Supporting Information for

Fusion and Planarization of BisBODIPY: a New Family of Photostable Near Infrared Dyes

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Contents:

1. General Information

Reagents and solvents were used as received from commercial suppliers unless noted otherwise. All reactions were performed in oven-dried or flame-dried glassware unless otherwise stated, and were monitored by TLC using 0.25 mm silica gel plates with UV indicator (HSGF 254). Flash column chromatography was performed using silica gel (200−400 mesh). For thin-layer chromatography (TLC). ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz or 125 MHz) spectra were recorded at 300 MHz or 500 MHz NMR spectrometer in $CDCl_3$ or d_6-DMSO. Chemical shifts (δ) are given in ppm relative to $CDCl_3$ (7.26 ppm for ^{1}H and 77 ppm for ^{13}C) or d_6-DMSO (2.54 ppm for ^{1}H and 39.9 ppm for ^{13}C) or to internal TMS (δ = 0 ppm) as internal standard. Data are reported as follows: chemical shift, multiplicity, coupling constants and integration. High-resolution mass spectra (HRMS) were obtained using APCI-TOF in positive mode.

Crystals of bisBODIPY **4** and BBP **1** suitable for X-ray analysis were obtained by by slow evaporation of a concentrated solution of the compound in a mixture of CH_2Cl_2/n-hexane. Diffraction was performed on a Bruker SMART APEXII CCD area detector diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293(2) K, with φ and ω scan techniques. An empirical absorption correction was applied using the SADABS program.[1] All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations based on F^2 using the SHELXTL program package.[2] The hydrogen atom coordinates were calculated with SHELXTL by using an appropriate riding model with varied thermal parameters. The residual electron densities were of no chemical significance.

UV-visible absorption spectra and Fluorescence emission spectra were recorded on a commercial spectrophotometer (190-1100 nm scan range, Shimadzu UV-4100, Edinburgh Instrucments FS5 and FLS 920). Relative fluorescence quantum efficiencies of BODIPY derivatives were obtained by comparing the areas under the corrected emission spectrum of the test sample in various solvents with fluorescein in 0.1 M NaOH aqueous solution (ϕ = 0.90)[3a], Rhodamine B (ϕ = 0.49 in ethanol)[3b], 1,7-diphenyl-3,5-di(*p*-methoxyphenyl)-azadipyrromethene (ϕ = 0.36 in chlorofrm)[3c], and and ICG (ϕ = 0.12 in DMSO)[3d]. Non-degassed, spectroscopic grade solvents and a 10 mm quartz cuvette were used. Dilute solutions (0.01<A<0.05) were used to

minimize the reabsorption effects. Quantum yields were determined using the following equation[3e]:

$$\Phi_X = \Phi_S (I_X/I_S) (A_S/A_X) (n_X/n_S)^2$$

Where Φ_S stands for the reported quantum yield of the standard, I stands for the integrated emission spectra, A stands for the absorbance at the excitation wavelength and *n* stands for the refractive index of the solvent being used. X subscript stands for the test sample, and S subscript stands for the standard. The photostabilities of BBPs **2a** and **3a** were studied by continuous irradiation with a Xe lamp (500 W) in DMSO.

Cyclic voltammetry experiments were performed with a Bioanalytical Systems Inc. (BASi) Epsilon potentiostat and analyzed using BASi Epsilon software. Electrochemical cells consisted of a three-electrode setup including a glassy carbon as working electrode, platinum wire as counter electrode, and saturated calomel electrode (SCE) as pseudo reference electrode. Experiments were run at 20 mV s^{-1} scan rates in degassed dichloromethane solutions of BODIPY **M**, BBPs **1-3**, and bisBODIPY **4** (~1 mM) and supporting electrolyte (0.1 M tetrabutylammonium hexafluorophosphate) at room temperature. Cyclic voltammograms were referenced against an external standard (~1 mM potassium ferricyanide) and corrected for external cell resistance using the BASi Epsilon software.

2. X-ray crystal dimer and packing diagram

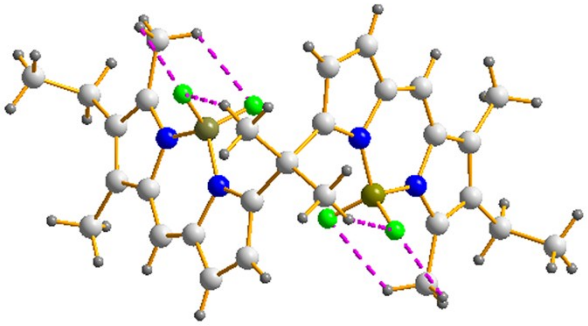


Figure S1. The dimer structures of cabon-bridged bisBODIPY **4**. C, light gray; H, gray; N, blue; B, dark yellow; F, bright green.

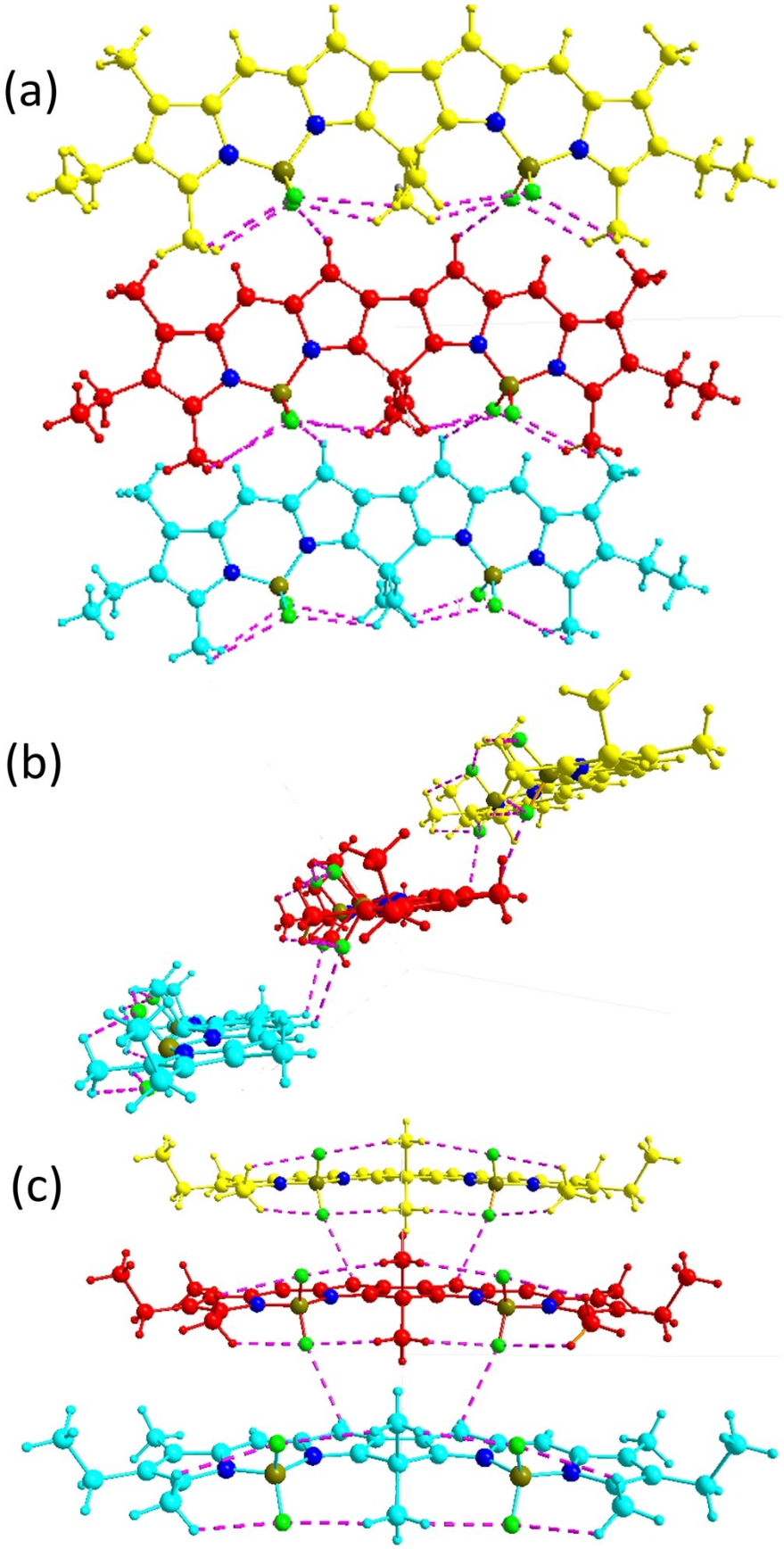


Figure S2. (a) top, (b) side, and (c) front views of X-Ray structure packing of BBP **1**.

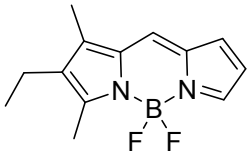
3. Photophysical Properties

Table S1: Photophysical properties of BODIPY **M**, BBPs **1-3**, and bisBODIPY **4** in different solvents at room temperature.

dyes	solvents	λ_{abs}^{max} (nm)	λ_{em}^{max} (nm)	ε_{max}[a]	ϕ[b]	Stokes Shift (cm^{-1})
M	Hexane	510	515	41000	0.577	190
	Toluene	510	521	40500	0.582	414
	DCM	500	519	33500	0.539	732
	THF	502	517	40400	0.582	578
	Acetonitrile	494	516	34700	0.536	863
	MeOH	498	516	35600	0.489	700
4	Hexane	538	600	133900	0.187	1921
	Toluene	538	603	107000	0.137	2004
	DCM	534	596	109000	0.167	1948
	THF	534	597	110600	0.193	1976
	Acetonitrile	530	540	93700	0.073	349
	MeOH	532	585	106300	0.059	1703
1	Hexane	696	700	117600	0.450	82
	Toluene	696	705	135500	0.547	183
	DCM	688	701	132900	0.544	270
	THF	686	697	149600	0.569	230
	Acetonitrile	676	690	116900	0.310	300
	MeOH	678	690	144000	0.304	257
2a	Hexane	750	754	167200	0.320	71
	Toluene	748	761	139400	0.463	228
	DCM	744	758	131100	0.217	248
	THF	742	753	138000	0.283	197
	Acetonitrile	728	746	120100	0.106	331
	DMSO	736	746	128100	0.112	182
	MeOH	730	754	107600	0.104	436
2b	Hexane	764	773	81400	0.174	152
	Toluene	772	789	76600	0.316	279
	DCM	766	791	65800	0.063	413
	THF	762	785	69800	0.058	385
	Acetonitrile	751	788	63600	0.005	625
	DMSO	763	779	68500	0.004	269
	MeOH	752	798	59800	0.008	767
3a	Hexane	796	804	69000	0.274	140
	Toluene	800	807	61500	0.211	154
	DCM	792	807	58700	0.098	219
	THF	788	804	59800	0.139	157
	Acetonitrile	776	796	50600	0.031	292
	DMSO	786	795	61300	0.075	144

	MeOH	778	803	47000	0.046	400
	Hexane	832	845	55600	0.070	185
	Toluene	842	861	61400	0.057	262
	DCM	834	866	68900	0.008	443
3b	THF	830	865	71400	0.015	487
	Acetonitrile	820	867	65000	0.001	661
	DMSO	834	877	74100	0.002	588
	MeOH	820	865	59600	0.002	634

[a]Molar absorption coefficient are in the maximum of the highest peak. [b]Fluorescence quantum yields were calculated using Fluorescein（ϕ = 0.90 in 0.1 M NaOH solution）for BODIPY **M**, Rhodamine B (ϕ = 0.49 in ethanol) for bisBODIPY **4**, 1,7-diphenyl-3,5-di(*p*-methoxyphenyl)-azadipyrromethene (ϕ = 0.36 in chloroform) for BBP **1**, and ICG (ϕ = 0.12 in DMSO for BBP **2a-b** and **3a-b** as the reference, and excited wavelengths were 460 nm for BODIPY **M**, 485 nm for bisBODIPY **4**, 640 nm for BBP **1**, 700 nm for BBP **2a-b** and **3a**, and 740 nm for BBP **3b**. The standard errors are less than 5%.



monomeric BODIPY **M**

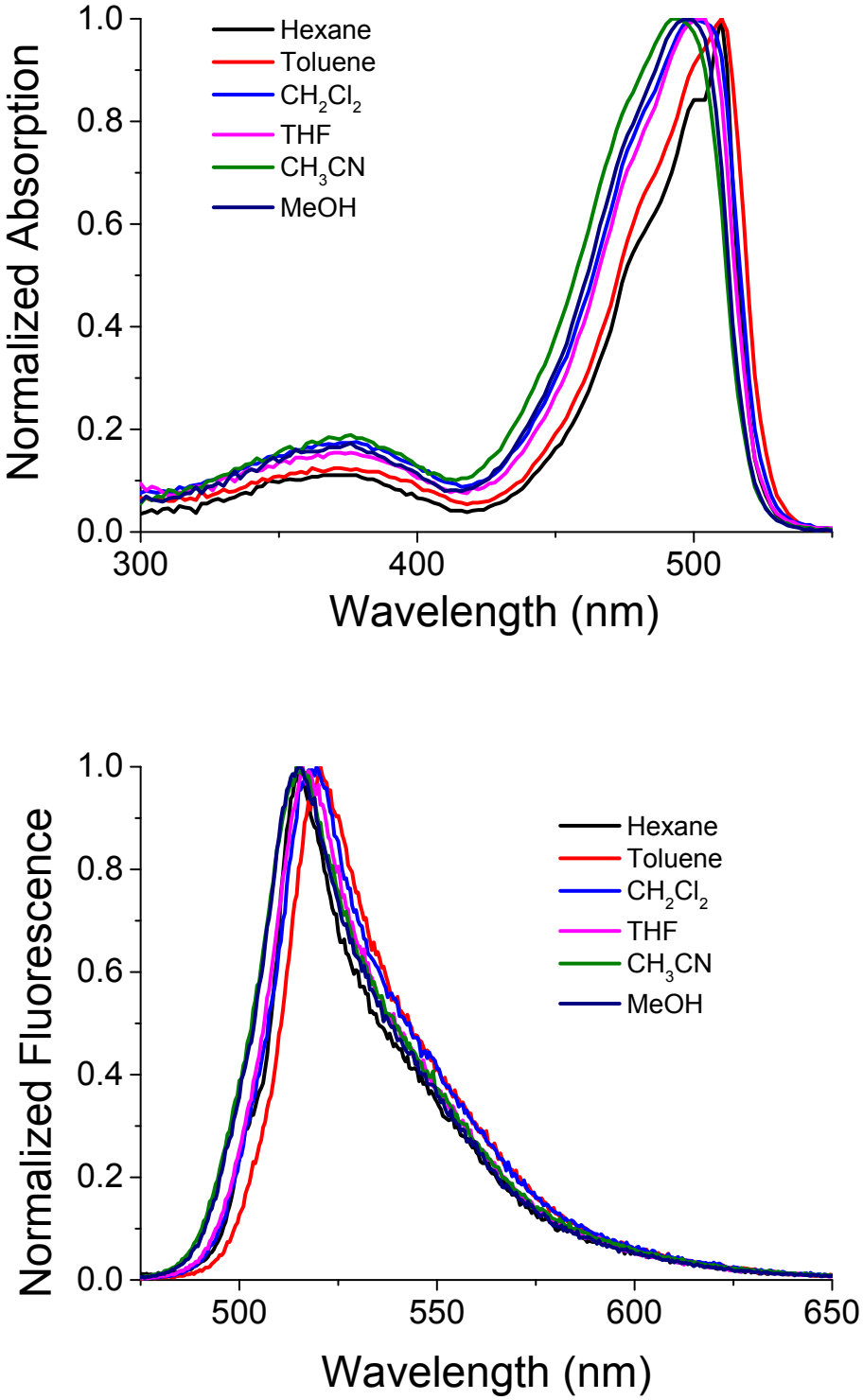


Figure S3. Normalized absorption (top) and emission (bottom) spectra of BODIPY **M** recorded in different solvents, excited at 460 nm.

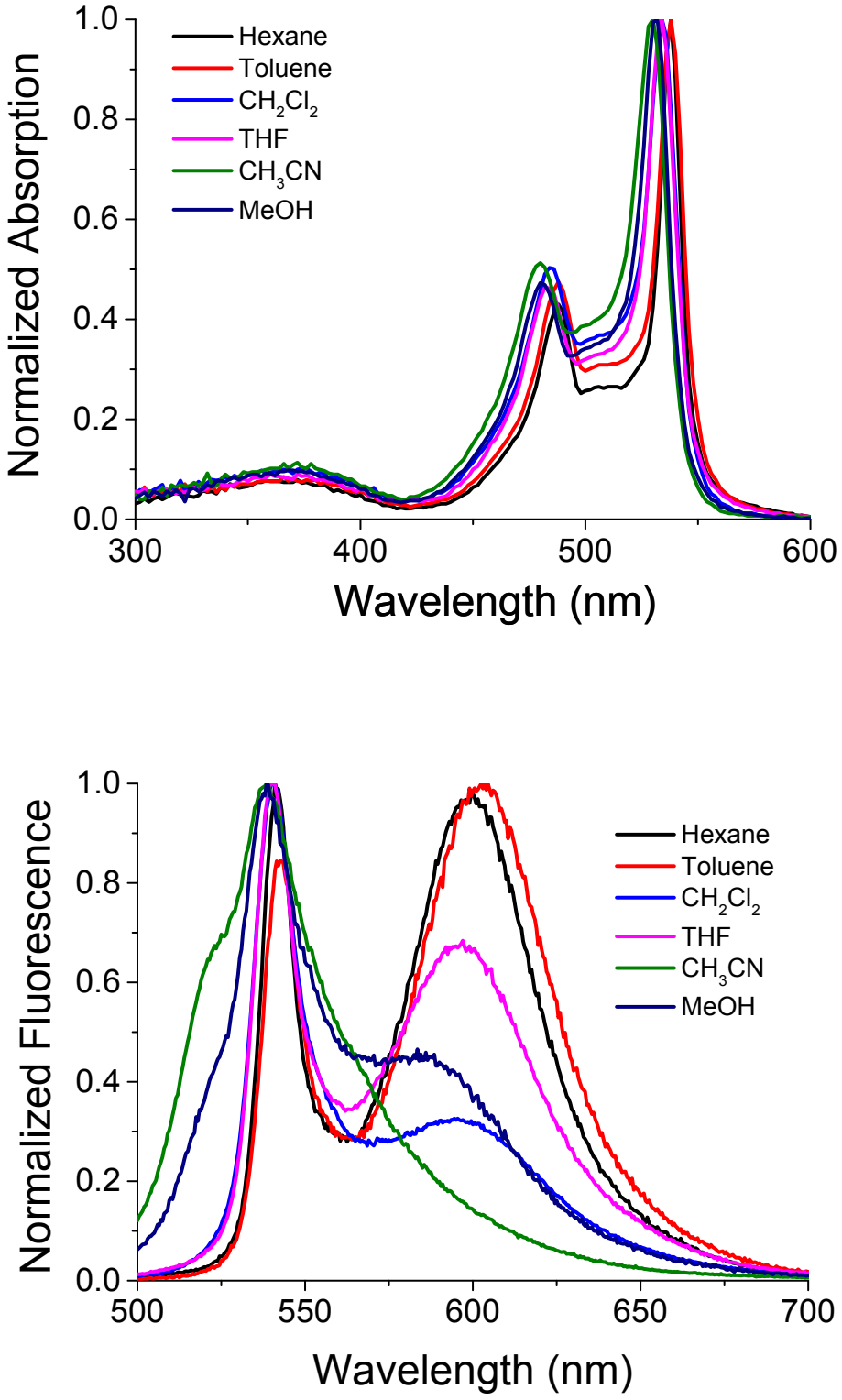


Figure S4. Normalized absorption (top) and emission (bottom) spectra of bisBODIPY **4** recorded in different solvents, excited at 485 nm.

