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Supporting Information for

Aggregation-Induced Emission Enhancement of a *meso*-Trifluoromethyl BODIPY via *J*-Aggregation

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Table of Contents:

Experimental

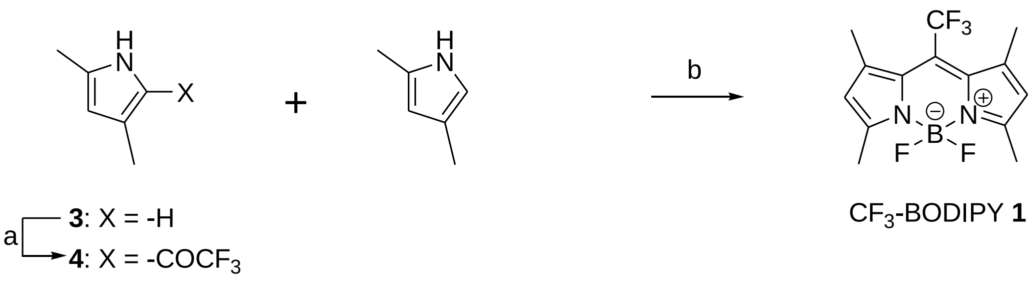
Materials

All reagents were of the highest commercial quality and used as received without further purification. All solvents were spectral grade unless otherwise noted. Anhydrous CH_2Cl_2 was obtained as a sure-seal bottle from Aldrich Co. Inc. (Milwaukee, WI). Silica gel (40 μm) was obtained from Merck Inc. Aqueous solutions were freshly prepared with deionized water from a water purification system (Human Corp. Korea). Compounds **4**,[1] and CH_3-BODIPY **2**[2] were prepared according to literature procedures.

General methods, instrumentation, and measurements

Synthetic manipulations that required an inert atmosphere (where noted) were carried out under argon using standard Schlenk techniques. NMR (^{1}H, ^{13}C and ^{19}F) spectra were recorded on JEOL 400 MHz spectrometer or Bruker Avance 500 MHz spectrometer. The ^{1}H and ^{13}C chemical shifts were reported as δ in units of parts per million (ppm), referenced to the residual solvent. ^{19}F-NMR chemical shifts are reported in units of δ (ppm), referenced to trifluoroacetic acid as a standard. Splitting patterns are denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Melting point determinations were performed using a Stuart Melting Point Apparatus SMP 10 instrument (open capillaries used). DLS data were obtained on a Malvern Zetasizer instrument. Life-time measurements were performed using a MicroTime-200 instrument at the National Center for Inter-University Research Facilities (Korea). SEM-images were obtained on Hitachi S-4300 scanning electron microscope. High-resolution mass spectra were obtained with JMS-700 (JEOL, Japan) using an electron impact source with an ionizing voltage of 70 V. FAB mass spectra were obtained at the National Center for Inter-University Research Facilities (Korea). Absorption spectra were obtained on an Optizen 2120UV spectrophotometer. Fluorescence measurements were recorded on a Hitachi F-7000 fluorescence spectrophotometer using 10 mm quartz cuvettes. Fluorescence quantum yields were determined by standard methods, using rhodamine 6G (Φ_F = 0.95 in EtOH)[3] for CF_3-BODIPY **1** and fluorescein (Φ_F = 0.95 in 0.1 M NaOH)[4] for CH_3-BODIPY **2** as standards, respectively.

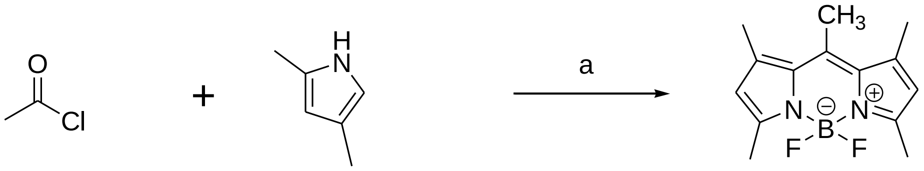
1. Synthesis of Compounds



Scheme S1. Synthetic scheme for CF_3-BODIPY **1**. (a) Trifluoroacetic anhydride, CH_2Cl_2, 0°C→RT, $NaHCO_3$, 3 hours, 94%; (b) $POCl_3$, $BF_3 \cdot OEt_2$, Et_3N, CH_2Cl_2, 4 hours, 0 °C→RT, 17%.

Compound 4.[1] To a stirred solution of 2,4-dimethylpyrrole (1 mL, 9.71 mmole) in dry dichloromethane (15 mL) at 0˚C was added trifluoroacetic anhydride (1.5 mL, 10.68 mmole) under argon atmosphere. The resulting solution was stirred at 0˚C for 30 minutes, and warmed to room temperature. After the reaction mixture was stirred at room temperature for 3 hours, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using progressively more polar hexanes to 1000:1 hexanes : ethyl acetate as the mobile phase to give compound **4** as a white solid (1.5 g, 94% yield). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.98 (d, 1H), 2.37 (s, 3H), 2.34 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 140.1, 120.9, 118.6, 116.4, 115.1, 114.1, 13.8 13.5; HR-MS (EI): calcd. for $C_8H_8F_3NO$ $[M]^+$ 191.0558, found 191.1539.

