Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Water dispersed fluorescent organic aggregates for detection of picomolar ClO_4^- in water, soil and blood serum and atto g by contact mode

Rahul Kumar, Sana Sandhu, Prabhpreet Singh* and Subodh Kumar*

Corresponding author. Address: Department of Chemistry, UGC Centre for Advanced Studies, Guru Nanak Dev University, Amritsar 143 005, India.

Corresponding author. Mobile: +91 9872361528.

E-mail address: subodh.chem@gndu.ac.in; prabhpreet.chem@gndu.ac.in

1. Experimental Details

General Remarks:

All reagents were purchased from commercial suppliers (Aldrich, Across, SDFCL, Spectrochem etc.) and used without further purification. Solvents were purified and dried by standard methods prior to use. 1-(4-Biphenyl)benzimidazole (1) was synthesized by CuI, benzotriazole catalyzed N-arylation of benzimidazole with 4-bromobiphenyl as reported in literature. TLC analyses were performed on silica gel plates and column chromatography was carried out over silica gel (100 - 200 mesh).

^1H and ^{13}C NMR spectra were recorded on BRUKER Bio spin AVANCE-III FT NMR HD-500 using $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal standard. Data are reported as follows: chemical shifts in ppm relative to the tetramethylsilane (TMS) as an internal

standard, coupling constants J in Hz; multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet). HRMS spectra were recorded on Brucker MicroToff/QII. The time resolved fluorescence spectra were recorded with ISS Chronos-BH time-resolved fluorescence spectrophotometer. DLS experiments were performed on Malvern-Zetasizer.

For UV-Vis, fluorescence, DLS and FESEM studies, all the solutions were prepared in deionized water obtained from ULTRA UV/UF Rions Lab Water System Ultra 370 series.

UV-Vis and fluorescence studies. UV-Vis studies were carried out on Shimadzu UV-2450 machine using slit width of 1.0 nm and matched quartz cells. The cell holder was thermo stated at 25.0 ± 0.2^{o}C. The fluorescence experiments were performed on Shimadzu 2450 and BH-CHRONOS fluorescence spectrophotometers with a quartz cuvette of path length 1 cm. The cell holder was thermo stated at 25.0 ± 0.2 ^{o}C. All absorption and fluorescence scans were saved as ASCII files and were further processed in Microsoft Excel™ to produce all graphs shown. The stock solutions of **CS-1** and **CS-2** (1 mM) were prepared in DMSO. For experiments with **CS-1,** 3 ml of the solution containing **CS-1** (60 μL, 0.1mM) and 2.94 mL HEPES buffer (0.05 M, pH 7.4) were taken in cuvette. Stock solutions (0.1 M) of sodium salts (Na^+X^-), where X = CN^- , F^-, Cl^- , Br^- , I^- , ClO_4^- , NO_3^- , SO_4^{2-} , HSO_4^-, SCN^-, AcO^- and $H_2PO_4^-$ were prepared in deionized millipore water and were diluted as required. During titration experiments, after addition of each aliquot of ClO_4^- solution, the solution was allowed to remain stable for 2 minutes.

DLS and SEM sample preparation. The stock solutions of **CS-1** (1 mM, DMSO) and water were filtered through 0.02 micron filter membrane to remove interfering impurities. Solutions of **CS-1** (H_2O - 2% DMSO) and its mixtures with different concentrations of ClO_4^- were prepared. 2 ml of each of these solutions was taken in glass cuvette to record the DLS spectrum at 25 ^{o}C. The solutions prepared for DLS experiments were used for preparing thin films for SEM recording. 10 μL of each of the solution was added on the pre-cleaned surface of the separate glass slide and was allowed to dry in the incubator at 25 ^{o}C. The dried films were coated with Au before recording SEM images. The scanning electron microscope (SEM) images were obtained with a field emission scanning electron microscope SEM JEOL JSM-6610LV.

Paper strips preparation. Whatman filter paper strips (1 cm x 1 cm) were dipped into aqueous DMSO solution of **CS-1** (0.1 mM) and were dried under vacuum at room temperature. These paper strips were used for naked eye (under 365 nm light) visualization of 10^{-15} to 10^{-9} M ClO_4^-

solution. The 10^{-15}, 10^{-14}, 10^{-13}, 10^{-12}, 10^{-11} M solutions of ClO_4^- and 10^{-11} M, 10^{-9} M solution of all other anions were prepared in water and 6 µl aliquot of each of these solutions was added on separate paper strip. For control experiment, drop of water alone was added on the **CS-1** coated paper strip. The fluorescence spectra of paper strips bearing ClO_4^- ions were also recorded using front surface steady-state fluorescence on ISS Chronos BH fluorescence spectrophotometer.

Blood Serum. A real blood sample of a medically fit person was used for the experiments. The blood serum was isolated by centrifugation of the fresh blood sample after fasting at 4000 rpm for 30 min at 4 ^oC. The stock solution of the blood serum was prepared in 10 ml volumetric flask by diluting 1ml of serum with HEPES buffer (0.05 M) at pH 7.40.

Quantum yield calculations[1]. Fluorescence quantum yields (Φs) were determined by using an optically matching solution of QHS (Φr = 0.54 in 0.1 M H_2SO_4) as standard at excitation wavelength of 290 nm and quantum yield is calculated using equation

