Electronic Supplementary Material (ESI) for RSC Advances

BODIPY based fluorescent chemodosimeter for explosive picric acid in aqueous media and rapid detection in solid state

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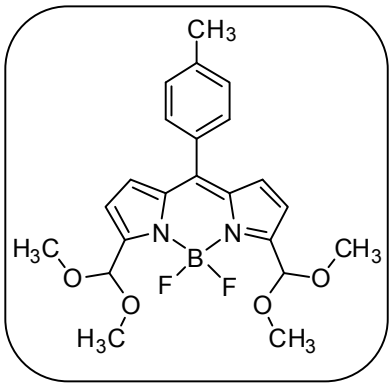
EXPERIMENTAL SECTION

The NMR experiments were performed with a 400 MHz spectrometer, and chemical shifts are expressed in parts per million with TMS as an internal reference. The mass spectra were recorded on Q-TOF instrument using electrospray ionization method. Absorption and steady state fluorescence studies were carried out with HPLC grade solvent. The elemental analyses were performed on a ThermoQuest microanalysis instrument. FT-IR spectra were measured on Perkin-Elmer spectrometer using KBr pellets. Cyclic Voltammetry studies were carried out with an electrochemical system utilizing the three electrode configuration consisting of a Glassy carbon (working electrode), platinum wire (auxillary electrode) and saturated calomel (reference electrode) electrodes. The experiments were done in dry dichloromethane using 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The time-resolved fluorescence decay measurements were carried out at magic angle using a picosecond diode laser based time correlated single photon counting (TCSPC) fluorescence spectrometer. For UV-vis and fluorescence titrations, the stock solution of BODIPY **2** (5×10^{-6} M) was prepared by using spectroscopic grade CH_3CN. The picric acid (PA) solution was prepared (1×10^{-2} M) in CH_3CN. The solution containing BODIPY **2** was placed in quartz cell (1 cm width), and PA solution was added in an incremental fashion. The association constant of the complex formed in solution has been estimated by using the standard Benesi–Hildebrand equation. In ^{1}H NMR titration, solution of BODIPY **2** in 0.4 mL of CD_3CN/D_2O (97.5/2.50; v/v) was prepared (5×10^{-3} M), and a 0.4 mL portion of this solution was transferred to a 5-mm NMR tube. A small aliquot of PA in CD_3CN was added in an incremental fashion, and their corresponding spectra were recorded.

Synthesis and Characterization for 3,5-bis(acetal) BODIPY 2: 3,5-diformyl-boron dipyrromethene **1** (100 mg, 0.295 mmol) in dry methanol (15 mL) was warmed until some parts of the solids were dissolved, giving a bright yellow suspension. Neat TFA (0.589 mmol) was added dropwise, causing the entire residual solid dissolve and yield a violet color solution. The mixture was stirred for 1 hr, and then TEA was added slowly in dropwise and continued stirring at room temperature for additional 30 min. The reaction mixture was evaporated and the crude product was purified using silica gel column chromatography with petroleum ether/ ethylacetate (85:15) and afforded pure 3,5-bis(acetal) BODIPY **2** as a orange solid. Yield: 78% (99 mg, 0.230 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.46 (s, 3H; -CH_3), 3.48 (s, 12H; -OCH_3), 5.87 (s, 2H; *meso*-CH), 6.68-6.69 (d, ^{3}J (H, H) = 4.24 Hz, 2H; py), 6.89-6.70 (d, ^{3}J (H, H) = 4.20 Hz, 2H; py), 7.30-7.32 (d, ^{3}J (H, H) = 7.96 Hz, 2H; Ar), 7.41-7.43 (d, ^{3}J (H, H) = 7.96 Hz, 2H; Ar). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 21.6, 29.9, 54.7, 98.5, 117.6, 129.3, 130.7, 131.1, 131.4, 135.0, 141.4, 147.9, 156.7. ^{11}B NMR (128.3 MHz, $CDCl_3$, δ in ppm): 0.78 (t, ^{1}J (B-F) = 31.5 MHz, 1B). ^{19}F NMR (376.4 MHz, $CDCl_3$, δ in ppm): -140.1 (q, ^{1}J (F-B) = 33.1 MHz, 2F). HRMS. Calcd for $C_{22}H_{25}BF_2N_2O_4$ [$(M+Na)^+$]: m/z 453.1773. Found: m/z 453.1769. Elemental analysis cald (%) for $C_{22}H_{25}BF_2N_2O_4$: C 61.41, H 5.86, N 6.51; found C 61.53, H 5.71, N 6.48.

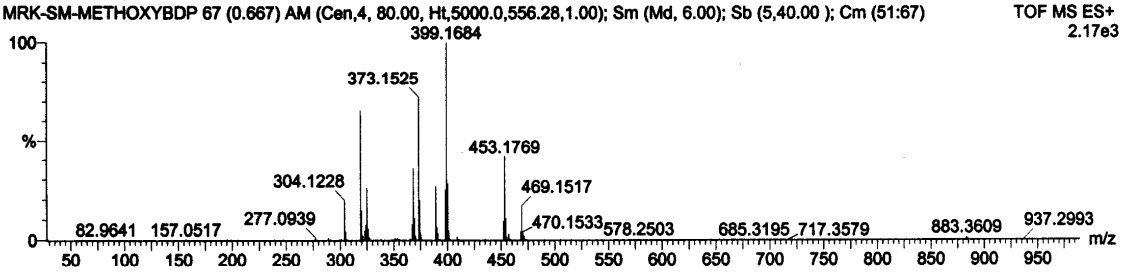


Elemental Composition Report **Page 1**

Single Mass Analysis (displaying only valid results)
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 200.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

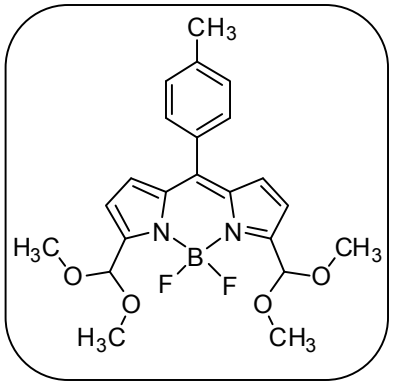
Monoisotopic Mass, Odd and Even Electron Ions
315 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Waters(Micromass) : Q-Tof micro(YA-105) Dept. Of Chemistry - I.I.T.(B) 21-Dec-201220:06:01
C22H25BF2N2O4
MRK-SM-METHOXYBDP 67 (0.667) AM (Cen,4, 80.00, Ht,5000.0,556.28,1.00); Sm (Md, 6.00); Sb (5,40.00); Cm (51:67) TOF MS ES+
2.17e3



