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Supplementary Information

PET governed fluorescence "Turn ON" BODIPY probe for selective detection of picric acid.

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Synthesis of BODIPY-1:

A solution of 3, 5-dinitrobenzoyl chloride (6.07g, 1eq.) and 2,4-dimethylpyrrole (5g, 2eq.) in dry dichloromethane(100ml) was stirred at 25°C for 24hours U/N_2. To deep red coloured reaction mass Et_3N (22.3ml, 6 eq.) was added slowly followed by BF_3-Et_2O (26.5ml, 8 eq.) after 30 min stirring. The solution was stirred for another 10 hours at 25°C. Then RM was washed thrice with 5% NaOH solution and then water. The organic layer was then dried over anhydrous Na_2SO_4, and concentrated in vacuo and purified by column chromatography on silica gel (hexane/dichloromethane as eluent) afford the pure BODIPY-1(Yield=58%).

Synthesis of BODIPY-2:

5% Pd/C (1.4g) and hydrazine(3ml) were added to the N_2 gas purged solution of BODIPY -1 (1g) in THF and MeOH (1:1,140 ml) and the RM was refluxed for 5 hours under N_2. Solid mass removed by filtration after completion of reaction and filtrate was concentrated and purified by silica gel column chromatography with dichloromethane followed by mix of dichloromethane and methanol. Orange solid (yield=75%) was obtained when solid from column was treated with hexane + dichloromethane mixture.

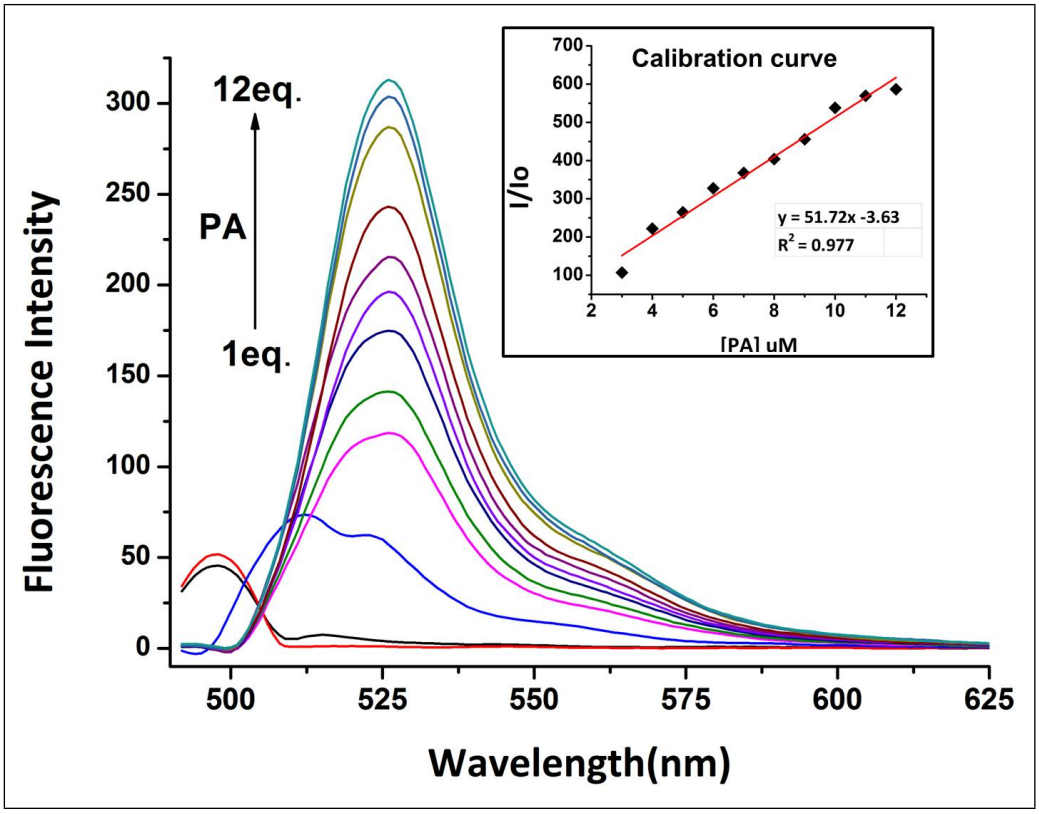

Fig.S1 - Fluorescence titration spectra of BODIPY-2 (1 µM) upon incremental addition of PA (1–12 equiv.) in absolute ethanol,λex = 499 nm. Inset: Calibration curve of fluorescence intensity as a function of PA equiv. to BODIPY probe.

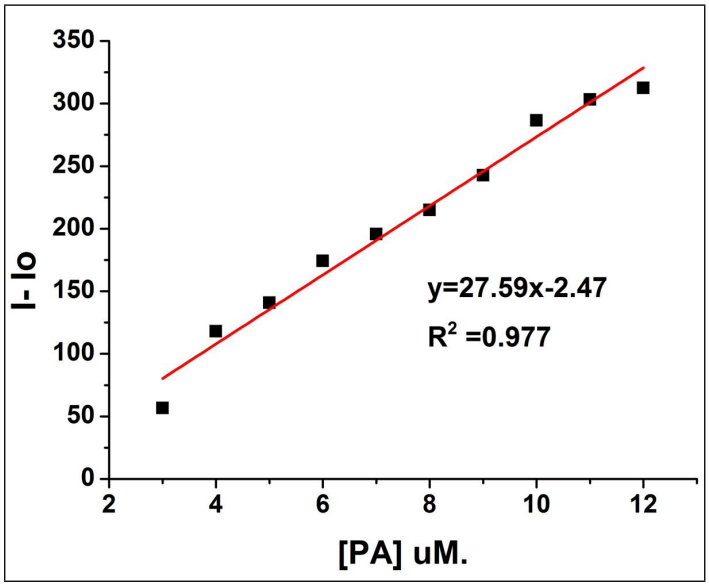

Fig. S2- Plot for detection limit calculation. LOD=0.655ppb was calculated by formula LOD=3xSD/slope. SD obtained from 10 blank readings.

