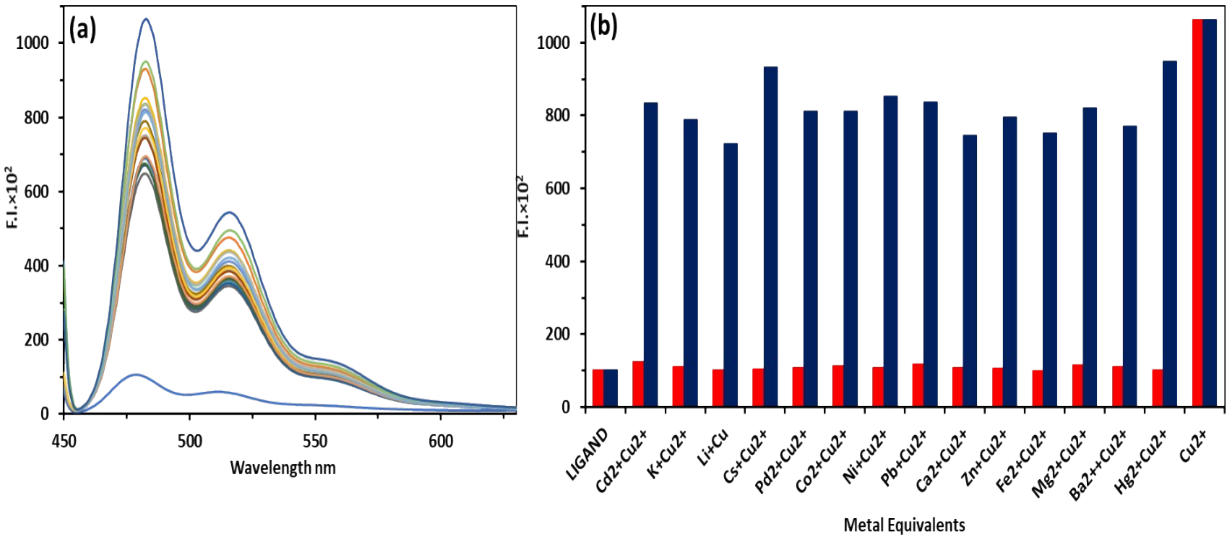

Figure S6: (a) Effect of the various metal ions on the fluorescence spectrum of the **TBP-PDI** (5 μM) recorded in 40% HEPES buffered:CH_3CN media; (b) bar graph representation of effect of the various metal ions on the fluorescence spectrum of the **TBP-PDI** (5 μM) recorded in 40% HEPES buffered:CH_3CN media.

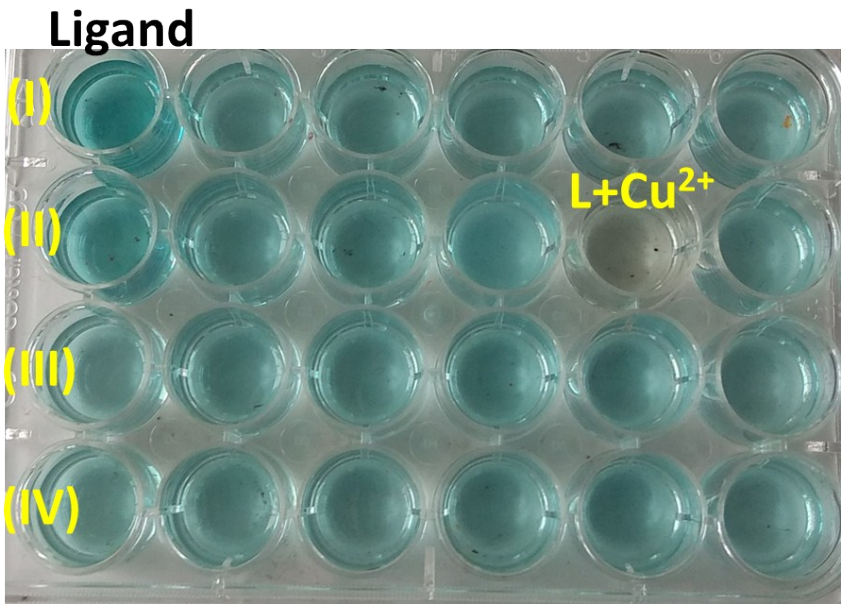

Figure S7. Color (*naked eye*) images of well plate containing **TBP-PDI** (20 μM) alone and **TBP-PDI** + different metal ions (20 equivalents). Row (IV) of the well plate showed simultaneous presence of two or three metal ions in the solution; Ligand (L) = **TBP-PDI**

