

Boron-Dipyrrin-Mercury(II) Complex as Fluorescence Turn-On Sensor for Chloride and Applications Towards Logic Gates

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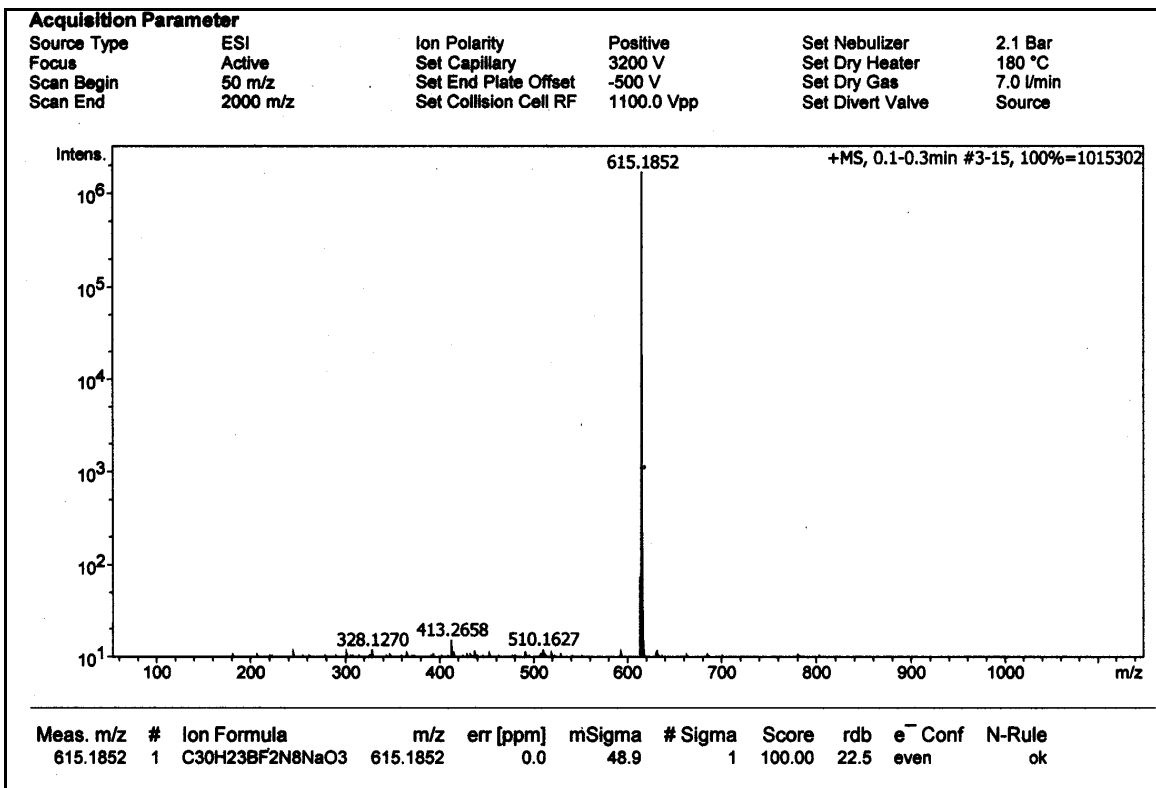
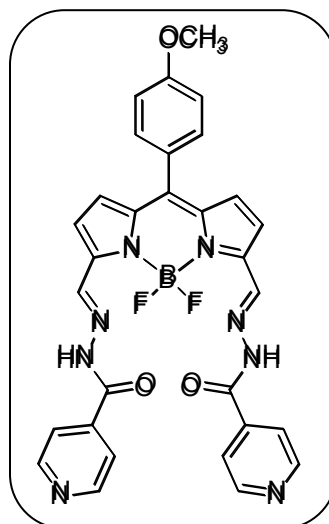


Figure S1: HRMS spectrum of compound 1

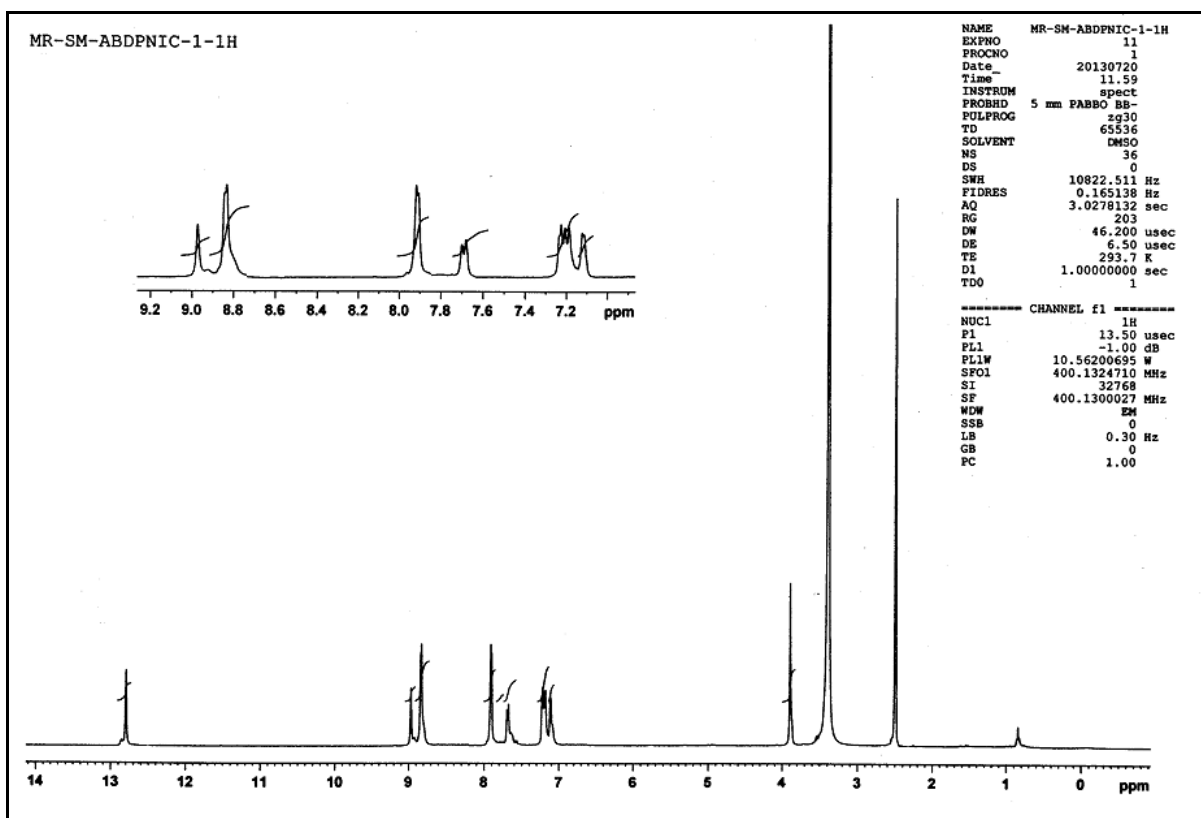
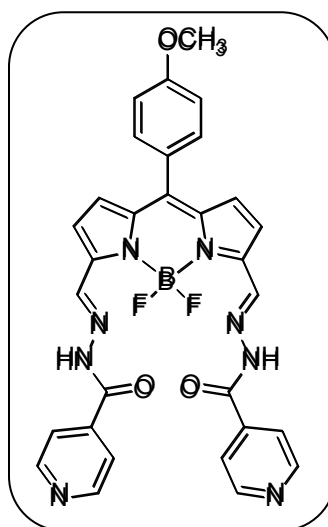


Figure S2: ¹H NMR spectrum of compound 1 recorded in DMSO-d₆

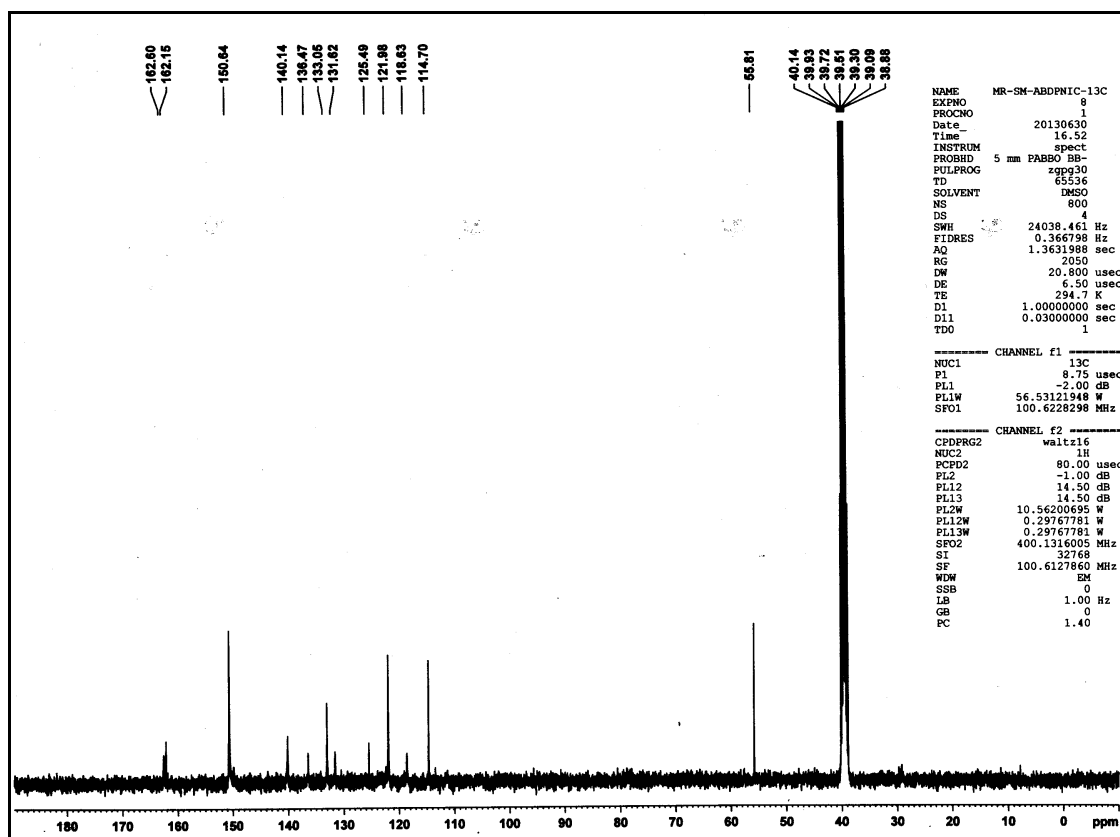
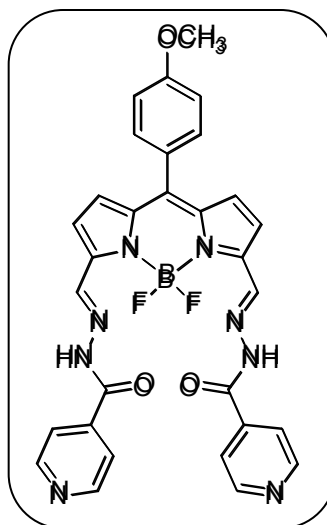