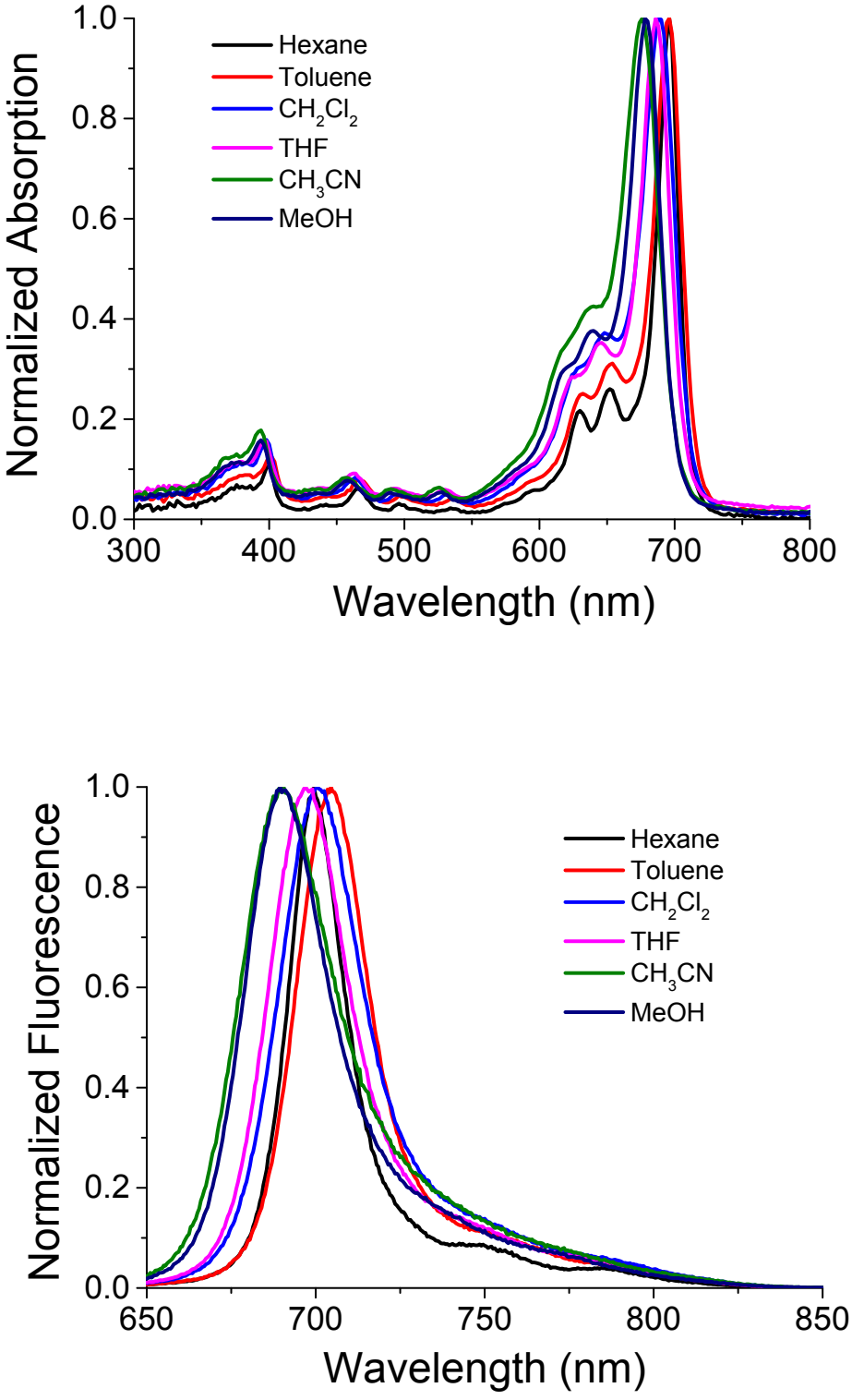


Figure S5. Normalized absorption (top) and emission (bottom) spectra of BBP **1** recorded in different solvents, excited at 640 nm.

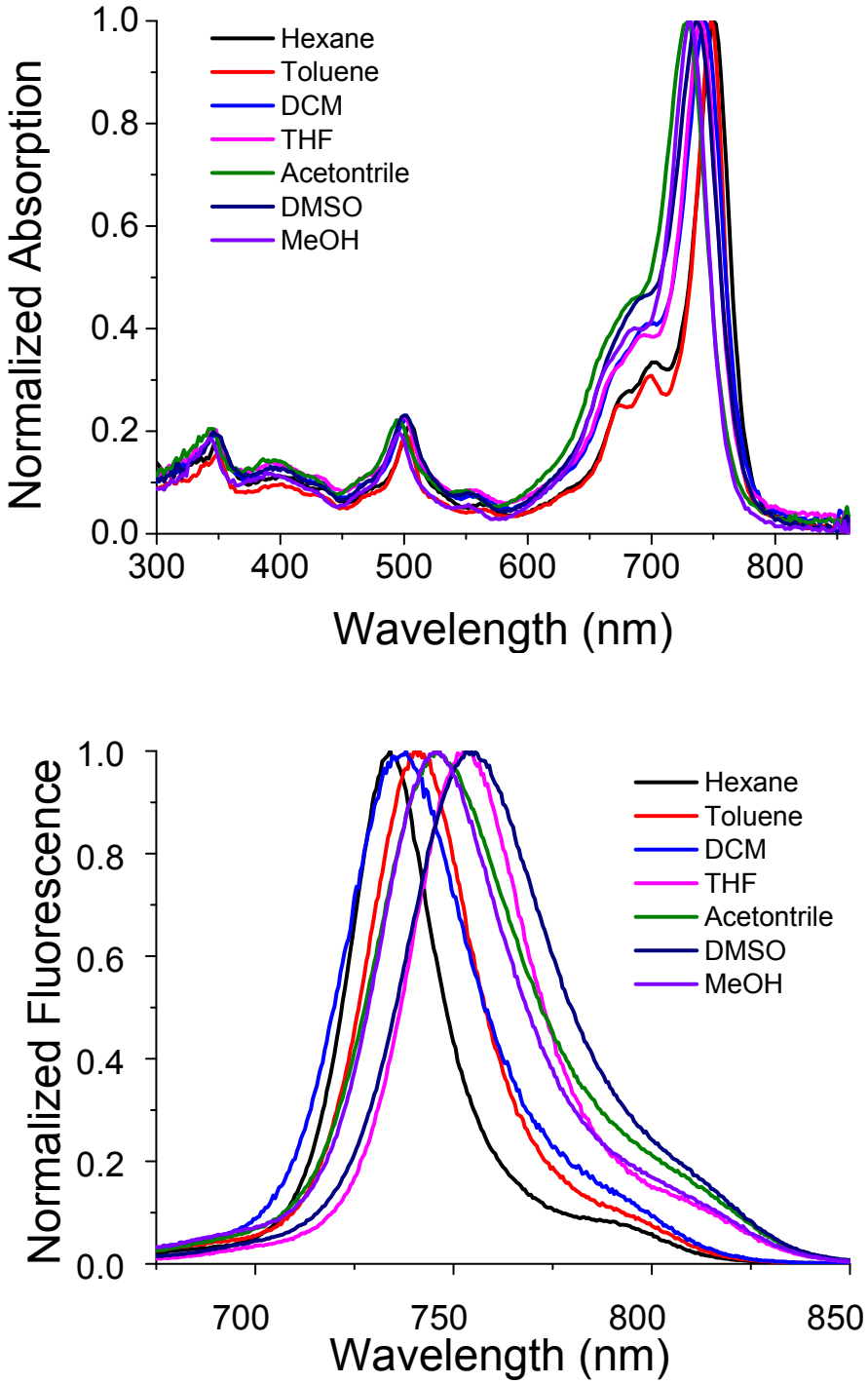


Figure S6. Normalized absorption (top) and emission (bottom) spectra of BBP **2a** recorded in different solvents, excited at 500 nm.

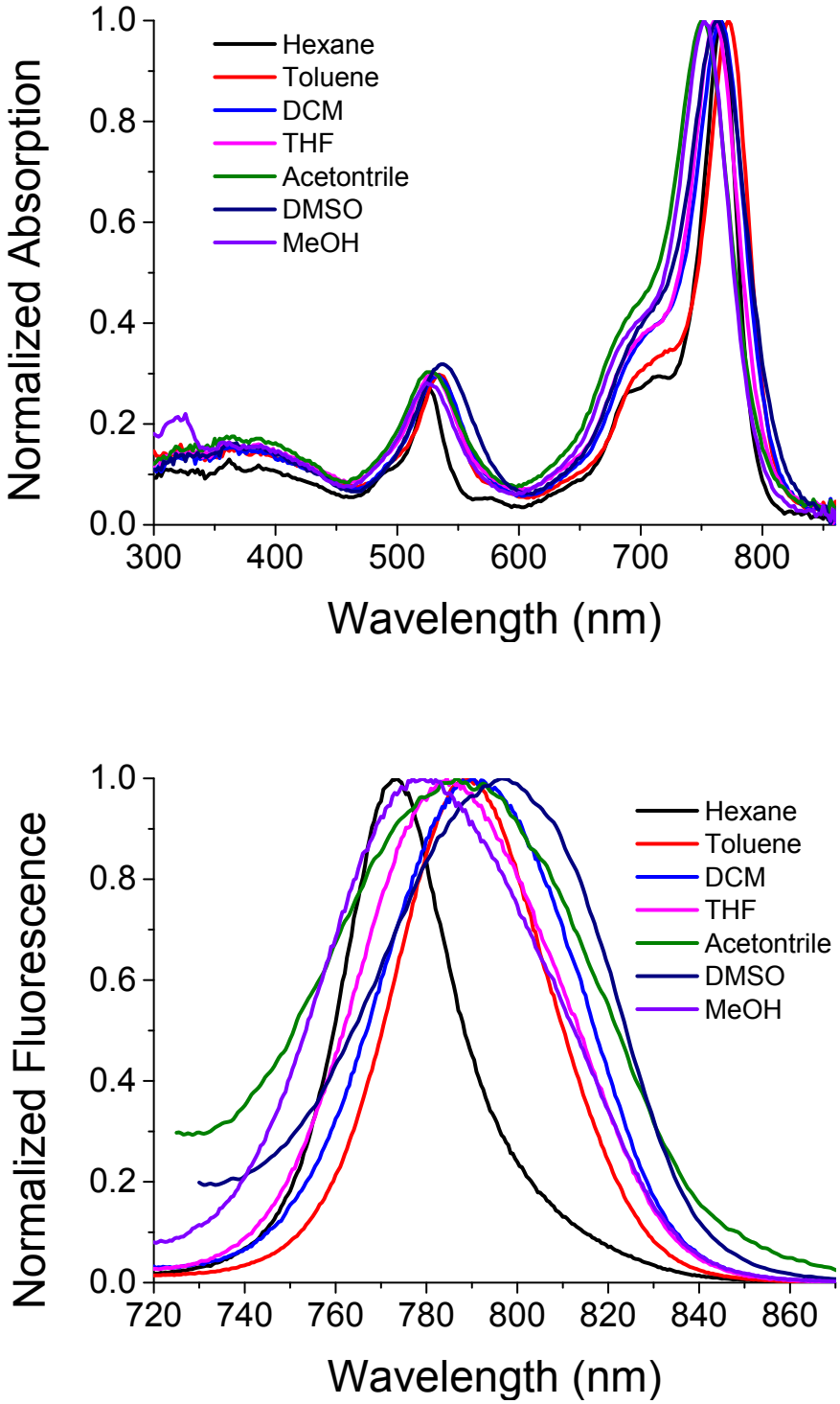


Figure S7. Normalized absorption (top) and emission (bottom) spectra of BBP **2b** recorded in different solvents, excited at 527 nm.

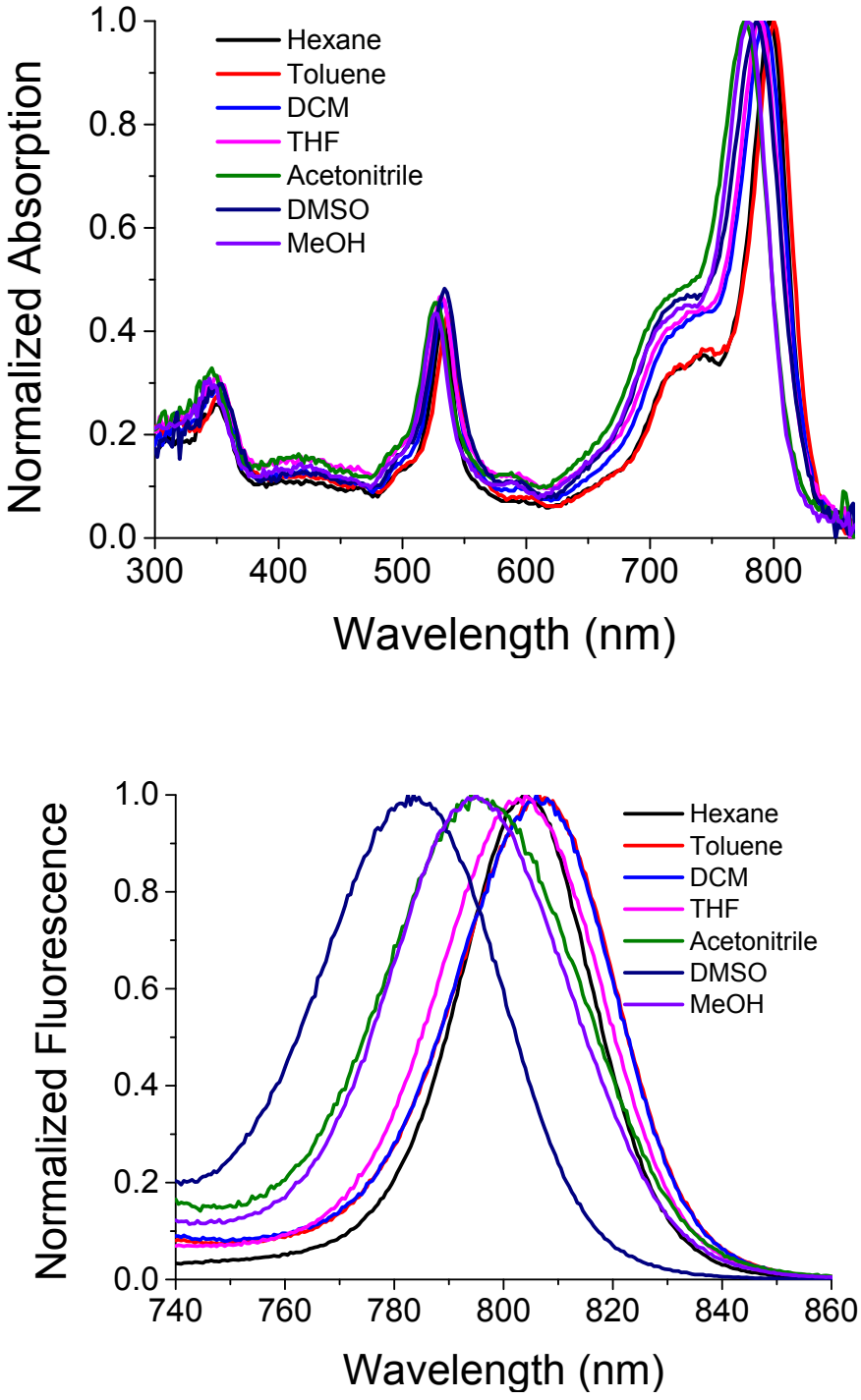


Figure S8. Normalized absorption (top) and emission (bottom) spectra of BBP **3a** recorded in different solvents, excited at 530 nm.

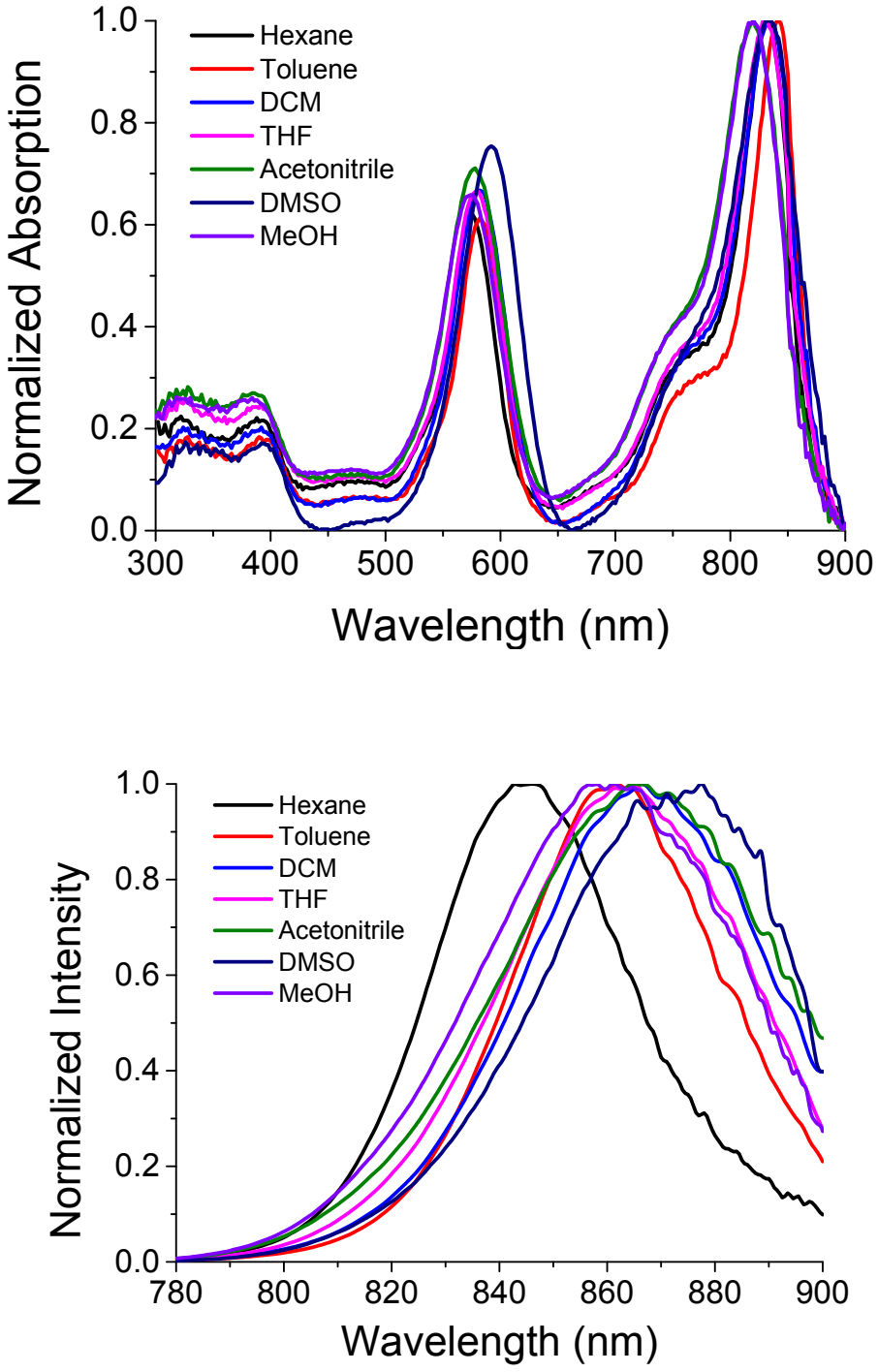


Figure S9. Normalized absorption (top) and emission (bottom) spectra of BBP **3b** recorded in different solvents, excited at 565 nm.