CF_3-BODIPY 1. To a stirred mixture of 2,4-dimethylpyrrole **3** (250 µL, 2.43 mmol) and compound **4** (300 mg, 1.62 mmol) in dry dichloromethane (5 mL) at 0 °C was added $POCl_3$ (220 µL, 1.62 mmol) under argon atmosphere. The reaction mixture was warmed to room temperature and stirred for 4 hours. This solution turned from colorless to red. To the reaction solution was added $BF_3 \cdot OEt_2$ (1 mL, 7.89 mmol) and triethylamine (1 mL, 7.17 mmol). After stirring for 10 min, the reaction mixture was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered, evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using progressively more polar 1000:1 to 100:1 hexanes : ethyl acetate to afford CF_3-BODIPY **1** as a red solid (85 mg, 17% yield). mp 172-173 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.15 (s, 2H), 2.54 (s, 6H), 2.30 (t, J = 3.6 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 158.9, 143.2, 131.4, 124.5, 123.8, 121.0, 16.0, 15.1; ^{19}F-NMR (470 MHz, $CDCl_3$): δ = -53.15 (t, 3F), -146.52 (q, 2F); HR-MS (FAB): calcd. for $C_{14}H_{14}BF_5N_2$ $[M]^+$ 316.1170, found 316.1173.



CH$_3$-BODIPY **2**

Scheme S2. Synthetic scheme for CH$_3$-BODIPY **2**. (a) BF$_3$·OEt$_2$, Et$_3$N, CH$_2$Cl$_2$, RT, 16 hours, 51%.

CH$_3$-BODIPY 2.[2] To a stirred solution of 2,4-dimethylpyrrole **3** (200 µL, 1.95 mmol) in dry dichloromethane (3 mL) at room temperature and an under argon atmosphere was added acetyl chloride (70 µL, 1.00 mmol). After the resulting solution was stirred at room temperature for 12 hours until TLC showed complete consumption of 2,4-dimethylpyrrole, BF$_3$·OEt$_2$ (4 mL, 31.56 mmol) and triethylamine (2 mL, 14.34 mmol) were added sequentially to the reaction mixture. The resulting solution was stirred for 4 hours. After the reaction was complete, the reaction solution was evaporated under reduced pressure and extracted with CH$_2$Cl$_2$. The crude product was purified by column chromatography on silica gel using progressively more polar 500:1 to 3:1 hexanes : ethyl acetate as the mobile phase to afford CH$_3$-BODIPY **2** as an orange solid (130 mg, 51% yield). mp 250-252 °C; ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 6.05 (s, 2H), 2.56 (s, 3H), 2.51 (s, 6H), 2.40 (s, 6H); ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 153.7, 141.5, 141.1, 132.1, 121.3, 17.4, 16.4, 14.5.

2. Studies of the Photophysical Properties

Table S1. Photophysical properties of CF$_3$-BODIPY **1** and CH$_3$-BODIPY **2** in various solvents

Compound	Solvent	$\lambda_{\text{abs. max}}$ [nm]	ε^a [M^{-1}cm^{-1}]	$\lambda_{\text{em. max}}{}^b$ [nm]	$\Phi_{FL}{}^c$
1	Toluene	557	48710	620	0.008
1	THF	553	43620	625	0.006
1	CHCl$_3$	553	50800	622	0.008
1	CH$_3$OH	550	45510	622	0.004
1	CH$_3$CN	549	46310	620	0.003
1	DMSO	554	30710	631	0.006
2	Toluene	501	100050	520	0.94
2	THF	496	100750	517	0.90
2	CHCl$_3$	499	115700	520	1.00
2	CH$_3$OH	493	88430	512	0.99
2	CH$_3$CN	492	92700	512	0.82
2	DMSO	495	103600	517	0.85

[a] Measured at each absorption maximum. [b] Excited at 530 and 460 nm for CF$_3$-BODIPY **1** and CH$_3$-BODIPY **2**, respectively. [c] Quantum yields vs. rhodamine 6G in ethanol (Φ_F = 0.95) for CF$_3$-BODIPY **1**[3] and fluorescein in 0.1 M NaOH (Φ_F = 0.95) for CH$_3$-BODIPY **2**.[4]