Figure S3: ^{13}C NMR spectrum of compound 1 recorded in DMSO-d_6

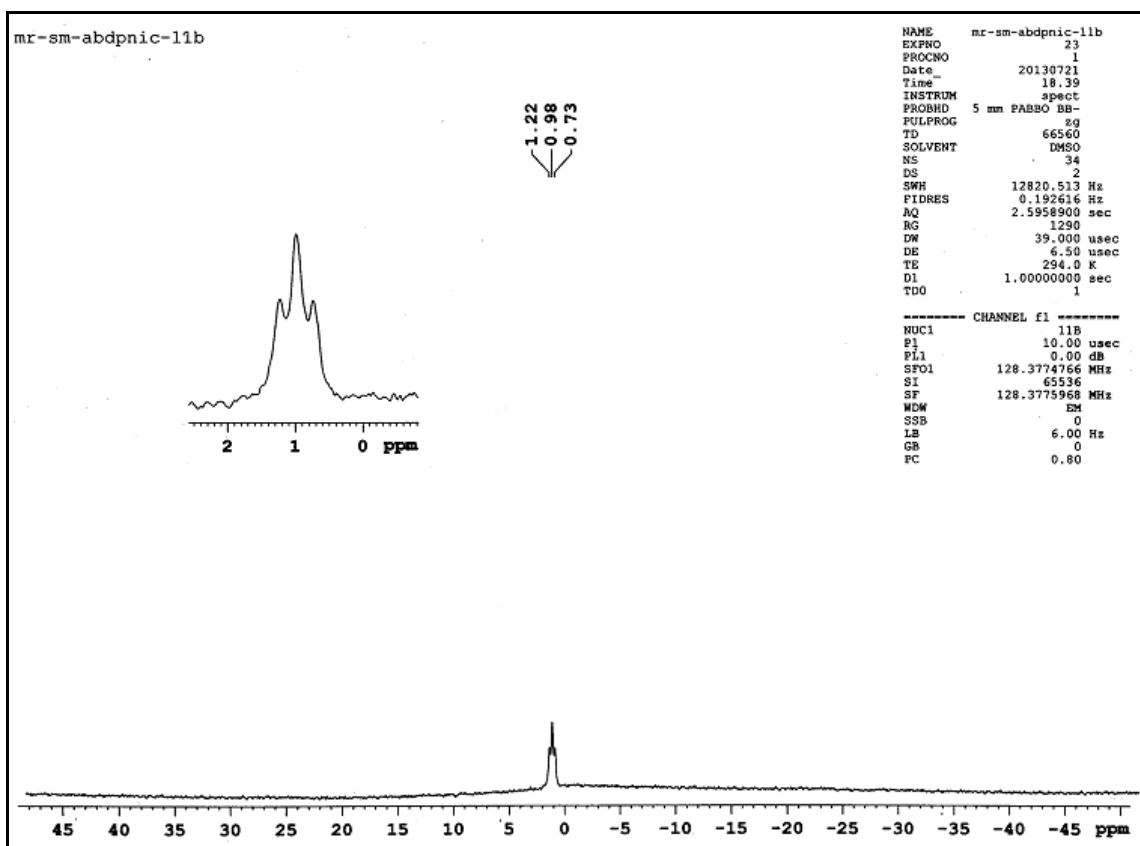
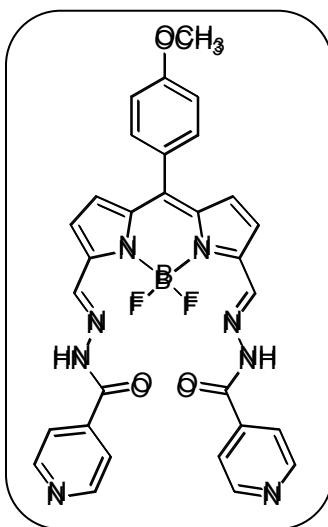


Figure S4: ^{11}B NMR spectrum of compound **1** recorded in DMSO- d_6 . Inset shows the expansion

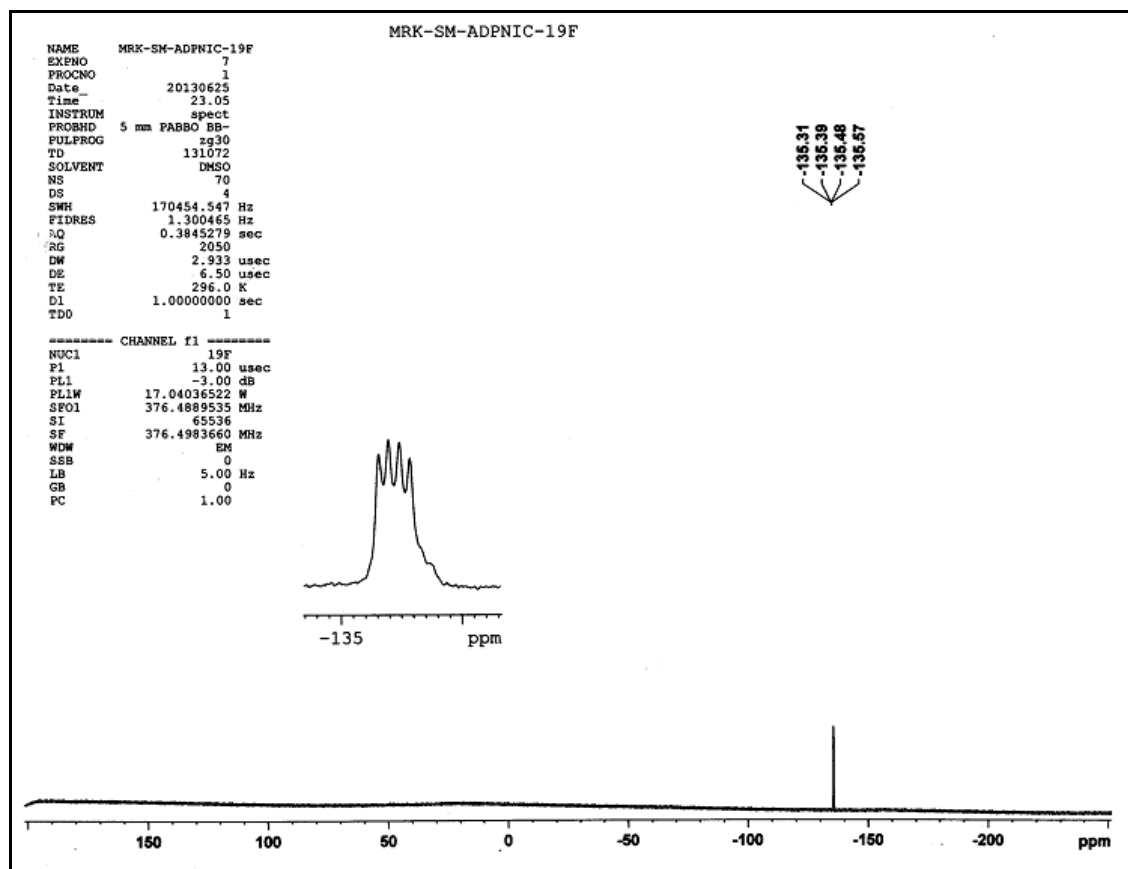
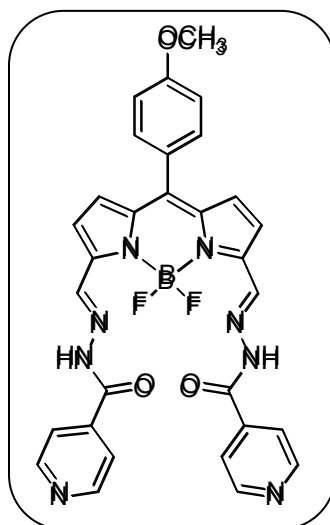


Figure S5: ^{19}F NMR spectrum of compound **1** recorded in DMSO-d_6 . Inset shows the expansion

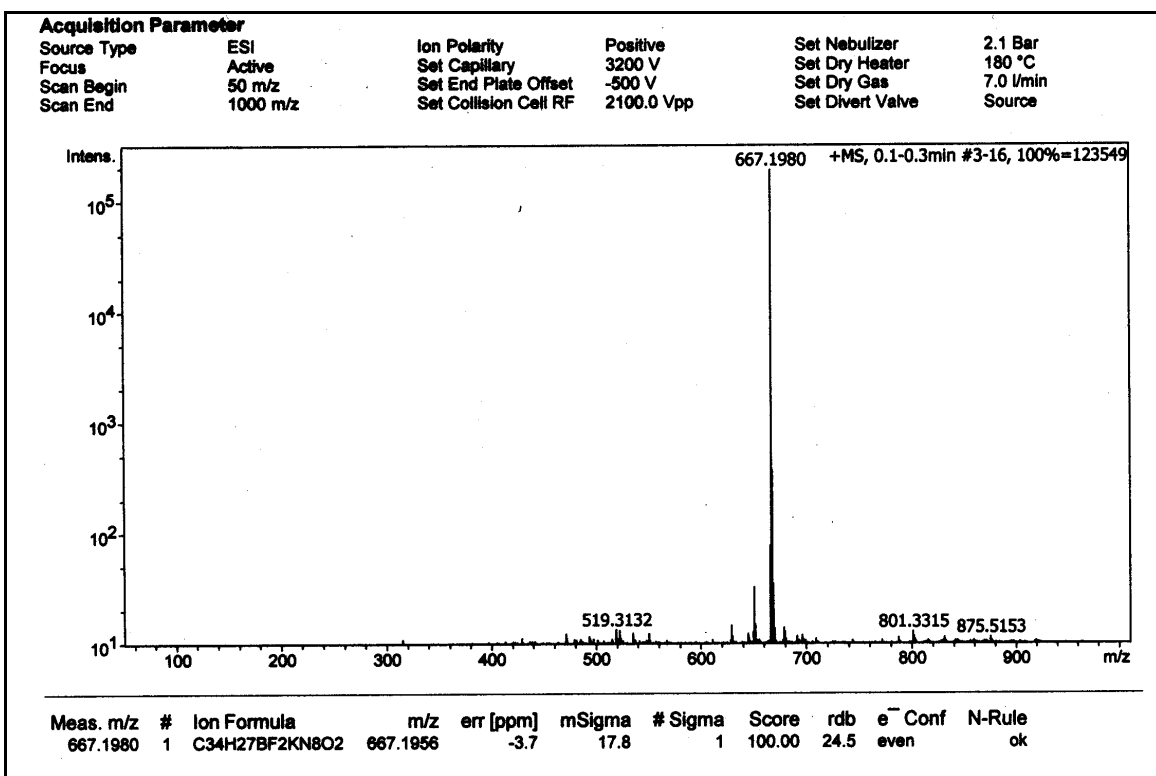
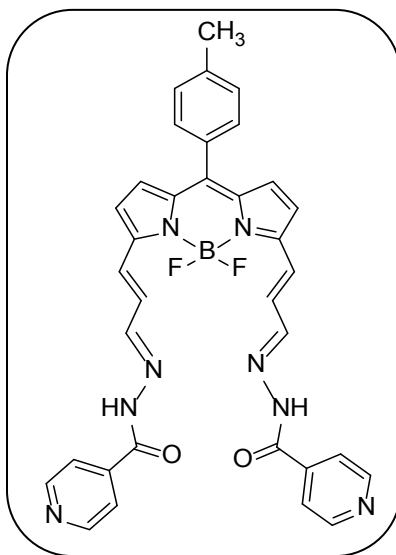