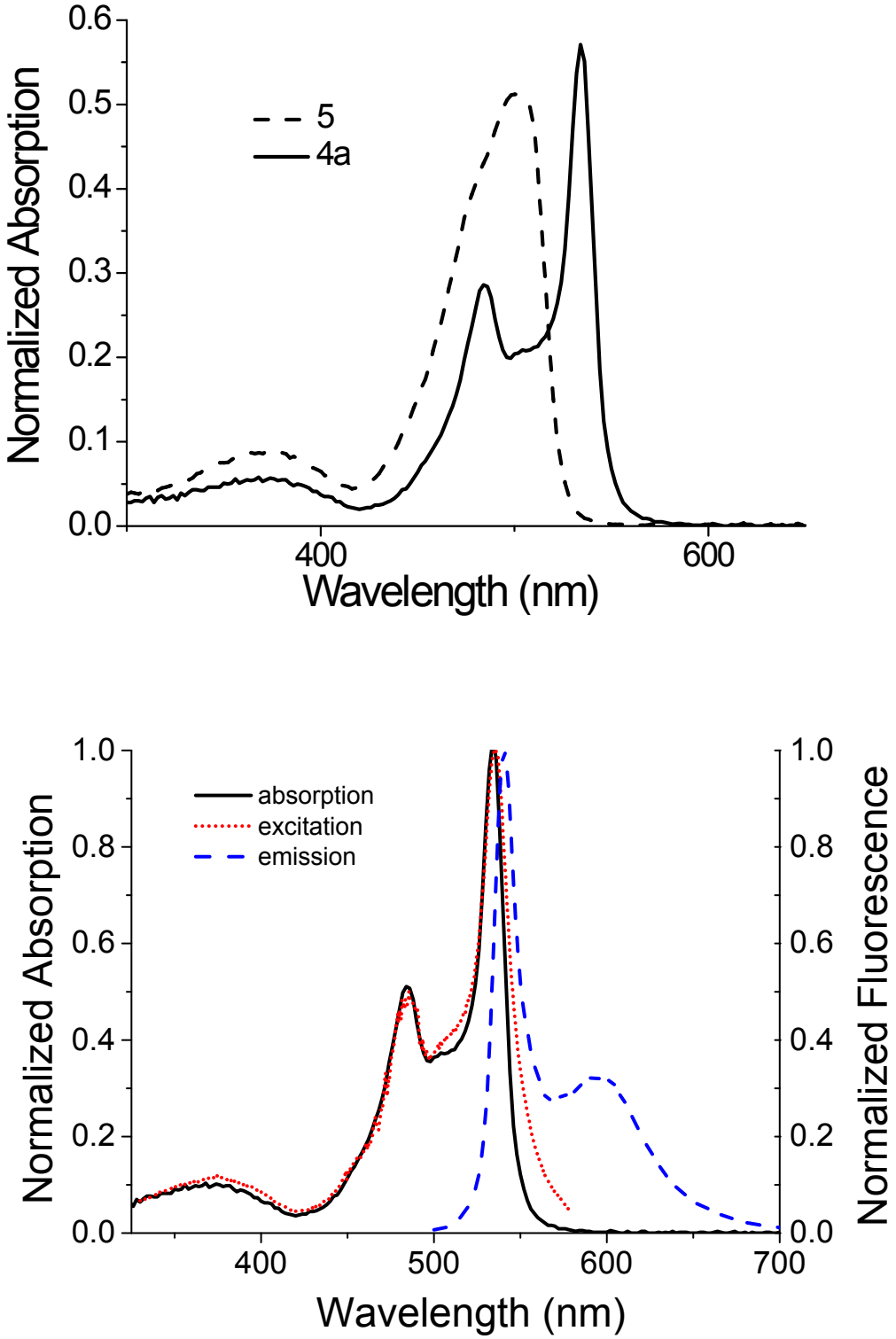


Figure S10. (a) UV−Vis spectrum of the novel carbon-bridged bisBODIPY **4** (solid) as compared to that of its monomeric BODIPY **M** (dash) in dichloromethane (top); (b) Normalized UV−vis spectra (solid), excited spectra registered at 600 nm (short dot) and fluorescence spectra excited at 485 nm (dash) of bisBODIPY **4** in dichloromethane (botton).

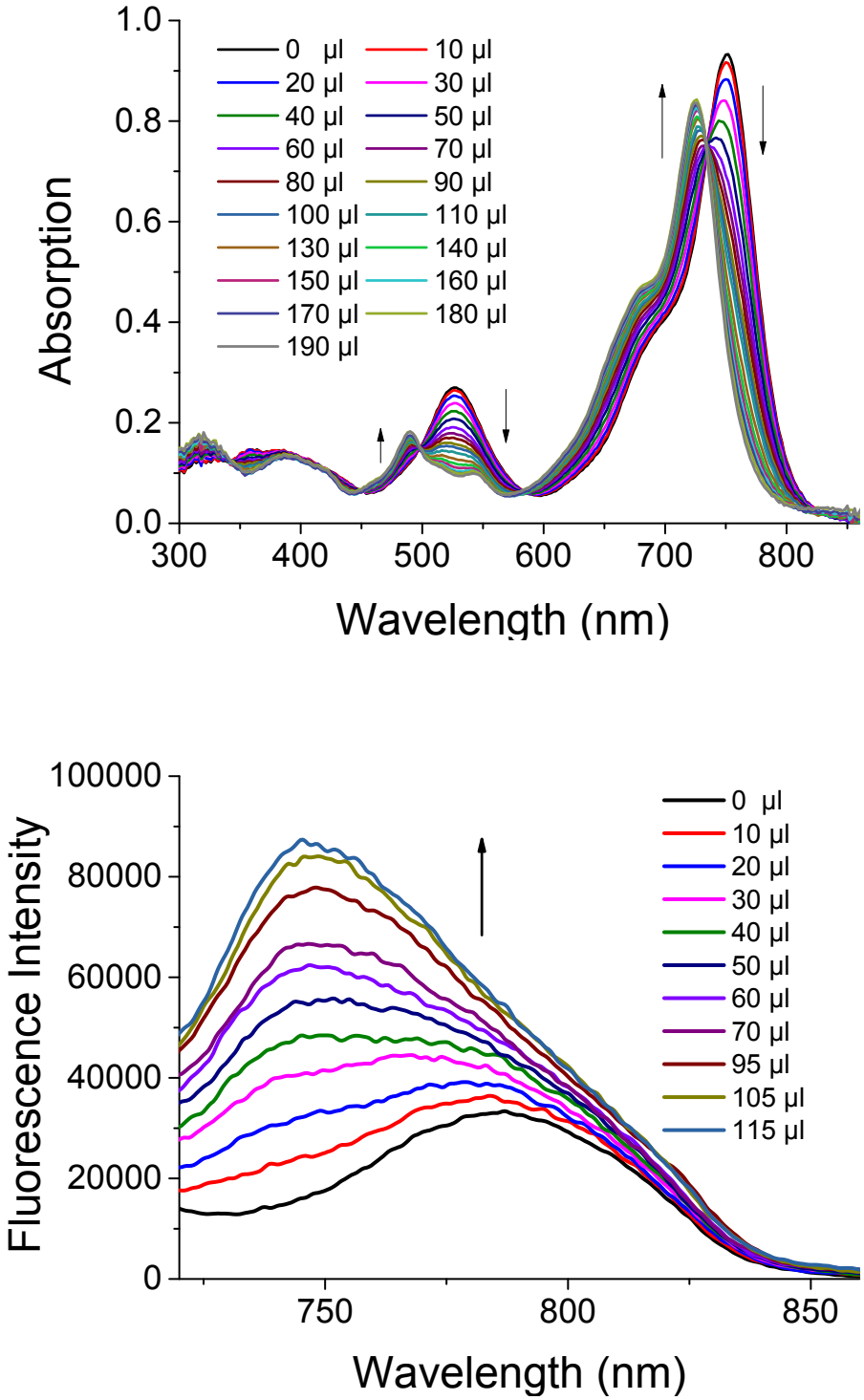


Figure S11. (a) Absorbance TFA (TFA: trifluoroacetic acid, 1.5 × 10^{-4} M) titration spectra of BBP **2b** in acetontrile (1.43 × 10^{-5} M); (b) Fluorescence TFA titration spectra (botton) of BBP **2b** (3.90 × 10^{-6} M) in acetonitrole after adding aliquots of TFA (1.5 × 10^{-4} M), excited at 527 nm.

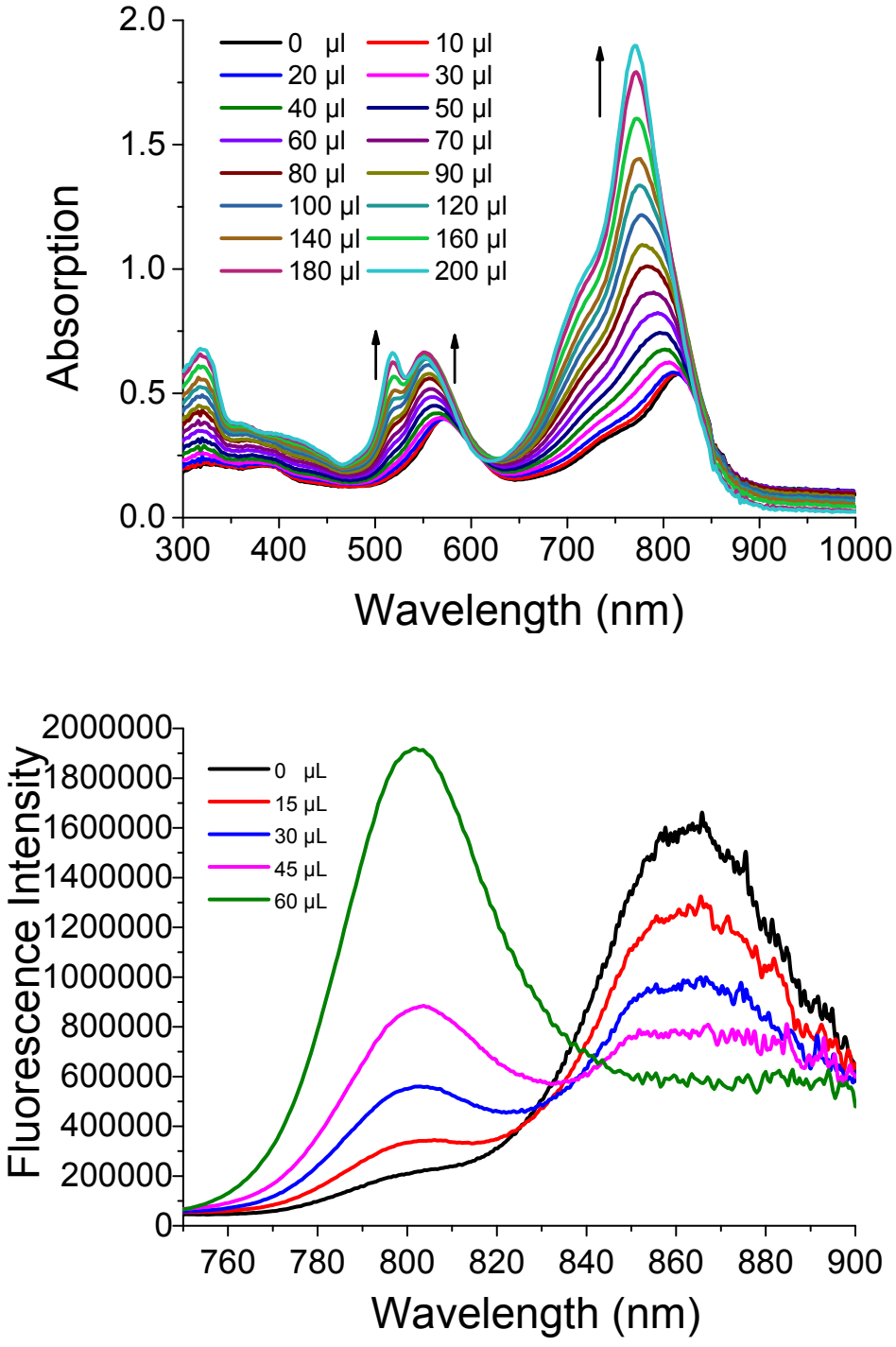


Figure S12. (a) Absorbance TFA (TFA: trifluoroacetic acid, 1.5 × 10^{-4} M) titration spectra of BBP **3b** in acetontrile (8.78 × 10^{-6} M); (b) Fluorescence TFA titration spectra (botton) of BBP **3b** (2.19 × 10^{-6} M) in dichloromethane after adding aliquots of TFA (1.5 × 10^{-4} M), excited at 565 nm.

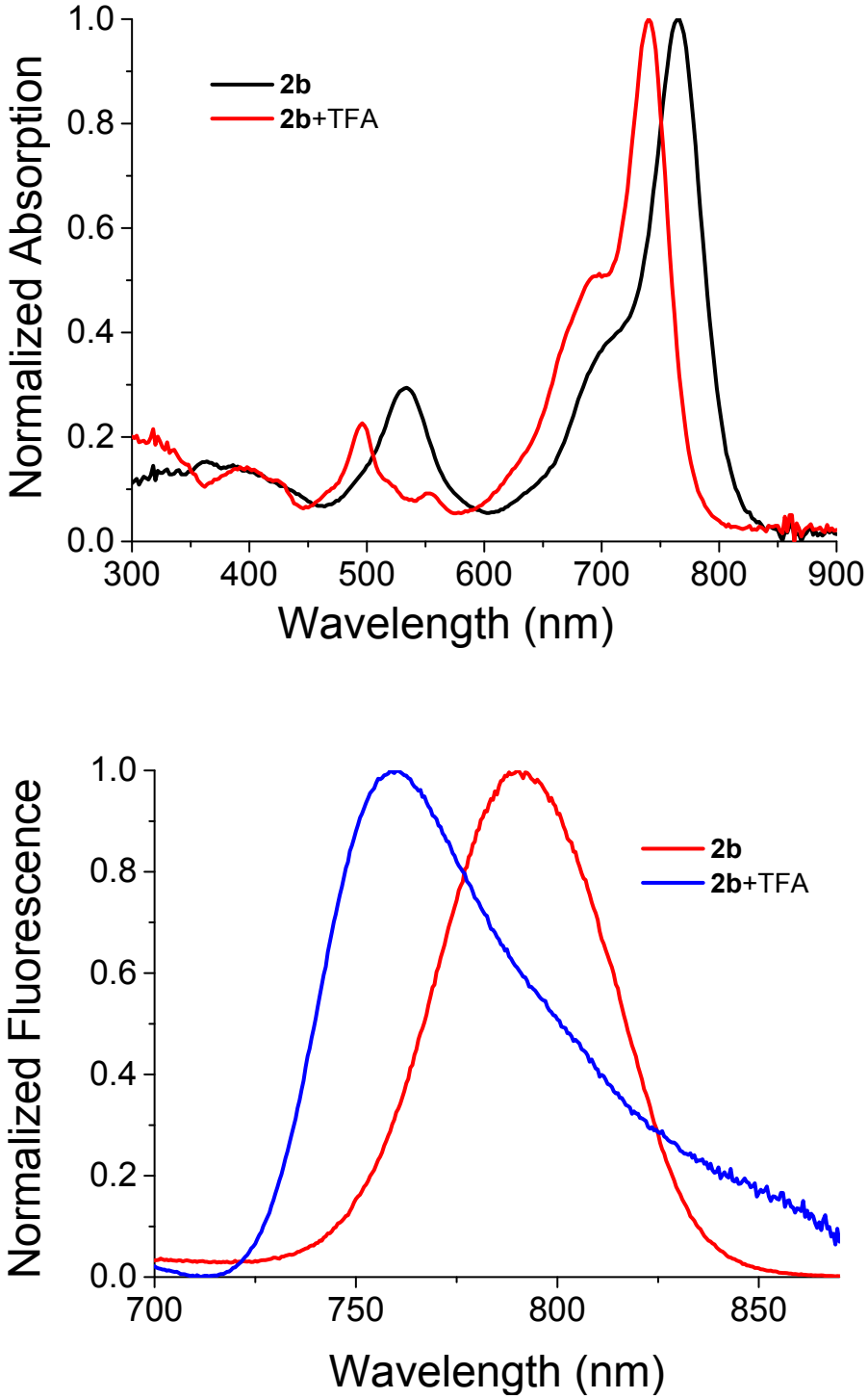


Figure S13. Normalized absorption and fluorescence spectra changes of BBP **2b** in dichloromethane after adding TFA. (TFA: trifluoroacetic acid).