Absorption and emission spectra of compounds in various solvents

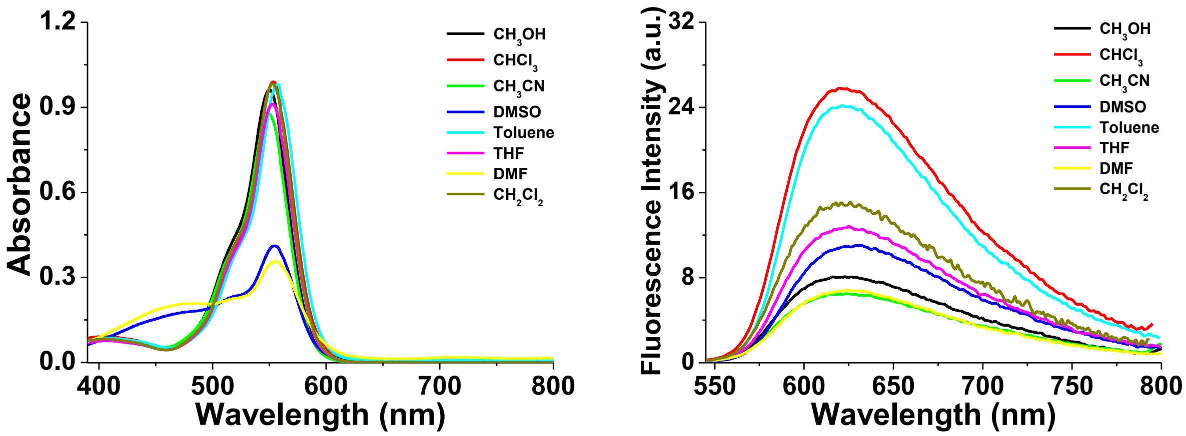


Figure S1. Absorption (left) and emission spectra (right) of CF_3-BODIPY **1** (20 μM) in various solvents at 25 °C. Excited at 530 nm.

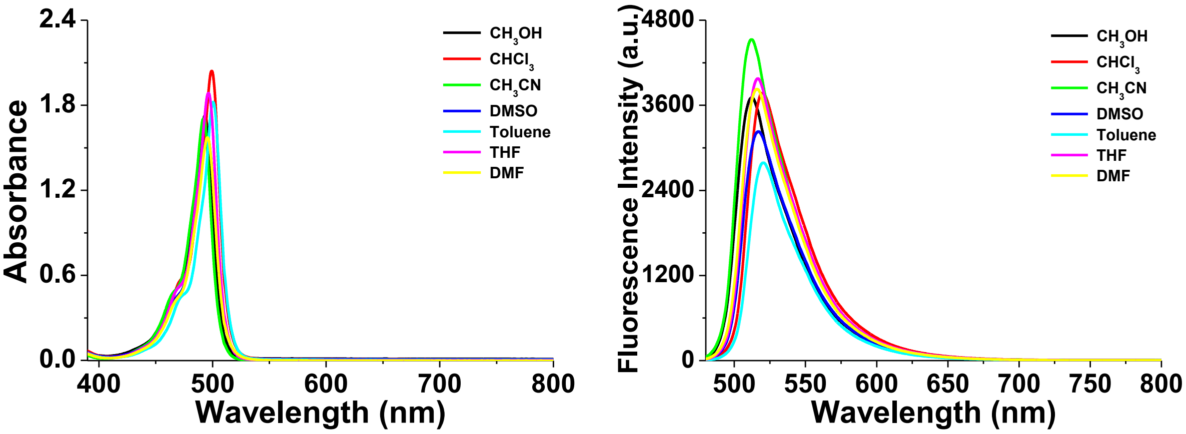


Figure S2. Absorption (left) and emission spectra (right) of CH_3-BODIPY **2** (20 μM) in various solvents at 25 °C. Excited at 460 nm.

3. Studies of AIEE Properties

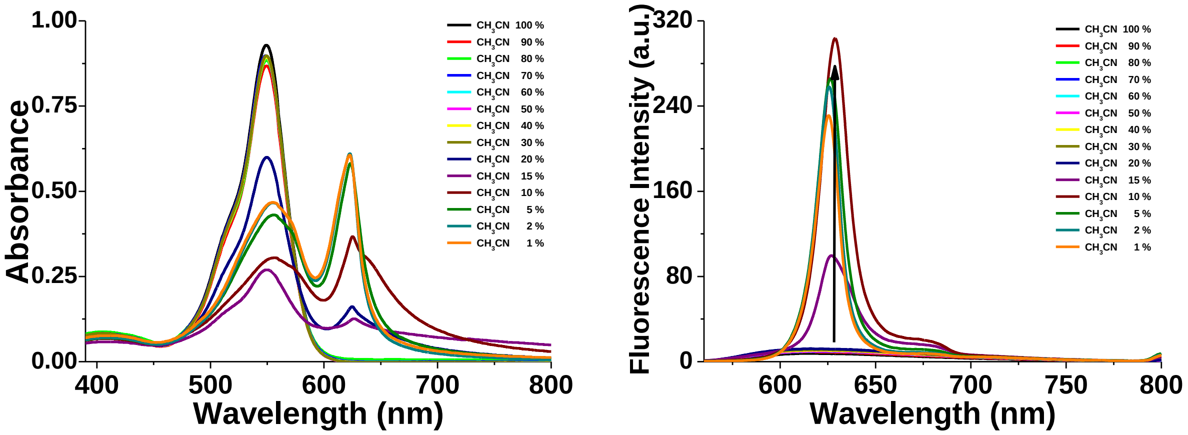


Figure S3. Absorption (left) and emission spectra (right) of CF_3-BODIPY **1** (20 μM) in acetonitrile-water mixtures of varying composition at 25 ^{o}C (volume fractions shown) . Excited at 530 nm.