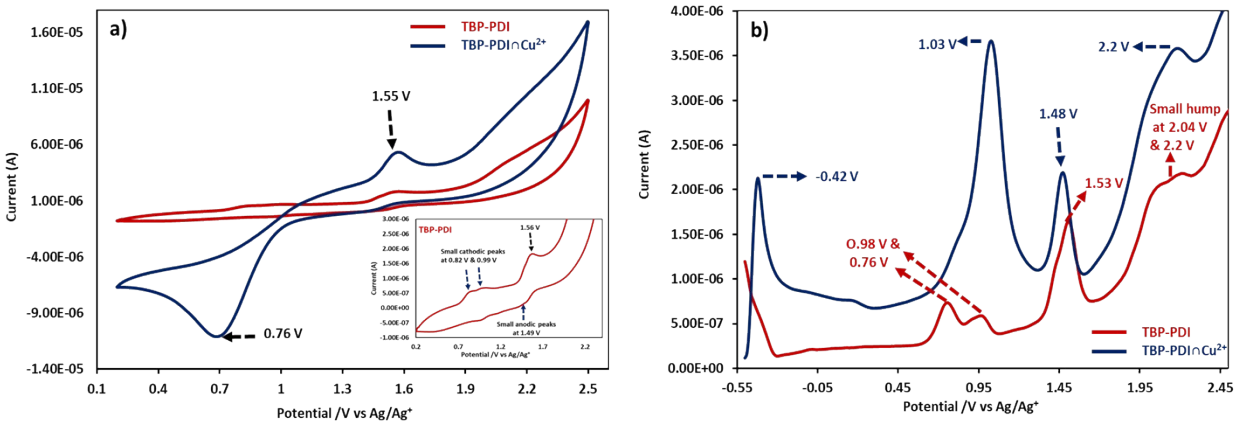

Figure S8: Cyclic voltammetric studies of **TBP-PDI** with Cu^{2+} ions; Red line correspond to **TBP-PDI** and blue line correspond to **TBP-PDI**∩Cu^{2+} complex.

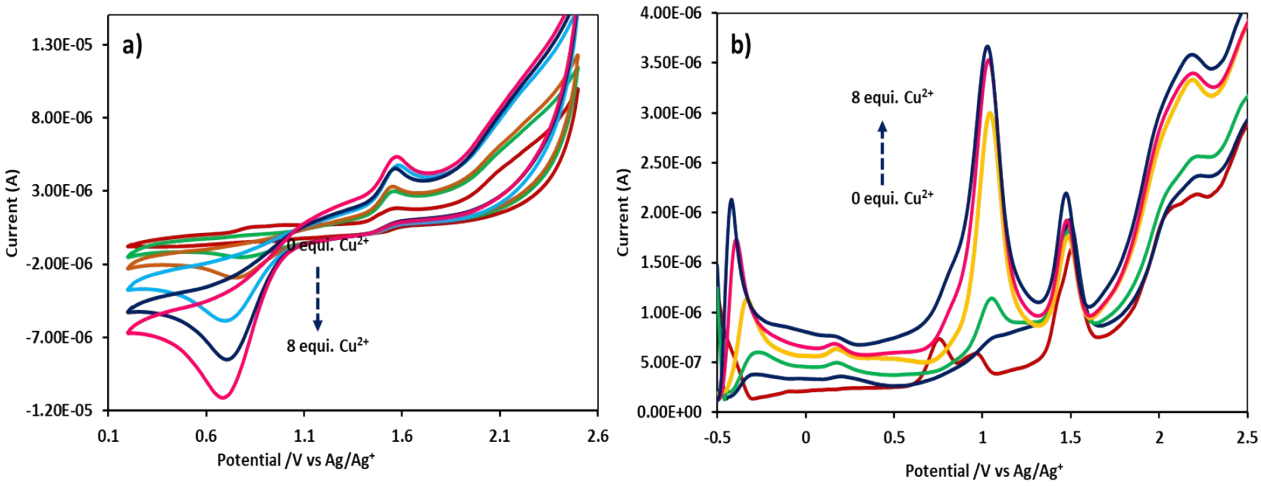

Figure S9: Differential pulse voltammetric (DPV) titration of **TBP-PDI** on addition of Cu^{2+} ions;