Figure S6: HRMS spectrum of compound 2

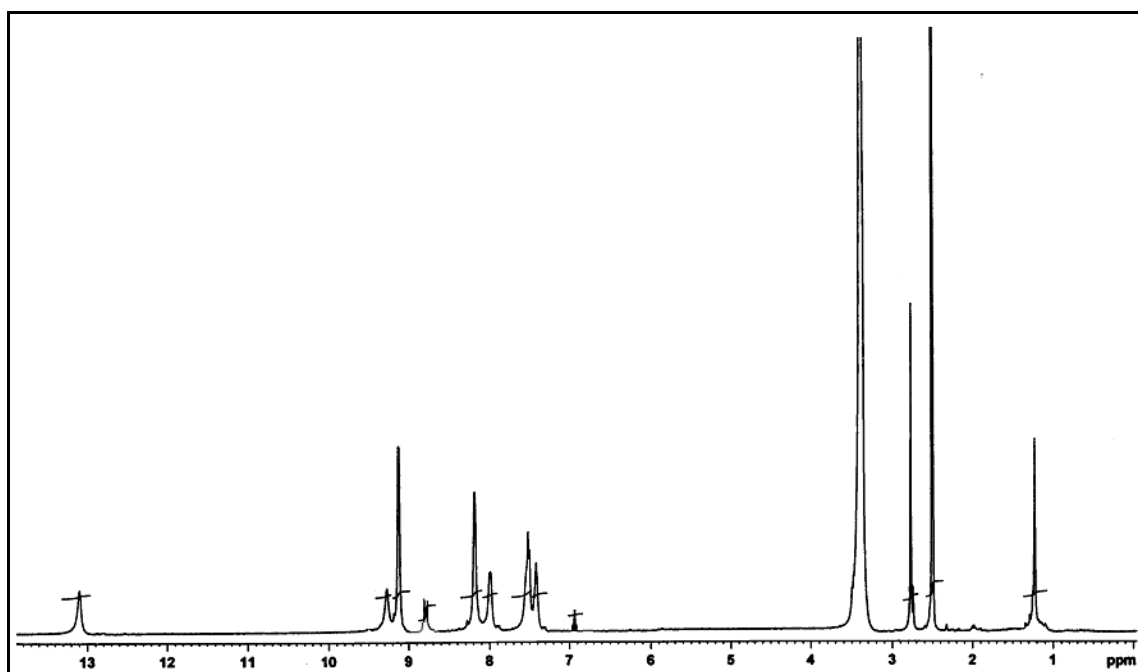
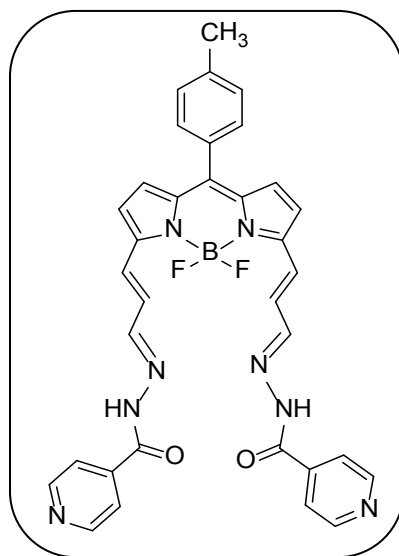


Figure S7: ¹H NMR spectrum of compound 2 recorded in DMSO-d₆

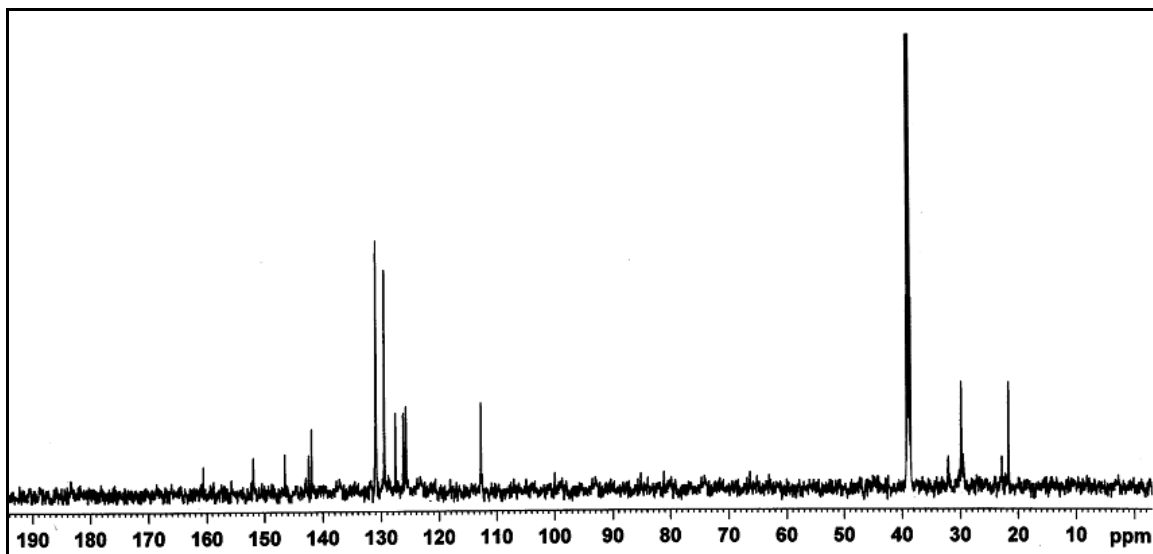
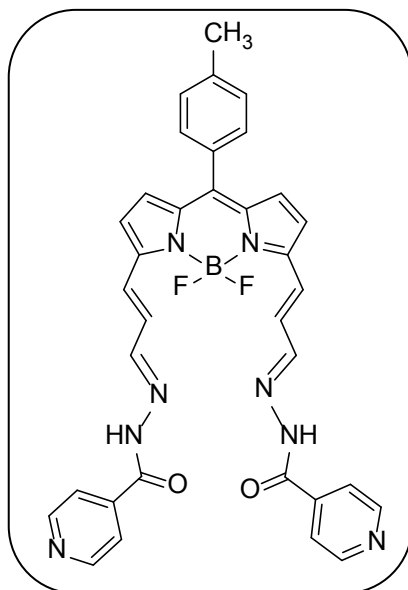


Figure S8: ¹³C NMR spectrum of compound **2** recorded in DMSO-d₆

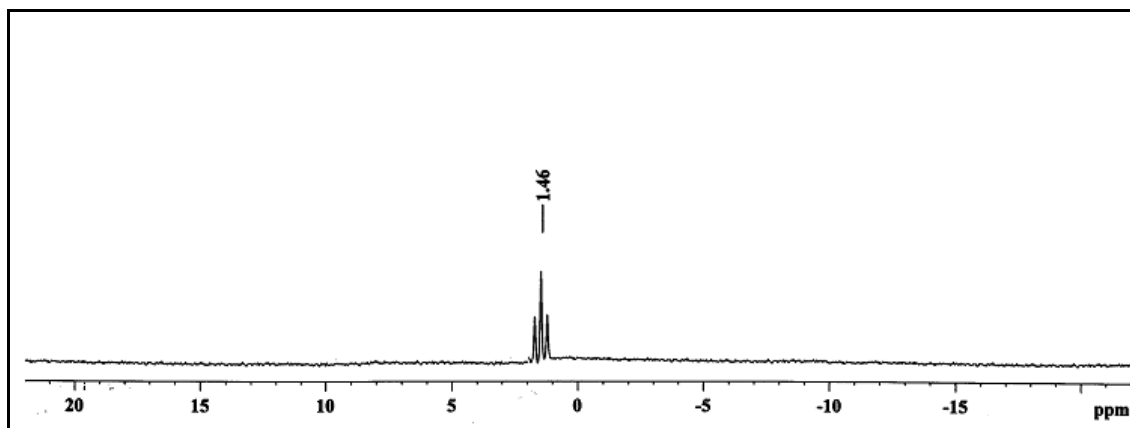
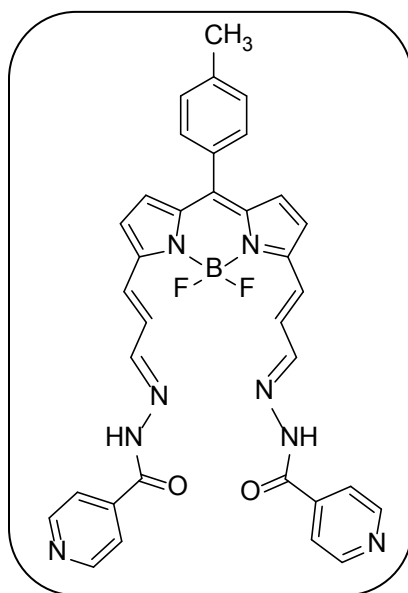


Figure S9: ¹¹B NMR spectrum of compound **2** recorded in DMSO-d₆. Inset shows the expansion