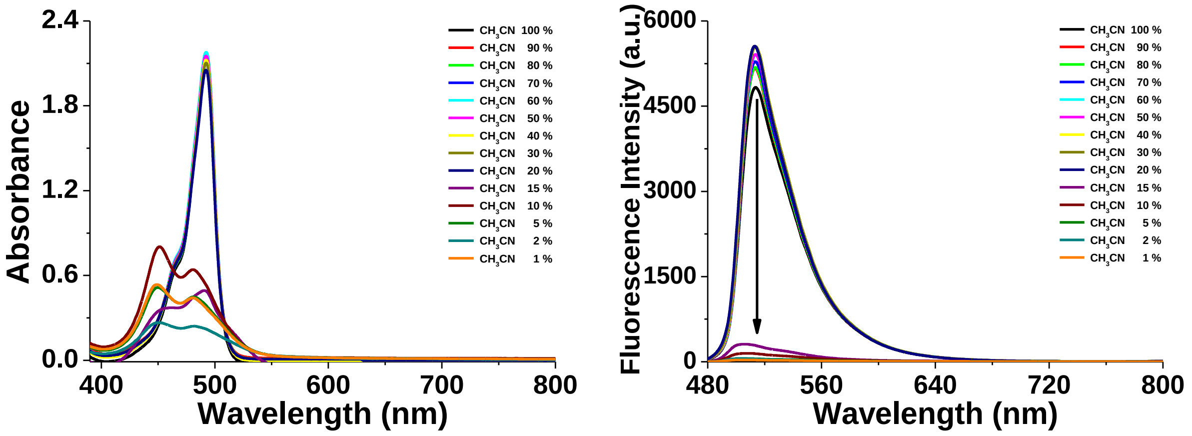


Figure S4. Absorption (left) and emission spectra (right) of CH_3-BODIPY **2** (20 μM) in acetonitrile-water mixtures of varying composition at 25 ^{o}C (volume fractions shown). Excited at 460 nm.

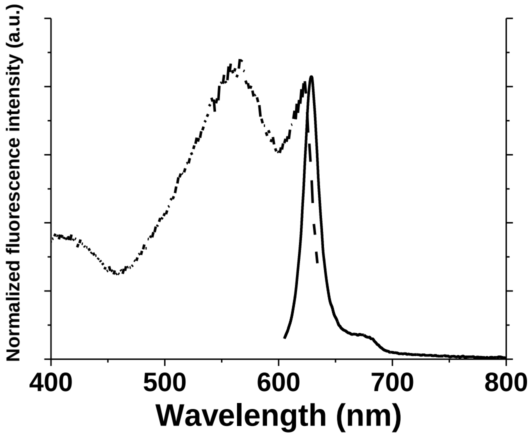


Figure S5. Excitation (dash-line) and emission (solid-line) spectra of CF_3-BODIPY **1** in 1/9 v/v acetonitrile-water at 25 °C. The excitation spectrum was obtained by monitoring at 650 nm, and the emission spectrum was obtained by excitation at 590 nm.

4. Dye-Doped PMMA Films

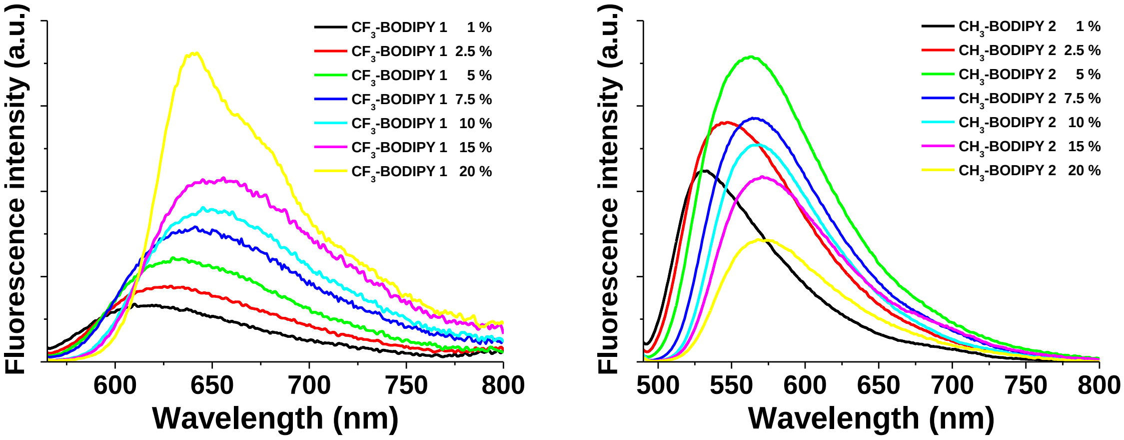


Figure S6. Emission spectra of different weight fraction of CF_3-BODIPY **1**-doped PMMA films (left) and CH_3-BODIPY **2**-doped PMMA films (right) at 25 °C. Excited at 530 nm for CF_3-BODIPY **1**-doped PMMA film and 460 nm for CH_3-BODIPY **2**-doped PMMA film, respectively.