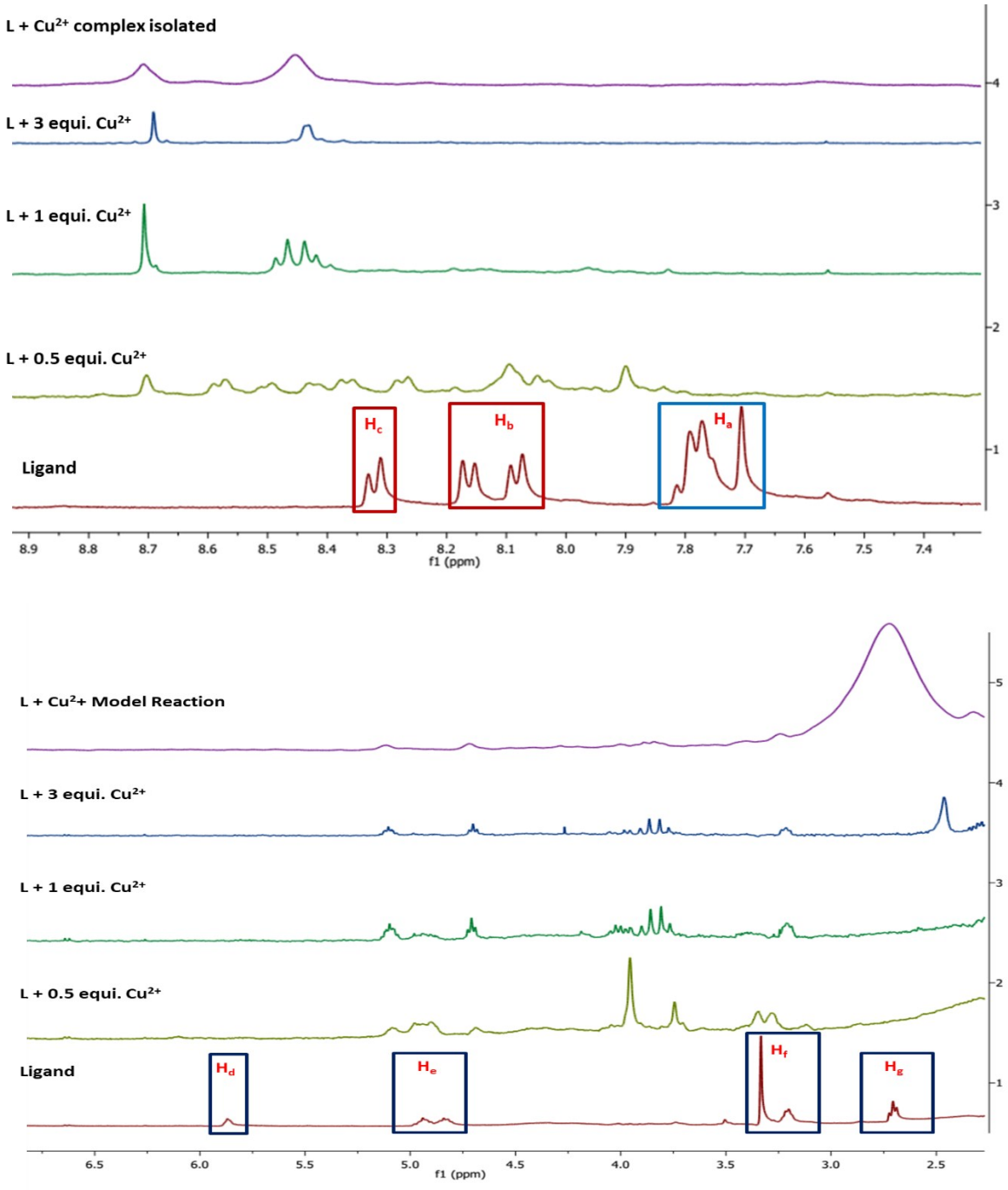

Figure S10: (Above) Partial ^{1}H NMR spectra (aromatic region) and (below) Partial ^{1}H NMR spectra (aliphatic region) of **TBP-PDI** (1 mM) with Cu^{2+} recorded in $CH_3CN(d_3)$; For comparison NMR spectrum of **TBP-PDI**∩Cu^{2+} complex has also been given; L = **TBP-PDI**.