Minimum:				-1.5		
Maximum:		50.0	5.0	200.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
453.1769	453.1773	-0.4	-0.9	10.5	1	C22 H25 N2 O4 Na F2 B

Figure S1: HRMS spectrum of BODIPY **2**



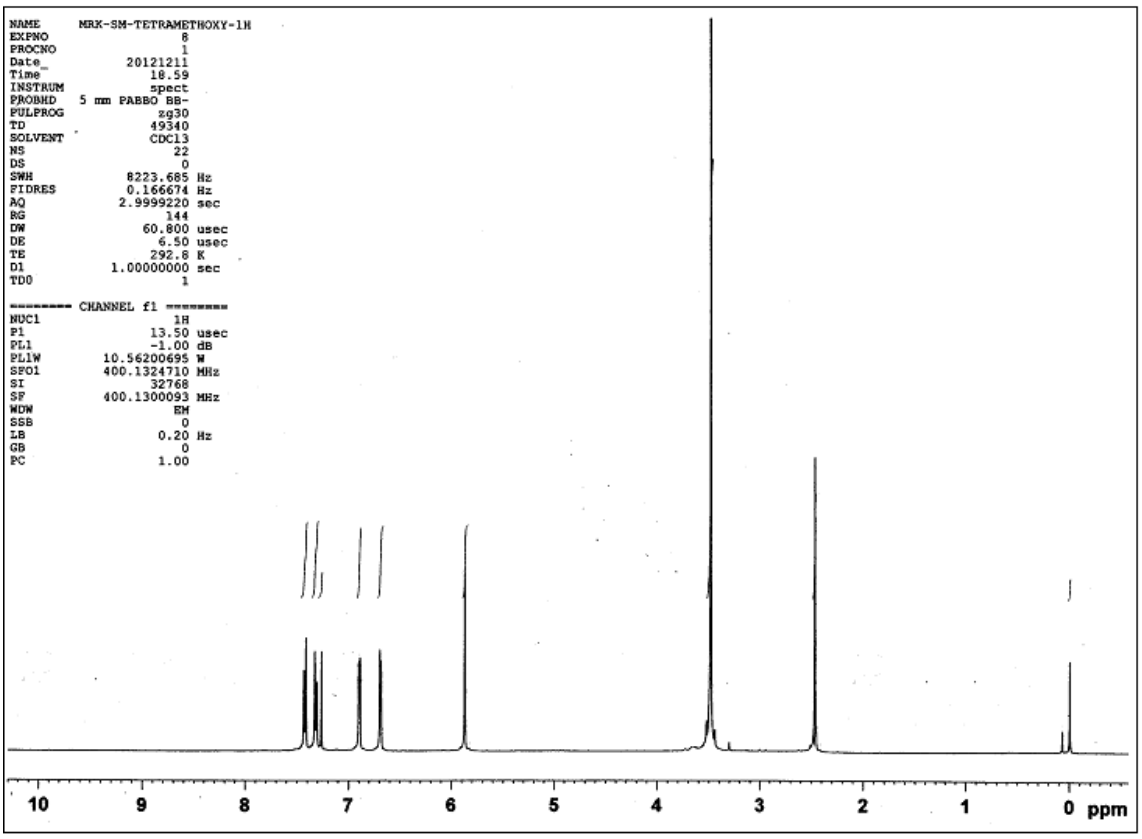
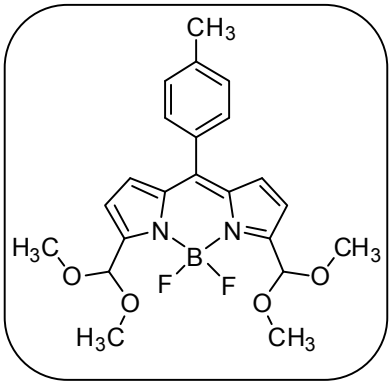


Figure S2: ^{1}H NMR spectrum of BODIPY **2** recorded in $CDCl_3$



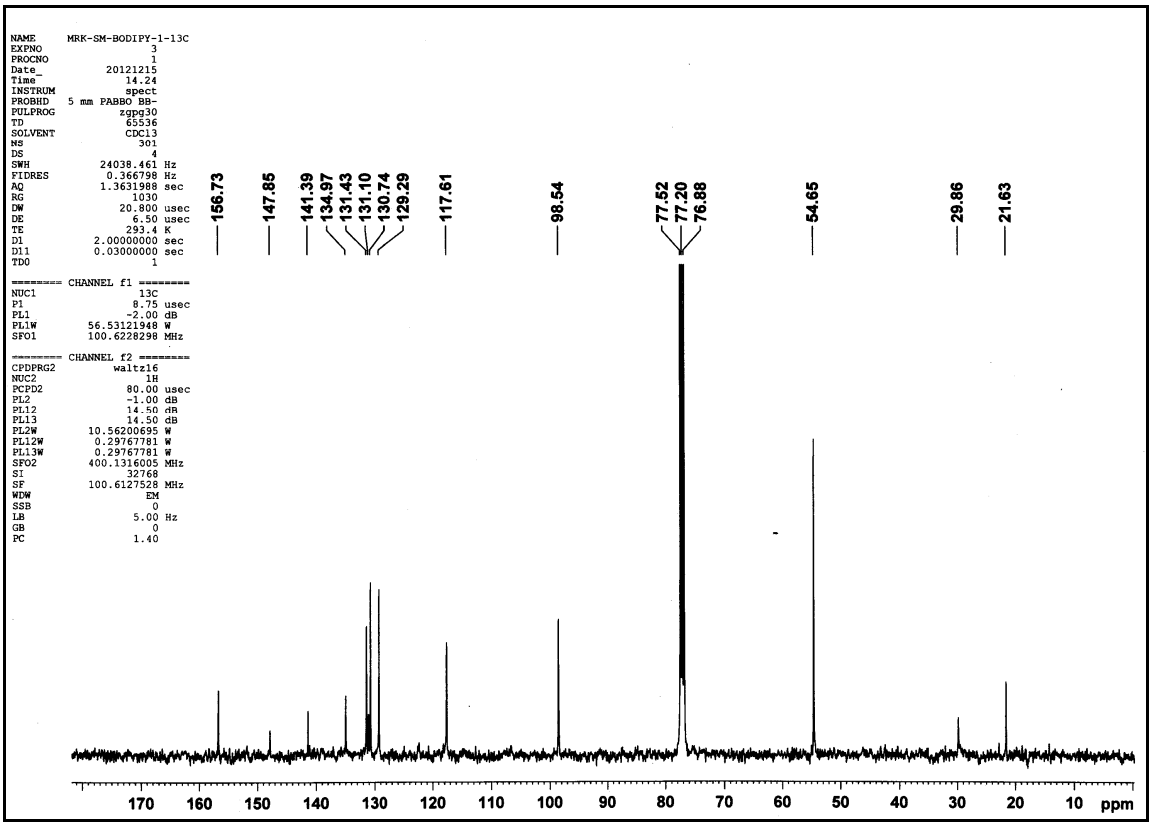
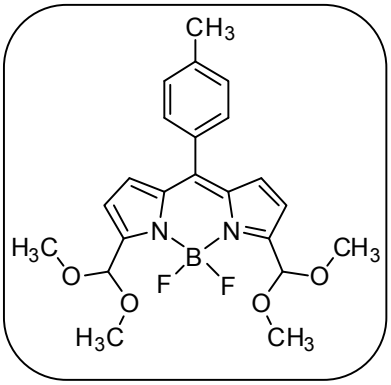