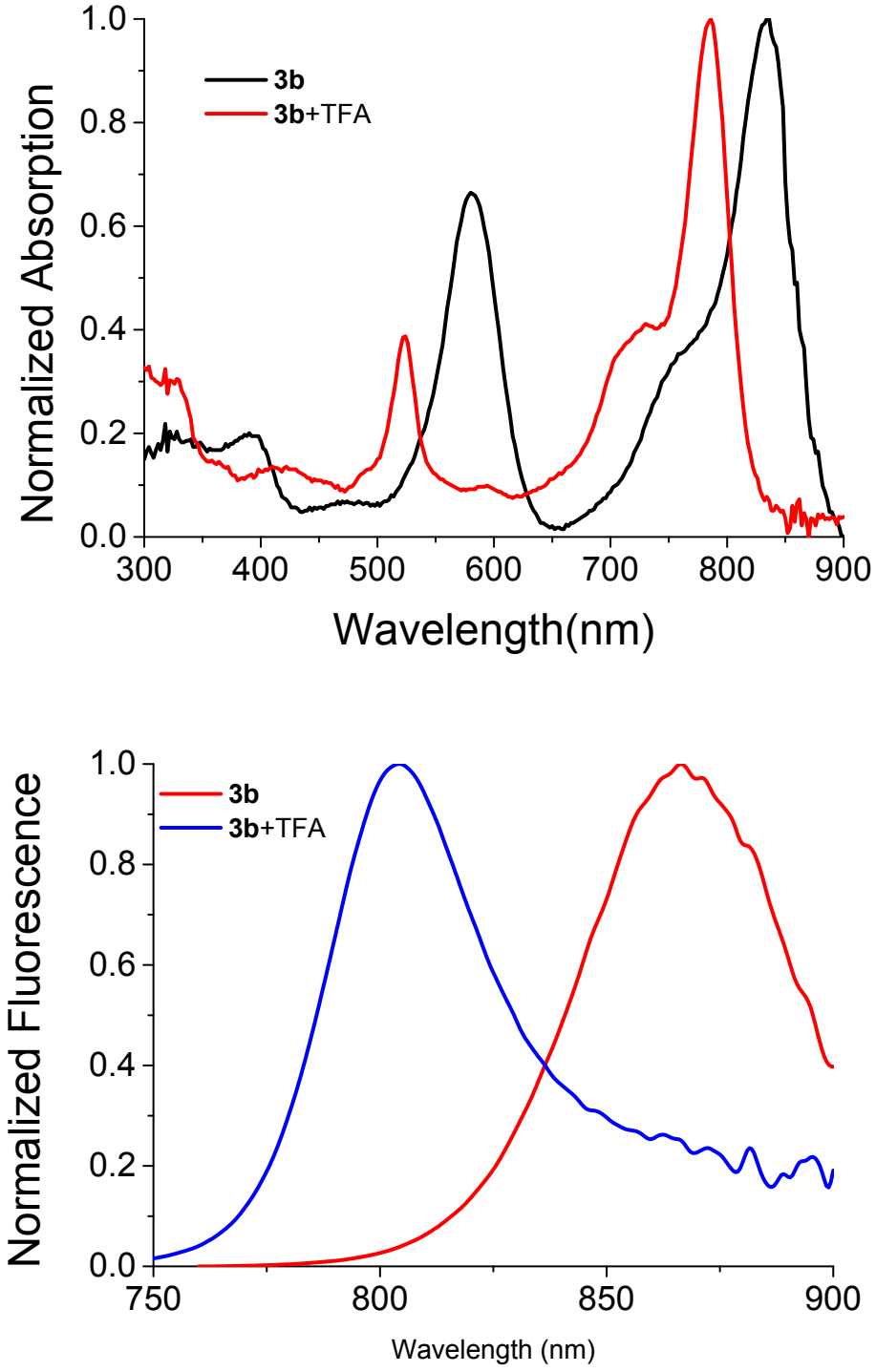


Figure S14. Normalized absorption and fluorescence spectra changes of BBP **3b** in dichloromethaneafter adding TFA. (TFA: trifluoroacetic acid).

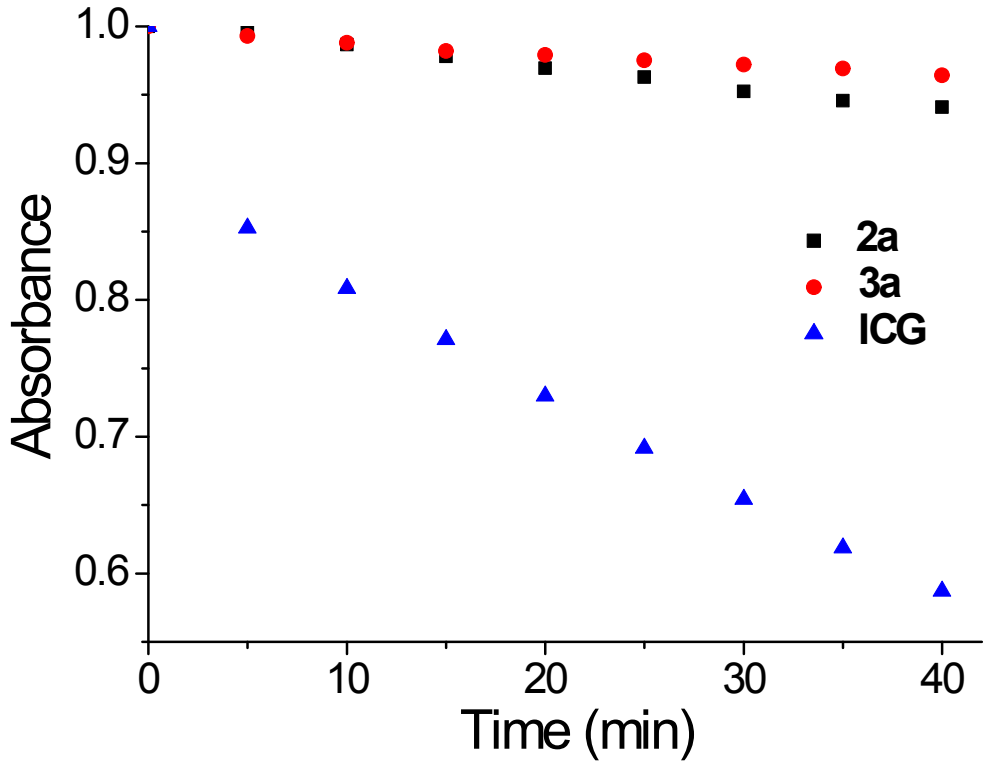


Figure S15. Comparison of the photostability of BBPs **2a, 3a** and **ICG** at the same absorption in DMSO under continuous irradiation with a 500 W Xe lamp over 40 min; 21 $mW.cm^{-2}$; > 590 nm light used, 25^0C.

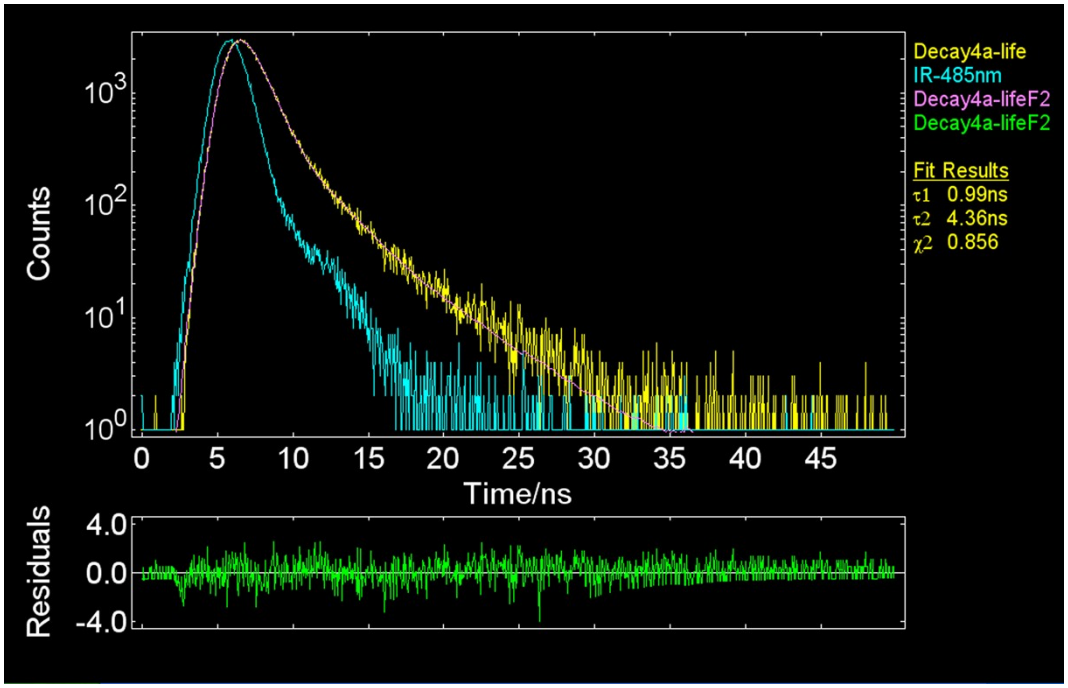


Figure S16. The fluorescence decay of **4** in distilled CH_2Cl_2 measured by single photon counting method with emission was monitored at 541 nm, excited at 485 nm.

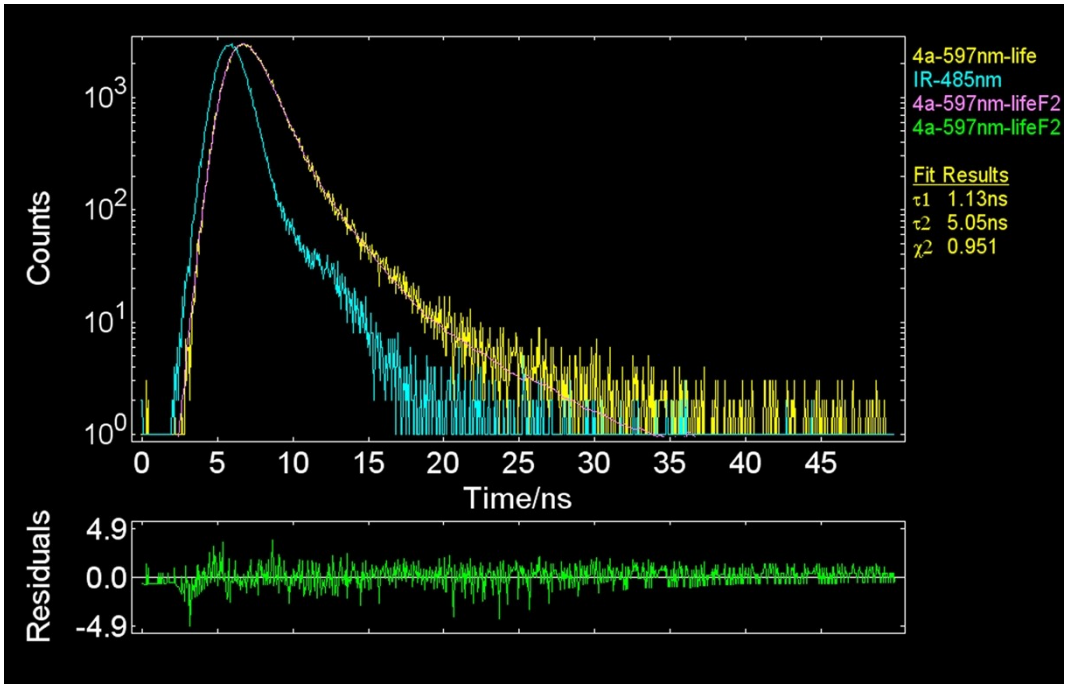


Figure S17. The fluorescence decay of **4** in distilled CH_2Cl_2 measured by single photon counting method with emission was monitored at 597 nm, excited at 485 nm.

4. Cyclic voltammograms of BODIPY M, BBPs 1-3 and bisBODIPY 4

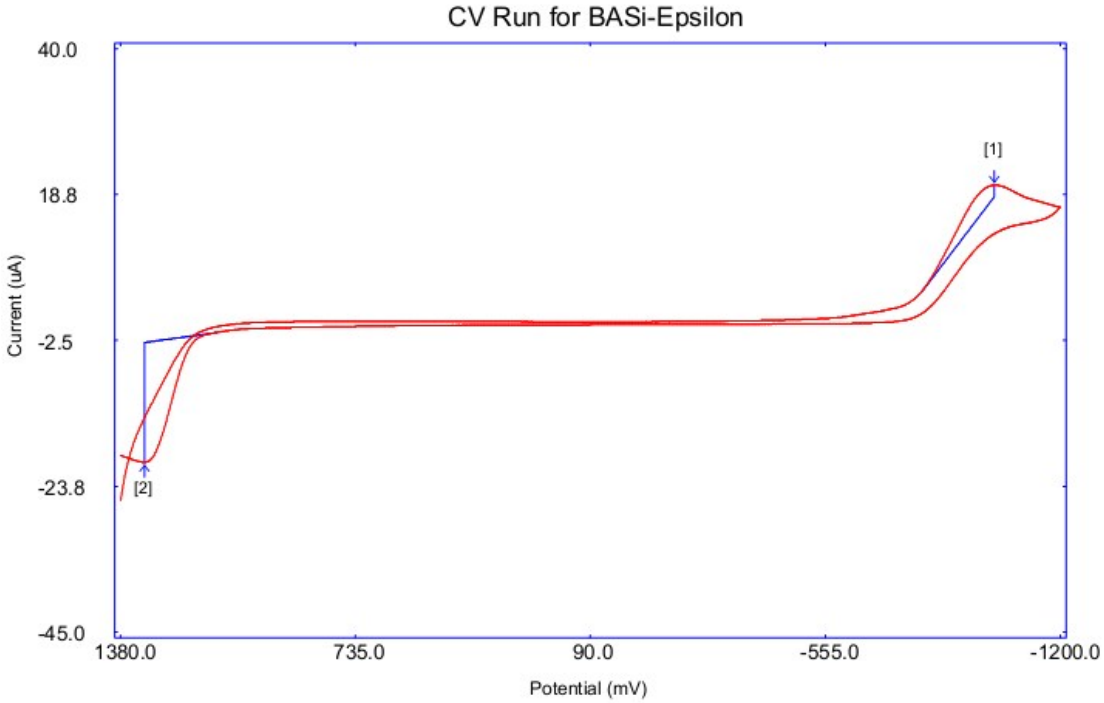


Figure S18. Cyclic voltammogram of BODIPY **M** in dichloromethane and scanning rate of 20 mV s^{-1}

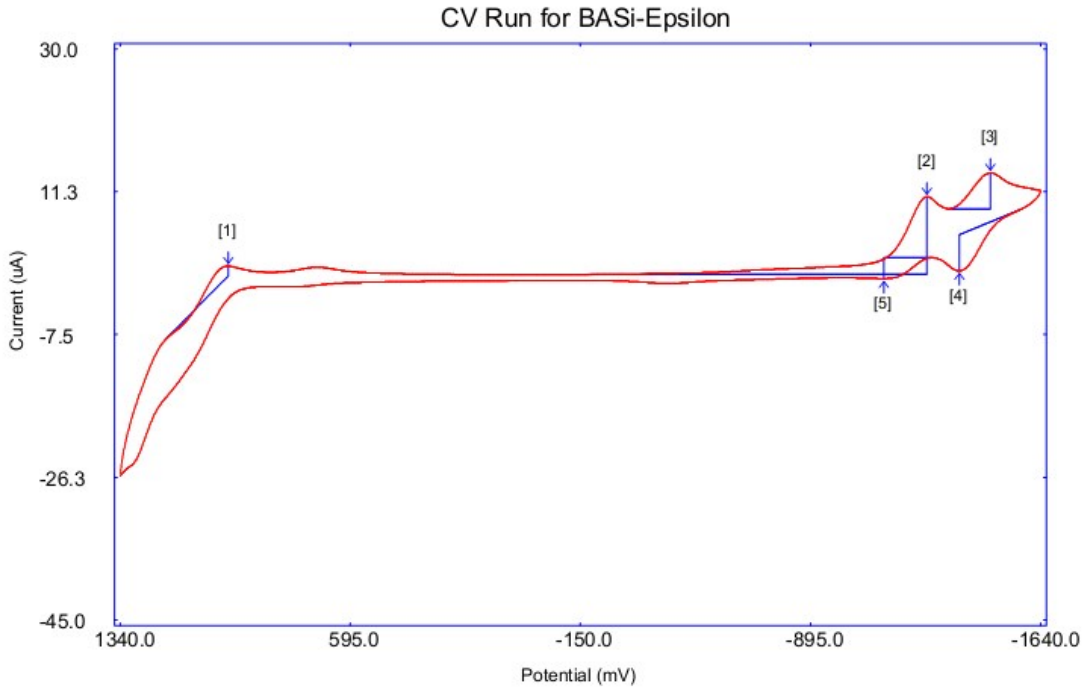


Figure S19. Cyclic voltammogram of bisBODIPY **4** in dichloromethane and scanning rate of 20 mV s^{-1}

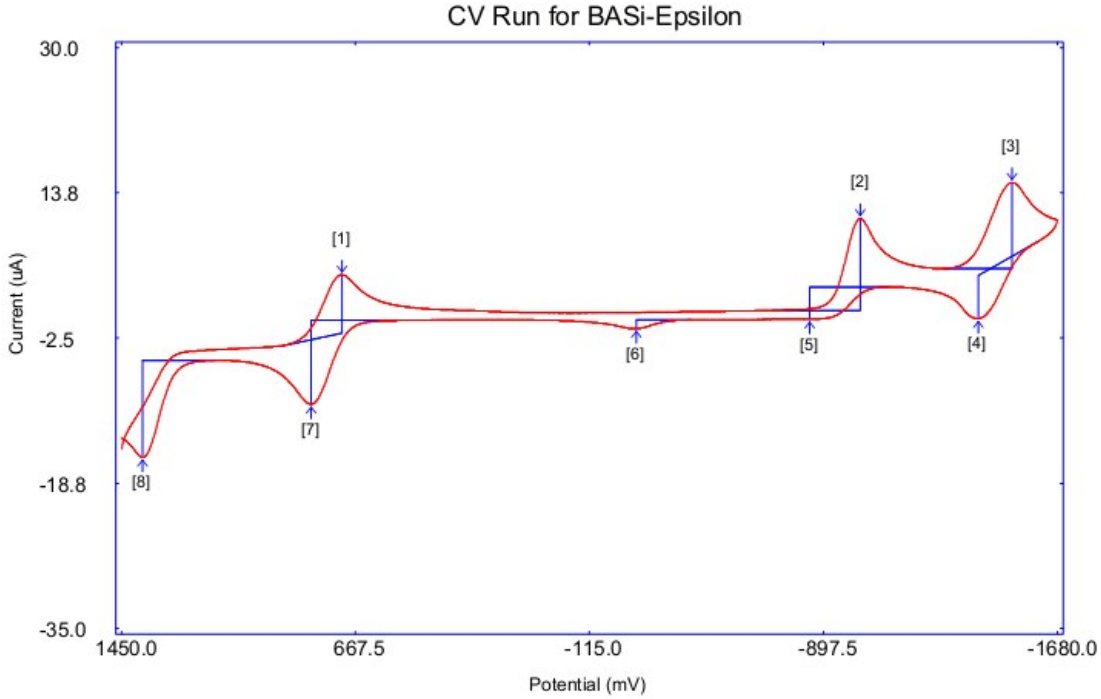


Figure S20. Cyclic voltammogram of BBP **1** in dichloromethane and scanning rate of 20 mV s^{-1}