5. Time-Resolved Photoluminescence Decay Dynamics

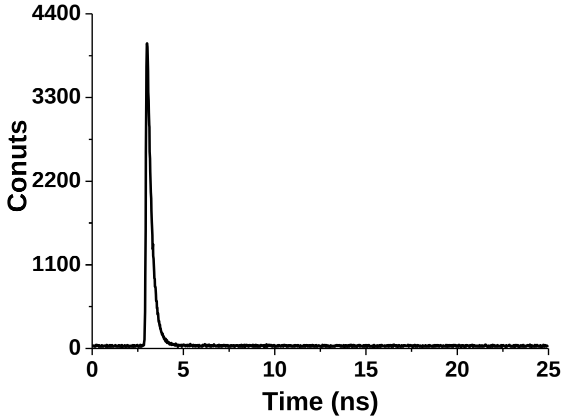


Figure S7. Time-resolved emission decays of CF_3-BODIPY **1** in chloroform. **1** bi-exponential decays gave lifetimes of 0.246 ns (82%) and 0.041 ns (18%) for 620 nm. Average lifetime of 0.210 ns.

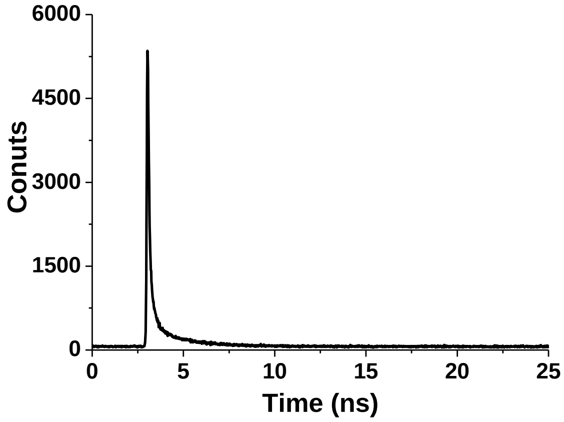


Figure S8. Time-resolved emission decays of CF_3-BODIPY **1** in acetonitrile. **1** tri-exponential decays gave lifetimes of 0.091 ns (85%), 0.351 ns (11%) and 1.923 ns (4%) for 620 nm. Average lifetime of 0.190 ns.

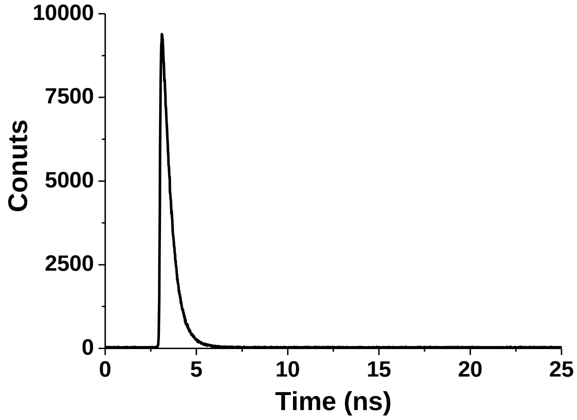


Figure S9. Time-resolved emission decays of CF_3-BODIPY **1** in acetonitrile-water mixture (10/90, v/v). **1** bi-exponential decays gave lifetimes of 0.477 ns (82%) and 0.053 ns (18%) for 630 nm. Average lifetime of 0.400 ns.

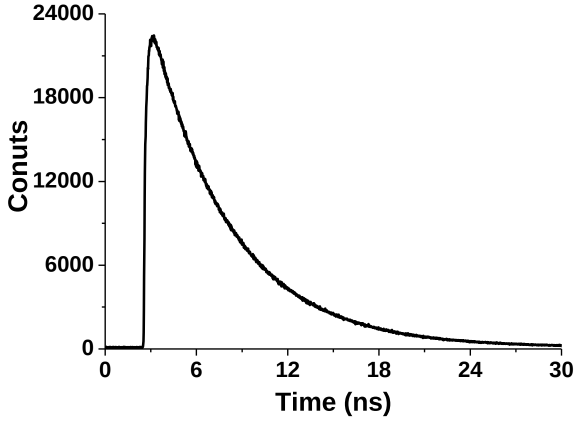


Figure S10. Time-resolved emission decays of CH_3-BODIPY **2** in chloroform. **2** mono-exponential decays gave lifetime of 5.22 ns (100%) for 520 nm.

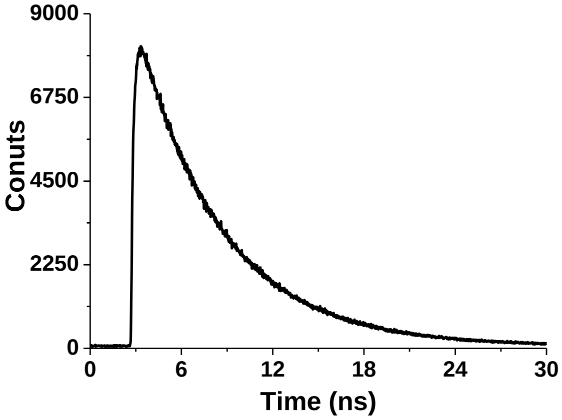


Figure S11. Time-resolved emission decays of CH_3-BODIPY **2** in acetonitrile. **2** mono-exponential decays gave lifetime of 5.51 ns (100%) for 510 nm.