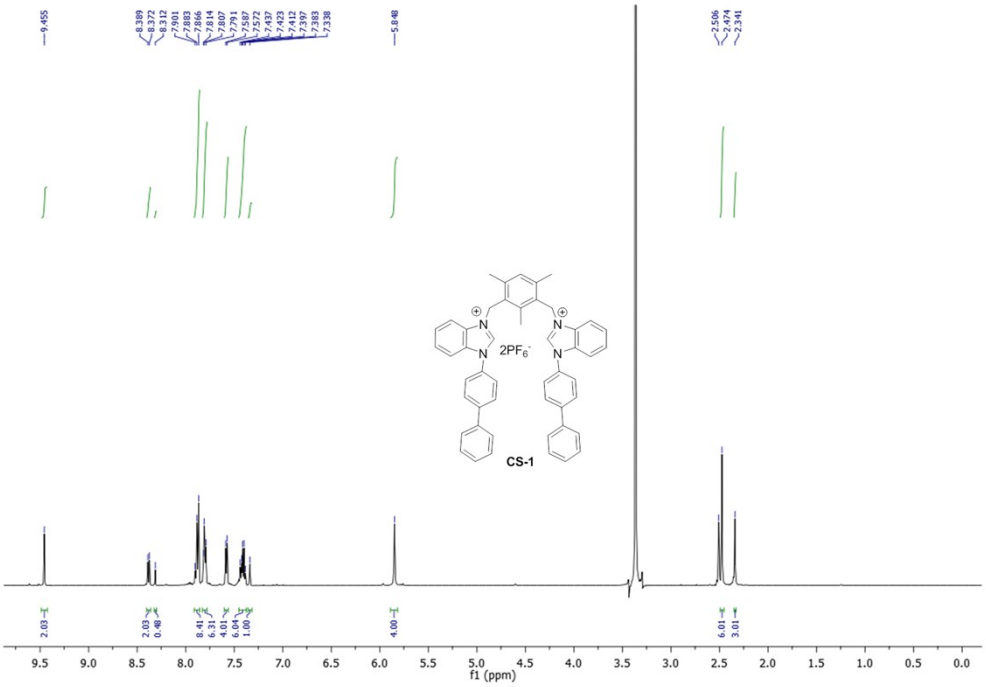
$$\Phi_{fs} = \Phi_{fr} \times \frac{1-10^{-ArLr}}{1-10^{-AsLs}} \times \frac{Ns^2}{Nr^2} \times \frac{Ds}{Dr}$$

Φfs and Φfr are the radiative quantum yields of sample and the reference, respectively. Ds and Dr are the respective areas of emission for the sample and reference, respectively. As and Ar are the absorbance; Ls and Lr are the lengths of the absorption cells; Ns and Nr are the refractive indices of the sample and reference solutions, respectively.

Detection limit[2]. The detection limit was calculated based on the fluorescence titration. To determine the S/N ratio, the emission intensity of **CS-1** (2 µM) without perchlorate was measured by 10 times and the standard deviation of blank solution (without addition of perchlorate) measurements was determined. Under the present conditions, a good linear relationship between the fluorescence intensity and the perchlorate concentration could be obtained in the 10^{-11} – 10^{-7} M (R^2 = 0.9929) for **CS-1**.The detection limit is then calculated with the equation:

Detection limit = 3σbi/m

Where, σbi is the standard deviation of blank solution (without addition of perchlorate) measurements, m is the slope between intensity versus sample concentration. The detection limit was measured to be 10 pM for **CS-1** S/N = 3.



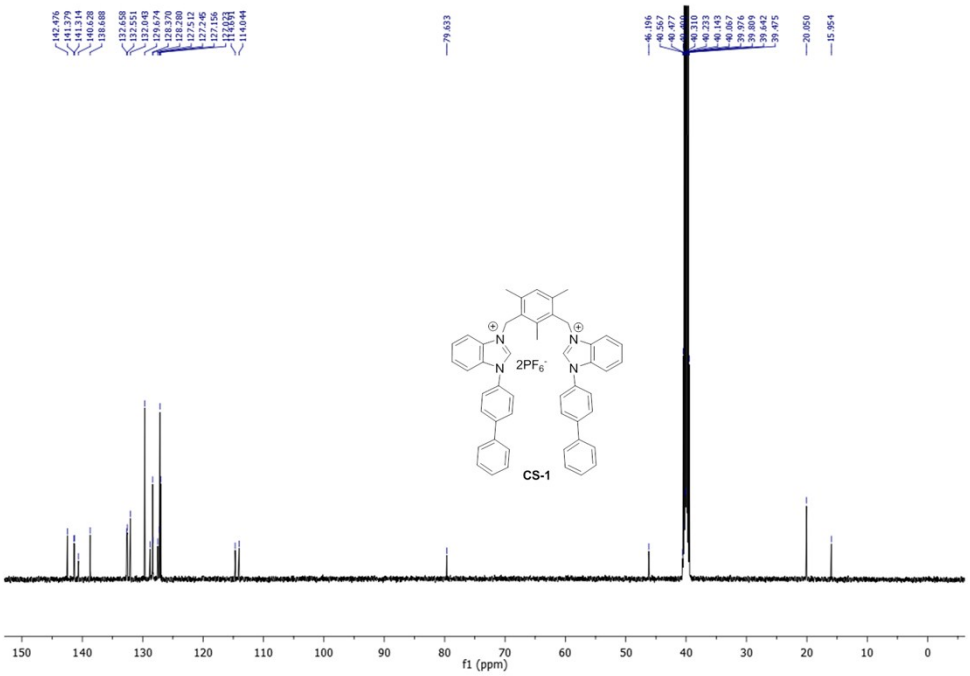
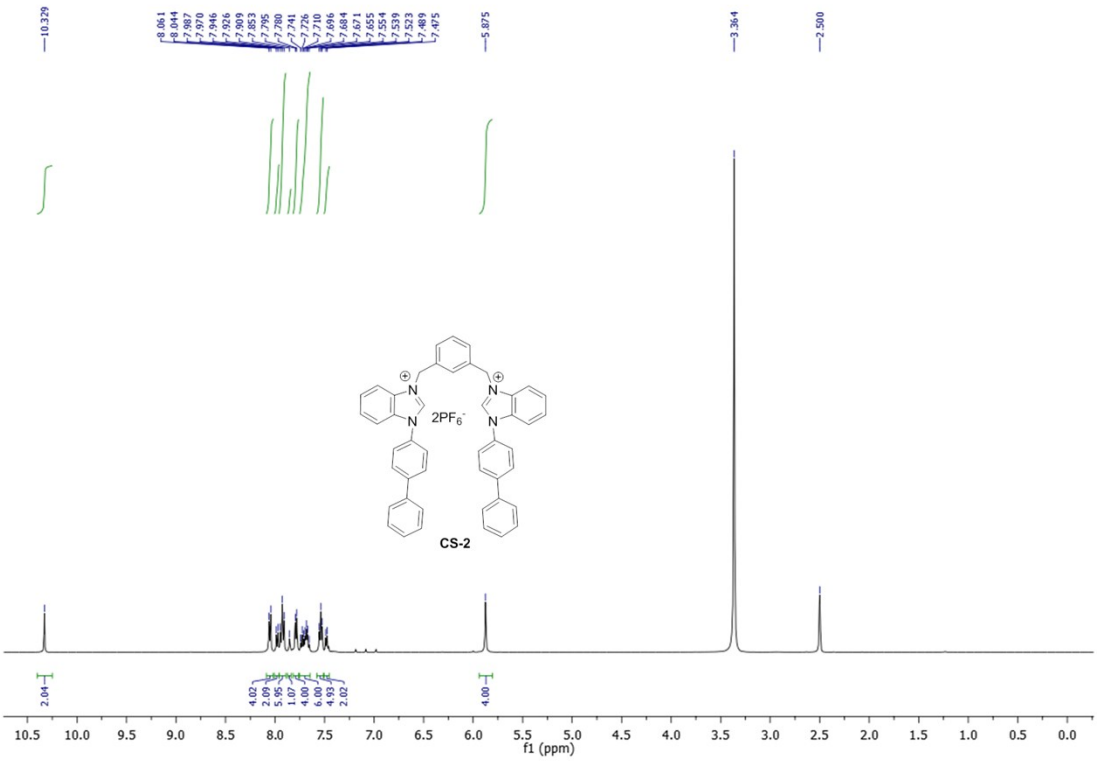