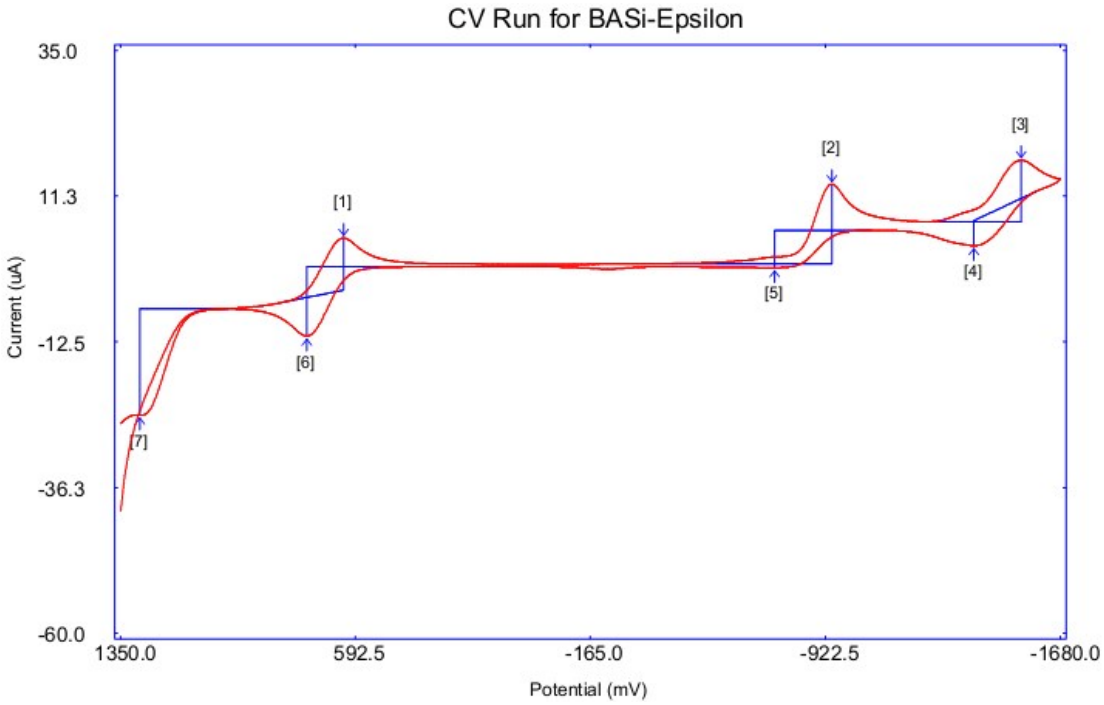


Figure S21. Cyclic voltammogram of BBP **2** in dichloromethane and scanning rate of 20 mV s^{-1}

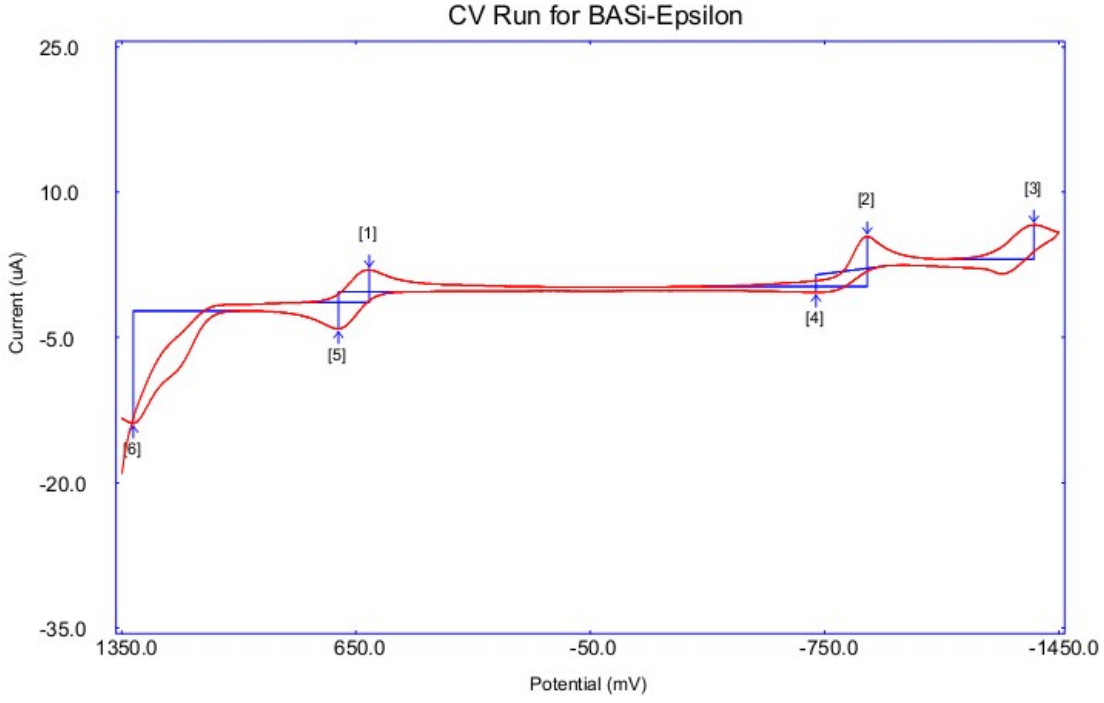


Figure S22. Cyclic voltammogram of BBP **3** in dichloromethane and scanning rate of 20 mV s^{-1}

5. Experiment Section

5,5-dimethyl-1,9-diformyldipyrromethane **5** were synthesized according to a reported literature[4]. $POCl_3$ (0.93 mL, 12 mmol) was added dropwise to DMF (1.1 mL, 12 mmol) at 0 ℃. The mixture was warmed to room temperature and stirred for 30 min. The ice bath was replaced to cool the mixture back to 0 ℃, then 20mL of CH_2Cl_2 was added to the mixture. A solution of dipyrrolmathane (870 mg, 5 mmol) in 50 mL of CH_2Cl_2 was added dropwise over 5 min at 0 ℃, the temperature was warmed to room temperature and comtinued to stir for 4 h. The reaction medium was poured into aqueous Na_2CO_3 slowly. The reaction mixture was further stirred for 6 h, and washed with water. The organic layers were combined, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The crude product was purified by chromatography (silica gel, petroleum ether and ethyl acetate) to afford a light yellow solid, affording the yield of 56% (644 mg). ^{1}H NMR (300 MHz, d_6-DMSO) δ 11.85 (br, s, 2H), 9.39 (s, 2H), 6.89 (s, 2H), 6.11 (s, 2H), 2.29 (s, 4H), 1.42 (s, 6H). ^{13}C NMR (75 MHz, d_6-DMSO) δ 179.2, 148.0, 133.2, 121.2, 108.2, 36.2, 27.7.

Syntheses of bisBODIPY 4: To compound **5** (230 mg, 1 mmol) in 100 mL toluene and 10 mL ethyl acetate was added distilled 3-ethyl-2,4-dimethylpyrrole (333 μL, 2.5 mmol) in 1 mL CH_2Cl_2 and $POCl_3$ (94 μL, 1 mmol) in 1 mL CH_2Cl_2 at ice-cold condition under argon. The reaction mixture was stirred at room temperature for 30 min. After 2 mL Et_3N was added into the reaction mixture, the mixture was stirred for 10 min, 4 mL $BF_3{\cdot}OEt_2$ was then added. The reaction mixture was left refluxing for 30 min, poured into water and extracted with ethyl acetate. Organic layers were combined, and solvent was removed under vacuum. The crude product was purified from chromatograph (silica gel, CH_2Cl_2) to give the desired compound **4** as red powder in 46% yield (246 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (s, 2H), 6.86 (d, J = 3.9 Hz, 2H), 6.42 (d, J = 3.9 Hz, 2H), 2.41 (s, 6H), 2.30 (q, J = 7.5 Hz, 4H), 2.11 (s, 6H), 2.00 (s, 6H), 0.98 (t, J = 7.5 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7, 159.4, 138.1, 134.8, 134.1, 133.6, 126.8, 123.1, 116.7, 40.3, 30.2, 17.2, 14.4, 13.1, 9.3. HRMS (APCI) Calcd. for $C_{29}H_{34}N_4B_2F_4$ $[M + H]^+$: 537.2969, found 537.2970.

Syntheses of BBP 1: To **4** (53.6 mg, 0.1 mmol) in 50 mL of dry dichloromethane was dropwisely added $FeCl_3$ (162 mg, 1 mmol, 10 eq) in 5 mL of CH_3NO_2. The reaction mixture

was stirred at room temperature for 5 min, and was quenched by adding saturated aqueous solution of $NaHCO_3$. The reaction mixture was diluted with dichloromethane, washed with water, dried over anhydrous Na_2SO_4, and evaporated under vacuum. The residue was purified by column chromatography on silica gel with CH_2Cl_2/petroleum ether as eluent to give the desired compound **1** in 70% isolated yield (37 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97 (s, 2H), 6.60 (s, 2H), 2.56 (s, 6H), 2.40 (q, *J* = 7.5 Hz, 4H), 2.14 (s, 6H), 1.94 (s, 6H), 1.07 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6, 143.1, 141.8, 137.4, 137.2, 135.6, 133.7, 124.6, 124.2, 35.2, 32.2, 18.6, 15.5, 14.5, 10.7. HRMS (APCI) Calcd. for $C_{29}H_{33}N_4B_2F_4$ [M + H]$^+$: 535.2827, found 535.2768.

Syntheses of BBP 2a: To compound tert-butyl-2-(4-formylphenoxy)acetate (38 mg, 0.16 mmol) and **1** (82 mg, 0.15 mmol) in 50 ml chlorotoluene were added piperidine (1 ml) through syringe, and a crystal of p-TsOH. The solution was refluxed over its boiling point up to 160℃ for 2 hours in a round-bottomed flask and any water formed during the reaction was removed by using a Soxhlet extractor containing anhydrous $CaCl_2$. Reaction was monitored by TLC. The resulting mixture was cooled to room temperature, poured into water and extracted with CH_2Cl_2. Organic layers were combined, and solvent was removed under vacuum. The crude product was purified from chromatograph (silica gel, petroleum/CH_2Cl_2 = 1/1, v/v) and then recrystallized from CH_3OH, affording the desired compound **2a** (35 mg) in 31% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59–7.54 (m, 3H), 7.33-7.26 (d, *J* = 20.4 Hz, 1H), 6.96-6.91 (m, 4H), 6.56 (d, *J* = 3.6 Hz, 2H), 4.57 (s, 2H), 2.68 (q, *J* = 7.2 Hz, 2H), 2.57 (s, 3H), 2.40 (q, *J* = 7.5 Hz, 2H), 2.12-2.11 (m, 6H), 1.97 (s, 6H), 1.26 (s, 9H), 1.08 (t, *J* = 7.5 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6, 174.5, 167.8, 158.8, 158.2, 152.5, 139.6, 138.4, 138.3, 138.1, 136.5, 135.1, 134.3, 133.1, 130.8, 129.0, 128.3, 127.3, 122.5, 121.1, 117.8, 115.0, 114.2, 113.6, 82.6, 65.8, 44.6, 29.7, 28.1, 23.7, 18.7, 17.3, 14.4, 13.9, 12.9, 9.4, 9.1. HRMS (APCI) Calcd. for $C_{42}H_{47}N_4B_2F_4O_3$ [M + H]$^+$: 753.3770, found 753.3767.

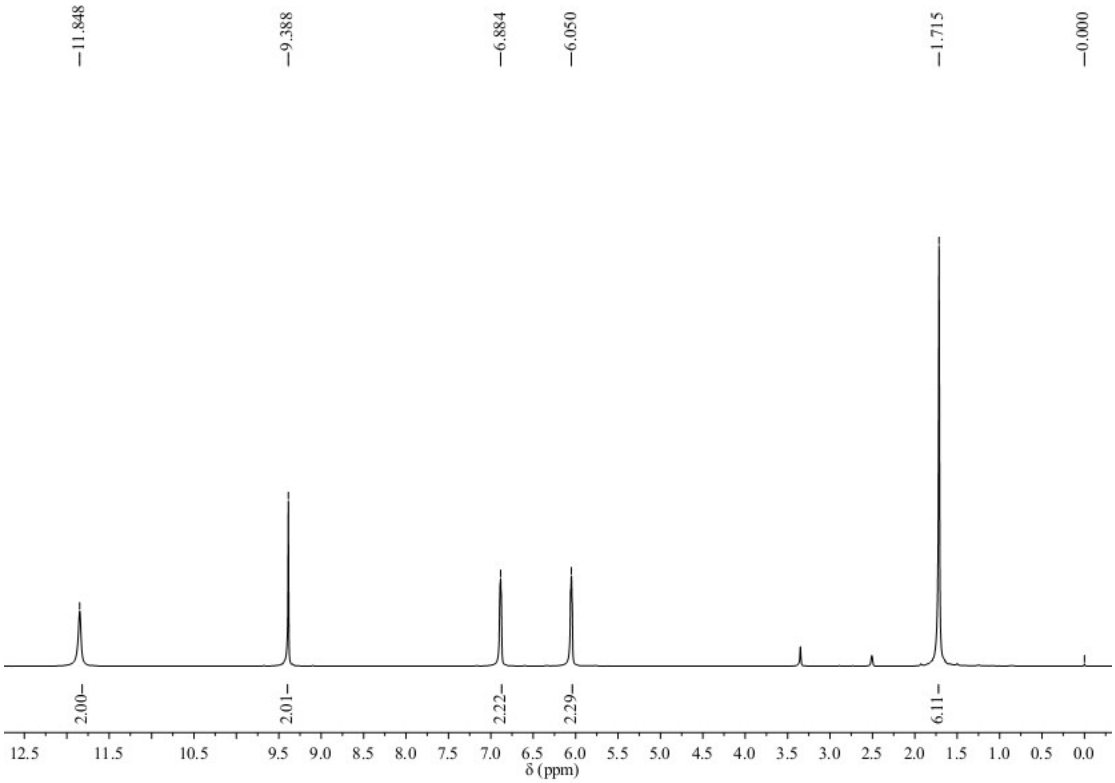
Syntheses of BBP 2b: Prepared using the above procedure from compound **1** (82 mg, 0.15 mmol) and 4-N,N-dimethylbenzaldehyde (24 mg, 0.16 mmol) affording gray power **2b** (34 mg) in 34% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56–7.51 (m, 3H), 7.36 (d, *J* = 17.1 Hz,

1H), 6.99 (s, 1H), 6.93 (s, 1H), 6.75–6.70 (m, 2H), 6.59 (d, *J* = 8.7 Hz, 2H), 3.05 (s, 6H), 2.71 (q, *J* = 7.5 Hz, 2H), 2.56 (s, 3H), 2.41 (q, *J* = 7.5 Hz, 2H), 2.18-2.17 (m, 6H), 1.97 (s, 6H), 1.23 (t, *J* = 7.5 Hz, 3H), 1.08 (t, *J* = 7.5 Hz, 3H). HRMS (APCI) Calcd. for $C_{38}H_{42}N_5B_2F_4$ [M + H]$^+$: 666.3562, found 666.3553.

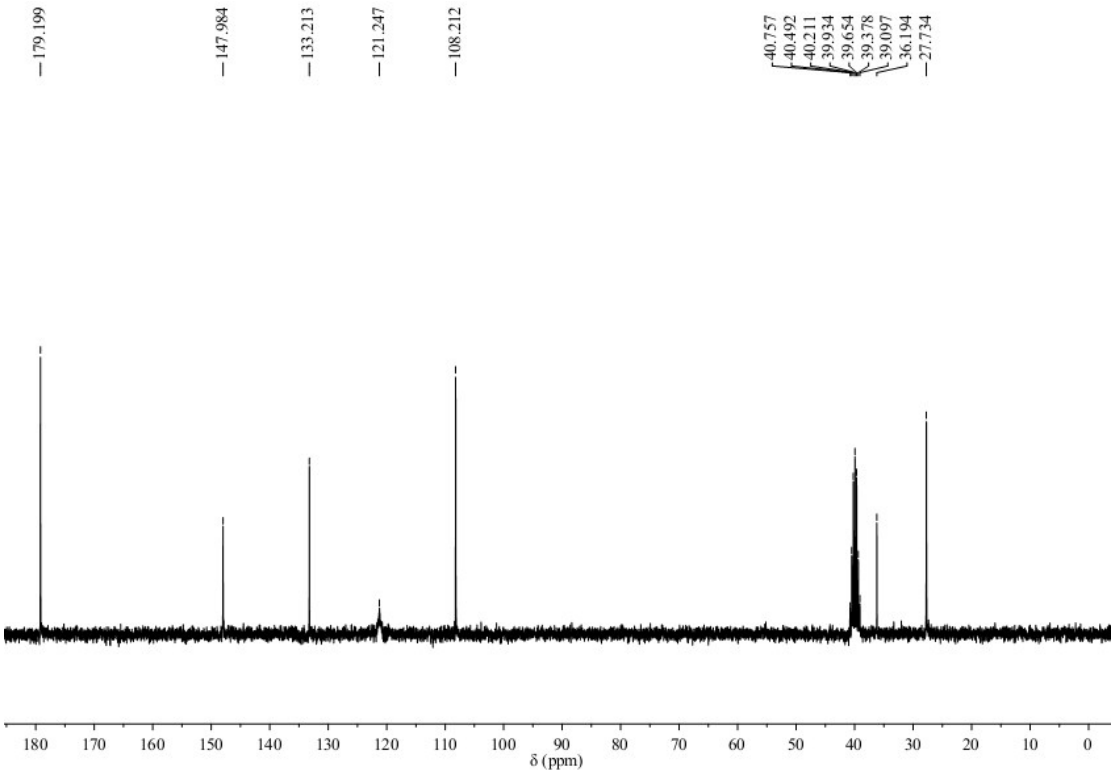
Syntheses of BBP 3a: To compound tert-butyl-2-(4-formylphenoxy)acetate (143 mg, 0.6 mmol) and **1** (82 mg, 0.15 mmol) in 50 ml chlorotoluene were added piperidine (1 ml) through syringe, and a crystal of p-TsOH. The solution was refluxed over its boiling point up to 160℃ for 30 min in a round-bottomed flask and any water formed during the reaction was removed by using a Soxhlet extractor containing anhydrous $CaCl_2$. Reaction was monitored by TLC. The resulting mixture was cooled to room temperature, poured into water and extracted with CH_2Cl_2. Organic layers were combined, and solvent was removed under vacuum. The crude product was purified from chromatograph (silica gel, petroleum/CH_2Cl_2 = 1/1, v/v) and then recrystallized from CH_3OH, affording the desired compound **3a** (33 mg) in 23% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60–7.55 (m, 6H), 7.32 (d, *J* = 16.8 Hz, 2H), 6.97-6.93 (m, 6H), 6.62 (s, 2H), 4.58 (s, 4H), 2.70 (q, *J* = 7.5 Hz, 4H), 2.17 (s, 6H), 2.00 (s, 6H), 1.23 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.7, 167.8, 158.9, 153.0, 139.6, 138.3, 136.8, 135.4, 133.4, 130.8, 129.0, 128.1, 121.1, 117.8, 115.0, 113.6, 82.6, 65.8, 44.8, 29.7, 28.1, 23.7, 18.7, 13.9, 9.2. HRMS (APCI) Calcd. for $C_{55}H_{61}N_4B_2F_4O_6$ [M + H]$^+$: 971.4713, found 971.4697.