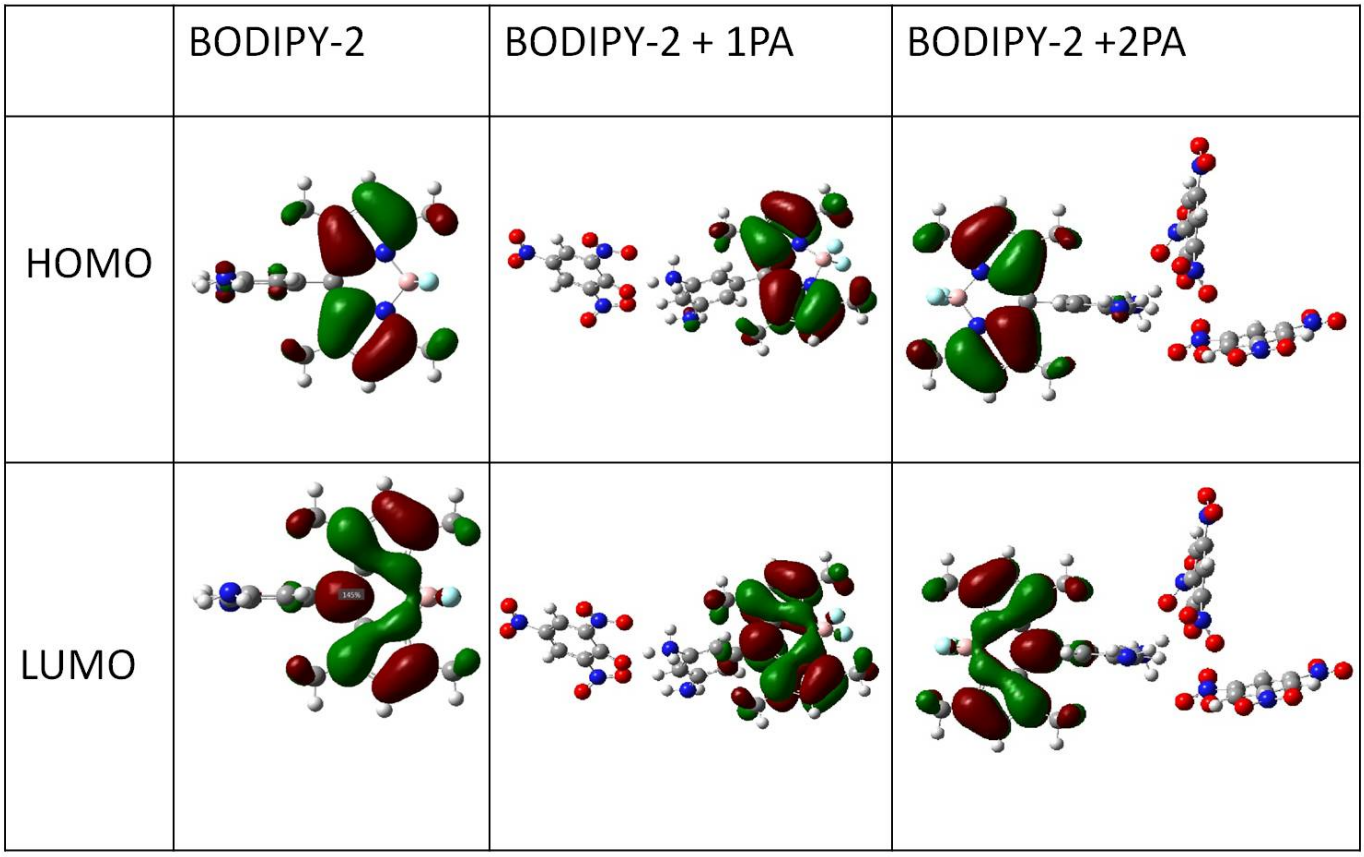

Fig. S3- Isodensity plots for BODIPY-2 and its association with 1 and 2 equivalent of PA from B3LYP/6-31g(d) level optimised output files.