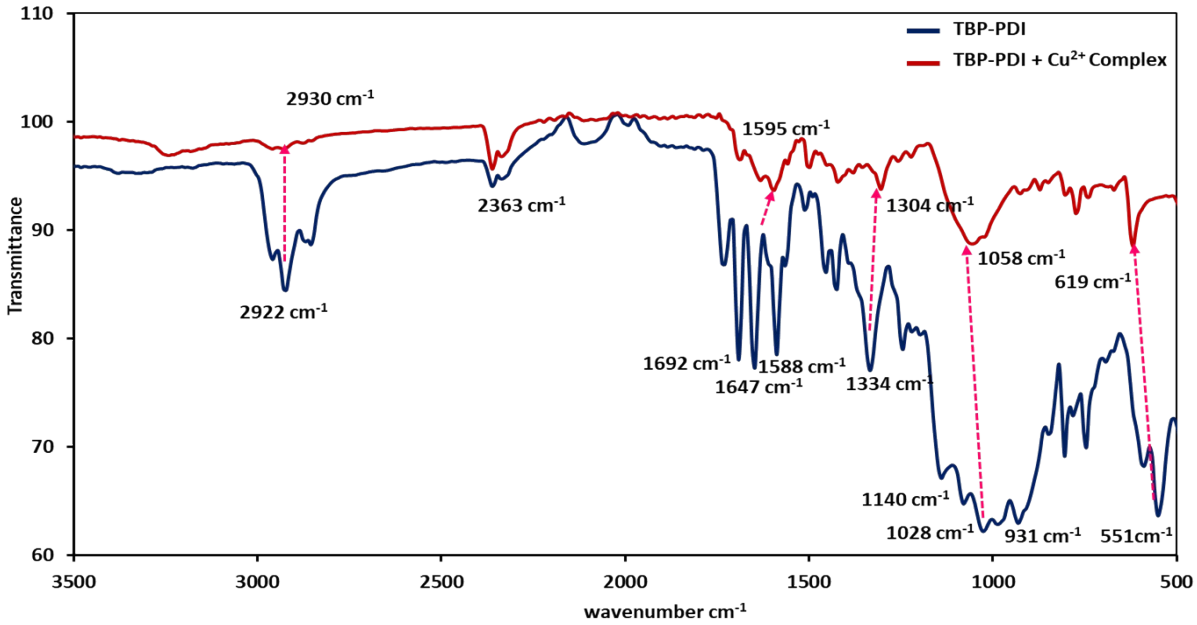

Figure S11: IR spectrum of **TBP-PDI** and **TBP-PDI**∩Cu^{2+}complex

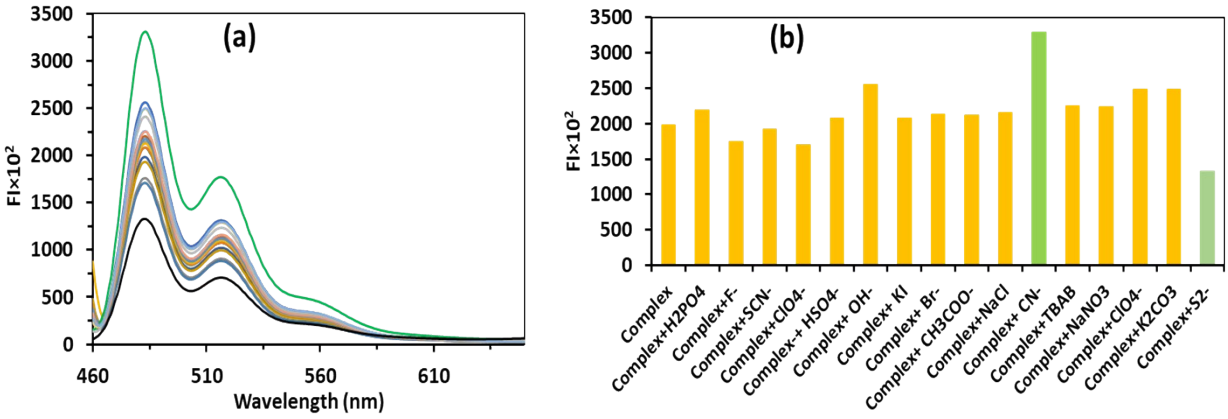

Figure S12: (a) Effect of the various anions on the fluorescence spectrum of the **TBP-PDI**∩Cu^{2+} (1:15) recorded in 40% HEPES buffered:CH_3CN media; (b) bar graph representation of