Syntheses of BBP 3b: Prepared using the above procedure from compound **1** (82 mg, 0.15 mmol) and 4-N,N-dimethylbenzaldehyde (90 mg, 0.6 mmol) affording **3b** (31 mg) in 26% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56–7.51 (m, 6H), 7.35 (d, *J* = 17.4 Hz, 2H), 6.94 (s, 2H), 6.74 (d, *J* = 8.4 Hz, 4H), 6.58 (s, 2H), 3.05 (s, 12H), 2.71 (d, *J* = 7.2 Hz, 4H), 2.19 (s, 6H), 2.00 (s, 6H), 1.23 (t, *J* = 7.2 Hz, 6H). HRMS (APCI) Calcd. for $C_{47}H_{51}N_6B_2F_4$ [M + H]$^+$: 797.4297, found 797.4285.

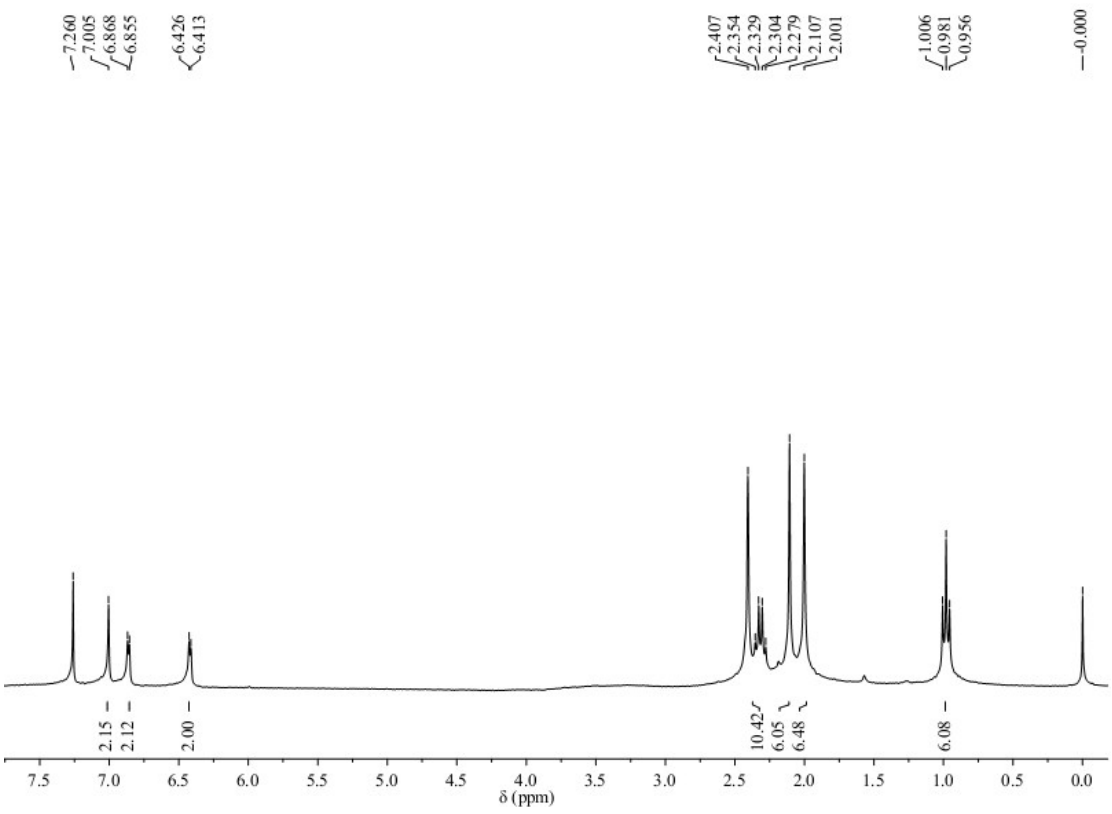
6. ^{1}H NMR and ^{13}C NMR spectra for all the compounds



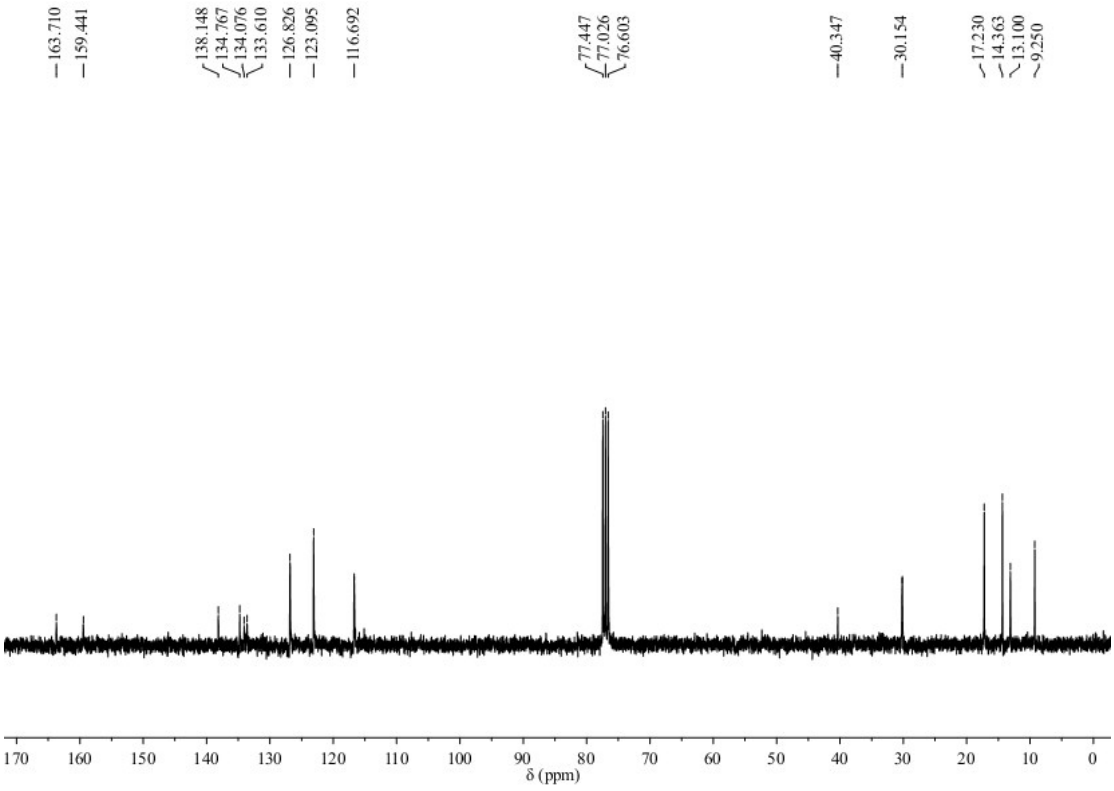
^{1}H NMR spectrum of **5** in d_6-DMSO solution



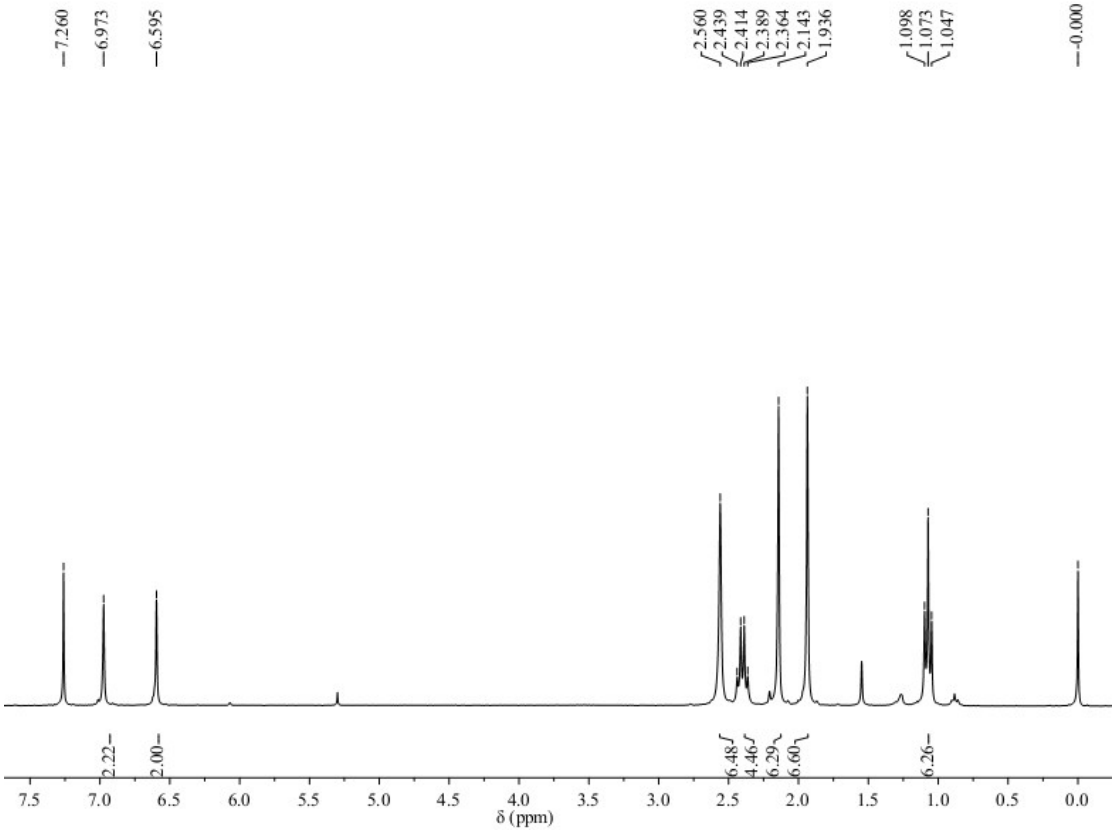
^{13}C NMR spectrum of **5** in d_6-DMSO solution



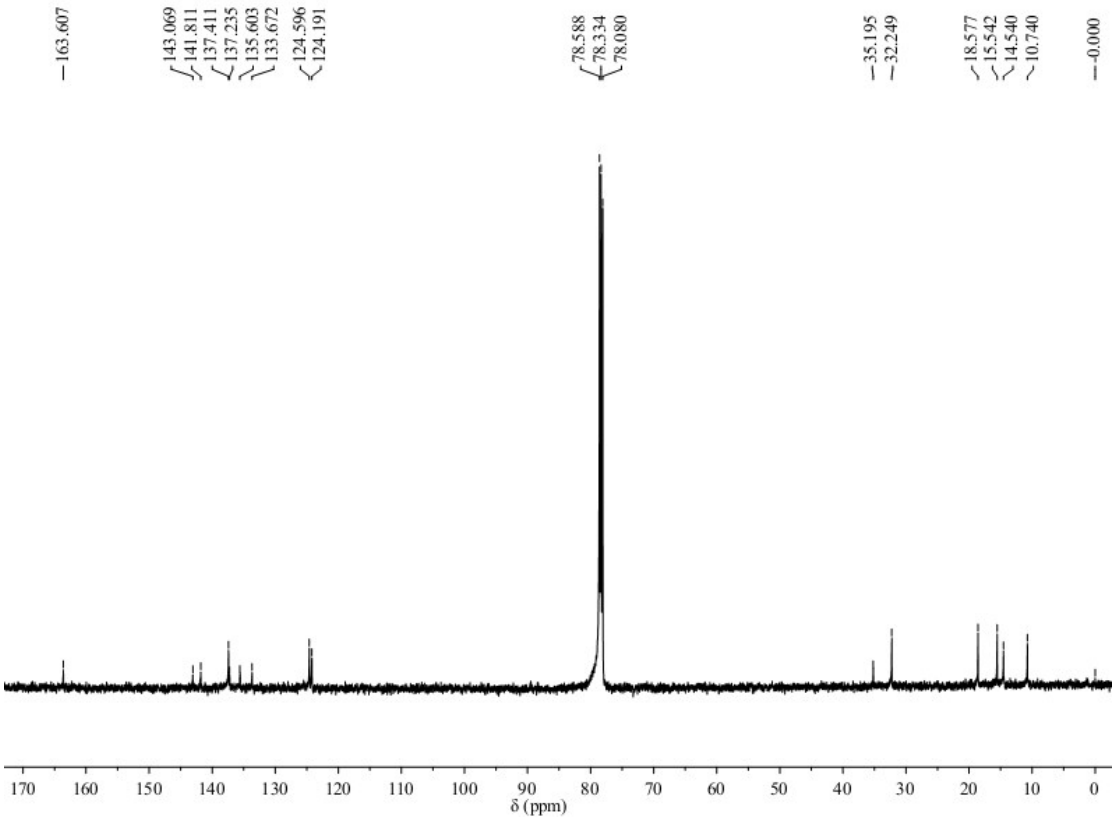
^{1}H NMR spectrum of bisBODIPY **4** in $CDCl_3$ solution



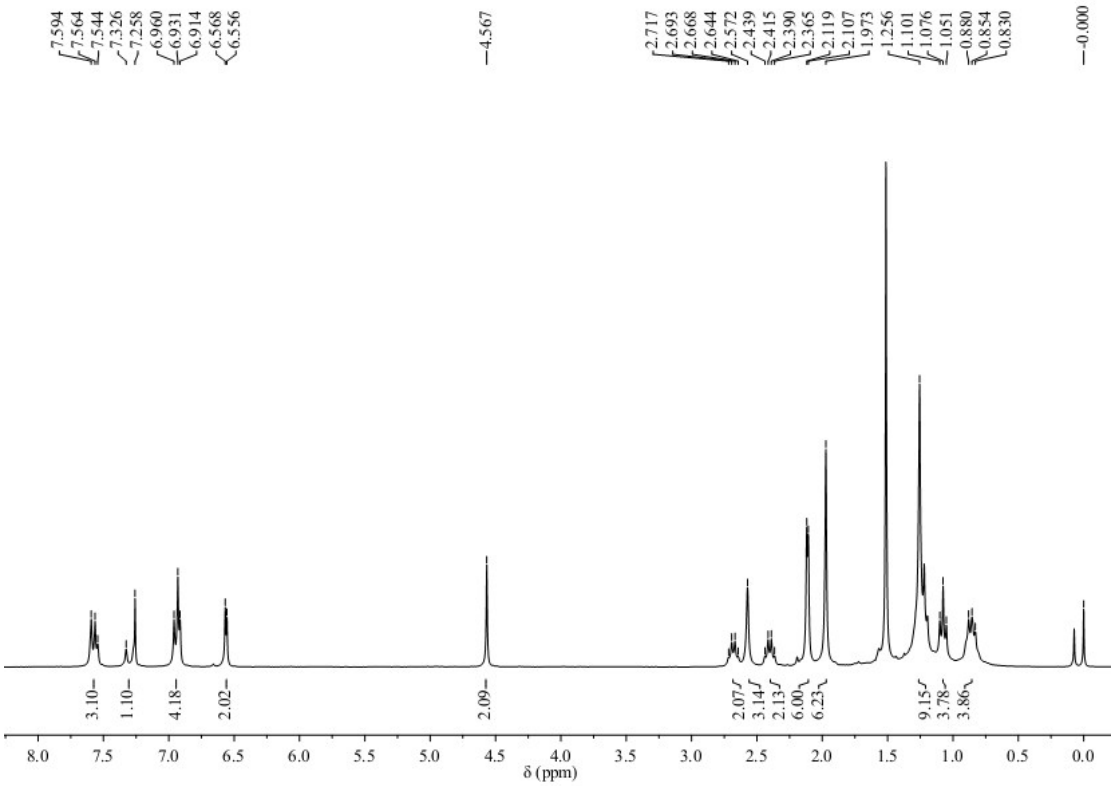
^{13}C NMR spectrum of bisBODIPY **4** in $CDCl_3$ solution



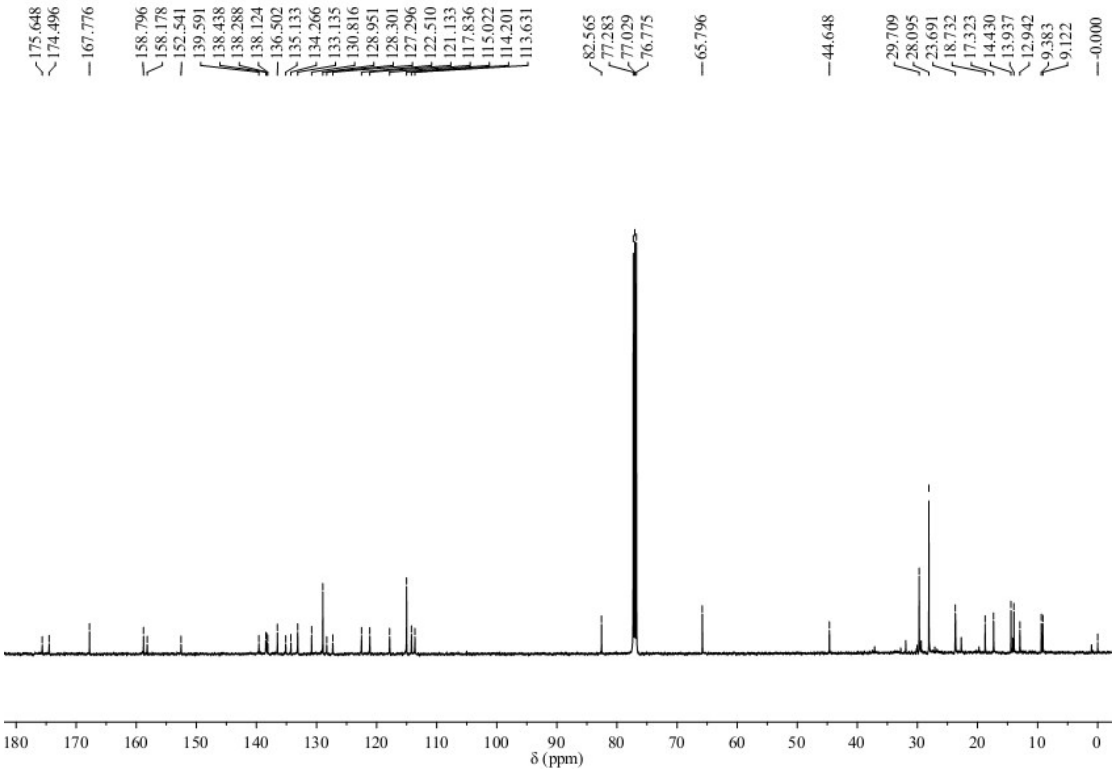
^{1}H NMR spectrum of BBP **1** in $CDCl_3$ solution