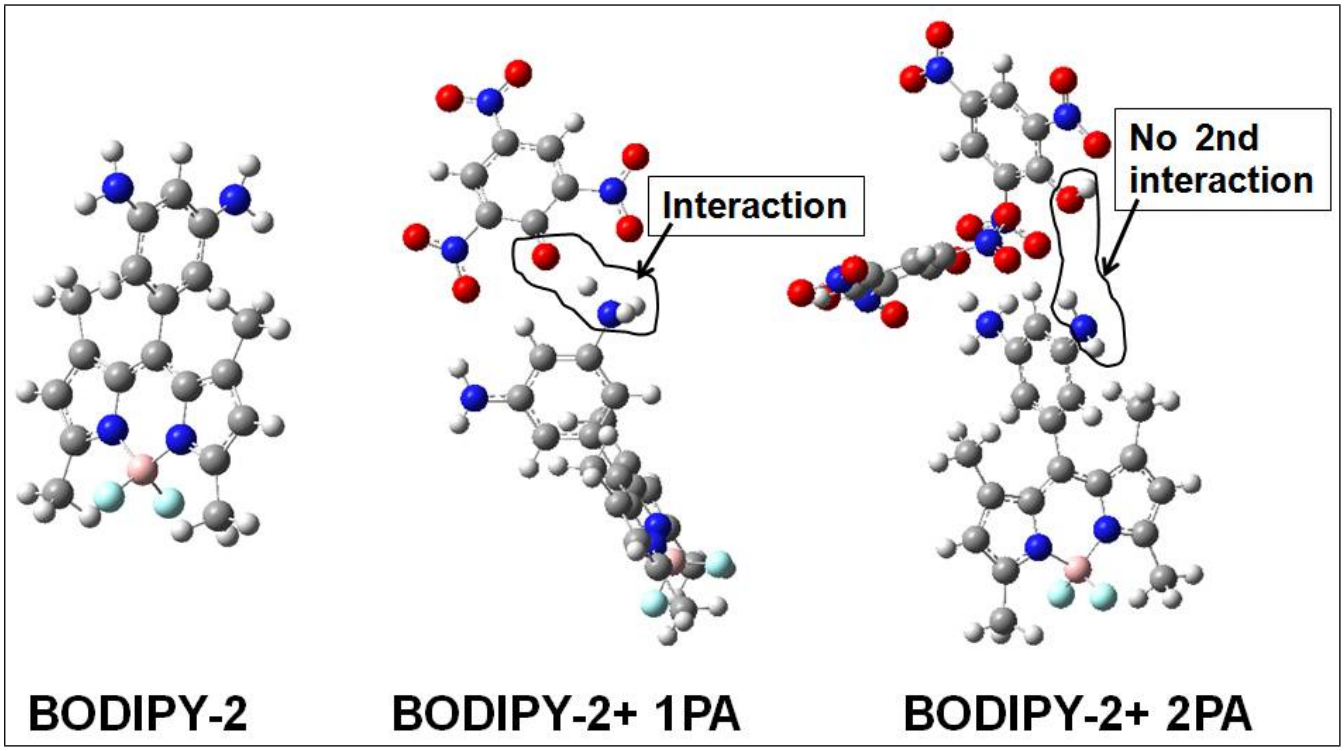

Fig. S4- B3LYP/6-31g(d) Optimised structures with ball–stick model for BODIPY-2 and its association with 1 and 2 equivalent of PA. Ball colour – atom: gray-carbon, dark blue-nitrogen, pink-boron, red-oxygen, sky blue-fluorine, white-hydrogen.

(The fig.S4 is repeated from main paper fig.7 for lager view)

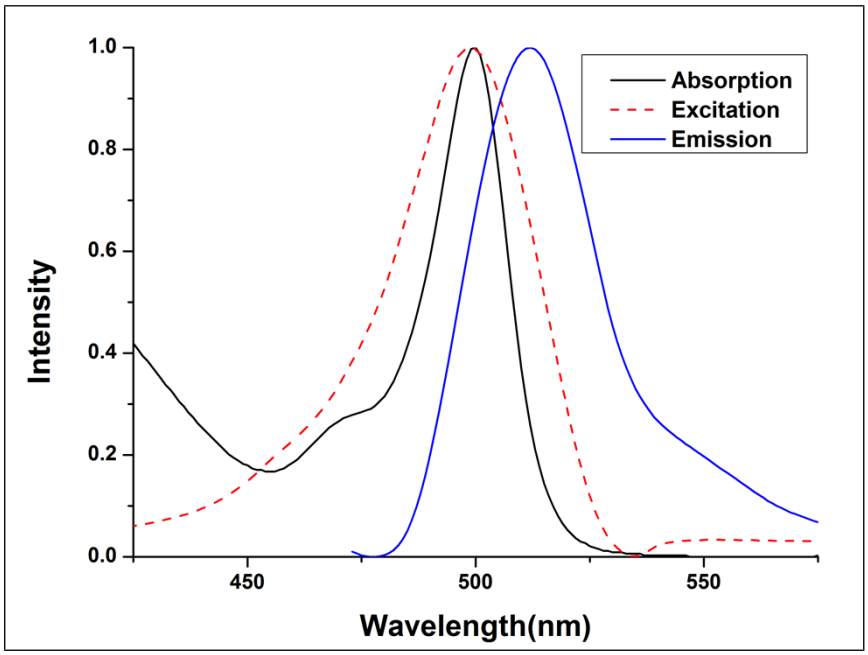

Fig. S5- Normalized absorption, excitation and emission plot of BODIPY-2 + PA.

(Emission & excitation graphs were not promising as unassociated BODIPY-2 is very weak emissive so all three plots were obtained from BODIPY-2 + PA in absolute EtOH.)