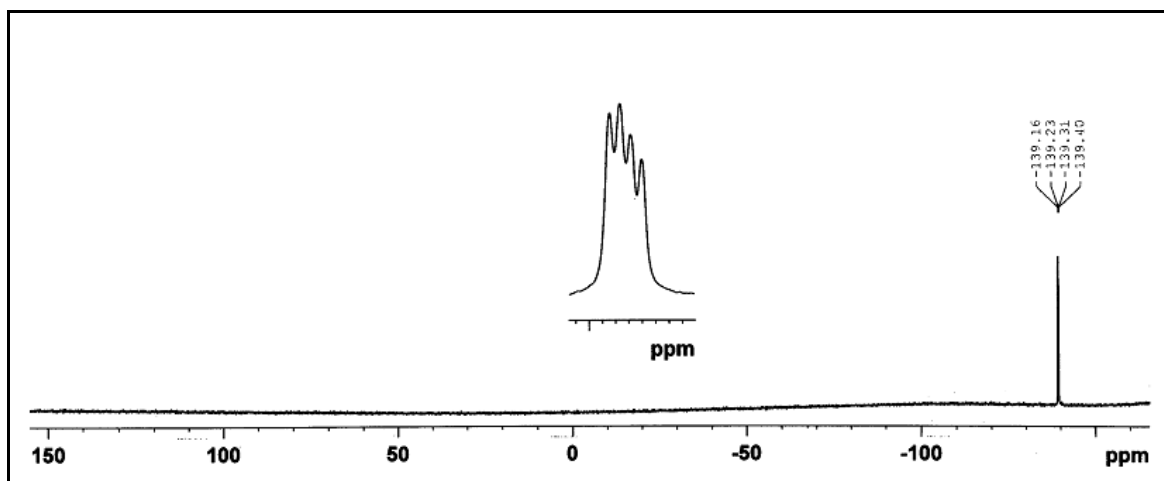
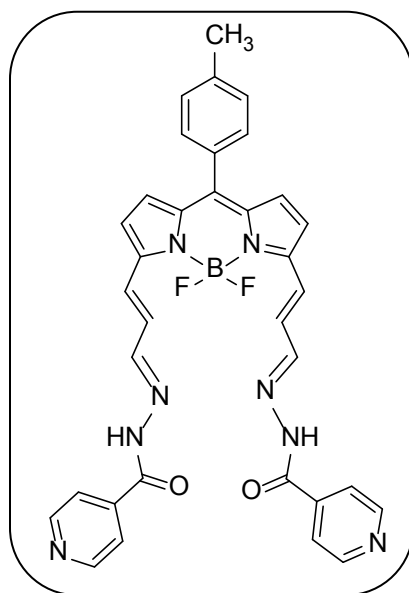


Figure S10: ¹⁹F NMR spectrum of compound **2** recorded in DMSO-d₆. Inset shows the expansion

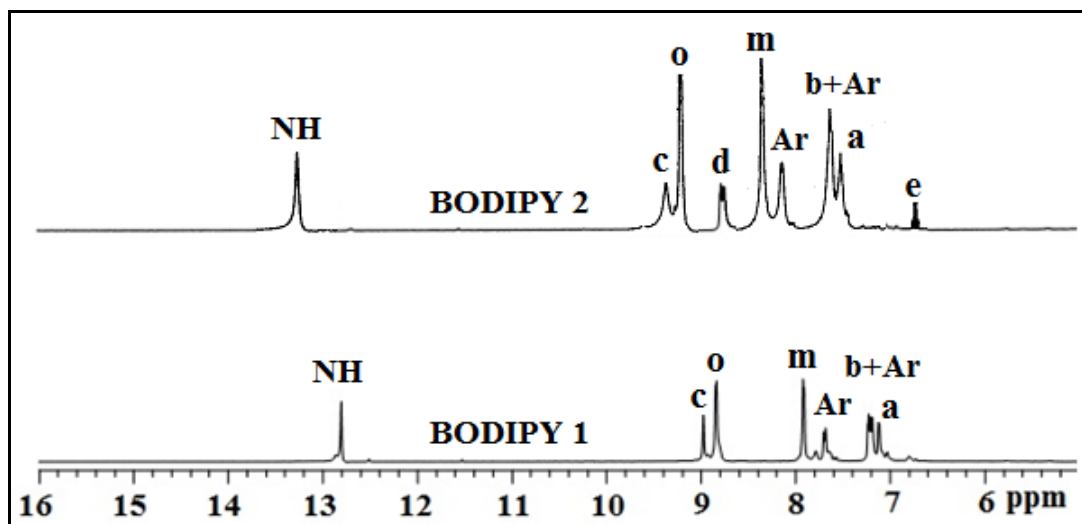


Figure S11: Comparison of the partial ¹H NMR spectra of BODIPYs **1** and **2** (16 mM) recorded in DMSO-d₆

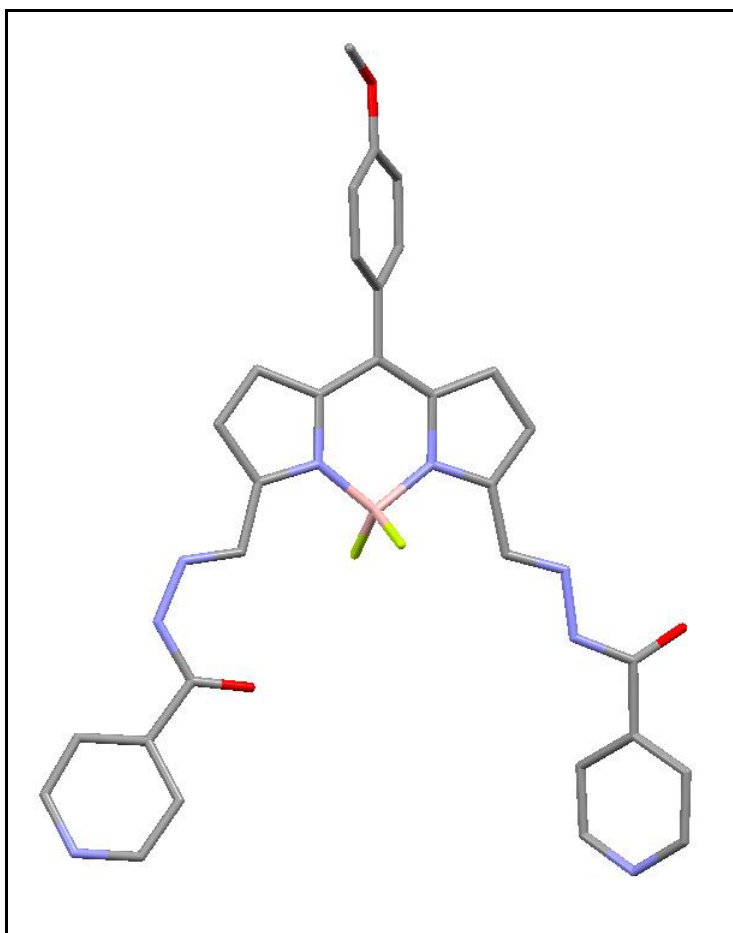


Figure S12: Crystal structure of BODIPY 1. Hydrogen atoms and solvent molecules are omitted for clarity.

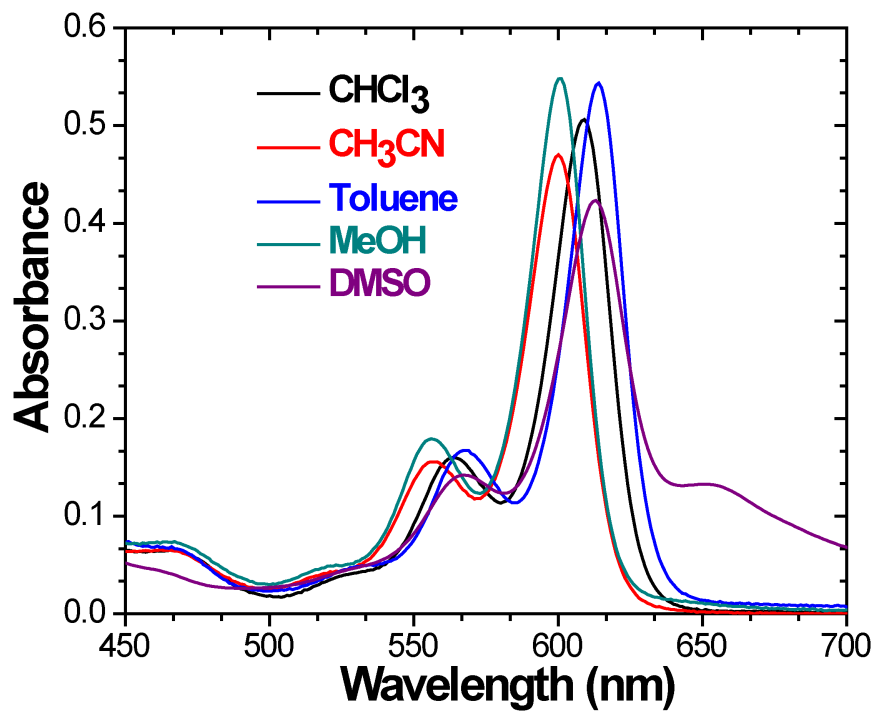


Figure S13: Absorption spectra of compound **1** (5 μM) recorded in different solvents

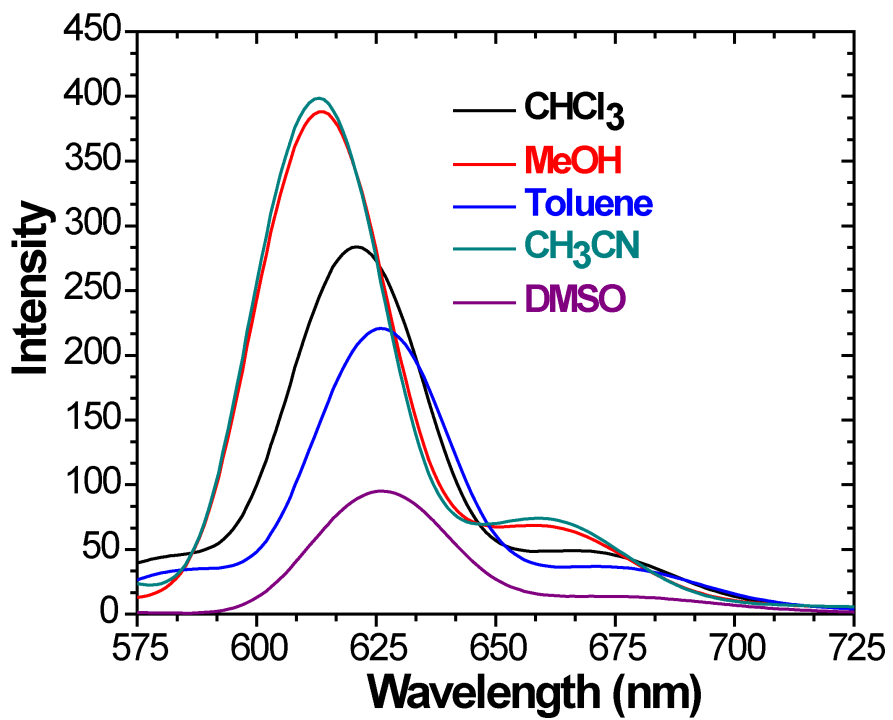


Figure S14: Emission spectra of compound **1** (5 μM) recorded in different solvents