Figure S1. ^{1}H NMR and ^{13}C NMR of **CS-1**



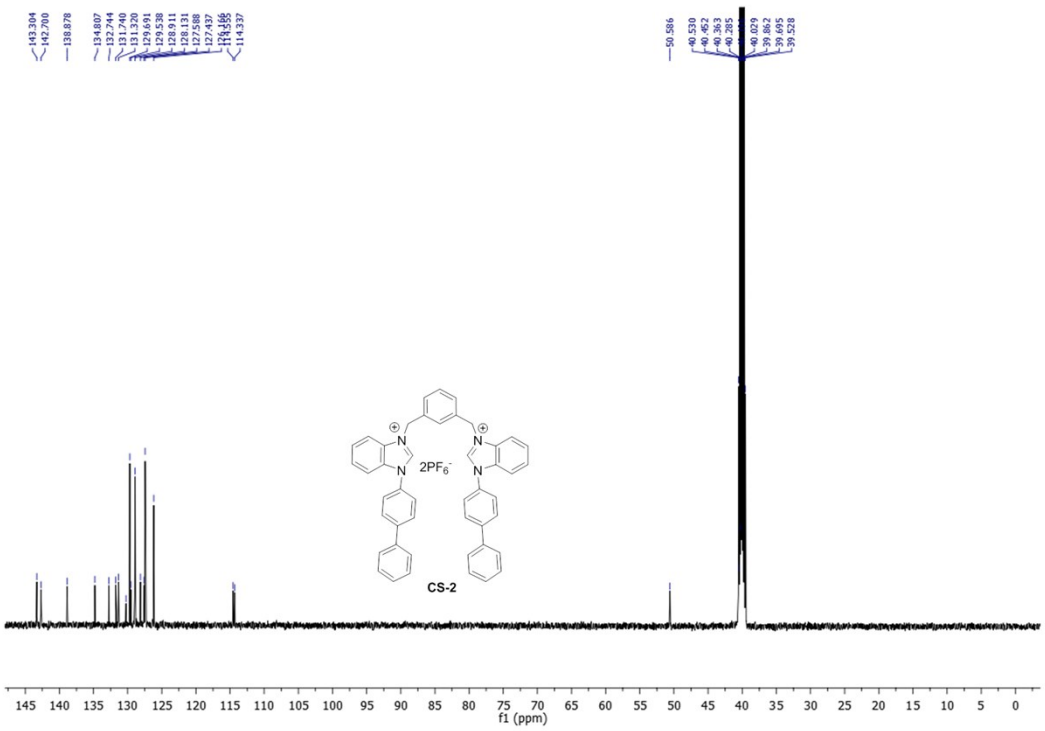


Figure S2. ^{1}H NMR and ^{13}C NMR of **CS-2**

Display Report

Analysis Info

Analysis Name	D:\MBBP\HRMS\MBBP.d	Acquisition Date	1/3/2015 4:31:00 PM
Method	tune_wide.m	Operator	Amrinder + Parteek
Sample Name	PP	Instrument	micrOTOF-Q II 228888.10356
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	650.0 Vpp	Set Divert Valve	Waste