^{1}H NMR BODIPY-2:

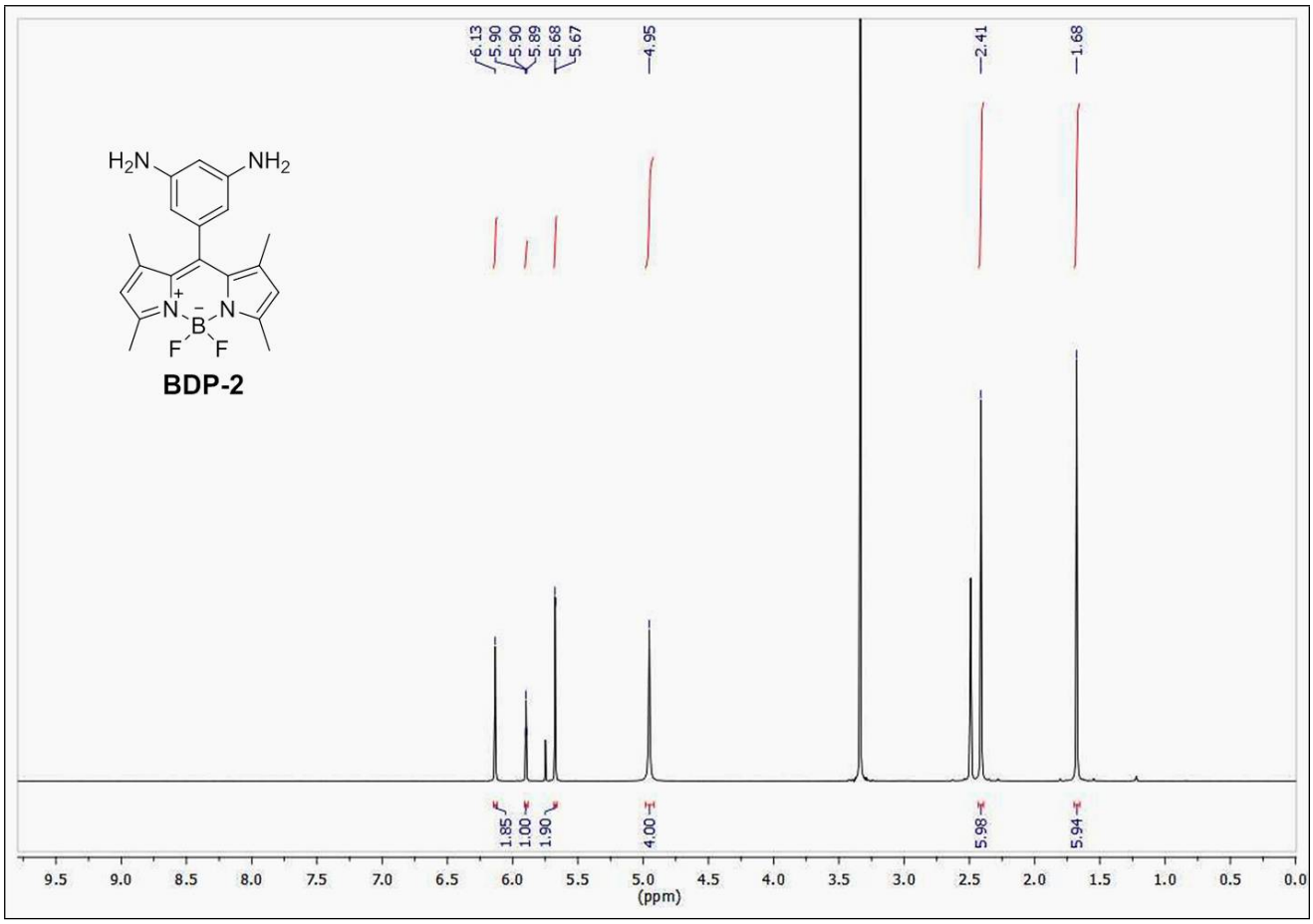

Fig.S6 - ^{1}H NMR (DMSO-d_6, 500 MHz) spectrum of BODIPY-2.

^{13}C NMR BODIPY-2:

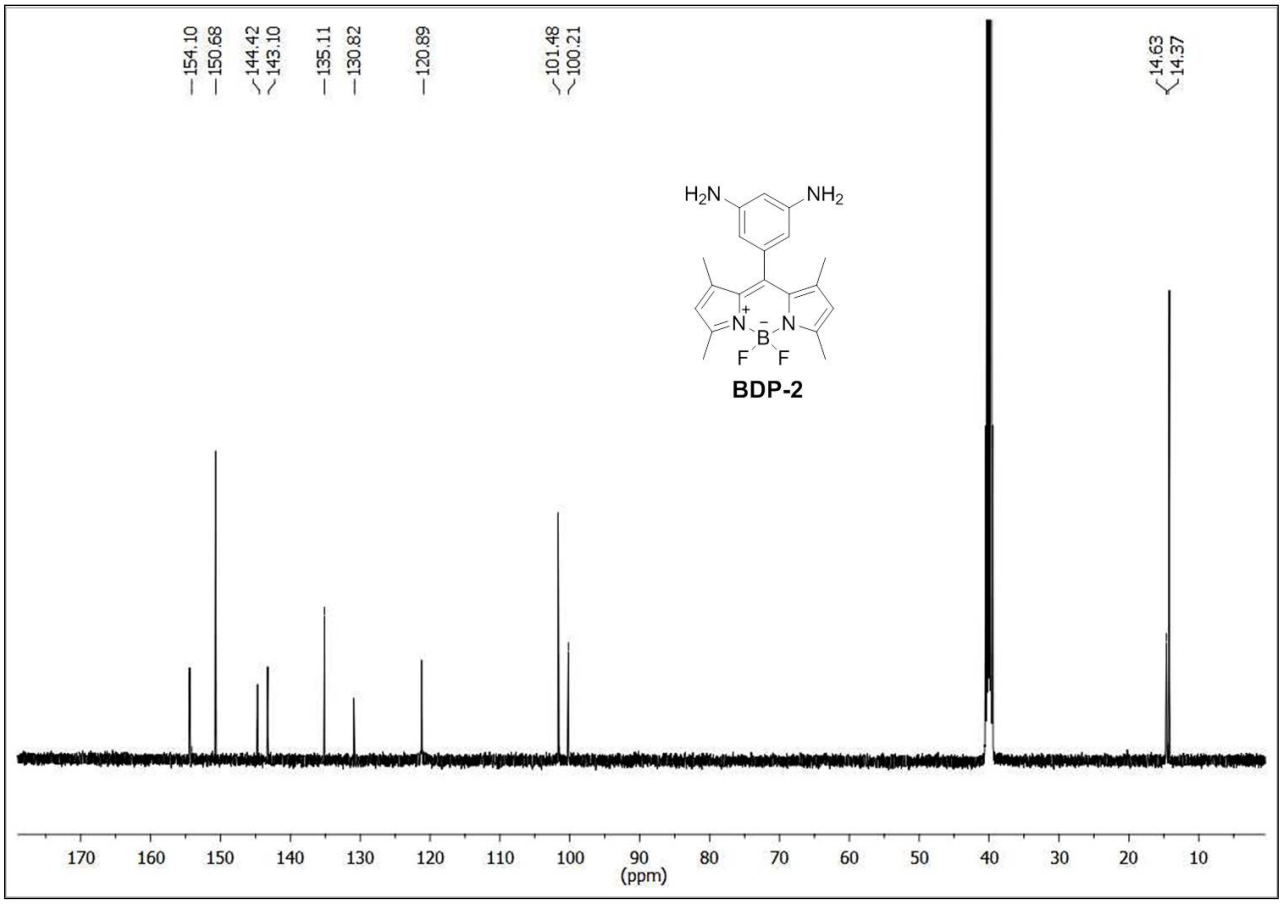

Fig.S7 - ^{13}C NMR (DMSO-d_6, 126 MHz) spectrum of BODIPY-2.

^{1}H NMR BODIPY-1:

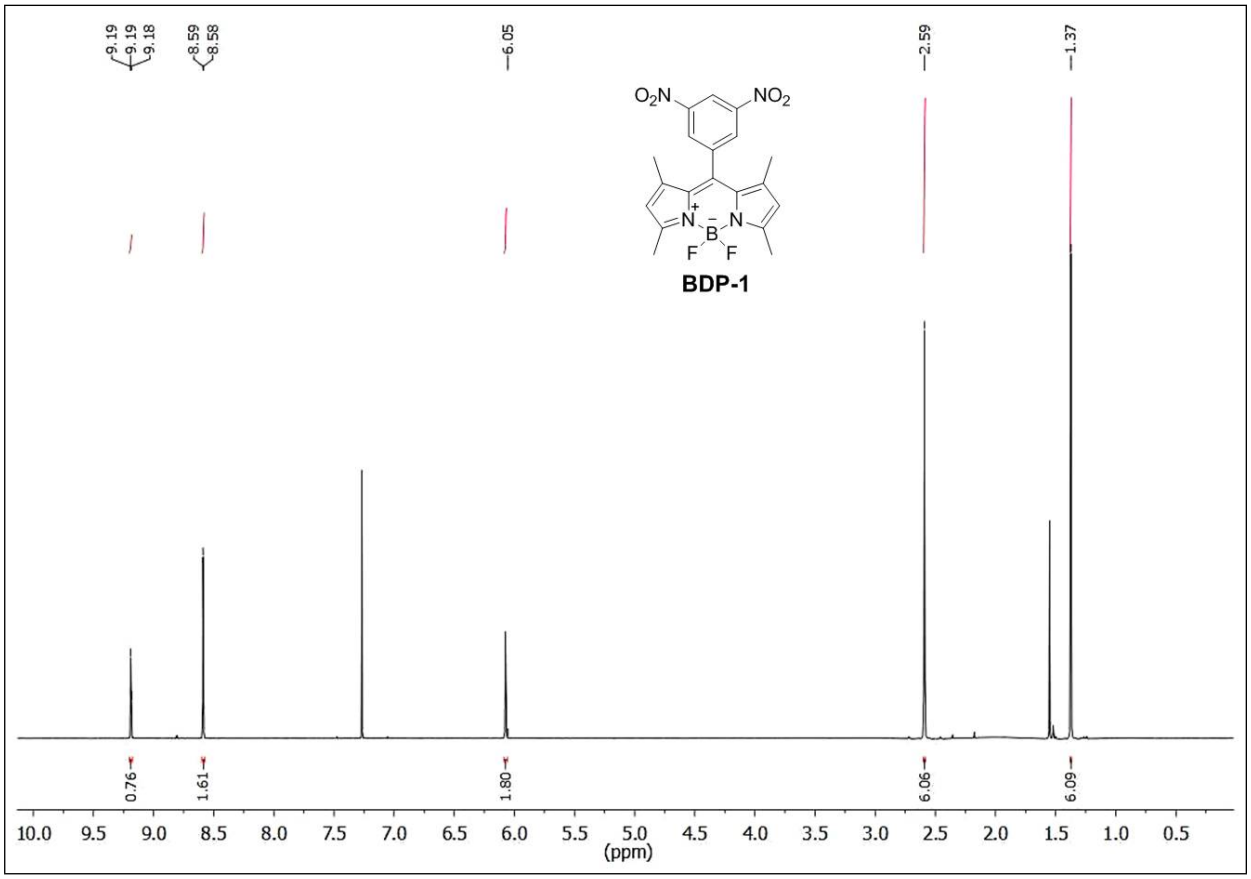

Fig.S8 - ^{1}H NMR ($cdcl_3$, 500 MHz) spectrum of BODIPY-1.