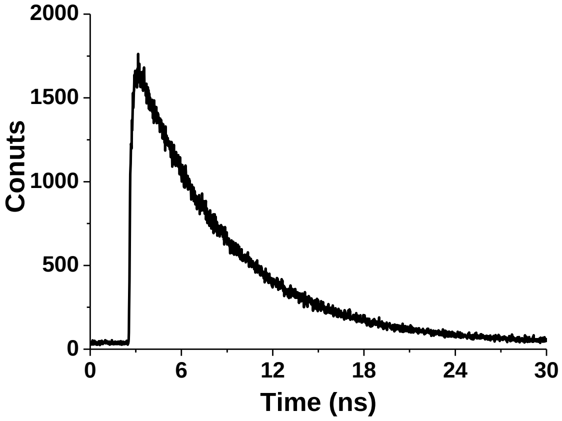


Figure S12. Time-resolved emission decays of CH_3-BODIPY **2** in acetonitrile-water mixture (10/90, v/v). **2** mono-exponential decays gave lifetime of 5.94 ns (100%) for 510 nm

6. DLS Studies of Aggregates of 1 and 2

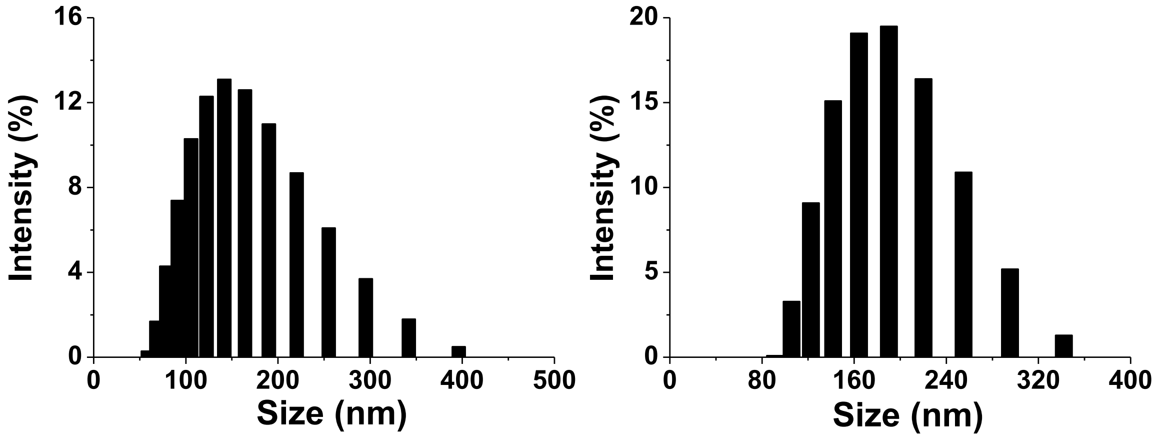


Figure S13. Size distribution by DLS of CF_3-BODIPY **1** aggregates (20 μM) in acetonitrle-water mixture solution (left: 1/99 (v/v), right: 10/90 (v/v)) at 25 °C.

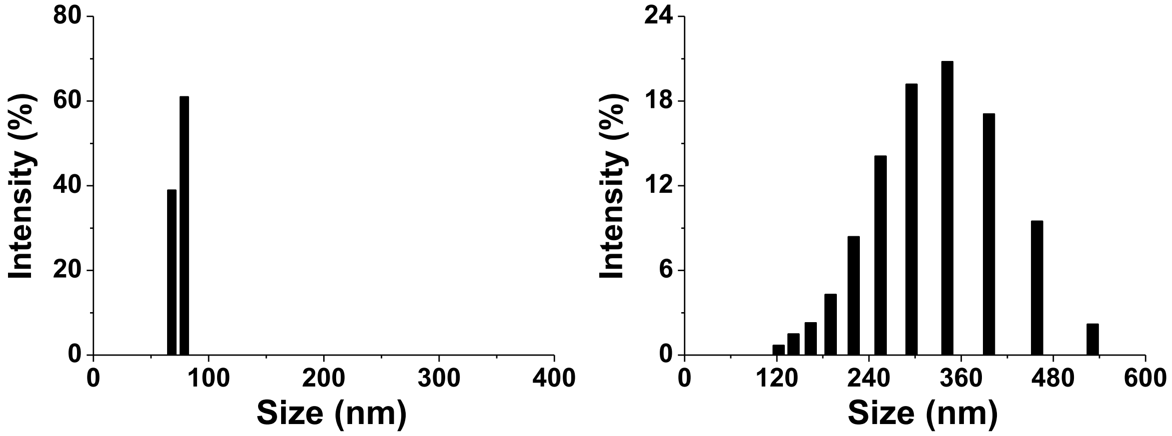


Figure S14. Size distribution by DLS of CH_3-BODIPY **2** aggregates (20 μM) in acetonitrle-water mixture solution (left: 1/99 (v/v), right: 10/90 (v/v)) at 25 °C.