Figure S3: ^{13}C NMR spectrum of BODIPY **2** recorded in $CDCl_3$



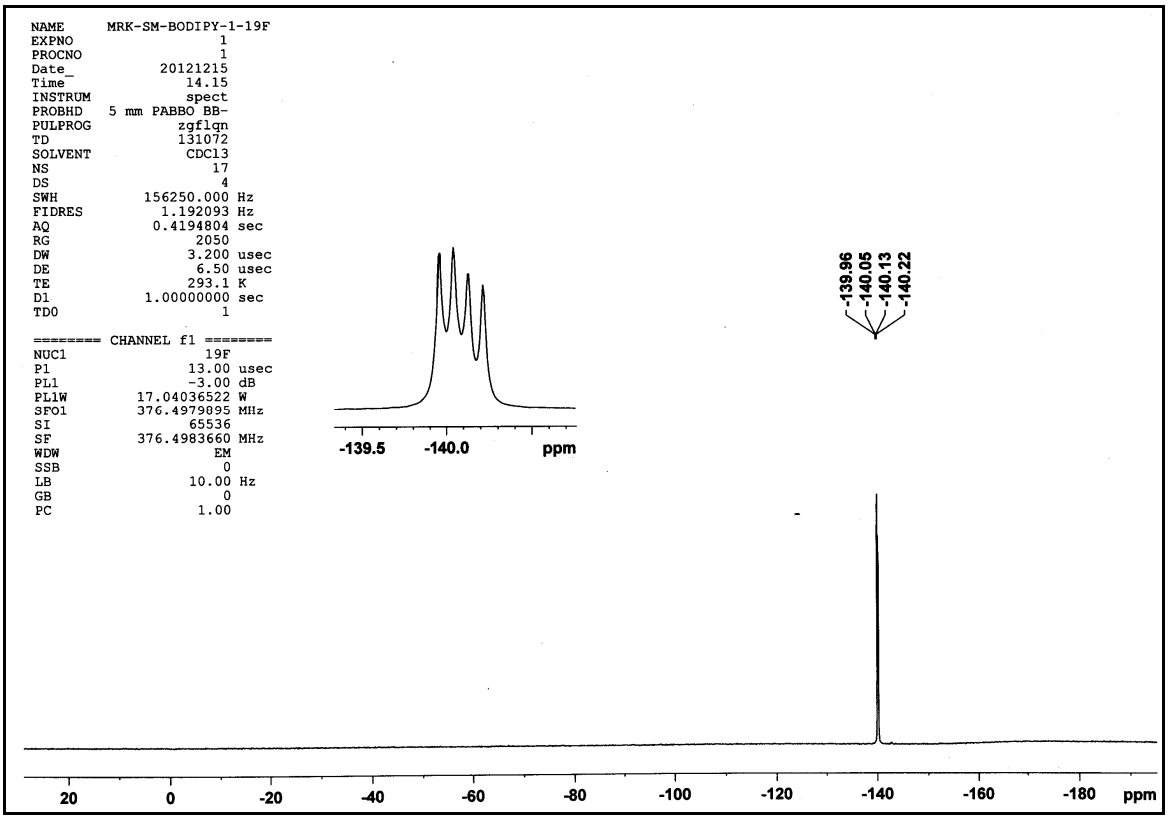
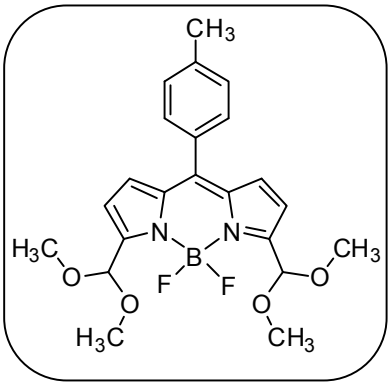


Figure S4: ^{19}F NMR spectrum of BODIPY **2** recorded in $CDCl_3$. Inset shows the expansion