effect of the various anions on the fluorescence spectrum of the **TBP-PDI**∩Cu^{2+} (1:15) recorded in 40% HEPES buffered:CH_3CN media.

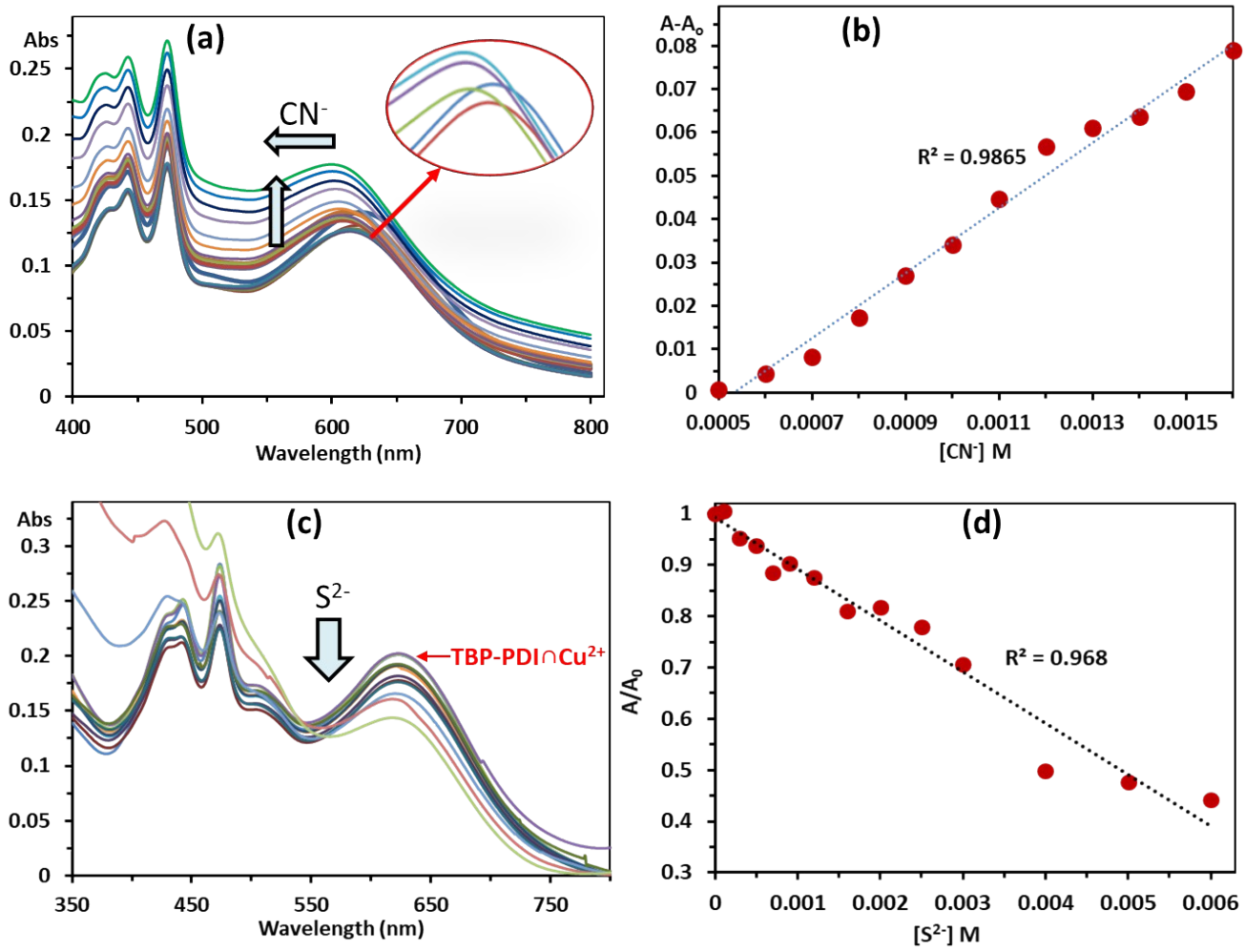

Figure S13: (a) Absorbance spectra and (b) absorbance profile of ensemble **TBP-PDI**∩Cu^{2+} after addition of S^{2-} ions in 40% HEPES buffered:CH_3CN media.