^{13}C NMR BODIPY-1:

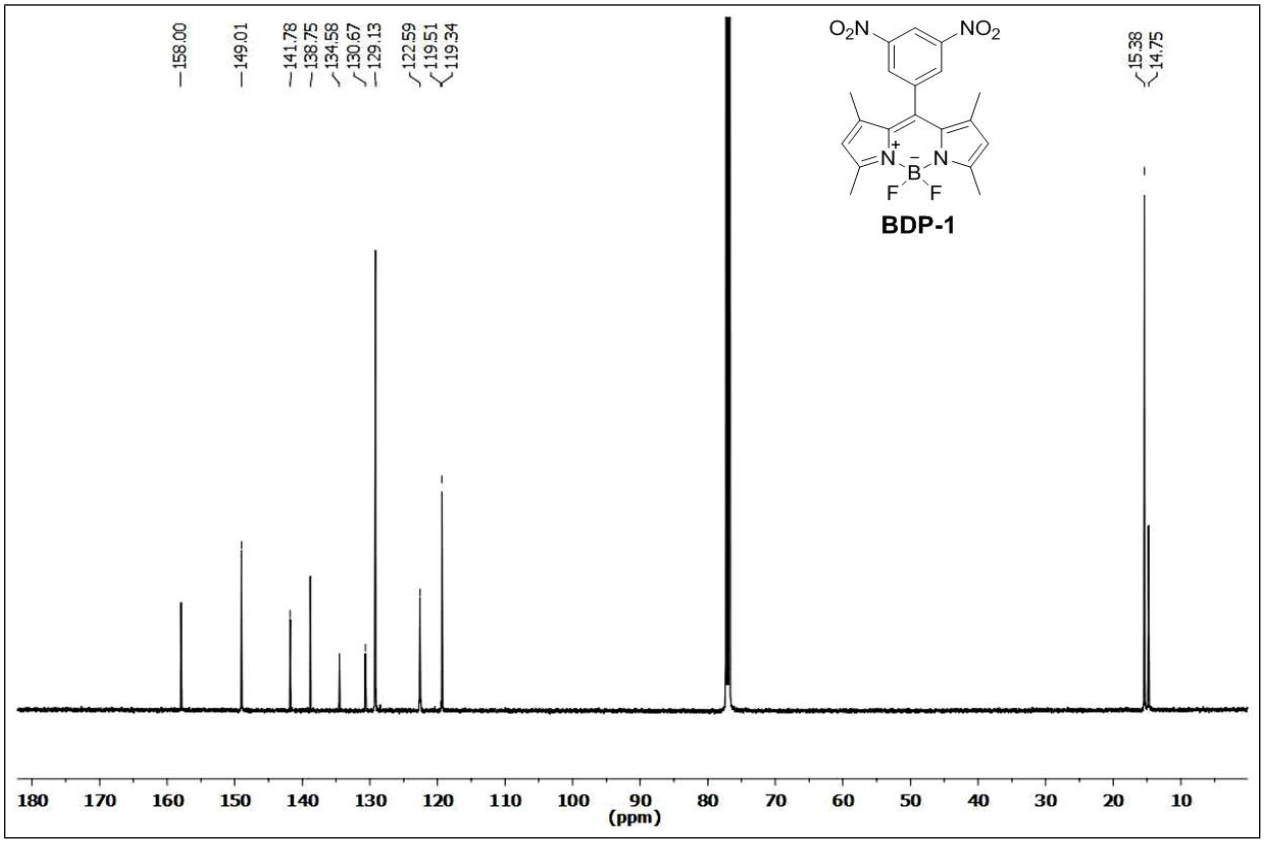

Fig.S9 - ^{13}C NMR (cdcl$_3$, 126 MHz) spectrum of BODIPY-1.

Calculation of Detection Limit:

Standard deviation from 10 blank readings of BODIPY probe (conc =1 × 10 −6mol/L) is SD(σ) = 0.05997. From the equation of titration plot(y = 27.59x-2.47, R^2 = 0.977, fig. S2) slope is = 27.468. So detection limit from formula DL= (3xSD)/slope = (3x0.05997)/27.468= 0.00655µM = 6.55x10^{-9} M (0.65ppb).

Calculation of Binding Constant:

Binding constant was determined from Benesi Hildebrand plot (fig.3, main paper). Binding constant = c/m. From plot (y =3.16x10^{-8}x + 6.03x10^{-4} , R^2 = 0.9875) intercept(c)= 6.03x10^{-4} and slope = 3.16x10^{-8}. Binding constant (Ka)= 1.91x10^4 M^{-1}.