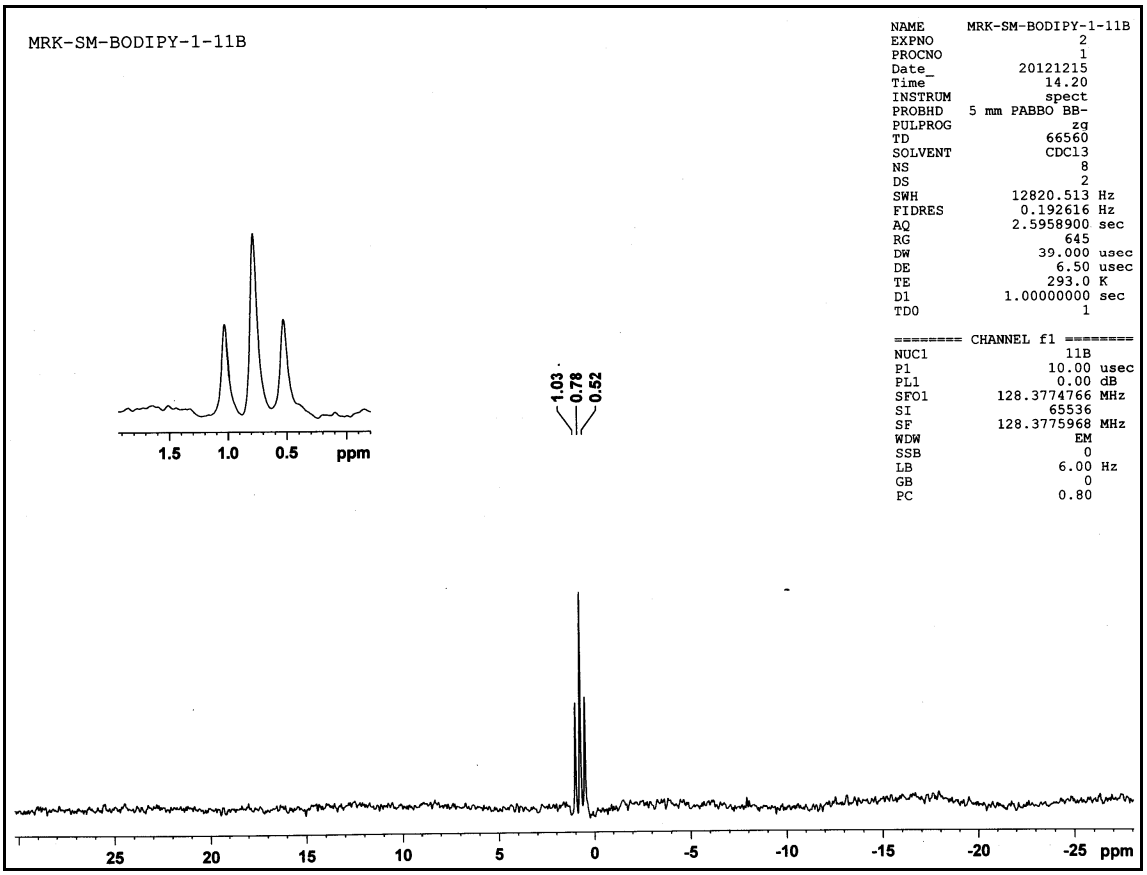


Figure S5: ^{11}B NMR spectrum of BODIPY **2** recorded in $CDCl_3$. Inset shows the expansion

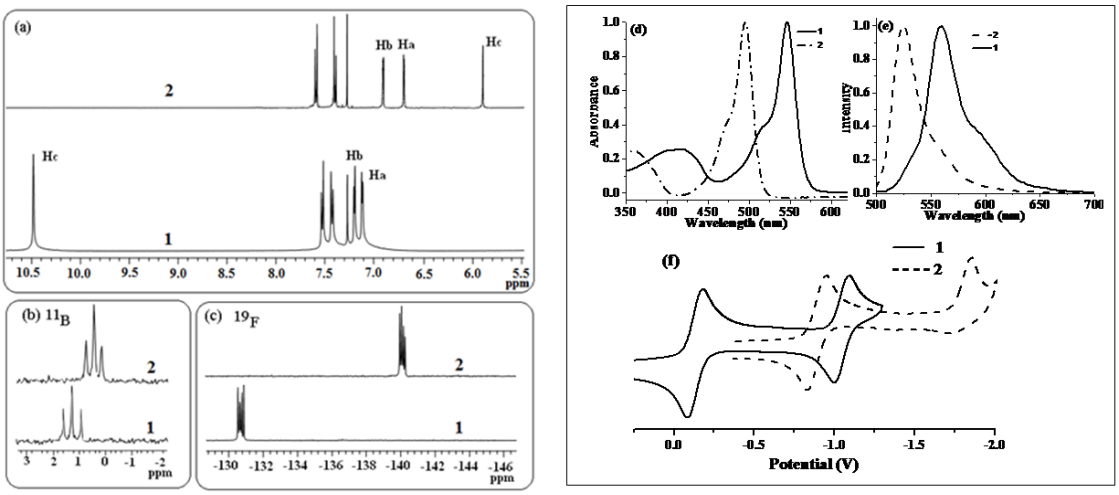


Figure S6. Comparison of (a) ^{1}H, (b) ^{11}B & (c) ^{19}F NMR spectra of BODIPYs **1** and **2** in selected region recorded in $CDCl_3$; and their normalized (d) absorption and (e) emission spectra recorded in chloroform. Comparison of reduction waves of (f) cyclic voltammograms of BODIPY **1** and **2** in dichloromethane containing 0.1 M TBAP as supporting electrolyte recorded at 50 mV s^{-1} scan rate.

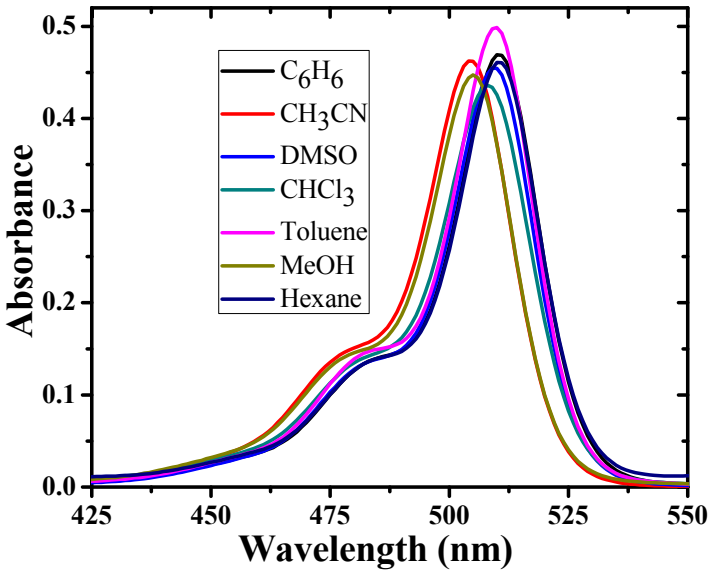


Figure S7: Absorption spectra of BODIPY **2** recorded in different solvents

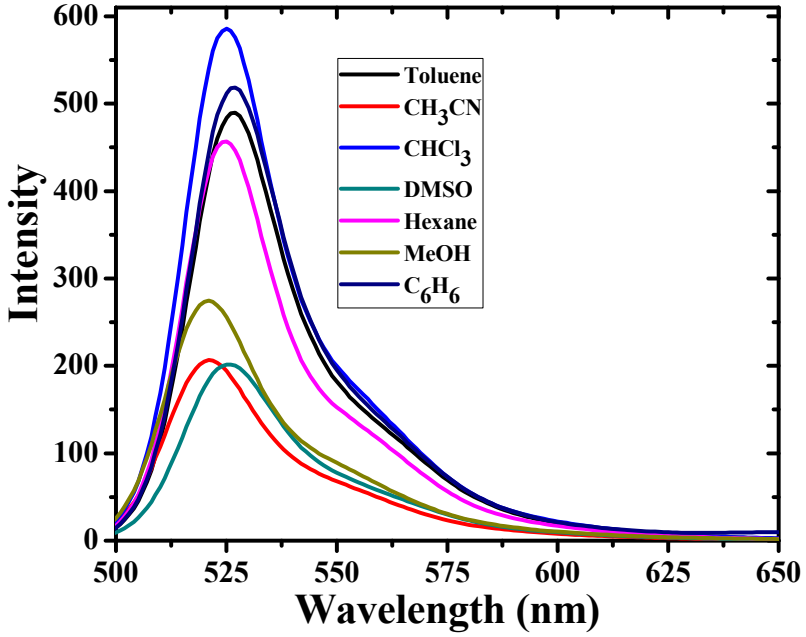


Figure S8: Emission spectra of BODIPY **2** recorded in different solvents. Excitation wavelength used was (λ_{ex}) 488 nm.