7. SEM Images of Aggregates of 1 and 2

To obtain more information about the aggregates of the *meso*-substituted BODIPY derivatives **1** and **2** formed in CH_3CN/water mixtures, the morphology of the aggregates of **1** and **2** was determined by scanning electron microscopy (SEM). The SEM images of the dried aggregates of **2** in 99% *f*w mixtures show a three-dimensional network of nanofibers, with nanorods 1.2 ± 0.5 μm in length and 92 ± 27 nm in width (Figure S17, *right*). The SEM images of the nanostructures of **1** show a three-dimensional network consisting of numerous, irregular, entangled nanoplates 189 ± 40 nm in size (Figure S17, *left*), which are consistent with the dynamic light scattering data.

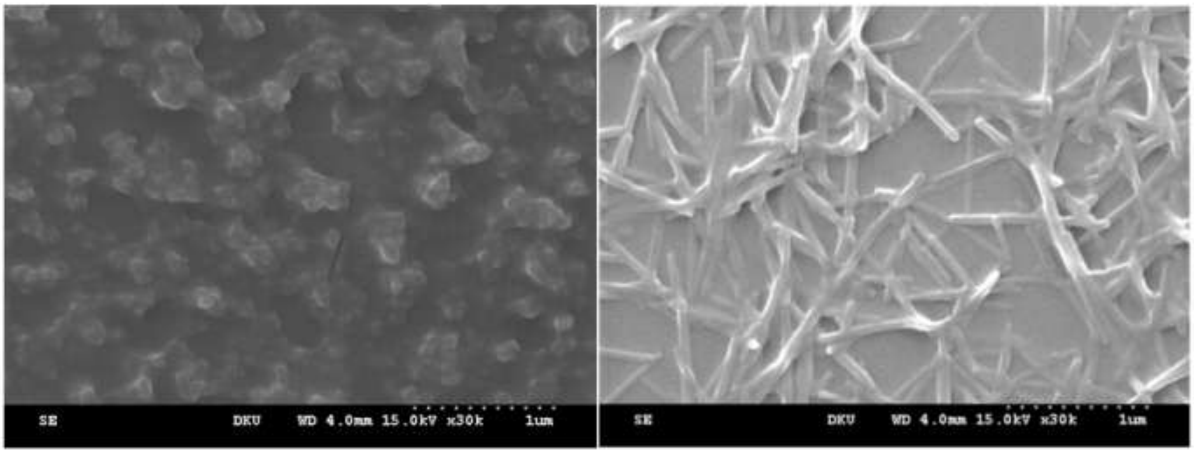


Figure S15. SEM images of **1** (left) and **2** (right) formed from evaporation of a CH_3CN/H_2O mixture (*f*w = 99%). Concentration of **1** and **2**: 20 μM.

8. X-ray Structures of 1 and 2

Single crystals of **1** and **2** suitable for X-ray structure analysis were obtained by diffusion of a solution of **1** in ethanol into water, and by slow evaporation from a CH_2Cl_2/pentane mixture solution for **2**.

Table S2. Crystal data and structure refinement for CF_3-BODIPY **1**.

Identification code	CF_3-BODIPY **1**
Empirical formula	$C_{14}\,H_{14}\,B\,F_5\,N_2$
Formula weight	316.08
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 6.4922(13) Å = 90°
	b = 12.393(2) Å = 90°
	c = 17.163(3) Å = 90°
Volume	1380.9(5) $Å^3$
Z	4
Density (calculated)	1.520 Mg/m^3
Absorption coefficient	0.137 mm^{-1}
F(000)	648
Crystal size	0.26 x 0.20 x 0.08 mm^3
Theta range for data collection	2.03 to 26.01°.
Index ranges	-7<=h<=8, -15<=k<=15, -14<=l<=21
Reflections collected	8739
Independent reflections	2715 [R(int) = 0.0740]

Completeness to theta = 26.01°	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2715 / 6 / 203
Goodness-of-fit on F^2	0.959
Final R indices [I>2sigma(I)]	R1 = 0.1080, wR2 = 0.2822
R indices (all data)	R1 = 0.1757, wR2 = 0.3340
Absolute structure parameter	-1(3)
Largest diff. peak and hole	1.271 and -0.466 e.$Å^{-3}$