Cartesian co ordinates of optimized files at B3LYP/6-31g(d) level :

BODIPY-2 : -

0 1

C	-0.51423600	-1.22312800	-0.00797500
C	0.17666400	-0.00002200	-0.00004400
C	-0.51419200	1.22310600	0.00793600
C	-1.19962800	3.37213400	0.03070800
H	-1.23185300	4.45435600	0.04269900
C	-1.19976700	-3.37212900	-0.03075200
H	-1.23204000	-4.45434900	-0.04277500
C	-3.77190200	-2.90856800	-0.02186700
H	-4.27815700	-2.50371000	0.86092400
H	-4.27983400	-2.48699000	-0.89580300
H	-3.88046400	-3.99619300	-0.03201700
C	-3.77178400	2.90868500	0.02176300
H	-3.88029800	3.99631600	0.03185400
H	-4.27803500	2.50380400	-0.86102000
H	-4.27975600	2.48717400	0.89570800
C	1.34712400	3.11606900	0.03386100
H	1.92232700	2.74404800	0.88819500
H	1.32671100	4.20938200	0.08477100
H	1.90365500	2.82710300	-0.86406200
C	1.34699200	-3.11618900	-0.03374900
H	1.92224400	-2.74421300	-0.88806900
H	1.90350800	-2.82723800	0.86418800
H	1.32652200	-4.20950200	-0.08464300
C	-2.32742000	-2.52662900	-0.01964300
C	-2.32731900	2.52668300	0.01959500
C	-0.05500800	2.58284400	0.02422600

C	-0.05511200	-2.58289000	-0.02417400
N	-1.91443200	1.24472200	0.00668100
N	-1.91447900	-1.24468700	-0.00664500
B	-2.84966300	0.00003600	0.00003500
F	-3.64622000	0.00603800	-1.14459600
F	-3.64618500	-0.00593600	1.14469200
C	3.77003400	-0.05596700	1.21741400
C	4.46189900	-0.00002300	0.00000000
C	3.77005900	0.05592700	-1.21742800
C	2.36365500	0.05414500	-1.21313200
C	1.67306600	-0.00003500	-0.00002900
C	2.36363100	-0.05418900	1.21308900
H	5.55040300	-0.00002000	0.00001100
H	1.81515000	0.10339800	-2.14989100
H	1.81510600	-0.10342900	2.14983800
N	4.46942200	0.17507200	-2.41999100
H	5.41150600	-0.19551300	-2.40822300
H	3.96107700	-0.12892400	-3.24100300
N	4.46937400	-0.17509700	2.41999200
H	5.41145700	0.19548900	2.40824000
H	3.96101300	0.12890800	3.24099000

BODIPY-2 + 1eq. PA:-

0 1

C	4.36108100	-0.98576600	0.44080700
C	3.41294000	-0.11776300	-0.12411700
C	3.78280500	1.13633900	-0.63651300
C	3.93477900	3.18703200	-1.56417900
H	3.71258500	4.13113100	-2.04518000
C	5.52477300	-2.65550200	1.41352200
H	5.81207400	-3.58431000	1.88978900
C	7.88094300	-1.52770700	1.31499100
H	8.41095900	-1.40217900	0.36479500
H	8.12925000	-0.65662400	1.93048500
H	8.23978700	-2.43340900	1.81022800
C	6.50943200	3.51067300	-1.25070300
H	6.35455600	4.49093800	-1.70825900
H	6.96212700	3.64053000	-0.26205600
H	7.22618700	2.94137100	-1.85214900
C	1.55395600	2.25631300	-1.55802700
H	1.21572400	1.42894100	-2.19045800
H	1.32810500	3.19268100	-2.07718500
H	0.94631000	2.22406300	-0.64665200
C	3.02588400	-3.15541800	1.19965200
H	2.25585300	-2.66221600	1.80309200
H	2.55770500	-3.41579900	0.24429700
H	3.30310200	-4.08650200	1.70335000
C	6.40677400	-1.60373200	1.08735700
C	5.21517900	2.77352200	-1.14026100
C	3.02321600	2.18381700	-1.26114200
C	4.24216700	-2.29474200	1.02106100

N	5.11943100	1.54946000	-0.58760900
N	5.70776200	-0.60976300	0.50745500
B	6.31030400	0.73830600	0.00743600
F	6.87343700	1.43265800	1.07540000
F	7.26232900	0.49817700	-0.97897500
C	0.15815900	-1.65351600	-1.37345900
C	-0.70862100	-1.32892000	-0.31051800
C	-0.21454100	-0.61777300	0.76707000
C	1.11347600	-0.20802600	0.87134000
C	1.97768900	-0.53825000	-0.18206400
C	1.50535300	-1.24923900	-1.28846300
H	-1.75548100	-1.60563900	-0.35345400
H	1.47618600	0.35281800	1.72760500
H	2.19206200	-1.49044900	-2.09579500
N	-1.17726400	-0.27417400	1.83661800
H	-1.00258000	-0.79724200	2.70028000
H	-1.15890100	0.71954500	2.08328400
N	-0.32308100	-2.38262200	-2.43662600
H	-1.32953500	-2.40569800	-2.55853900
H	0.20471700	-2.36461100	-3.29786000
C	-5.28915900	-0.79846900	-0.66982800
C	-6.55511500	-0.34458800	-0.97330700
C	-7.16011400	0.59838000	-0.13899600
C	-6.50669000	1.07789400	0.98854500
C	-5.23767500	0.61122000	1.30312100
C	-4.55247000	-0.40731600	0.52272500
H	-7.06940200	-0.70082200	-1.85689600
H	-6.98299700	1.81609200	1.62042800
N	-4.61991300	1.18649300	2.48585400