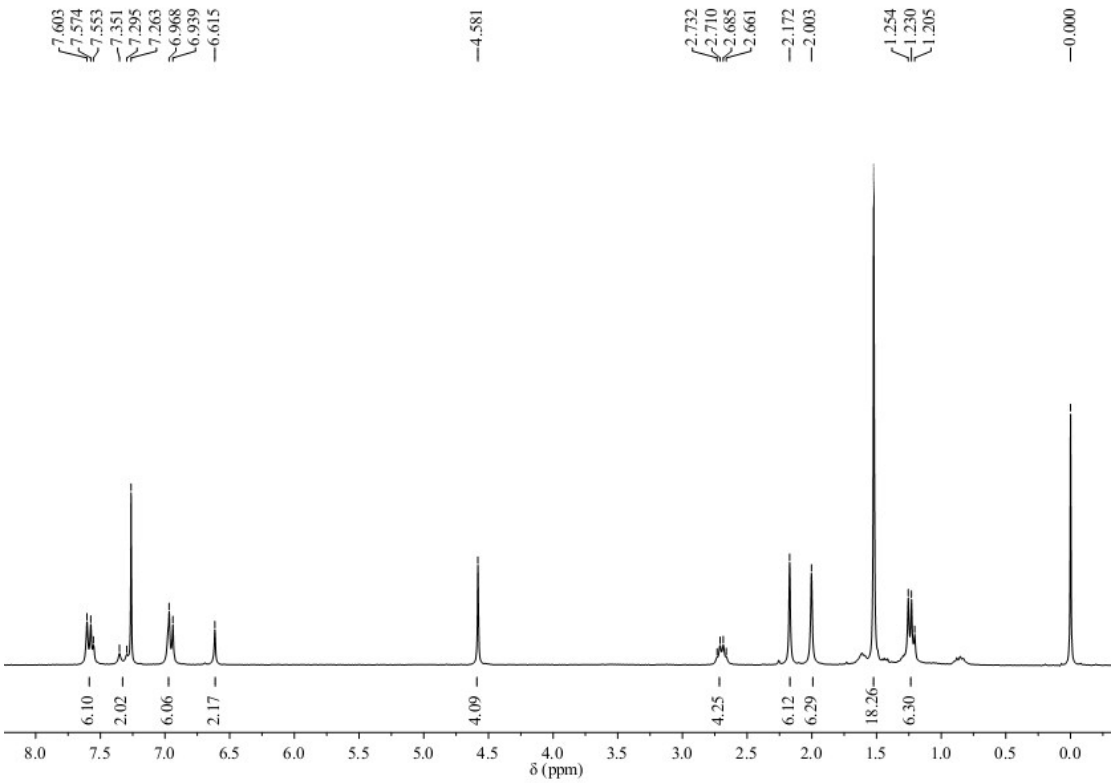
^{13}C NMR spectrum of BBP **1** in $CDCl_3$ solution



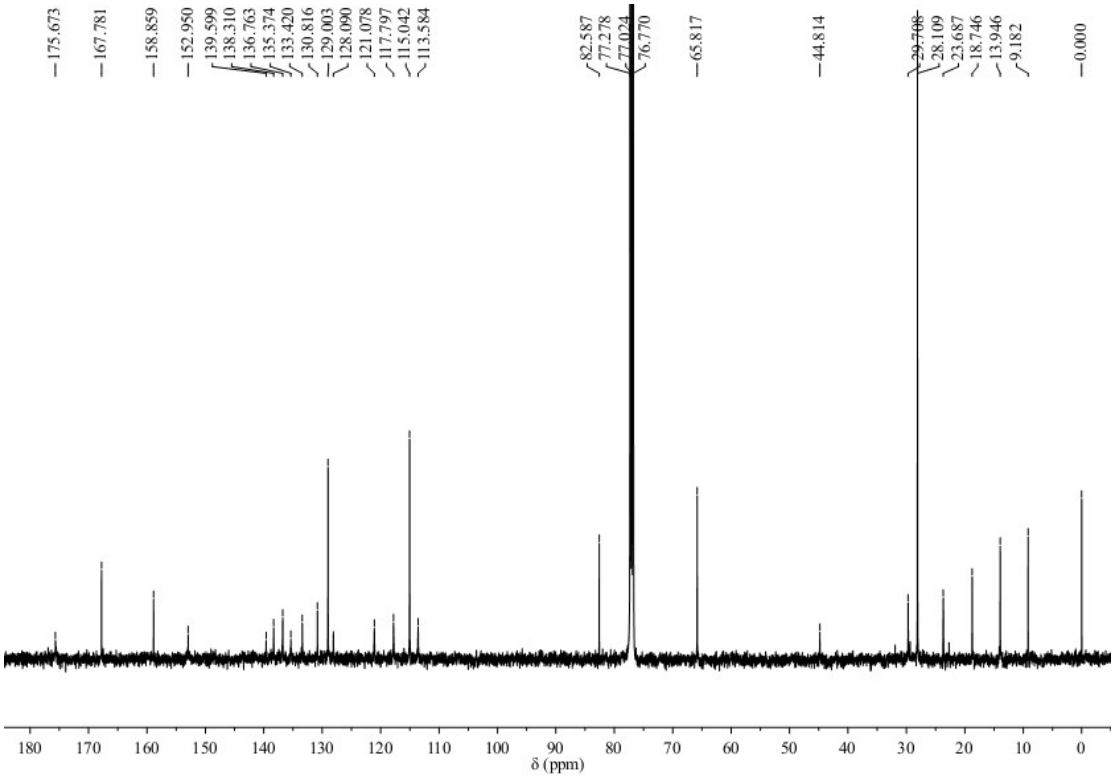
^{1}H NMR spectrum of BBP **2a** in $CDCl_3$ solution



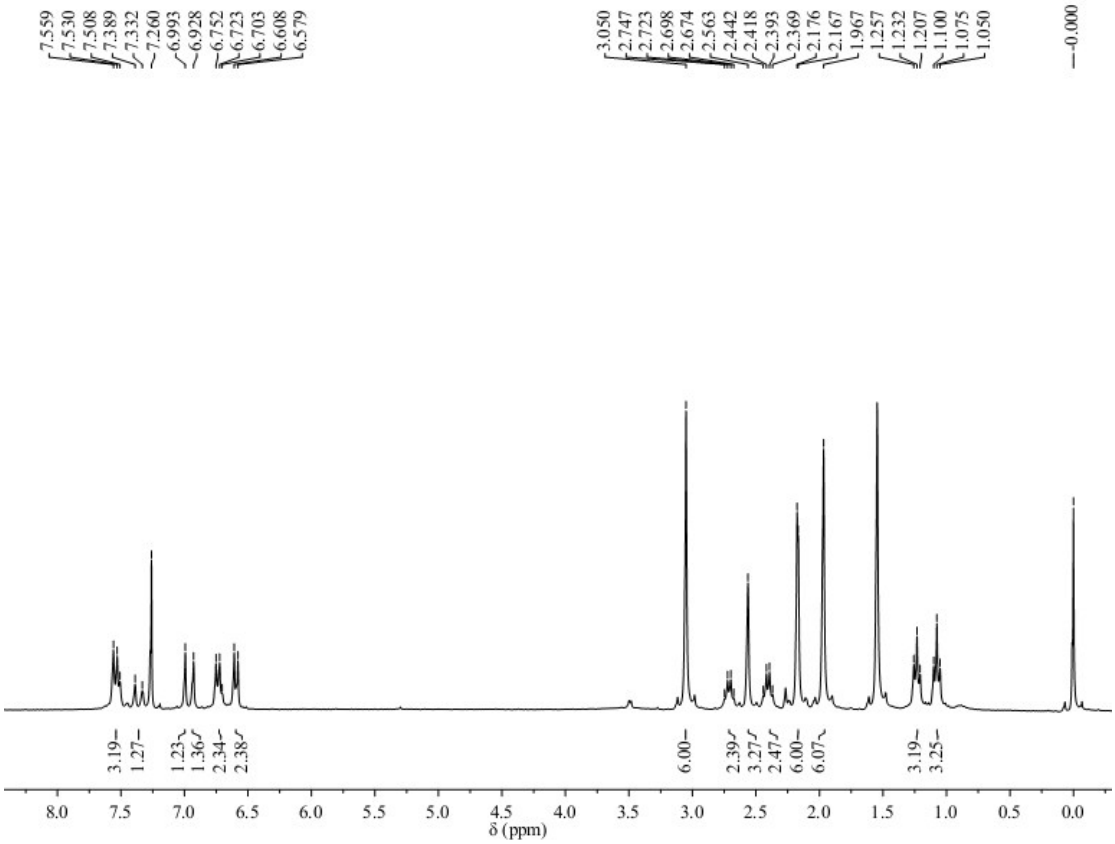
^{13}C NMR spectrum of BBP **2a** in $CDCl_3$ solution



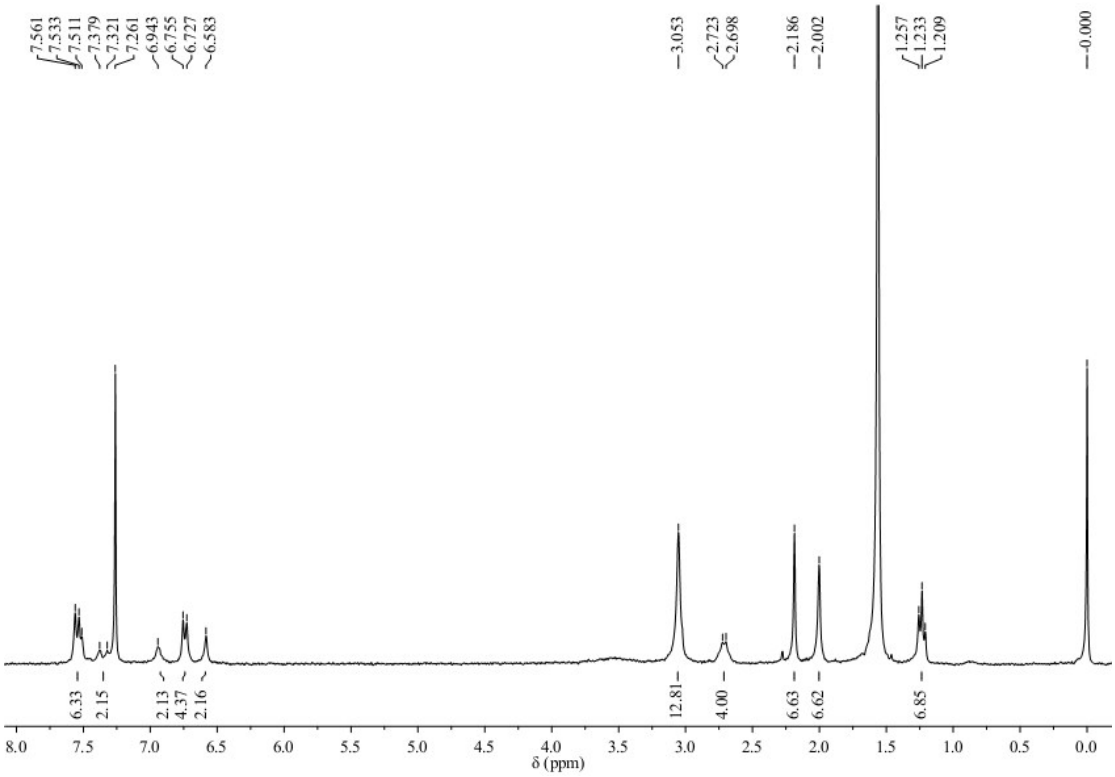
^{1}H NMR spectrum of BBP **3a** in $CDCl_3$ solution



^{13}C NMR spectrum of BBP **3a** in $CDCl_3$ solution



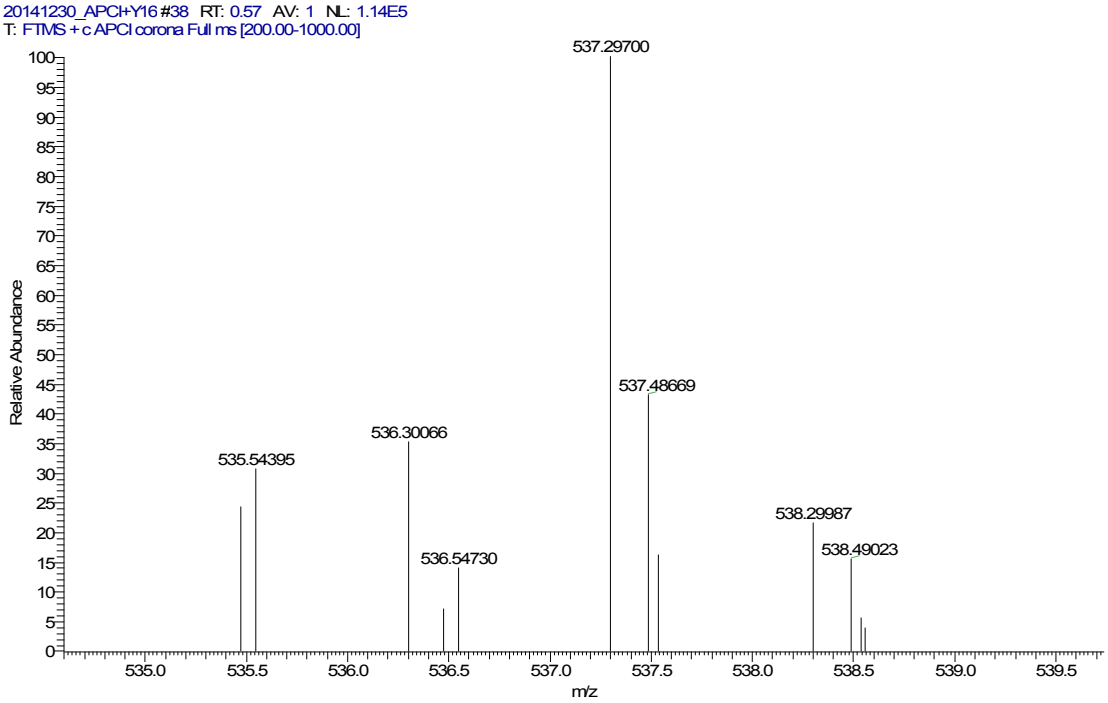
^{1}H NMR spectrum of BBP **2b** in $CDCl_3$ solution



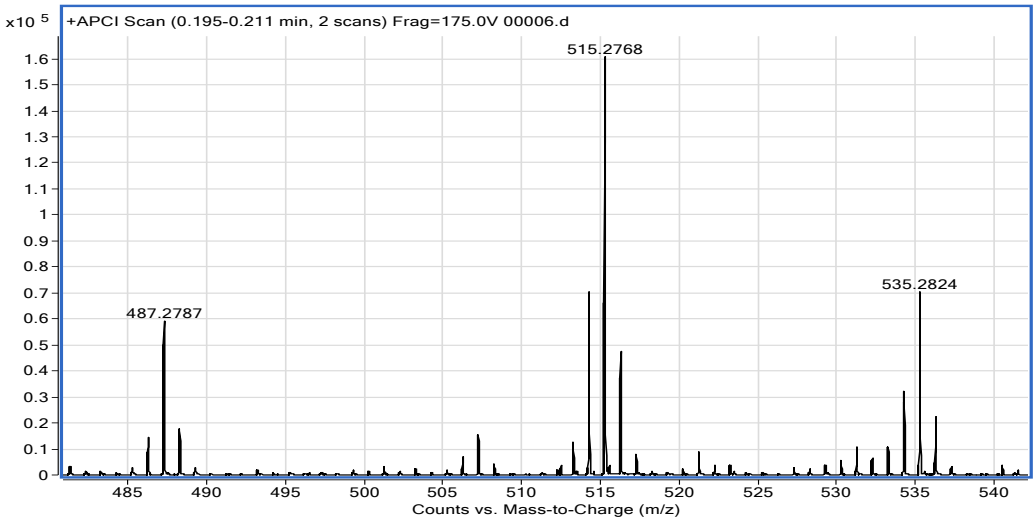
^{1}H NMR spectrum of BBP **3b** in $CDCl_3$ solution