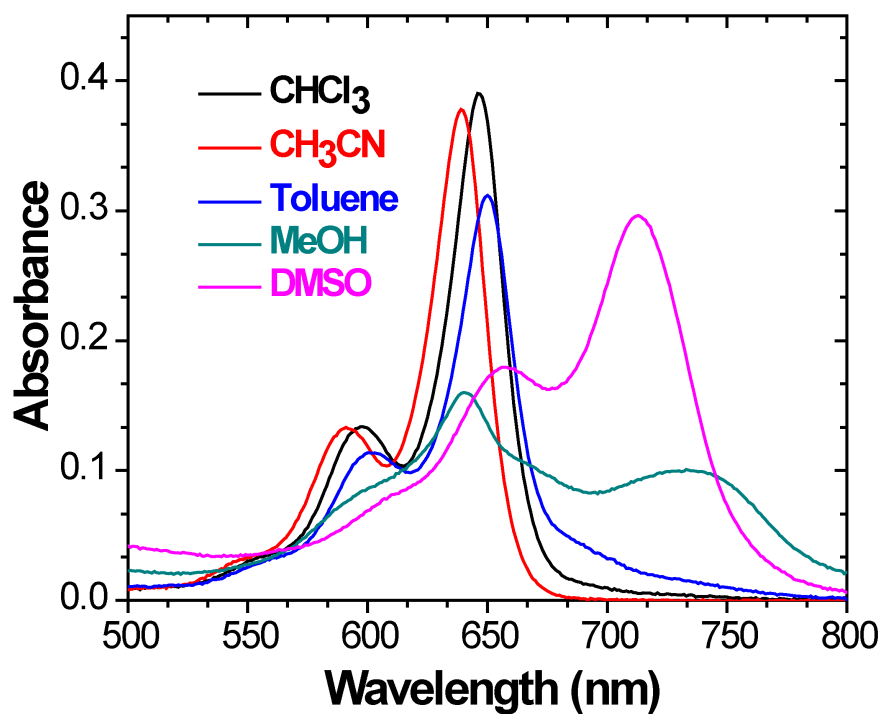


Figure S15: Absorption spectra of compound 2 (5 μM) recorded in different solvents

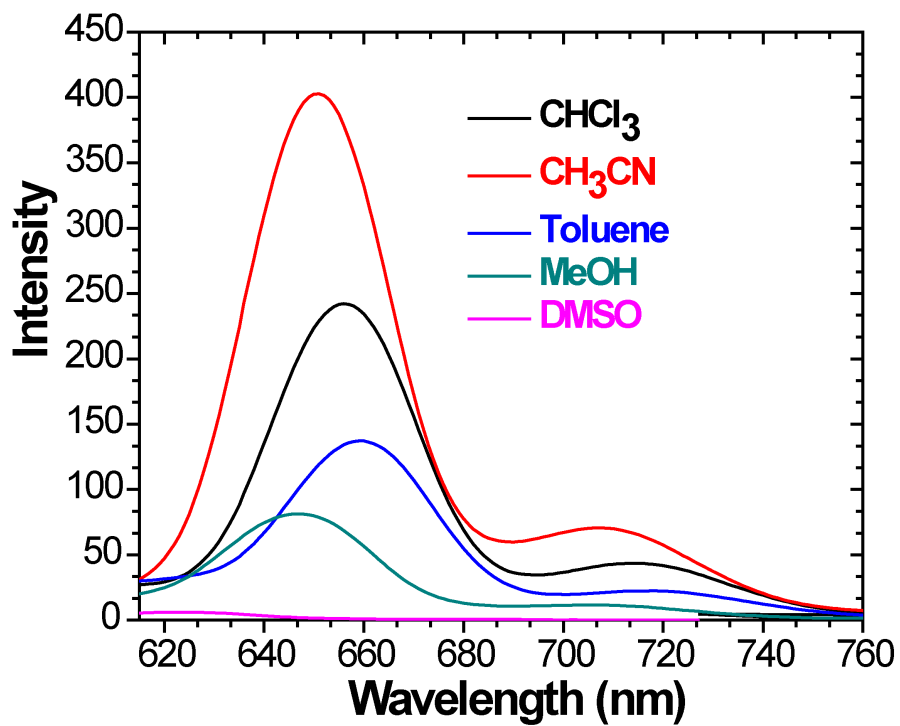


Figure S16: Emission spectra of compound 2 (5 μM) recorded in different solvents



Figure S17: Color change induced upon addition of various (excess equivalents of perchlorate salts) metal ions to BODIPY **1** (5×10^{-6} M) in $\text{CH}_3\text{CN}/\text{PBS}$ (7:3; v/v, pH 7.4) under daylight: From left to right: (1) no metal ion, (2) Na^+ , (3) K^+ , (4) Mn^{2+} , (5) Hg^{2+} , (6) Fe^{2+} , (7) Co^{2+} , (8) Ni^{2+} , (9) Cu^{2+} and (10) Zn^{2+} respectively.



Figure S18: Color change induced upon addition of various (excess equivalents of perchlorate salts) metal ions to BODIPY **1** (5×10^{-6} M) in $\text{CH}_3\text{CN}/\text{PBS}$ (7:3; v/v, pH 7.4) under UV lamp: From left to right: (1) no metal ion, (2) Na^+ , (3) K^+ , (4) Mn^{2+} , (5) Hg^{2+} , (6) Fe^{2+} , (7) Co^{2+} , (8) Ni^{2+} , (9) Cu^{2+} and (10) Zn^{2+} respectively.

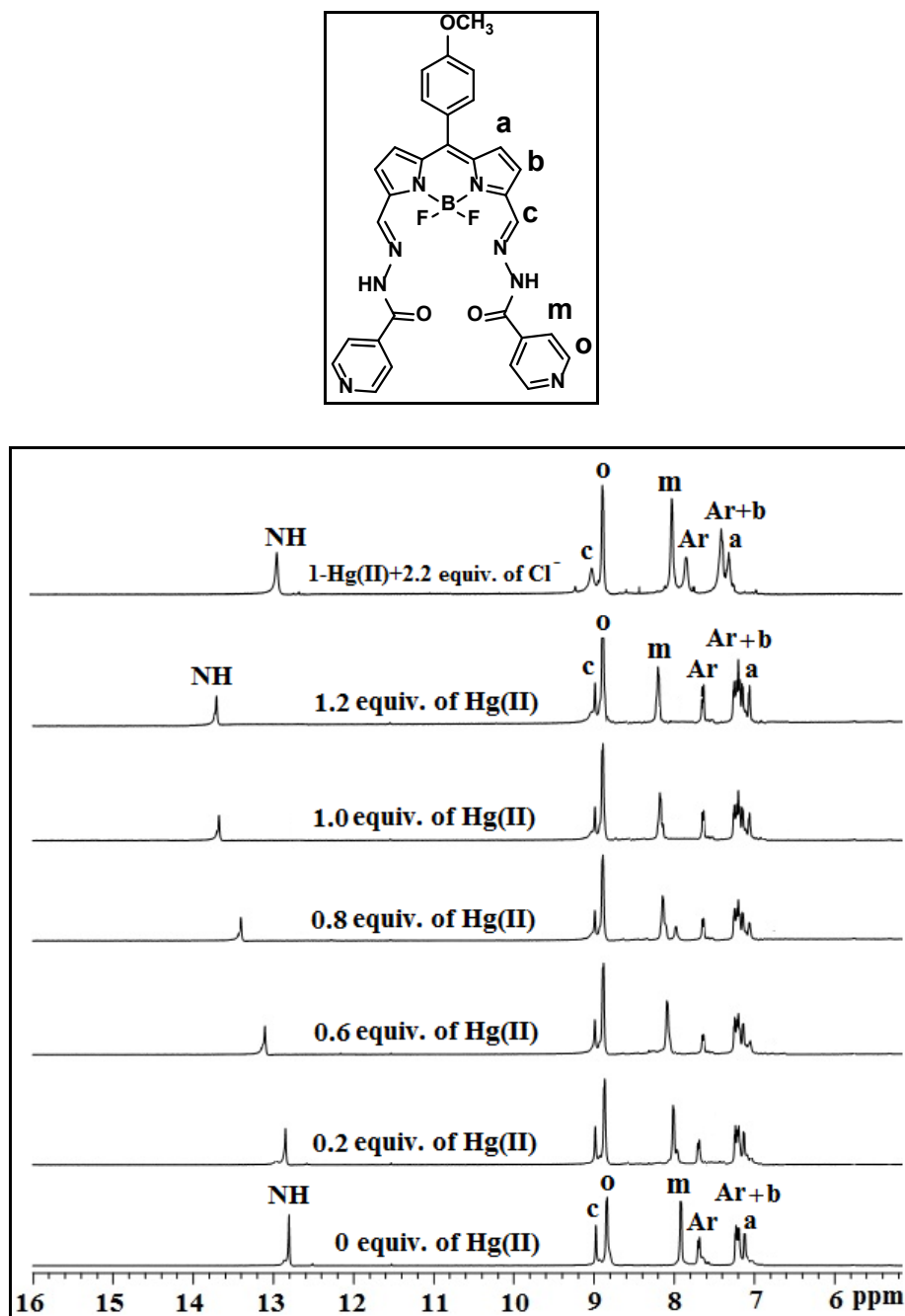


Figure S19: Partial ¹H NMR spectra of BODIPY 1 (16 mM) in the presence of increasing concentrations of Hg²⁺ ions (0-1.2 equiv.) recorded in CD₃CN/D₂O. Top: Partial ¹H NMR spectra of BODIPY 1-Hg(II) complex (16 mM) obtained upon addition of Cl⁻ (TBACl) ion (2.2 equiv.) recorded in CD₃CN/D₂O which is matching with the spectra of BODIPY 1 in absence of Hg²⁺ ion.