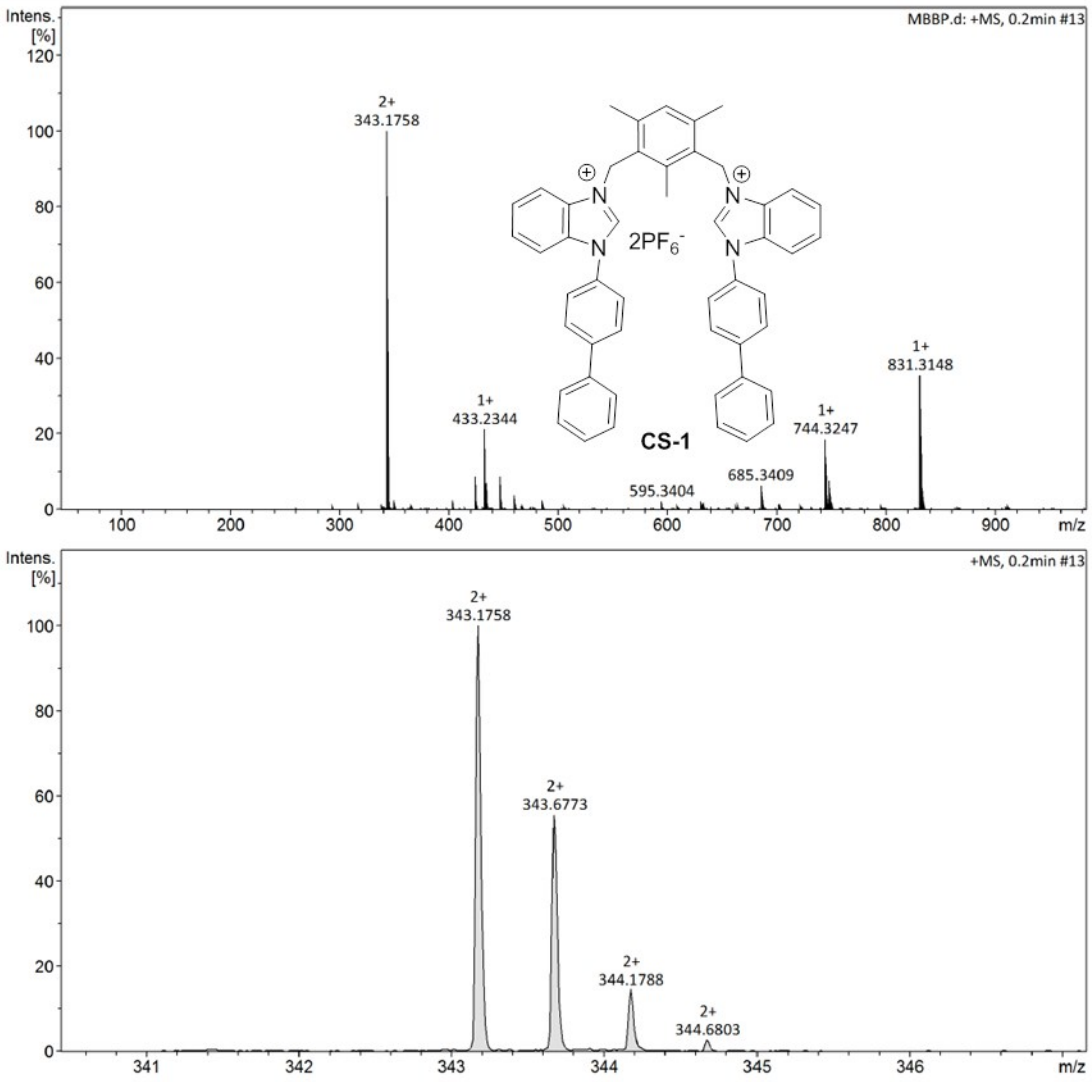


Figure S3. HRMS spectra of of **CS-1**

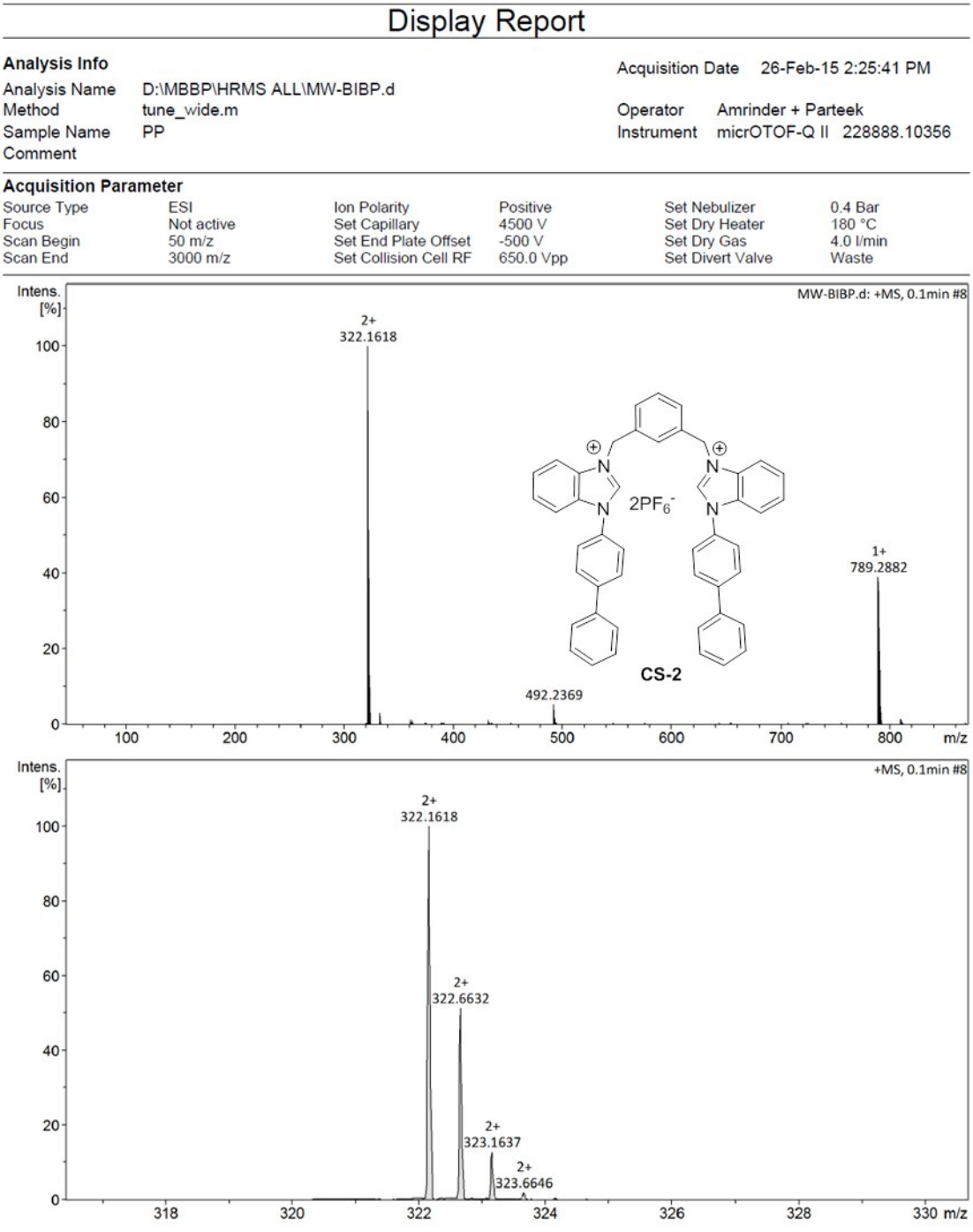


Figure S4. HRMS spectra of of **CS-2**

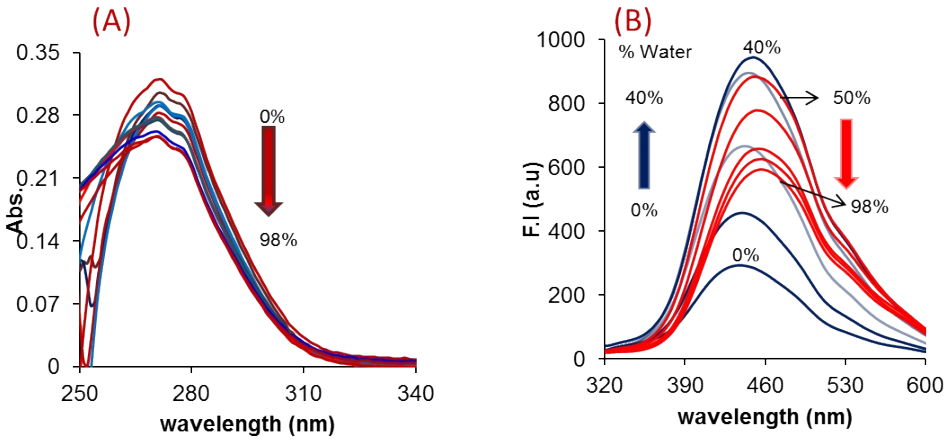


Figure S5. Change in absorption and emission spectrum of **CS-1** with increasing volume fractions of water.