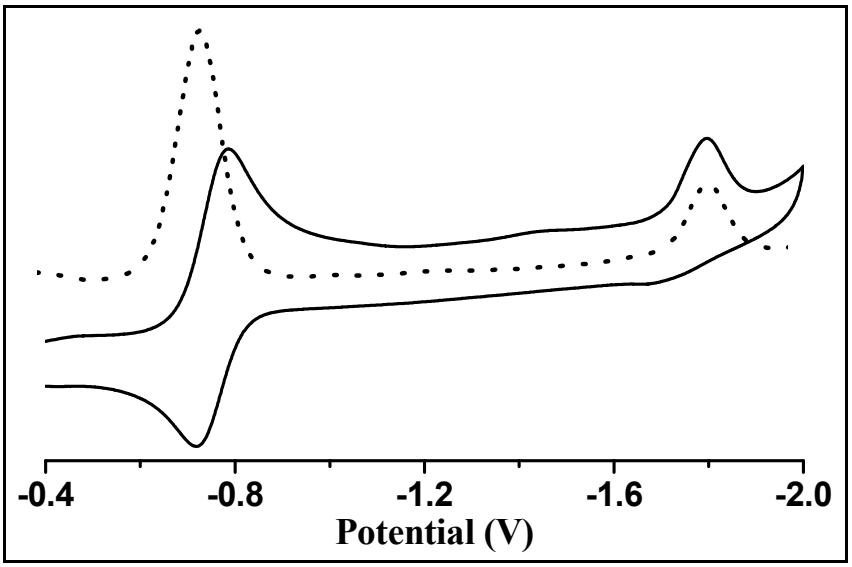


Figure S9: Reduction waves of the cyclic voltammogram and differential pulse voltammogram of BODIPY **2** in dichloromethane containing 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte recorded at a 50 mV s^{-1} scan rate.

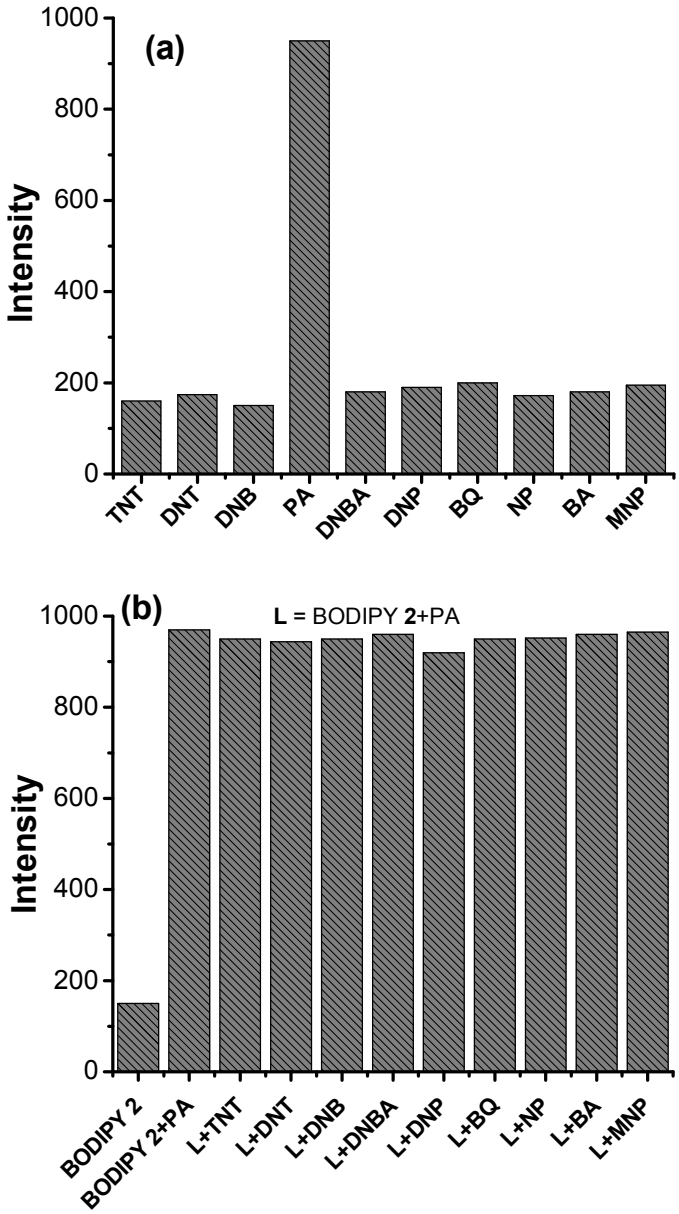


Figure S10: The histograms showing the fluorescence titration response of (a) BODIPY **2** in the presence of various nitroaromatic compounds, [BODIPY **2**] = 5 μM; [NAC = 20 μM]. (b) The histograms showing the competitive fluorescence titration response of [BODIPY **2**+PA] in the presence of various other nitroaromatic compounds. {[BODIPY **2**+PA] +NACs}; [BODIPY **2**] = 5 μM, [PA] = 20 μM; [NACs] = 30 μM,