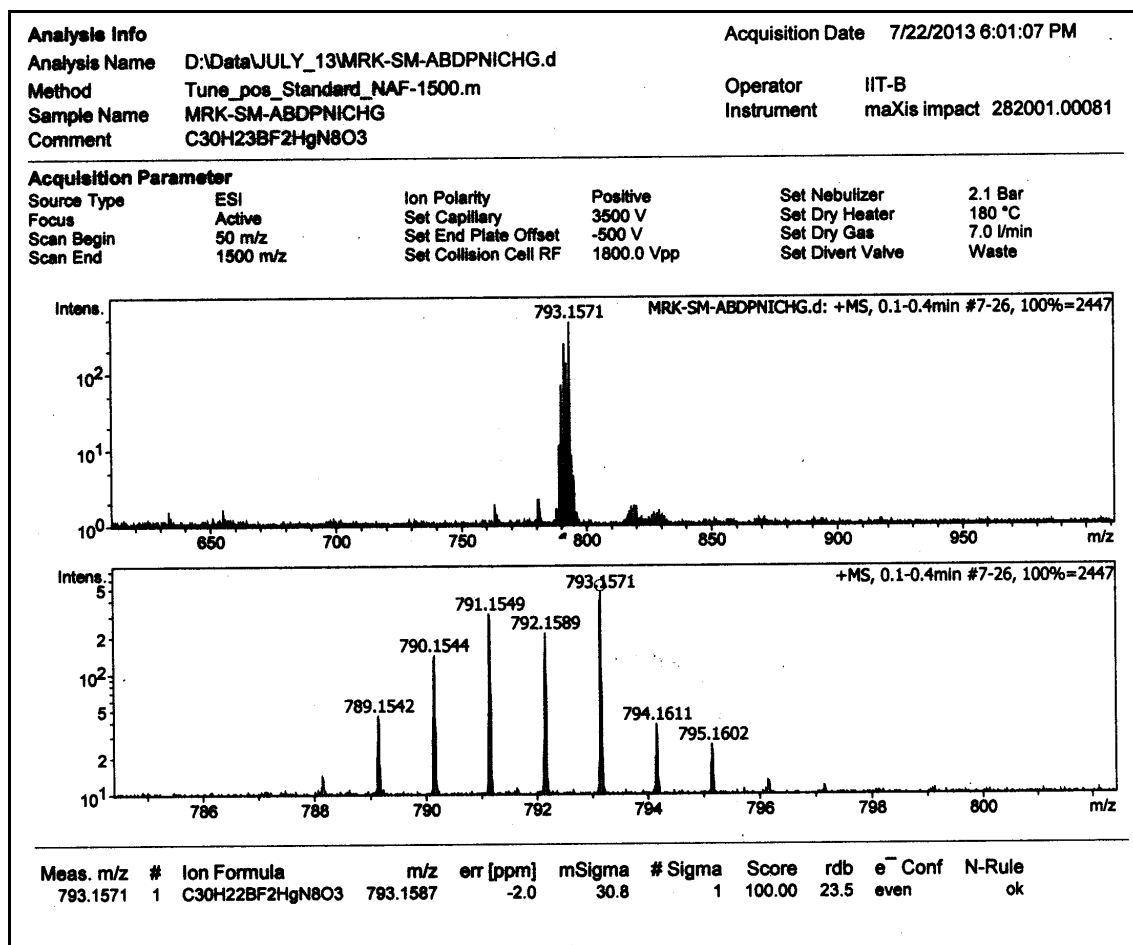


Figure S20: HR-MS spectrum showing the molecular ion peak for the 1:1 complex formed between compound **1** and Hg²⁺ ion during titration (top) and expansion of the molecular ion peak (down).

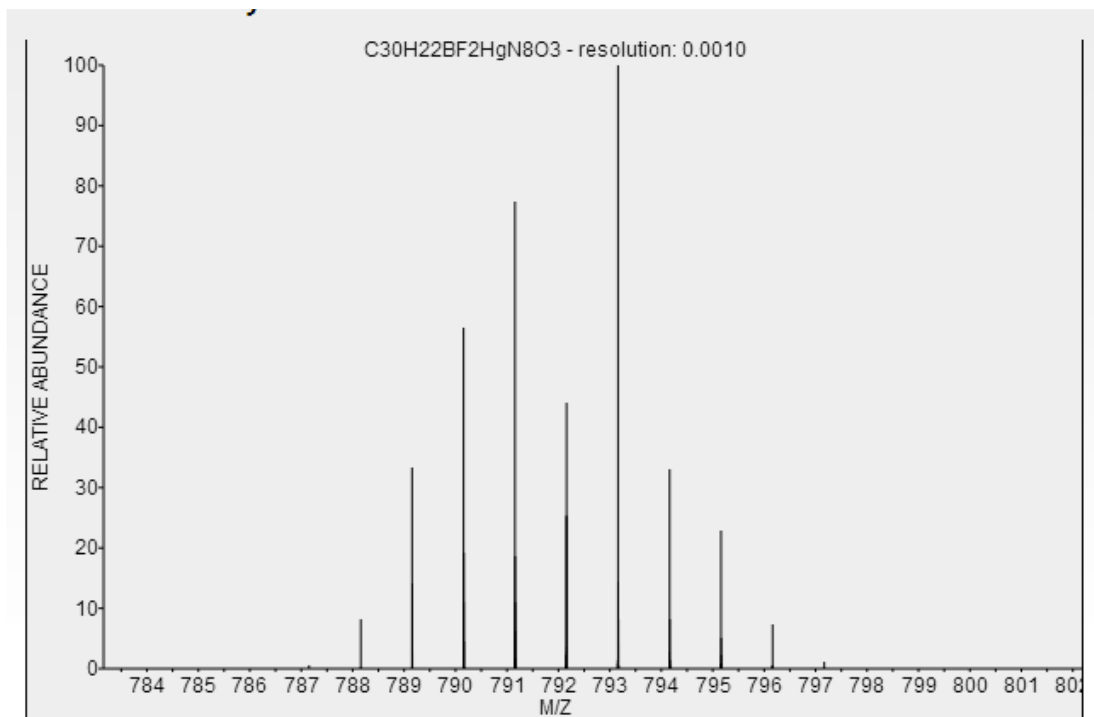


Figure S21: The calculated isotopic peak pattern for the 1:1 complex formed between BODIPY **1** and Hg⁺² ions.

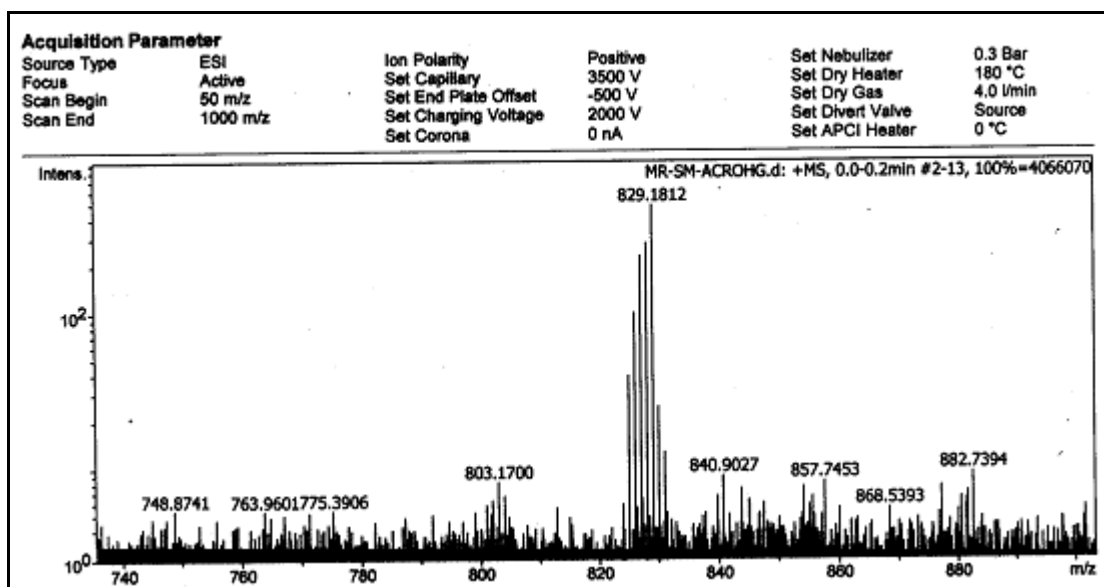


Figure S22: ESI mass spectrum showing the molecular ion peak for the 1:1 complex formed between BODIPY 2 and Hg^{+2} ions during titration.

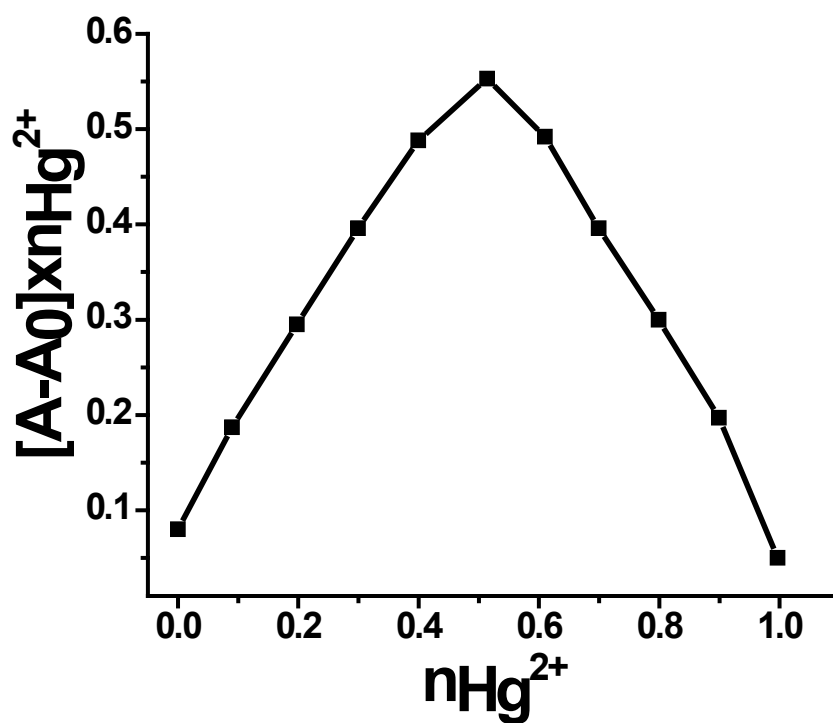


Figure S23. Job's plot for the evolution of binding stoichiometry between BODIPY **1** and Hg^{2+} in $\text{CH}_3\text{CN}/\text{PBS}$ (7:3; v/v, pH 7.4) solution. Where $n_{\text{Hg}^{2+}}$ is mole fraction of the Hg^{2+} ion added and A is absorbance of compound **1** in the presence of Hg^{2+} and A_0 is the absorbance of compound **1** in the absence of Hg^{2+} which forms 1:1 complex. The total $[\text{compound } \mathbf{1}] + [\text{Hg}^{2+}] = 1.0 \times 10^{-4} \text{ M}$.