7. High resolution mass spectroscopes for the compounds

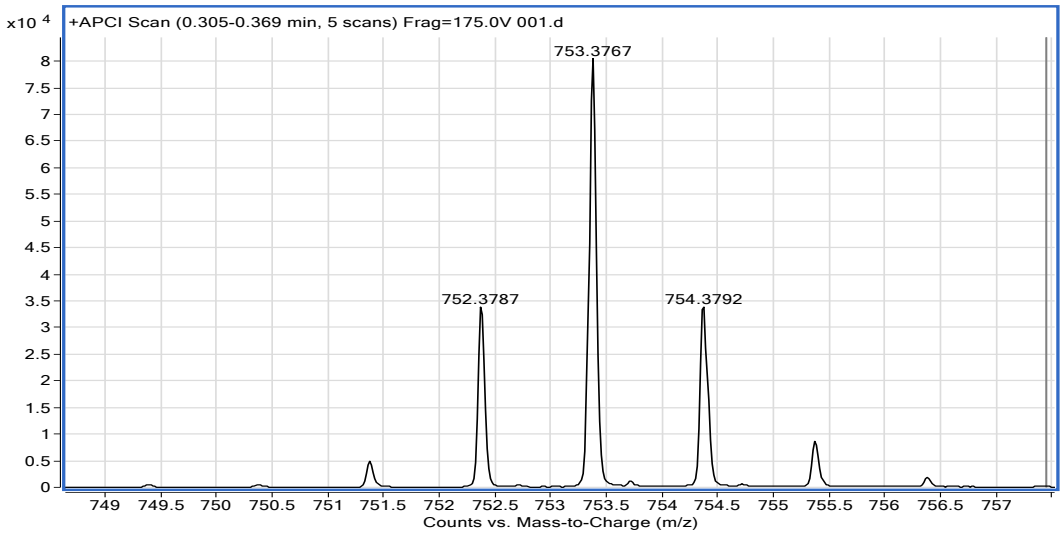
HRMS for bisBODIPY **4**



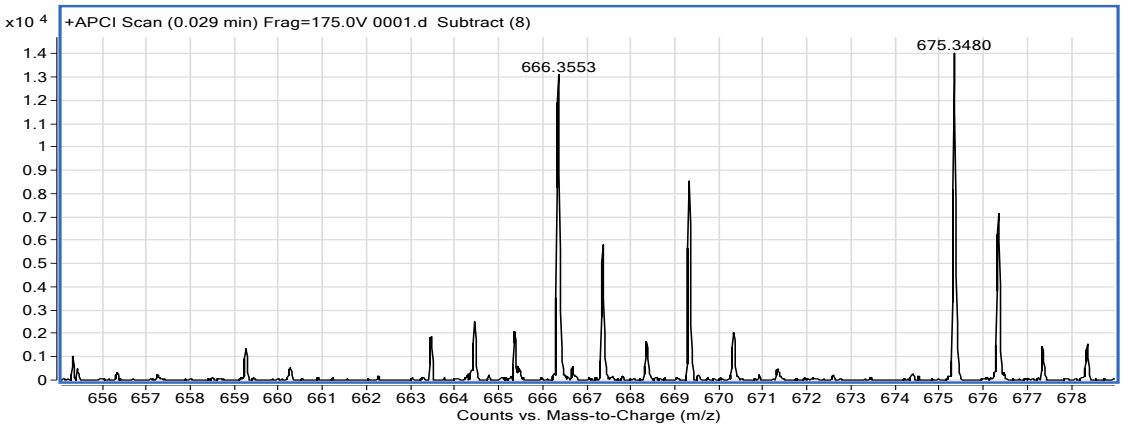
HRMS for BBP **1**



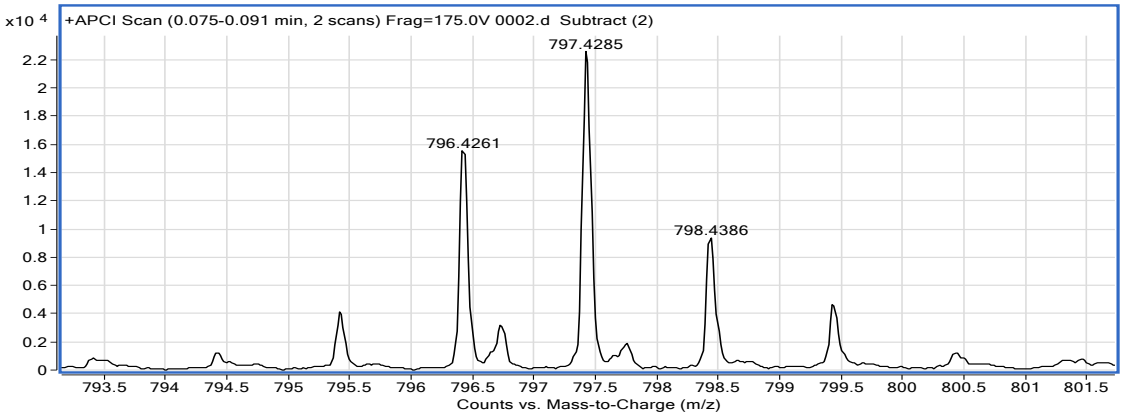
HRMS for BBP **2a**



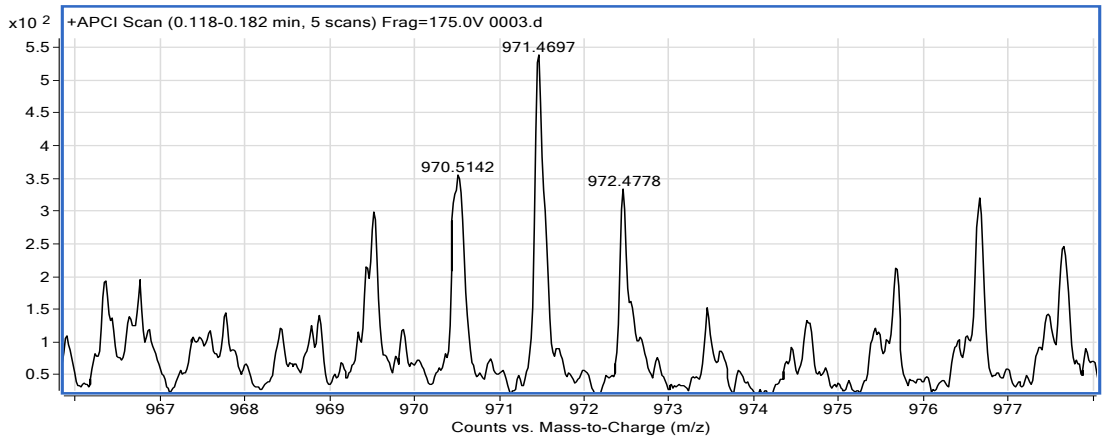
HRMS for BBP **2b**



HRMS for BBP **3a**



HRMS for BBP **3b**



8. DFT calculation

The ground state geometry was optimized by using DFT method at TPSSH/6-31G (d) level. The same method was used for vibrational analysis to verify that the optimized structures correspond to local minima on the energy surface. TDDFT computations were used to obtain the vertical excitation energies and oscillator strengths at the optimized ground state equilibrium geometries under the TPSSH/6-311G (2d, p) theoretical level. The TDDFT of all the molecules in dichloromethane were using the Self-Consistent Reaction Field (SCRF) method and th Polarizable Continuum Model (PCM). All of the calculations for BODIPY **M**, BBP **1** and bisBODIPY **4** were carried out in dichloromethane by the methods implemented in Gaussian 09 package[6].

BBP 1:

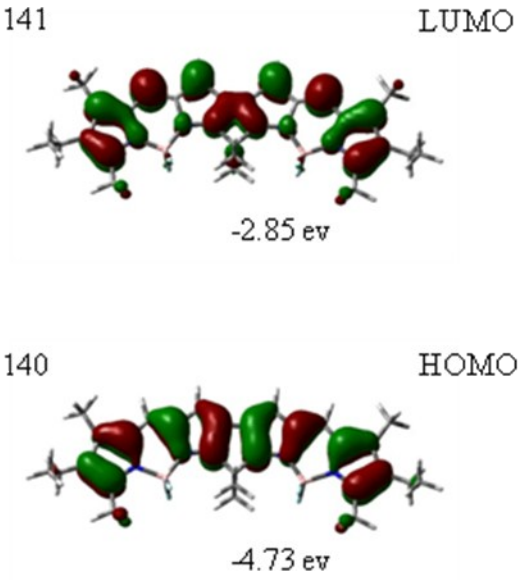


Figure S23. Frontier molecular orbitals (MO) and frontier orbital energy of BBP **1** calculated with

density functional theory (DFT) at the TPSSH /6-31G* level using Gaussian 09.

Selected TDDFT paramete :

Excited State	1:	Singlet-A"	1.9641 eV	631.26 nm	f=1.0936	<S**2>=0.000
140 → 141		0.70406				
Excited State	2:	Singlet-A'	2.2443 eV	552.44 nm	f=0.0007	<S**2>=0.000
139 → 141		-0.37131				
140 → 142		0.60051				

bisBODIPY 4 :

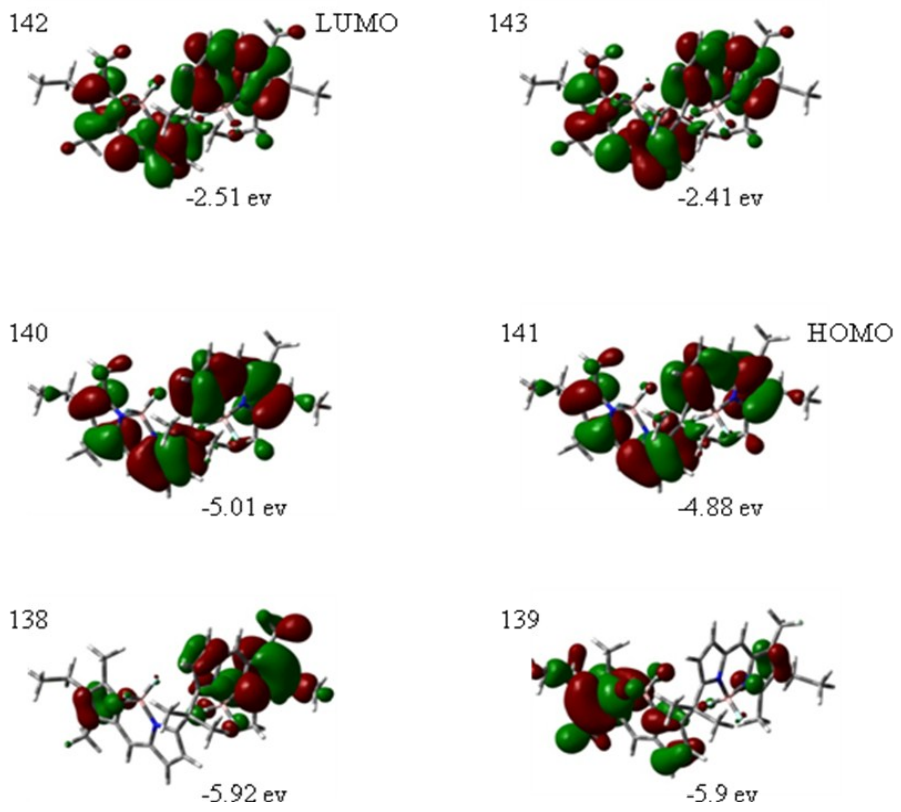


Figure S24. Frontier molecular orbitals (MO) and frontier orbital energy of bisBODIPY **4** calculated with density functional theory (DFT) at the TPSSH /6-31G* level using Gaussian 09.

Selected TDDFT paramete :

Excited State	1:	Singlet-A	2.2342 eV	554.95 nm	f=0.0481	<S**2>=0.000
140 -> 142		-0.20425				
140 -> 143		-0.31324				
141 -> 142		0.56315				
141 -> 143		0.20710				
Excited State	2:	Singlet-A	2.2707 eV	546.01 nm	f=0.0149	<S**2>=0.000
140 -> 142		-0.44244				
140 -> 143		0.21871				

141 -> 142	-0.20850					
141 -> 143	0.46126					
Excited State 3:	Singlet-A	2.7741 eV	446.93 nm	f=0.6367	<S**2>=0.000	
138 -> 142	0.10039					
140 -> 143	0.58328					
141 -> 142	0.36362					
Excited State 4:	Singlet-A	2.8854 eV	429.70 nm	f=0.4421	<S**2>=0.000	
138 -> 143	0.13644					
139 -> 142	-0.19859					
140 -> 142	0.47724					
141 -> 143	0.45798					

BODIPY M :

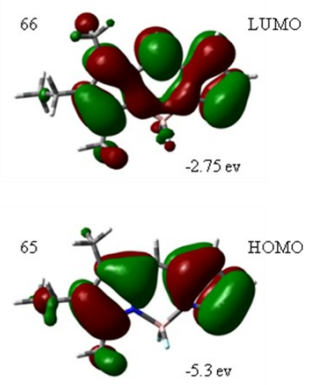


Figure S25. Frontier molecular orbitals (MO) and frontier orbital energy of BODIPY **M** calculated with density functional theory (DFT) at the TPSSH /6-31G* level using Gaussian 09.

Selected TDDFT paramete :

Excited State 1:	Singlet-A	2.8931 eV	428.55 nm	f=0.5090	<S**2>=0.000
64 -> 66	0.24356				
65 -> 66	0.66313				
65 <- 66	-0.10222				
Excited State 2:	Singlet-A	3.2867 eV	377.23 nm	f=0.2102	<S**2>=0.000
64 -> 66	0.66055				
65 -> 66	-0.24401				
Excited State 3:	Singlet-A	3.6583 eV	338.91 nm	f=0.0748	<S**2>=0.000
63 -> 66	0.69700				

DFT optimized coordinates for BODIPY **M**, BBP **1** and bisBODIPY **4**

BBP 1:

B	8.123800	6.190600	4.095200
C	10.380000	6.739500	2.870700

C	10.788900	7.414100	1.705300
C	9.659500	7.852100	1.047300
C	8.569500	7.437300	1.834600
C	7.198200	7.617200	1.641300
C	6.254700	7.153400	2.531900
C	4.835500	7.206300	2.531200
C	4.397400	6.602800	3.689600
C	5.556500	6.162900	4.393900
C	4.003700	7.772200	1.436700
C	3.014100	6.429800	4.175300
C	2.388700	5.089200	3.841400
C	5.632100	5.428400	5.685800
C	11.517500	6.160200	3.702200
C	11.517500	4.618000	3.610100
C	11.517500	6.590400	5.168500
F	8.311700	4.820900	4.195700
F	8.408700	6.787000	5.292200
N	9.040300	6.754100	2.974000
N	6.666600	6.486000	3.698000
B	14.911200	6.190600	4.095200
C	12.655000	6.739500	2.870700
C	12.246100	7.414100	1.705300
C	13.375500	7.852100	1.047300
C	14.465500	7.437300	1.834600
C	15.836800	7.617200	1.641300
C	16.780300	7.153400	2.531900
C	18.199500	7.206300	2.531200
C	18.637600	6.602800	3.689600
C	17.478500	6.162900	4.393900
C	19.031300	7.772200	1.436700
C	20.020900	6.429800	4.175300
C	20.646300	5.089200	3.841400
C	17.402900	5.428400	5.685800
F	14.723300	4.820900	4.195700
F	14.626300	6.787000	5.292200
N	13.994700	6.754100	2.974000
N	16.368400	6.486000	3.698000
H	9.624000	8.325500	0.246700
H	6.910500	8.068500	0.881400
H	3.600400	7.058100	0.939100
H	4.556300	8.297000	0.852600
H	3.317000	8.329100	1.811400
H	2.462400	7.131300	3.794300
H	3.008400	6.544000	5.139000

H	2.368000	4.973200	2.888300
H	1.495000	5.057100	4.187900
H	2.911600	4.385900	4.235700
H	5.894700	4.519800	5.522800
H	4.772900	5.440900	6.111800
H	6.277000	5.851400	6.256600
H	11.517500	4.355500	2.678100
H	10.941600	4.230600	4.252600
H	12.093400	4.230600	4.252600
H	10.752700	6.283400	5.672500
H	11.517500	7.545400	5.271800
H	12.282300	6.283400	5.672500
H	13.411000	8.325500	0.246700
H	16.124500	8.068500	0.881400
H	19.434600	7.058100	0.939100
H	18.478700	8.297000	0.852600
H	19.718000	8.329100	1.811400
H	20.572600	7.131300	3.794300
H	20.026600	6.544000	5.139000
H	20.667000	4.973200	2.888300
H	21.540000	5.057100	4.187900
H	20.123400	4.385900	4.235700
H	17.140300	4.519800	5.522800
H	18.262100	5.440900	6.111800
H	16.758000	5.851400	6.256600

bisBODIPY 4 :

B	2.11100300	0.64415000	0.49751200
C	0.70110200	2.28820600	-1.07090300
C	0.56662100	2.49724700	-2.46542300
C	1.41753100	1.61776800	-3.10651800
C	2.07191000	0.87379900	-2.10067000
C	3.01132900	-0.14383900	-2.24521700
C	3.56613100	-0.80295200	-1.16106000
C	4.53313400	-1.84510500	-1.07713400
C	4.70907400	-2.11432100	0.28116100
C	3.84652500	-1.23240100	0.99408100
C	3.65845700	-1.11539900	2.47208200
C	5.64961300	-3.11712500	0.89190800
C	7.03002600	-2.53202600	1.24636700
C	5.22407700	-2.49830500	-2.23575100
C	0.00026500	3.11793500	0.00238500
C	1.06524300	4.04948900	0.64771200

F	1.05339700	0.04122000	1.15961900
F	2.74025200	1.58439700	1.31765000
N	1.62566200	1.31334900	-0.85018900
N	3.17016700	-0.45506900	0.12609400
B	-2.11348800	0.64744500	-0.49687700
C	-0.70021400	2.28608400	1.07426600
C	-0.56412100	2.49149100	2.46915900
C	-1.41481100	1.61083400	3.10892900
C	-2.07061000	0.86974400	2.10189400
C	-3.00976300	-0.14835800	2.24494600
C	-3.56523000	-0.80524700	1.15980000
C	-4.53165300	-1.84782000	1.07438900
C	-4.70852400	-2.11419100	-0.28434100
C	-3.84716800	-1.23011100	-0.99603700
C	-3.66067400	-1.10949200	-2.47394400
C	-5.64884900	-3.11632600	-0.89651400
C	-7.02984300	-2.53135100	-1.24891600
C	-5.22119500	-2.50400000	2.23215700
C	-1.06481200	4.05046600	-0.64131600
F	-1.05682800	0.04832000	-1.16390000
F	-2.74596000	1.58993700	-1.31198600
N	-1.62558200	1.31230100	0.85205900
N	-3.17052100	-0.45431000	-0.12691000
H	-0.10558000	3.20271200	-2.92857500
H	1.56639400	1.49376400	-4.17144800
H	3.31149100	-0.42070500	-3.25120000
H	4.06454100	-0.16503000	2.83750200
H	4.15525300	-1.93419900	2.99820700
H	2.59296800	-1.11921200	2.72013300
H	5.20123500	-3.54878000	1.79589700
H	5.78586400	-3.95557000	0.19686600
H	7.52525600	-2.12668600	0.35687600
H	7.68217900	-3.30011100	1.67846800
H	6.93817600	-1.71692000	1.97283000
H	5.29436100	-3.58345800	-2.09680000
H	6.24934400	-2.12503500	-2.36100700
H	4.69504600	-2.32153700	-3.17756300
H	0.58298900	4.76090900	1.32667900
H	1.55548300	4.62531800	-0.14383500
H	1.82520200	3.48459800	1.18514000
H	0.10904600	3.19532400	2.93337700
H	-1.56250200	1.48410200	4.17370100
H	-3.30888300	-0.42766100	3.25056500
H	-4.06755600	-0.15839000	-2.83657100

H	-4.15768800	-1.92720600	-3.00154700
H	-2.59545000	-1.11220600	-2.72311900
H	-5.20078500	-3.54587800	-1.80166000
H	-5.78414400	-3.95625100	-0.20307900
H	-7.52475100	-2.12808400	-0.35830400
H	-7.68180900	-3.29896600	-1.68213400
H	-6.93894500	-1.71474600	-1.97381100
H	-5.29070900	-3.58891900	2.09101900
H	-6.24666900	-2.13181600	2.35894700
H	-4.69161200	-2.32875300	3.17394200
H	-0.58260600	4.76346700	-1.31865500
H	-1.55543500	4.62450100	0.15129800
H	-1.82452400	3.48653100	-1.18008900

BODIPY M :

B	1.13015400	-1.25682600	-0.03257400
C	3.61266600	-0.49856400	0.16761100
C	4.36495100	0.69089100	0.22426000
C	3.45531000	1.74303900	0.15413900
C	2.16435000	1.16809200	0.05623900
C	0.89597400	1.75185900	-0.03954900
C	-0.25989100	0.99100700	-0.12279700
C	-1.63251300	1.37914400	-0.21706000
C	-2.37640800	0.20147500	-0.27475500
C	-1.44588500	-0.88068700	-0.21357200
C	-2.14243900	2.78921100	-0.22525200
C	-3.87272200	0.06394100	-0.35031300
C	-4.40985258	0.05225931	-1.79497682
C	-1.72334300	-2.34903800	-0.23810700
F	1.09905500	-2.05102600	1.10584400
F	1.27849300	-2.02607700	-1.17983500
N	2.29985300	-0.21699100	0.06798600
N	-0.19043900	-0.40381700	-0.12407900
H	3.66839400	2.80392700	0.17054600
H	0.82015500	2.83492200	-0.04504600
H	-2.37931400	3.13624400	0.78931000
H	-1.40795300	3.48320000	-0.64700800
H	-3.05869300	2.87345600	-0.81908900
H	-4.17792317	-0.86175208	0.15309226
H	-4.34984663	0.88244875	0.20384323
H	-3.98265340	-0.78093389	-2.36336156
H	-5.50103268	-0.05024893	-1.80324554
H	-4.15001210	0.97951271	-2.31722413
H	-1.42552200	-2.80558800	0.71245800

H	-2.78363100	-2.54660500	-0.41222800
H	-1.12956700	-2.83170800	-1.02075300
H	5.44122700	0.75431000	0.30676400
H	3.95089800	-1.52534300	0.19276100

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