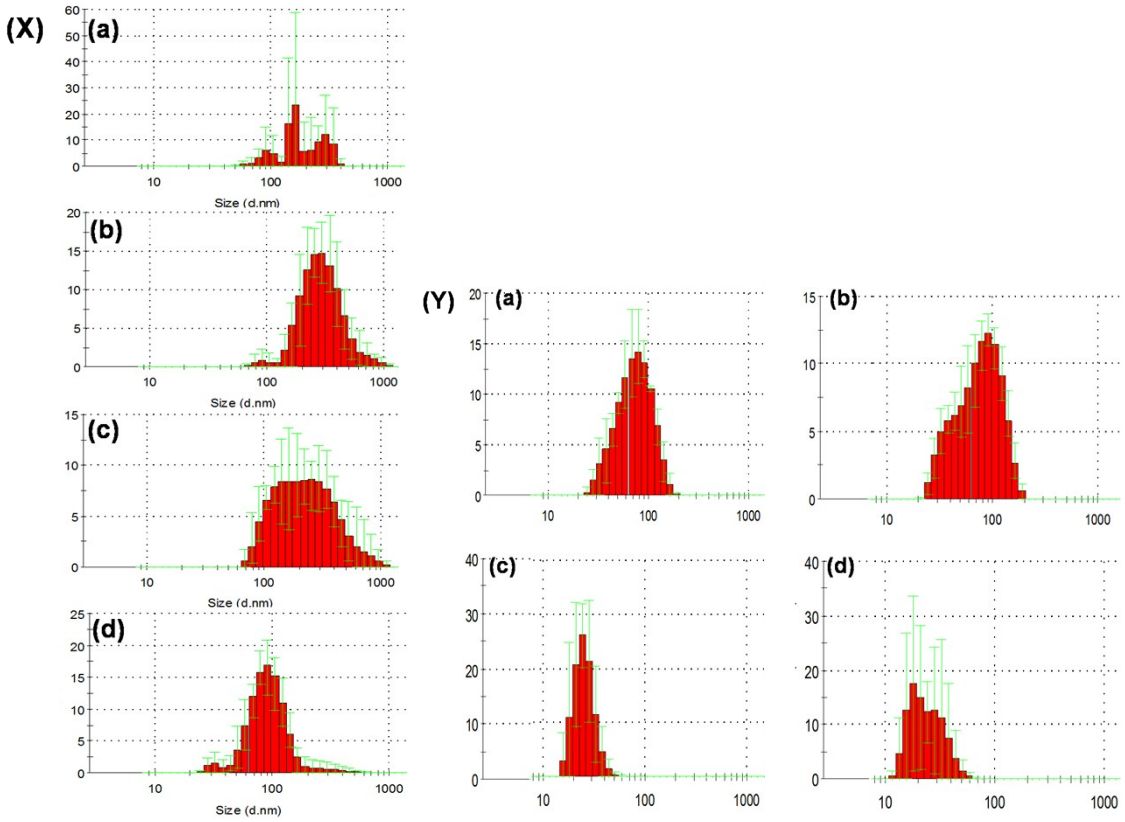


Figure S6 : (X) DLS studies of CS-1 (HEPES- DMSO 98:2) in the presence of ClO_4^-. (a) only CS-1; (b) CS-1 + ClO_4^- (10^{-11} M); (c) CS-1 + ClO_4^- (10^{-9} M); (d) CS-1 + ClO_4^- (10^{-6} M); **(Y)** DLS of CS-1 (a) after 1h (b) after 24h; DLS of CS-1+10^{-5} M ClO_4^- in water (c) after 1h (d) after 24 h.

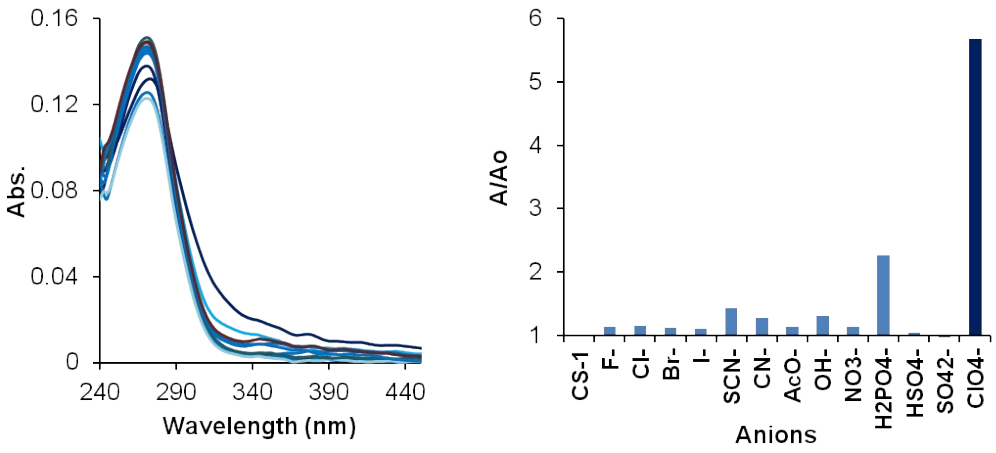


Figure S7. Effect of various anions (100 μM) on absorption spectrum of **CS-1** (2 μM) in HEPES buffer – 2% DMSO (pH 7.4).

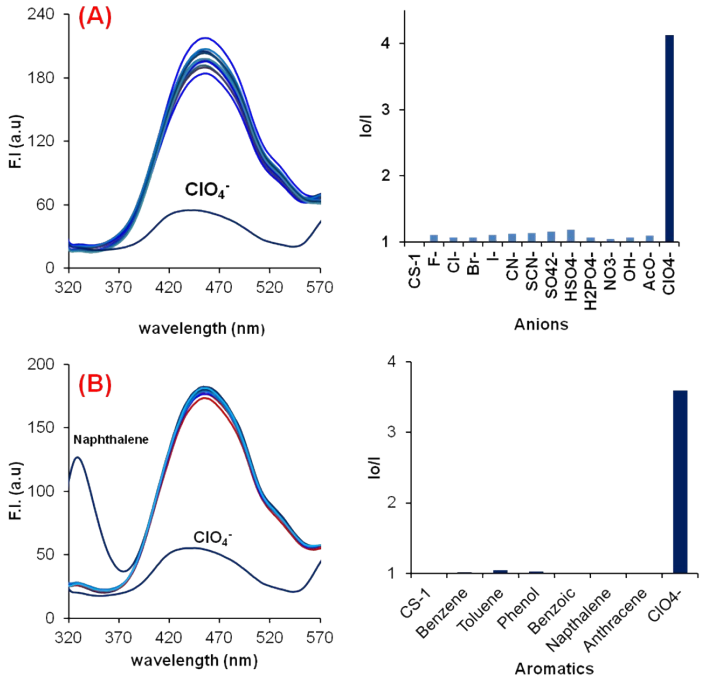


Figure S8. (A) Effect of various anions (100 μM) on emission spectrum (λex = 290 nm) of **CS-1** (2 μM) in HEPES buffer – 2% DMSO (pH 7.4); (B) Effect of various aromatic hydrocarbons (50 μM) on the emission spectrum (λex = 290 nm) of CS-1 (2 μM) in in HEPES buffer – 2% DMSO (pH 7.4).