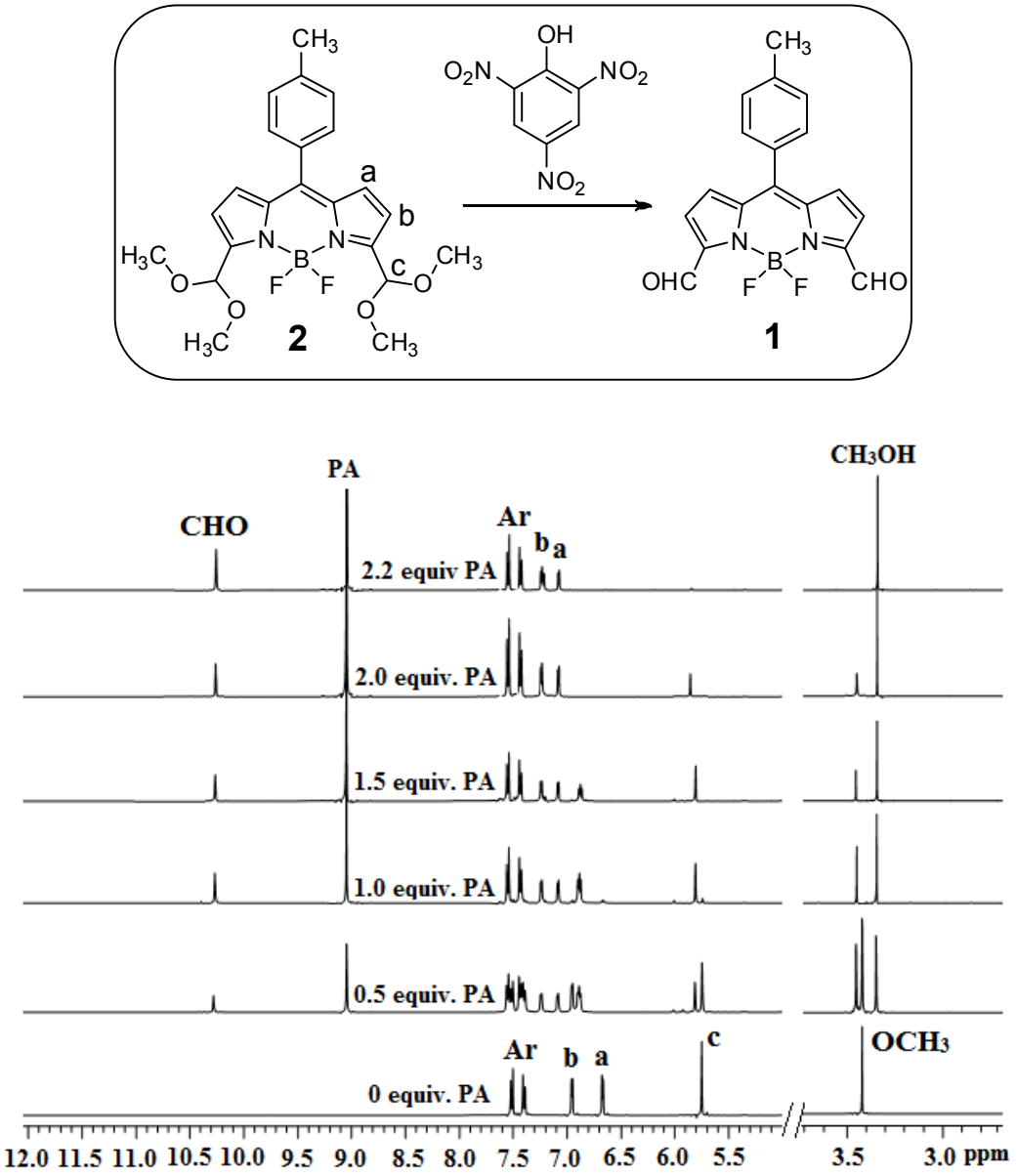


Figure S11: Partial ^{1}H NMR spectra of BODIPY **2** (2.2×10^{-2} M) in the presence of different concentrations of PA in 0.4 mL of CD_3CN/D_2O (97.5/2.5; v/v). Concentration of PA was varied from 0 to 2.2 equiv.