N	-8.48542700	1.10343300	-0.47078200
N	-4.68119500	-1.71334500	-1.63466600
O	-3.47911900	-0.98024700	0.85178000
H	-2.20466000	-0.47496900	1.53455700
O	-3.45972700	-1.64092400	-1.81741400
O	-5.33766500	1.77202500	3.29513100
O	-9.02766100	0.65937100	-1.48516400
O	-5.42328900	-2.47253300	-2.25528200
O	-8.98416200	1.94277500	0.28144900
O	-3.38895900	1.09030200	2.62623800

BODIPY-2 +2 eq. PA :-

0 1

C	5.30815800	-1.64763200	-0.04828700
C	4.56390500	-0.46009700	-0.14085500
C	5.18048600	0.79851700	-0.05882000
C	5.74939600	2.98022600	0.01437900
H	5.72728100	4.06256000	0.00989700
C	6.09810700	-3.75826900	0.04860100
H	6.18702800	-4.83720000	0.05651300
C	8.62174700	-3.15985600	0.37564500
H	9.21077700	-2.74252400	-0.44817000
H	8.99639300	-2.69769200	1.29491300
H	8.78322600	-4.23968800	0.42226300
C	8.31996700	2.64752700	0.35395700
H	8.37411400	3.73897800	0.35520700
H	8.72559100	2.26492400	1.29668700
H	8.95787000	2.25453400	-0.44466100

C	3.24325600	2.60156200	-0.31864700
H	2.80930200	2.23937200	-1.25687900
H	3.21508000	3.69524900	-0.33539200
H	2.58301100	2.26198500	0.48697400
C	3.56503000	-3.64201400	-0.28026800
H	2.86531700	-3.33541600	0.50503900
H	3.10788300	-3.36324100	-1.23569100
H	3.64471300	-4.73299600	-0.25146200
C	7.17158000	-2.85406400	0.19023100
C	6.90980400	2.19245400	0.16807900
C	4.65690300	2.13491500	-0.12907600
C	4.92407600	-3.03107600	-0.10117100
N	6.56542000	0.89168500	0.12319900
N	6.69520600	-1.59602800	0.13222900
B	7.55721800	-0.30344900	0.25757600
F	8.18166900	-0.26574900	1.50180200
F	8.49984000	-0.25891700	-0.76592900
C	1.14503500	-0.67792000	-1.81349100
C	0.30495000	-0.71789600	-0.68432600
C	0.86924700	-0.63847500	0.58089500
C	2.23992300	-0.55280800	0.79676200
C	3.08108800	-0.54141400	-0.32622000
C	2.53875300	-0.59776400	-1.60953800
H	-0.76973500	-0.80354300	-0.79643800
H	2.65776400	-0.49345500	1.79730800
H	3.20481400	-0.57467500	-2.46824300
N	-0.05228300	-0.63576700	1.73242300
H	-0.45190800	-1.57529100	1.90632100
H	0.39089900	-0.28909300	2.58584900

N	0.60769500	-0.75822800	-3.08249900
H	-0.34570700	-0.42929400	-3.20110300
H	1.21249700	-0.47501000	-3.84223900
C	-2.60474300	2.01286200	-1.06081700
C	-2.74111700	3.30548100	-1.52828100
C	-2.70327600	4.36148400	-0.61902500
C	-2.44970000	4.13195900	0.73172200
C	-2.23114500	2.83999300	1.17685500
C	-2.34907600	1.66722100	0.32857800
H	-2.88446800	3.50085900	-2.58379300
H	-2.40001900	4.96202600	1.42504400
C	-6.51274300	-2.07738200	-0.31134500
C	-5.34800600	-2.43474400	-0.97669700
C	-4.08873000	-2.55065700	-0.31276400
C	-4.09423700	-2.24077900	1.07719800
C	-5.25313700	-1.87322400	1.74506000
C	-6.45307000	-1.81004900	1.04795300
H	-7.44896900	-2.00804100	-0.85010400
H	-5.21621800	-1.62894100	2.79873000
N	-1.86138000	2.69091800	2.57924500
N	-2.89646500	5.72387100	-1.09404900
N	-2.61341900	0.94735900	-2.04804200
N	-5.45564500	-2.69266400	-2.41041700
N	-2.86393300	-2.24047300	1.86035400
N	-7.68251100	-1.44093100	1.76349400
O	-2.98446200	-2.90532800	-0.92817800
H	-3.20956500	-2.99019600	-1.89554500
O	-2.21985800	0.47680700	0.72573200
H	-0.89775500	-0.00904900	1.53307500

O	-3.17589500	-0.11370400	-1.77111800
O	-2.25146300	3.54220300	3.37536000
O	-3.11837600	5.88279900	-2.29669100
O	-1.86260900	-2.79779300	1.38955800
O	-7.58619100	-1.22069100	2.96809100
O	-4.42287200	-3.02837500	-3.02627400
O	-6.54596100	-2.57725200	-2.94529400
O	-8.71833300	-1.38219200	1.10564900
O	-2.87436600	-1.67380100	2.94920200
O	-2.02846600	1.15281800	-3.12182000
O	-2.82536900	6.63443200	-0.26664700
O	-1.13856200	1.73600400	2.89691700