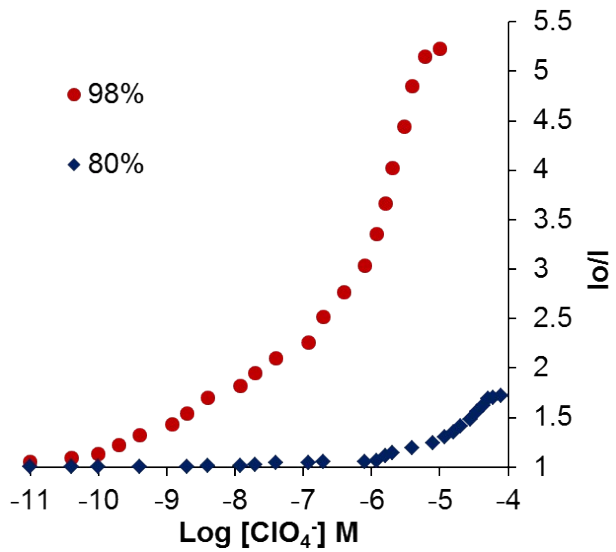


Figure S9. Effect of different water - DMSO ratio (80 : 20 and 98 : 2) on the sensitivity of **CS-1** for determination of ClO_4^-.

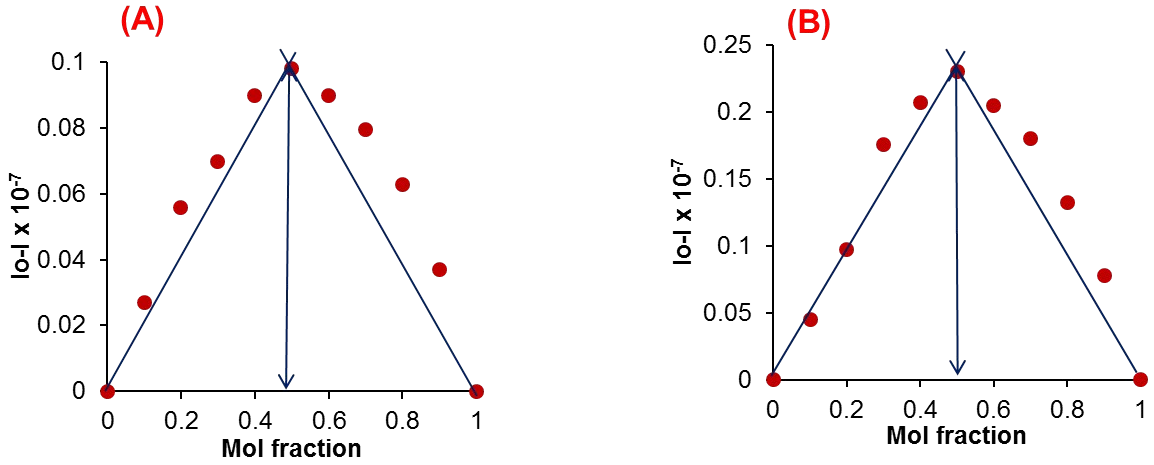


Figure S10. Job's plot of chemosensor **CS-1** (A) through absorption, (B) through emission in HEPES buffer – 2% DMSO solution (pH 7.4).

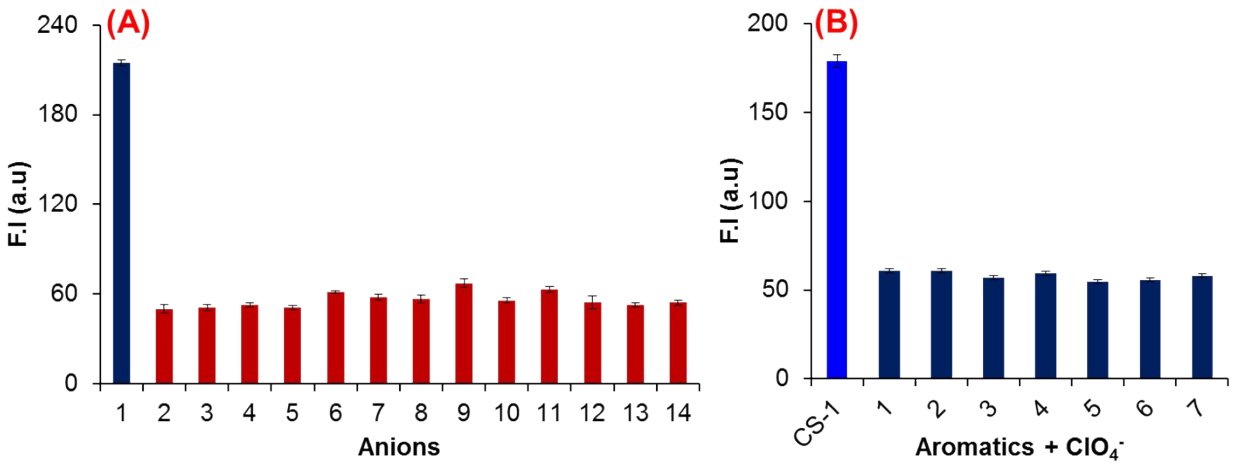


Figure S11. (A) Effect of different anions on the fluorescence quenching by ClO_4^- (1) **CS-1** only; (2) ClO_4^- only; (3) F^- + ClO_4^-; (4) Cl^- + ClO_4^-; (5) Br^- + ClO_4^-; (6) I^- + ClO_4^-; (7) CN^- + ClO_4^-; (8) OH^- + ClO_4^-; (9) SO_4^{2-} + ClO_4^-; (10) HSO_4^- + ClO_4^-; (11) $H_2PO_4^-$ + ClO_4^-; (12) AcO^- + ClO_4^-; (13) NO_3^- + ClO_4^-; (14) SCN^- + ClO_4^-. **(B)** Effect of various aromatic hydrocarbons (50 μM) on the emission spectrum (λex = 290 nm) of **CS-1** (2 μM) in the presence of ClO_4^- ions (1000 nM) (1) ClO_4^- only; (2) Benzene; (3) Toluene; (4) Phenol; (5) Benzoic acid; (6) Naphthalene; (7) Anthracene (error less than 3.1%).