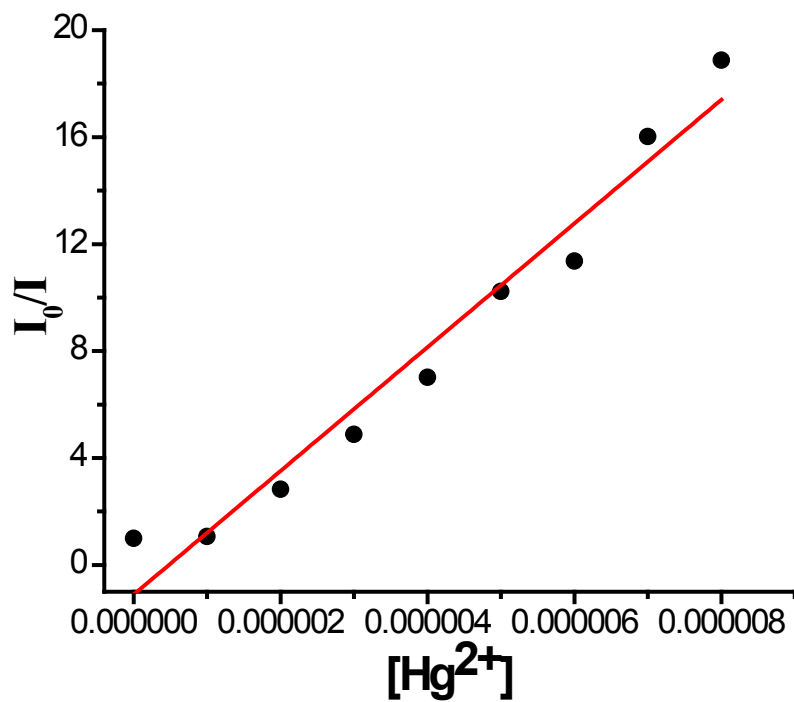


Figure S24: Determination of Stern-Volmer quenching constant for compound **1**- Hg^{2+}

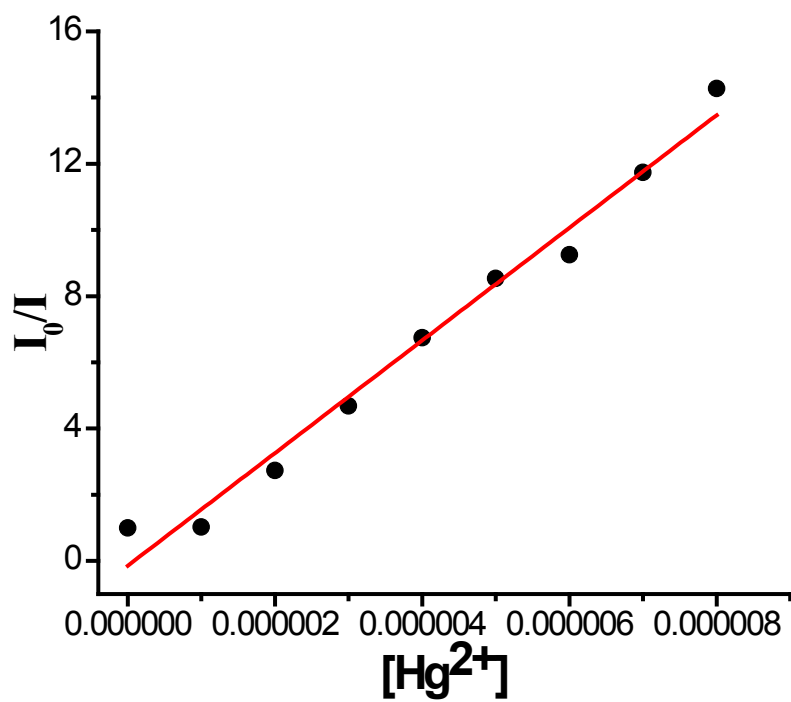


Figure S25: Determination of Stern-Volmer quenching constant for compound **2**- Hg^{2+}



Figure S26: Color change induced upon addition of various (excess equivalents of Bu_4N^+ salts) anions to BODIPY **1**- Hg^{2+} complex (5×10^{-6} M) in $\text{CH}_3\text{CN}/\text{PBS}$ (7:3; v/v, pH 7.4) under daylight: From left to right: (1) F^- , (2) CN^- , (3) N_3^- , (4) OH^- , (5) Cl^- , (6) Br^- , (7) I^- , (8) H_2PO_4^- , (9) HSO_4^- and (10) ClO_4^- respectively.

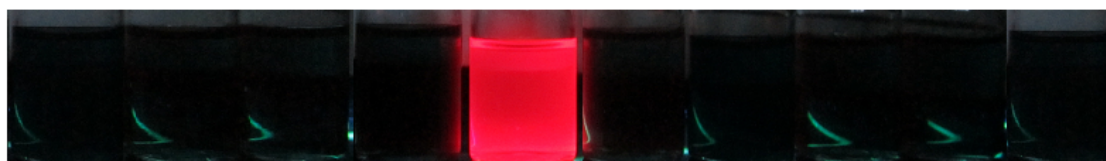


Figure S27: Color change induced upon addition of various (excess equivalents of Bu_4N^+ salts) anions to BODIPY **1**- Hg^{2+} complex (5×10^{-6} M) in $\text{CH}_3\text{CN}/\text{PBS}$ (7:3; v/v, pH 7.4) under UV lamp: From left to right: (1) F^- , (2) CN^- , (3) N_3^- , (4) OH^- , (5) Cl^- , (6) Br^- , (7) I^- , (8) H_2PO_4^- , (9) HSO_4^- and (10) ClO_4^- respectively.

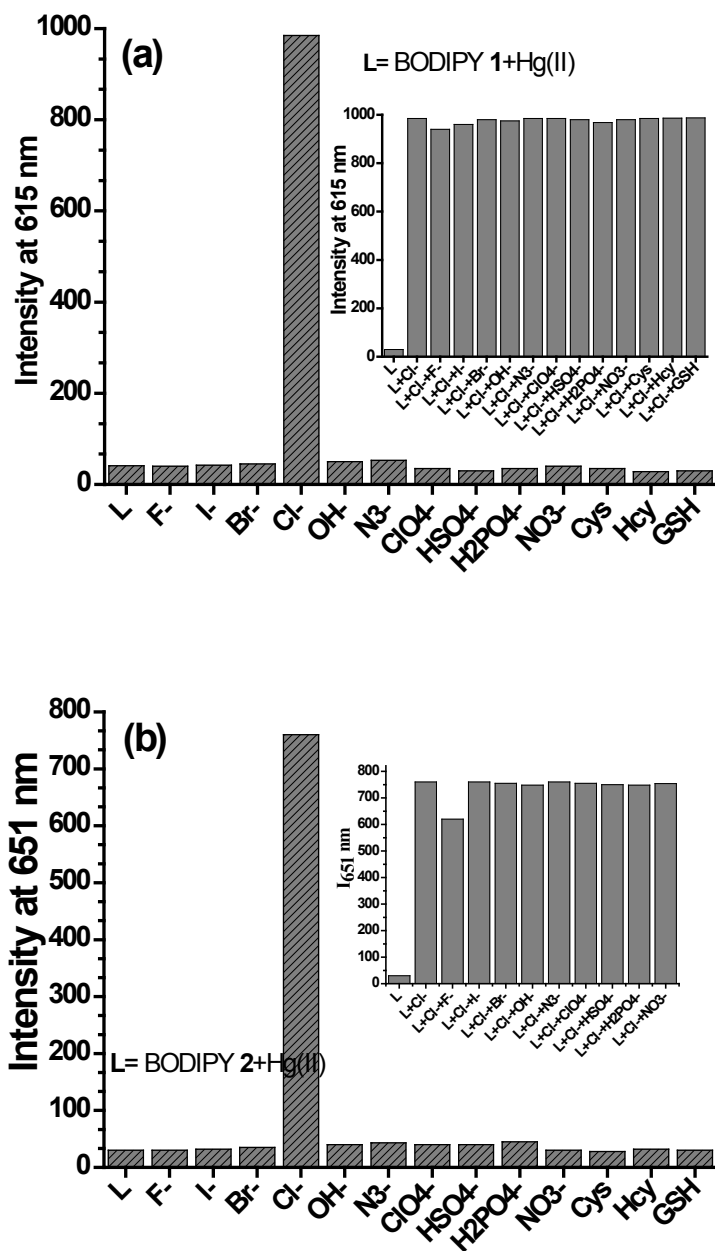


Figure S28: The histograms showing the fluorescence titration response of (a) **1**-Hg²⁺ and (b) **2**-Hg²⁺ in the presence of various anions; [BODIPYs **1,2**] = 5 μM; [Aⁿ⁻] = 20 μM]. The inset histograms showing the competitive fluorescence titration response of (a) **1**-Hg²⁺ and (b) **2**-Hg²⁺ in the presence of different anions; {[**1**+Hg²⁺, **2**+Hg²⁺] + Aⁿ⁻}; [**1, 2**] = 5 μM, [Cl⁻] = 20 μM, [A⁻] = 30 μM.

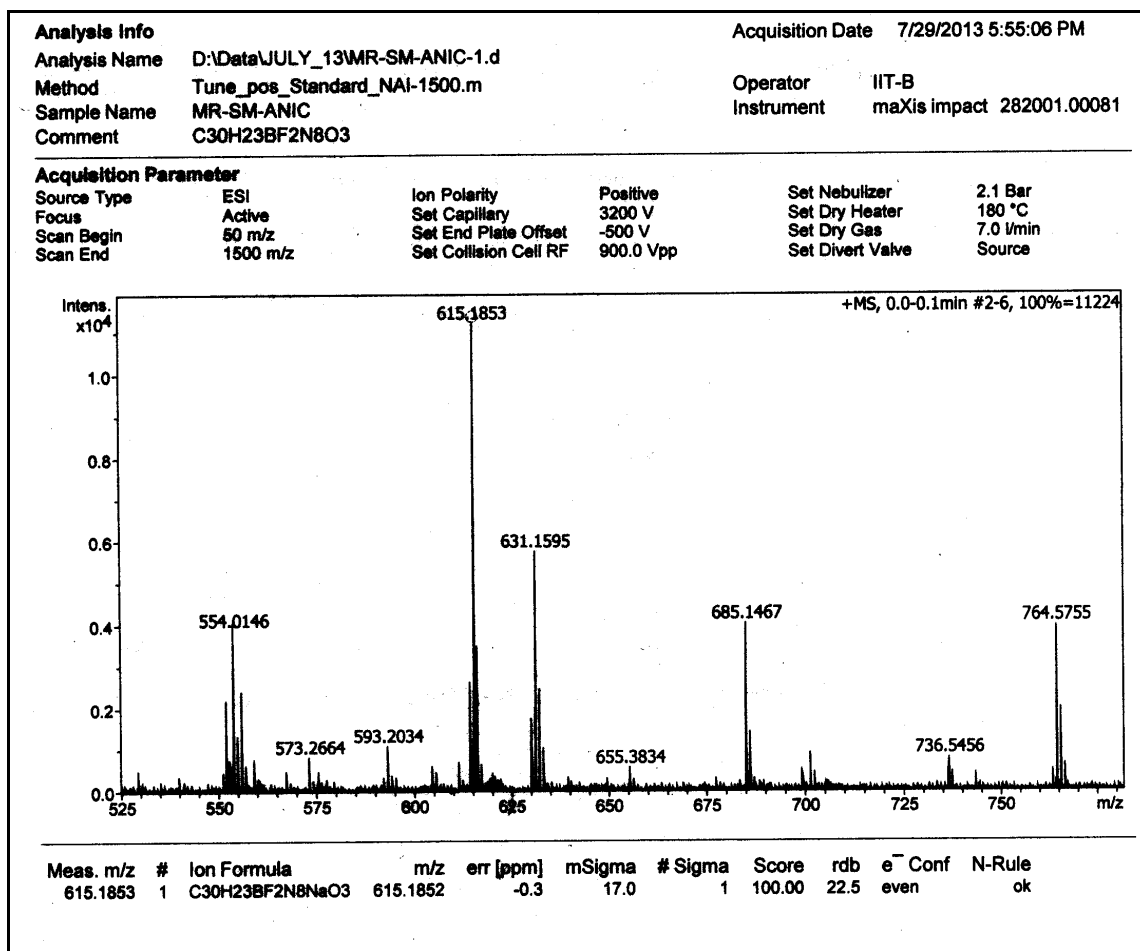


Figure S29: HR-MS spectrum showing the molecular ion peak for the formation of compound **1** during titration of BODIPY **1**-Hg²⁺ complex with Cl⁻ ion.