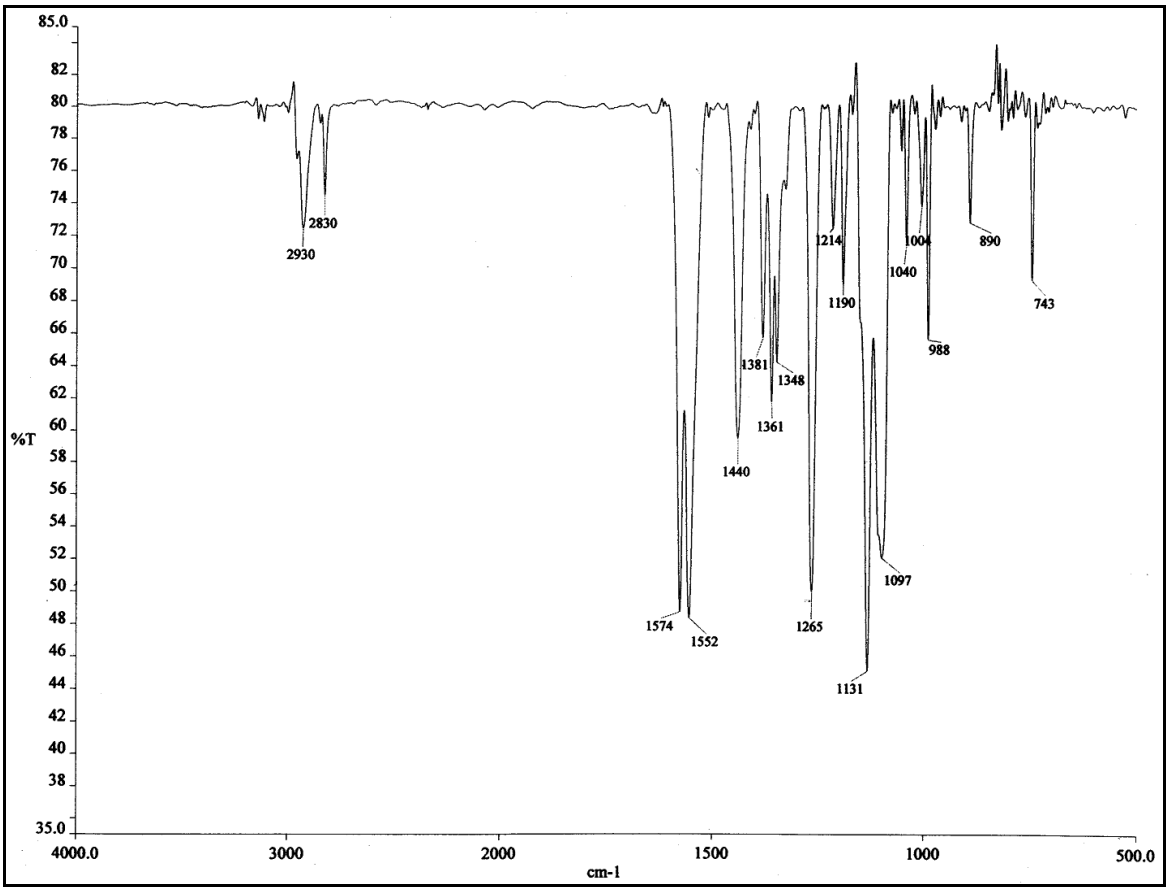


Figure S12: IR spectrum of picric acid

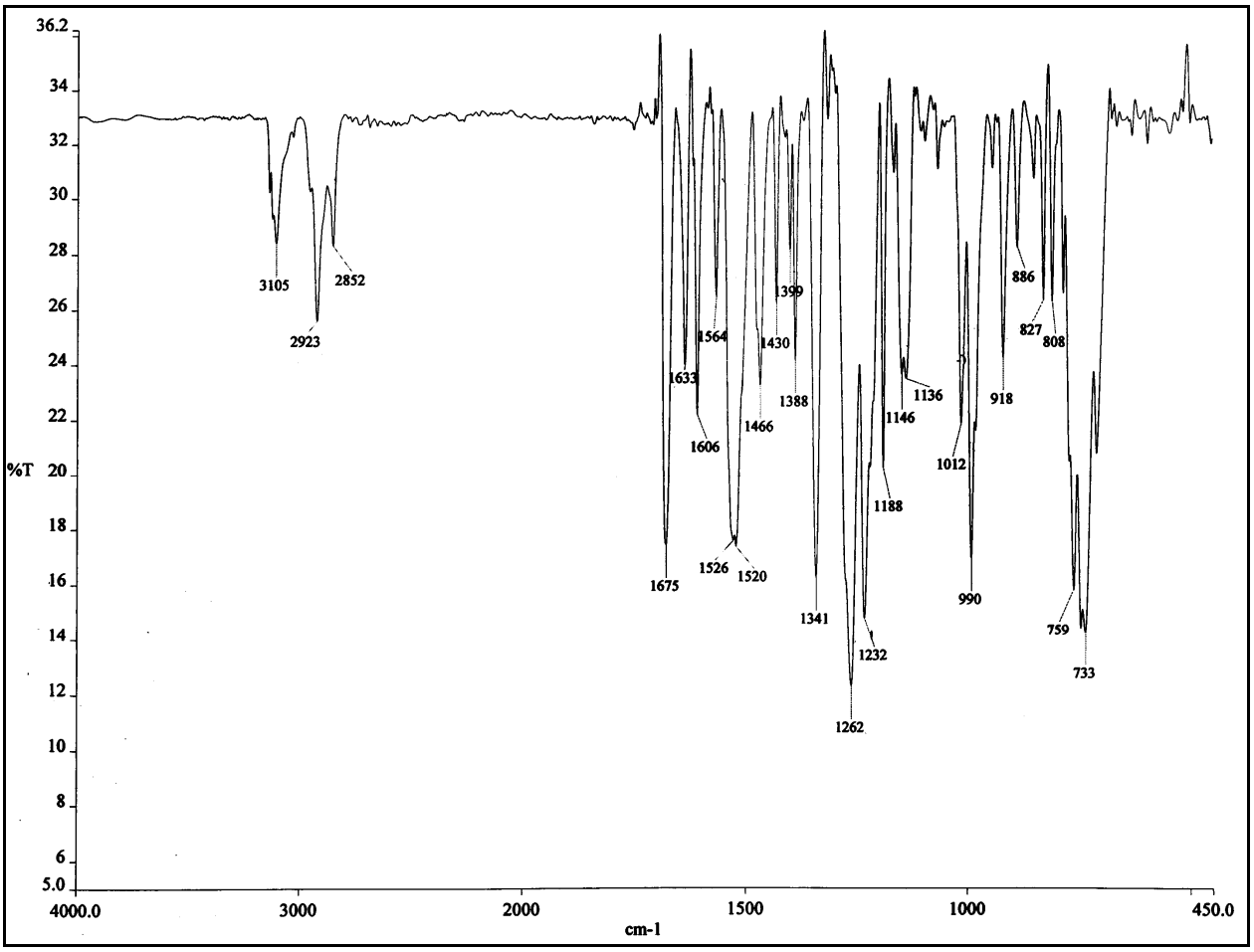


Figure S13: IR spectrum of BODIPY **2** upon treating with picric acid

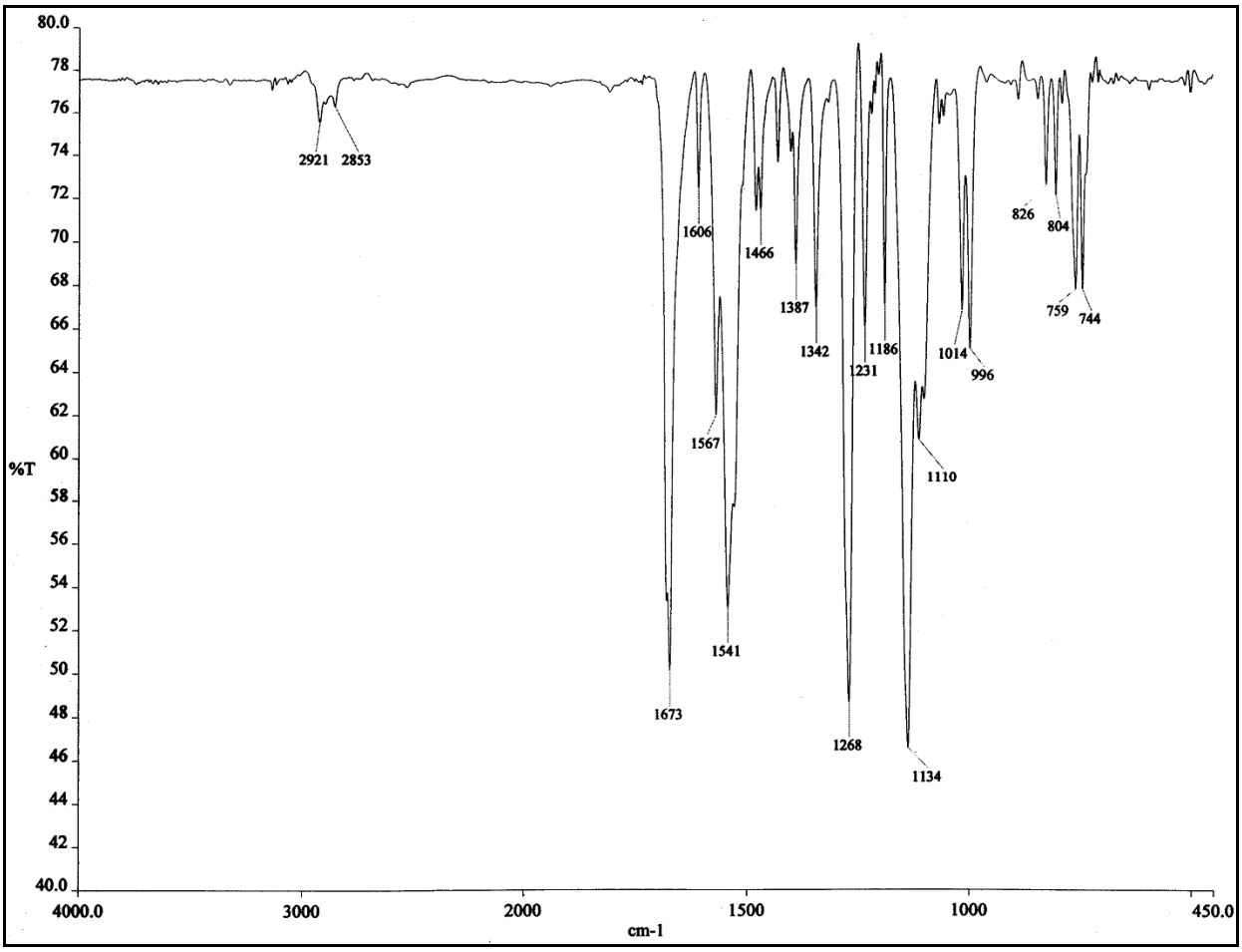


Figure S14: IR spectrum of BODIPY **1**

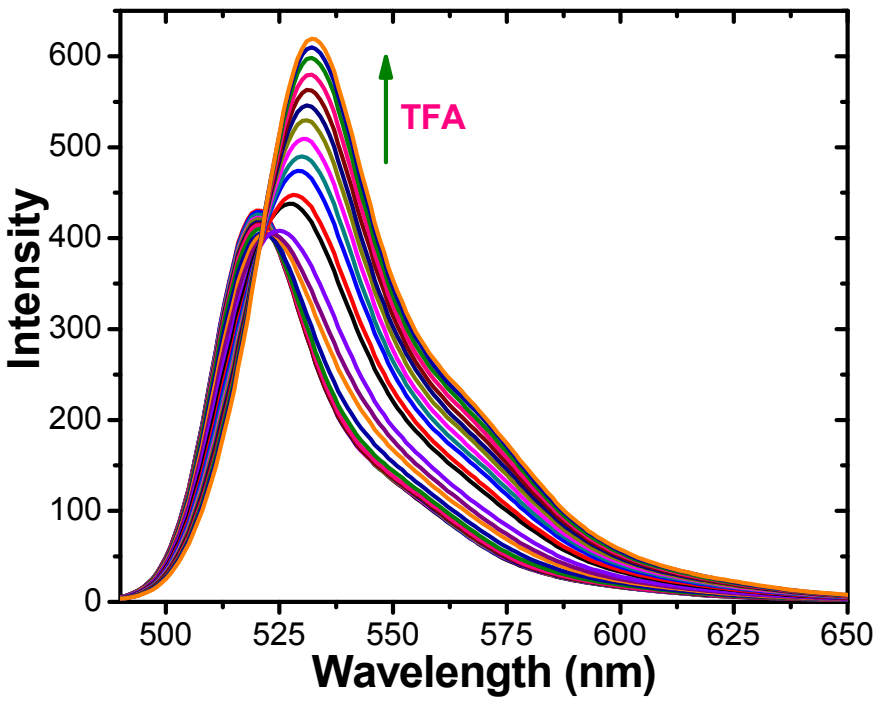


Figure S15: Changes in fluorescence spectra of BODIPY **2** (5 μM) upon titration with TFA (0 to 30 equiv.) in CH_3CN/H_2O (9:1; v/v) solution. (λ_{ex} = 488 nm).

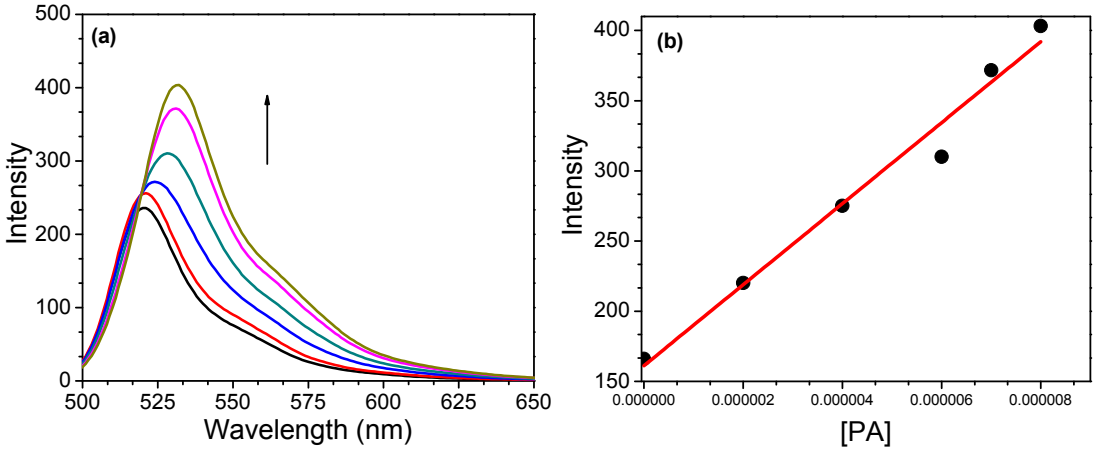


Figure S16: (a) Fluorescence spectral traces of BODIPY **2** during titration with PA to determine LOD. (b) The linear dynamic fluorescence response for the titration of BODIPY **2** with PA to determine the detection limit (LOD). The LOD was derived by using the formula 3σ/K where σ = standard deviation of the blank (10 blank samples) and K = is the slope of linear calibration curve.

Table S1: Photophysical data of BODIPY **2** recorded in different solvents

Solvent	λ_{abs}(nm)	λ_{em}(nm)	$\Delta\nu_{st}$(cm^{-1})	logε	Φ	τ(ns)	K_r(10^9s^{-1})	K_{nr}(10^9s^{-1})
Hexane	510	525	560	4.49	0.18	1.22	0.148	0.672
$CHCl_3$	508	525	637	4.48	0.25	1.72	0.145	0.436
CH_3CN	505	521	608	4.55	0.08	0.48	0.166	1.916
Toluene	510	527	633	4.46	0.21	1.60	0.131	0.494
C_6H_6	509	528	707	4.45	0.20	1.32	0.152	0.606
MeOH	505	521	608	4.53	0.13	0.62	0.210	1.403
DMSO	509	526	635	4.49	0.10	0.58	0.172	1.552

log(ε/mol^{-1}dm^3 cm^{-1})-molar extinction coefficient, λ_{abs} (absorption maxima), λ_{em} (emission maxima), Δν (Stokes shift), Φ (quantum yield), τ (lifetime), k_r (radiative decay), and k_{nr} (nonradiative decay).