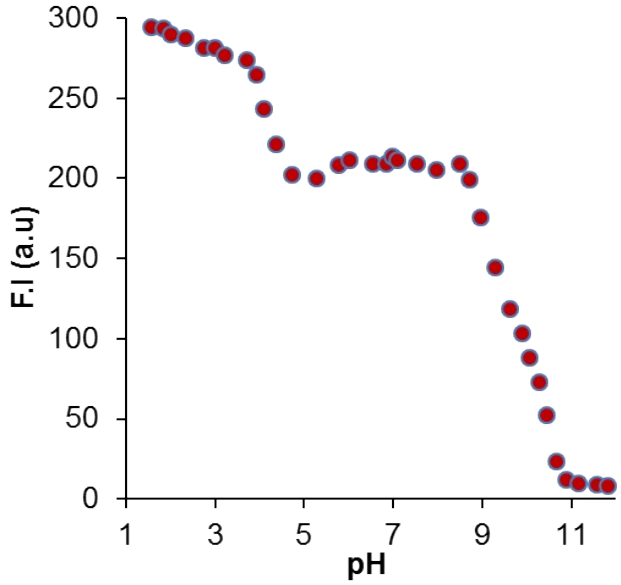


Figure S12: Effect of pH on the fluorescence intensity of **CS-1** (H_2O – DMSO, 98:2)

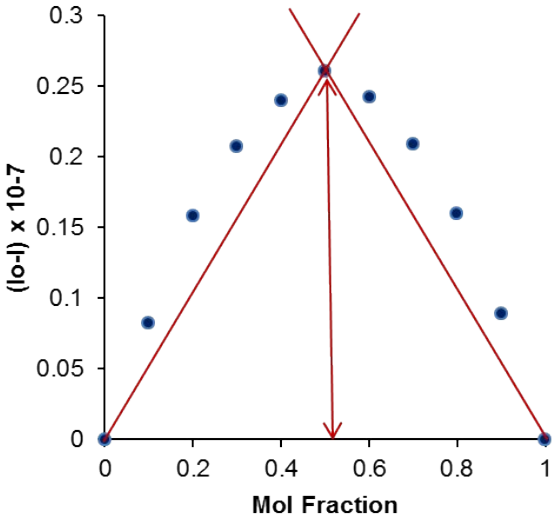


Figure S13. Job's plot of **CS-2** in HEPES buffer – 2% DMSO solution (pH 7.4).

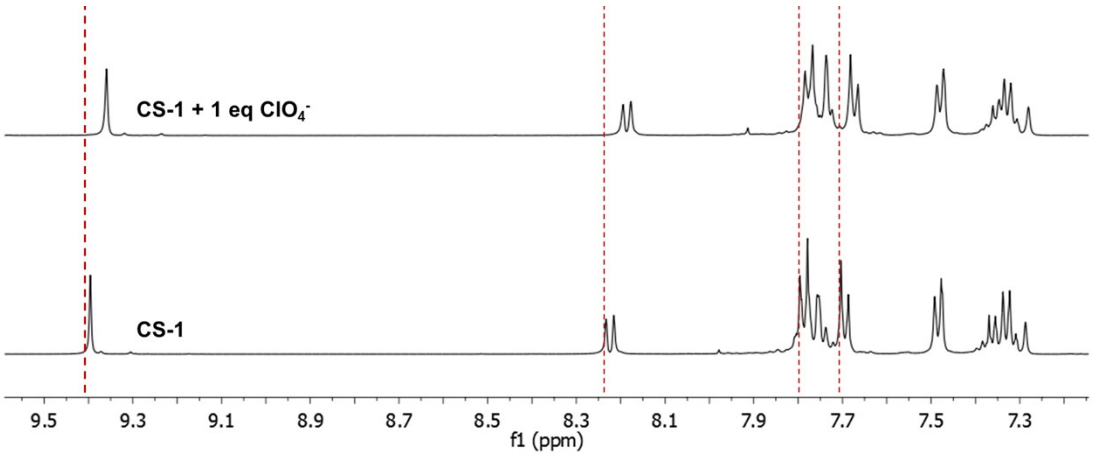


Figure S14. ^{1}H NMR titration of **CS-1** with ClO_4^- in DMSO - Water (7:3) ratio.

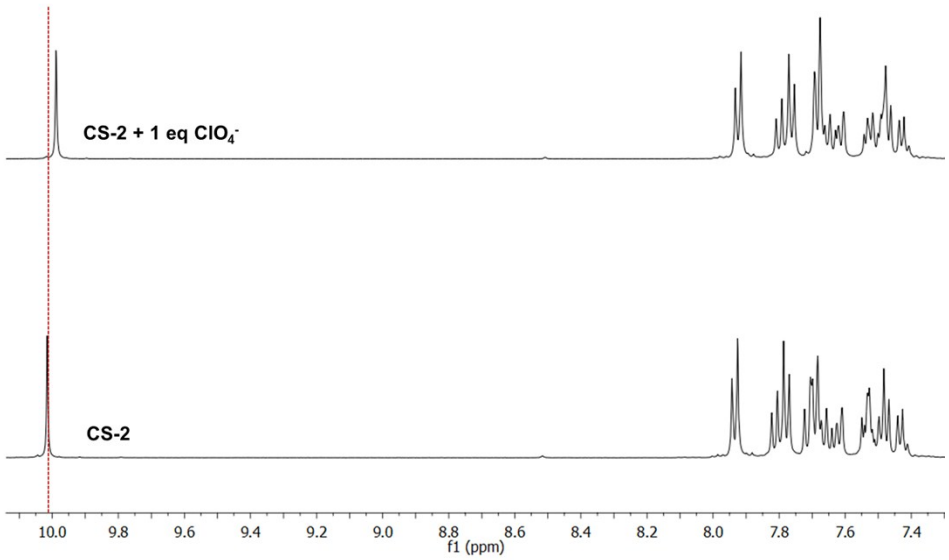


Figure S15. ^{1}H NMR titration of **CS-2** with ClO_4^- in DMSO - Water (7:3) ratio.