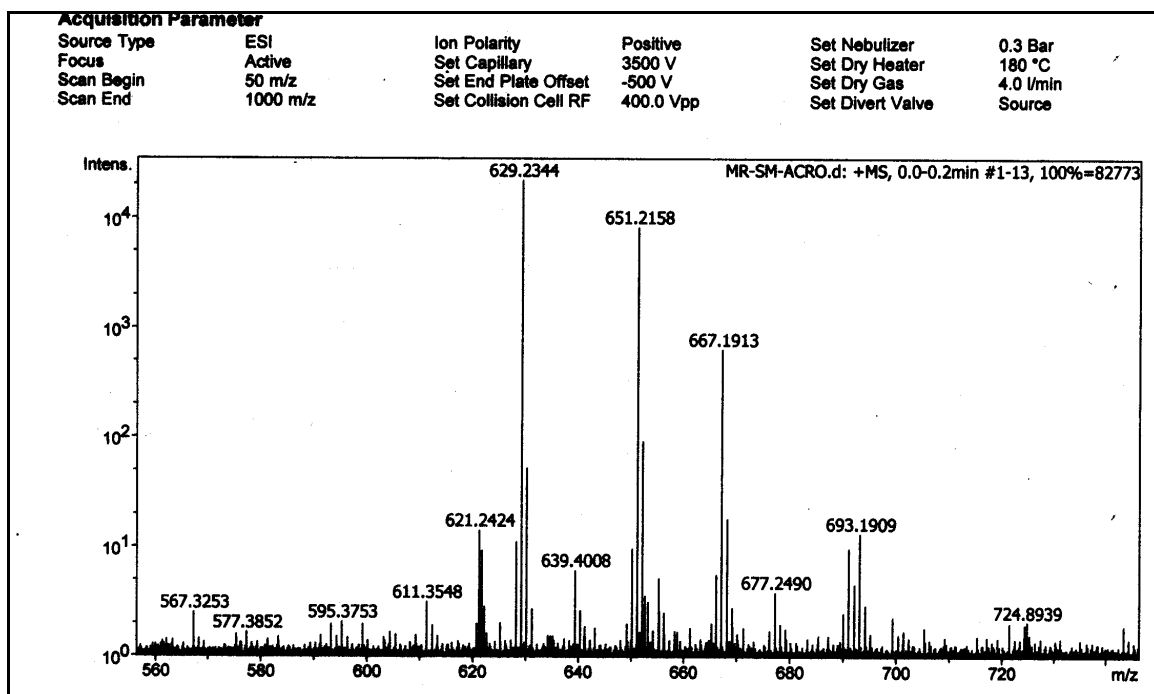


Figure S30: HR-MS spectrum showing the molecular ion peak for the formation of compound **2** during titration of **2**-Hg²⁺ complex with Cl⁻ ion.

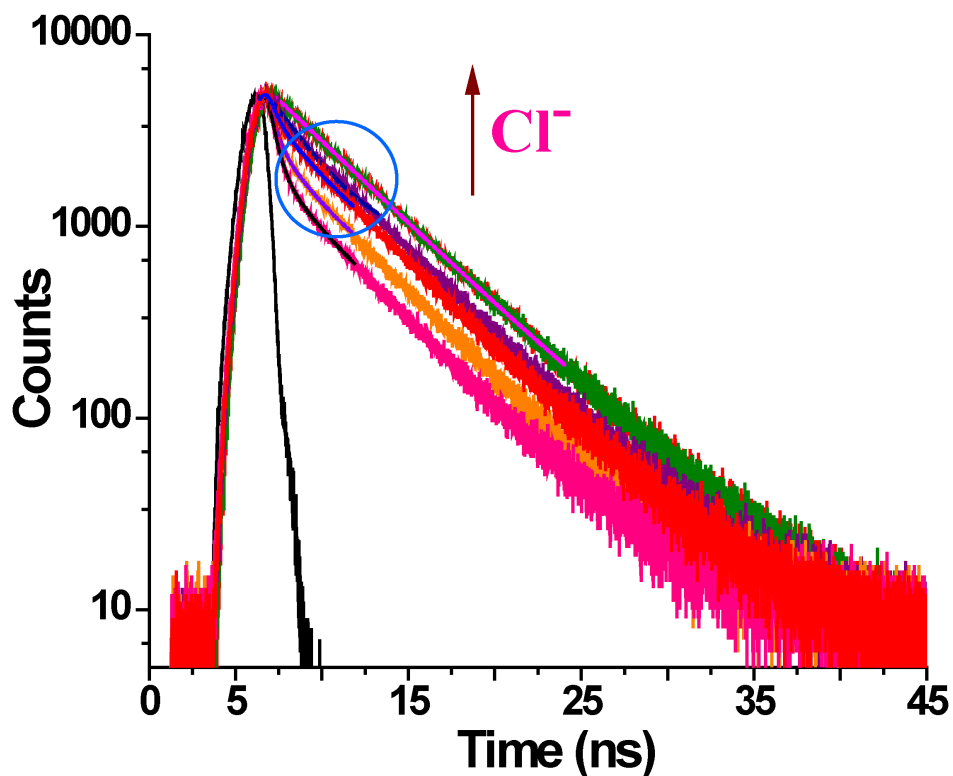


Figure S31: Time-resolved luminescence decay profiles of BODIPY 1-Hg²⁺ complex (5 μ M) in CH₃CN/PBS (7:3; v/v, pH 7.4) solution upon titration with different concentrations of Cl⁻ ions (TBACl). The excitation wavelength used was 540 nm and emission was detected at the emission-peak maxima (615 nm) of BODIPY 1-Hg²⁺ in chloroform.

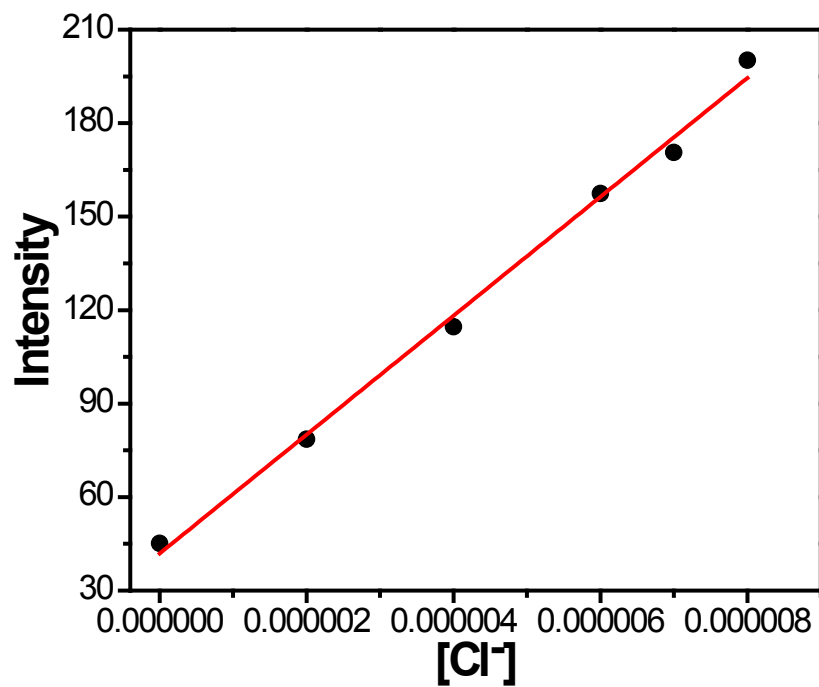


Figure S32: (a) The linear dynamic fluorescence response for the titration of BODIPY 1- Hg^{2+} complex with Cl^- to determine the detection limit (LOD). The LOD was calculated using the formula $3\sigma/k$, where σ = standard deviation of blank (10 samples) and k = is the slope of linear calibration curve.

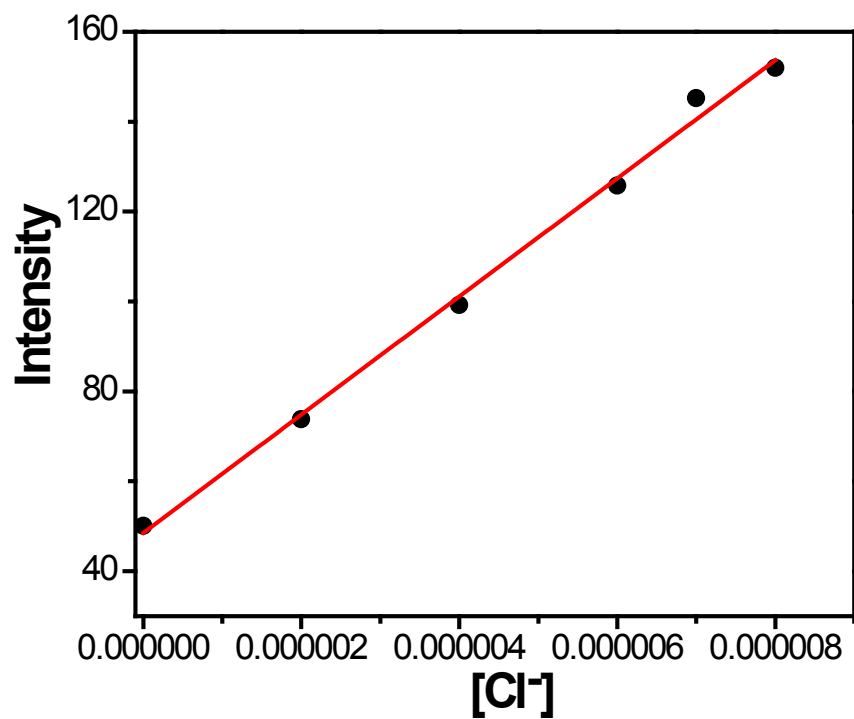


Figure S33: (a) The linear dynamic fluorescence response for the titration of BODIPY 2- Hg^{2+} complex with Cl^- to determine the detection limit (LOD). The LOD was calculated using the formula $3\sigma/k$, where σ = standard deviation of blank (10 samples) and k = is the slope of linear calibration curve.

Table S1: Electrochemical data of BODIPYs **1-4** recorded in acetonitrile containing 0.1M TBAP as supporting electrolyte

| Compound | $E_{\text{red}}(\text{V})$ I | $E_{\text{red}}(\text{V})$ II |
|----------|---------------------------------|----------------------------------|
| 1 | -0.514 | -0.897 |
| 2 | -0.561 | -0.875 |
| 3 | -0.148 | -1.055 |
| 4 | -0.342 | -0.946 |