Table S1: Comparison of the literature report for Cu^{2+} complex and its application as ensemble with present report.

S.No.	Papers Detail	Solvent medium	λ_{ex}	λ_{abs} / λ_{em}	LOD for Cu^{2+} ion	Applications as ensemble
	This manuscript	CH_3CN/H_2O (v/v, 6: 4) CH_3CN	490 nm	ratiometric fluorescent '*turn-on*' (F_{482}/F_{680} nm) and colorimetric (A_{476}/A_{630})	4.8 µM 2.5 nM	ensemble for CN^- with detection limit of 6.95 nM, and for S^{2-}, with detection limit of 2.39 mM
1.	Bioorganic & Medicinal Chemistry Letters 23 (2013) 2538–2542	EtOH/HEPES, v/v = 9:1	418 nm	541 nm	Association Constant (Ka) = 2.9×10^2	Ensemble for thiols with detection limit of 0.42 µM for Cys, 0.105 µM for Hcy and 4.34 µM for GSH.
2.	Journal of Photochemistry and Photobiology A: Chemistry 324 (2016) 152–158	DMSO	504 nm	545 nm	5.25 µM	Application in molecular logic gate
3.	Dalton Trans., 2012, 41, 11413–11418	DMSO	275 nm	384 nm	3.12 µM	Ensemble for CN^- ions with detection limit of 5.93 µM.
4.	Dalton Trans., 2013, 42, 4450–4455	EtOH–H_2O (8: 2) mixture;e buffered with HEPES	293 nm	386 nm	1.5 µM	Ensemble for CN^- ions with detection limit of 0.026 ppm.
5.	J. Fluoresc, 2014, 24, 909–915	Chloroform	500 nm	579 nm	0.5 µM	Ensemble for CN^- ions with detection limit of 8 µM.
6.	J. Mater. Chem. C, 2016, 4, 2488-2497	CH_3CN	490 nm	537 nm	17.5 µM	Not an ensemble
7.	New J. Chem.,	CH_3CN	450 nm	554 nm	0.21-5.12	_

	2019,43, 7393-7402				µM	
8.	Dalton Trans., 2015, 44, 6490–6501	Fluorescence turn-on CH3CN/H2O (v/v, 7: 3)	446 nm		1.53 µM	Ensemble for S^{2-} ion with detection limit of 11.4 µM.
9.	Sensors, 2017,17, 1980–1993	Fluorescence turn-off, CH_3CN	395 nm	489 nm	9 µM	Real time analysis
10.	Journal of Luminescence 175 (2016) 122–128	THF: HEPES¼5:5, 20 mM, pH¼7.4	420 nm		55 nM	Ensemble for thiols with detection limit of 1.5µM for Cys, 1.8µM for Hcy and 2.2 µM for GSH.
11.	Sensors and Actuators B, 2013,177 213–217	CH_3CN	530 nm	590 nm	10 µg/L	-
12.	J Fluoresc, 2014, 24, 1331–1336	EtOH–H_2O (5: 5) mixture buffered with Tris–HCl, pH=7.2	399 nm	514 nm	0.07 µM	Visualize the change of intracellular Cu^{2+} in living cells
13.	J Fluoresc, 2012, 22, 1603–1608	CH_3CN: H_2O, 1:1, v/v, HEPES, 10 mM, pH=7.0	530 nm	578 nm	5.3 µM	-
14.	Inorganica Chimica Acta, 2015, 438, 37-41	DMSO	300 nm	385 nm	0.27 µM	Cu^{2+} Sensing in a drug sample
15.	**RSC Adv.,** 2016**,6,** 71543-71549	10% aq.-DMSO solution (HEPES buffer 7.4)	440 nm & 470 nm	-	Not mentioned	3.5 µM for CN^- ion