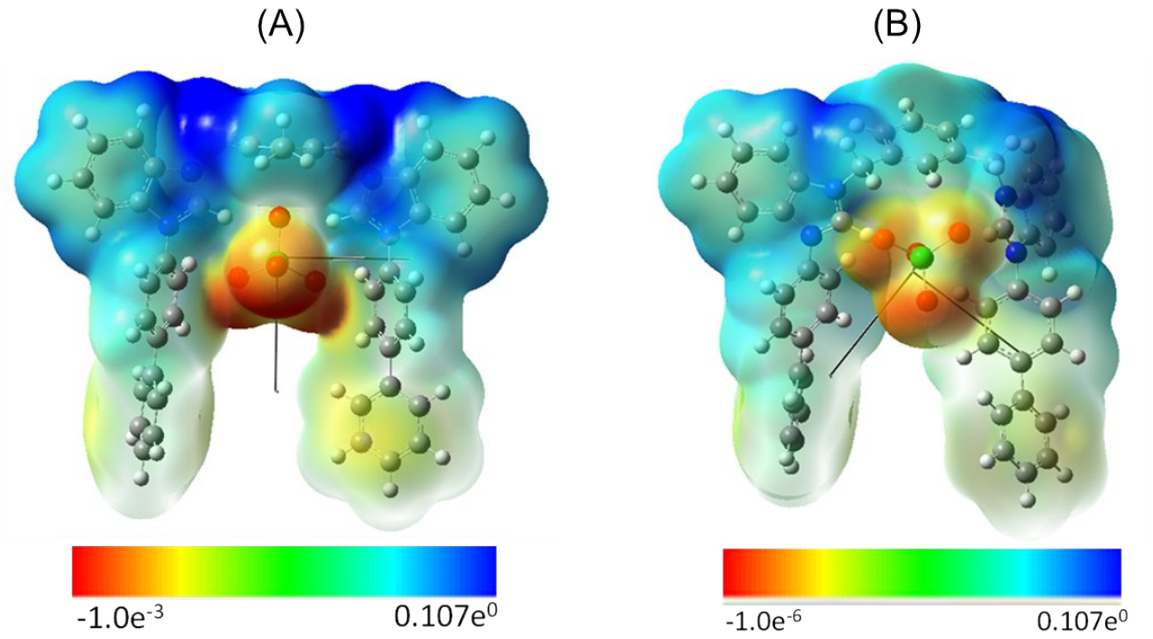


Figure S16. Isosurface energy map of (**A**) **CS-1** with ClO_4^- and (**B**) **CS-2** with ClO_4^-.

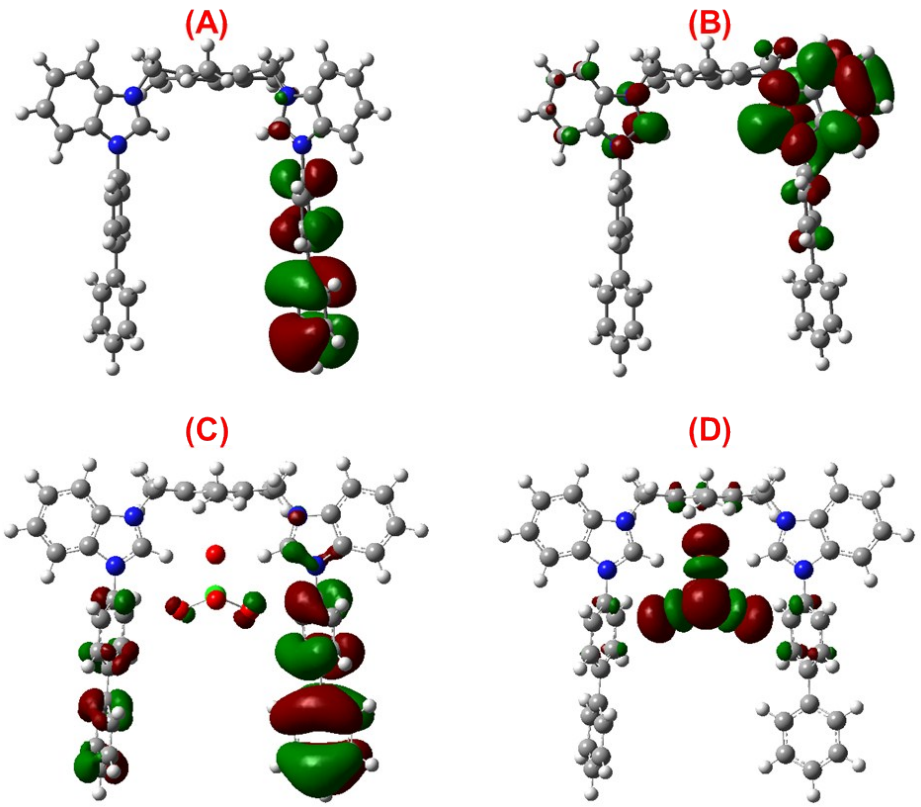


Figure S17. (**A**) HOMO of **CS-1**, (**B**) LUMO of **CS-1**, (**C**) HOMO of **CS-1** + ClO_4^- Complex, (**D**) LUMO of **CS-1** + ClO_4^-.

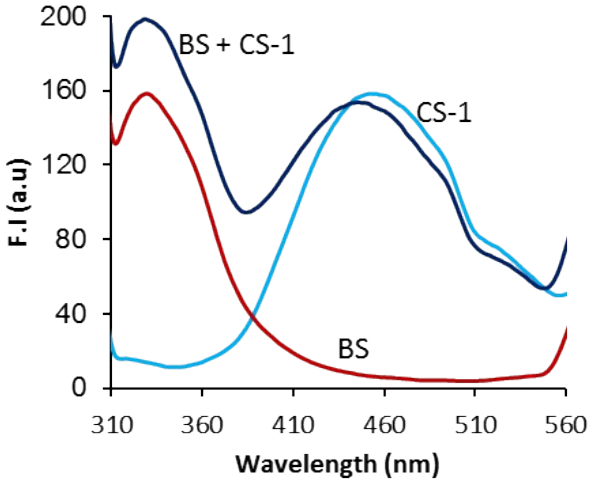


Figure S18. Emission spectrum of **CS-1**, blood serum (BS) and **CS-1** + blood serum in 98% aqueous buffered solution.