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for CF_3-BODIPY **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	2934(16)	6513(8)	6520(6)	53(3)
F(1)	2207(8)	5768(4)	5980(3)	63(2)
F(2)	4170(7)	7261(4)	6128(3)	62(1)
N(1)	4220(10)	5928(5)	7140(3)	38(2)
N(2)	1150(8)	7061(5)	6926(3)	37(2)
C(1)	5887(13)	5335(6)	7003(5)	48(2)
C(2)	6777(15)	5131(8)	6215(6)	71(3)
C(3)	6594(15)	4930(7)	7718(7)	69(3)
C(4)	5389(14)	5312(7)	8321(5)	56(2)
C(5)	5729(19)	4997(8)	9164(6)	82(3)
C(6)	3805(12)	5965(7)	7941(5)	49(2)
C(7)	2202(12)	6567(7)	8219(4)	48(2)
C(8)	1961(16)	6749(12)	9108(8)	89(4)
F(3)	675(16)	6141(7)	9407(5)	132(3)
F(4)	3600(16)	6874(6)	9466(3)	116(3)
F(5)	1191(15)	7866(7)	9276(4)	134(3)
C(9)	788(13)	7115(6)	7730(4)	43(2)
C(10)	-1033(12)	7731(6)	7865(4)	46(2)
C(11)	-2216(17)	8071(9)	8573(5)	80(3)
C(12)	-1683(13)	8043(7)	7139(5)	57(2)
C(13)	-343(12)	7628(6)	6561(4)	46(2)
C(14)	-455(15)	7775(7)	5713(4)	59(2)

Table S4. Bond lengths [Å] and angles [°] for CF_3-BODIPY **1**.

B(1)-F(1)	1.391(11)
B(1)-F(2)	1.399(10)
B(1)-N(2)	1.512(11)
B(1)-N(1)	1.534(11)
N(1)-C(1)	1.329(10)
N(1)-C(6)	1.401(10)
N(2)-C(13)	1.351(9)
N(2)-C(9)	1.402(9)
C(1)-C(3)	1.403(12)
C(1)-C(2)	1.492(12)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-C(4)	1.381(14)
C(3)-H(3)	0.9500
C(4)-C(6)	1.462(11)
C(4)-C(5)	1.515(12)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-C(7)	1.366(11)
C(7)-C(9)	1.417(10)
C(7)-C(8)	1.552(16)
C(8)-F(3)	1.236(13)
C(8)-F(4)	1.238(13)
C(8)-F(5)	1.500(15)
C(9)-C(10)	1.426(10)
C(10)-C(12)	1.372(11)
C(10)-C(11)	1.498(11)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800

C(12)-C(13)	1.416(11)
C(12)-H(12)	0.9500
C(13)-C(14)	1.469(9)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
F(1)-B(1)-F(2)	108.3(7)
F(1)-B(1)-N(2)	110.2(7)
F(2)-B(1)-N(2)	111.3(7)
F(1)-B(1)-N(1)	109.5(7)
F(2)-B(1)-N(1)	109.5(7)
N(2)-B(1)-N(1)	108.1(7)
C(1)-N(1)-C(6)	110.4(6)
C(1)-N(1)-B(1)	125.6(7)
C(6)-N(1)-B(1)	124.0(7)
C(13)-N(2)-C(9)	108.1(6)
C(13)-N(2)-B(1)	124.8(6)
C(9)-N(2)-B(1)	127.1(6)
N(1)-C(1)-C(3)	108.0(8)
N(1)-C(1)-C(2)	124.8(7)
C(3)-C(1)-C(2)	127.3(9)
C(1)-C(2)-H(2A)	109.5
C(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(4)-C(3)-C(1)	110.4(8)
C(4)-C(3)-H(3)	124.8
C(1)-C(3)-H(3)	124.8
C(3)-C(4)-C(6)	104.7(8)
C(3)-C(4)-C(5)	123.0(9)
C(6)-C(4)-C(5)	132.2(9)
C(4)-C(5)-H(5A)	109.5

C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(7)-C(6)-N(1)	120.5(7)
C(7)-C(6)-C(4)	133.0(8)
N(1)-C(6)-C(4)	106.5(8)
C(6)-C(7)-C(9)	123.3(7)
C(6)-C(7)-C(8)	120.0(8)
C(9)-C(7)-C(8)	116.6(8)
F(3)-C(8)-F(4)	116.8(12)
F(3)-C(8)-F(5)	105.0(9)
F(4)-C(8)-F(5)	94.3(12)
F(3)-C(8)-C(7)	112.8(12)
F(4)-C(8)-C(7)	114.8(8)
F(5)-C(8)-C(7)	110.9(9)
N(2)-C(9)-C(7)	116.8(7)
N(2)-C(9)-C(10)	109.0(6)
C(7)-C(9)-C(10)	134.2(7)
C(12)-C(10)-C(9)	104.9(6)
C(12)-C(10)-C(11)	120.0(8)
C(9)-C(10)-C(11)	135.1(8)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-C(13)	110.2(8)
C(10)-C(12)-H(12)	124.9
C(13)-C(12)-H(12)	124.9
N(2)-C(13)-C(12)	107.8(7)
N(2)-C(13)-C(14)	124.0(8)

C(12)-C(13)-C(14)	128.2(8)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($Å^2$x 10^3) for CF_3-BODIPY **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
(1)	56(6)	63(6)	41(5)	8(4)	0(5)	9(5)
F(1)	69(3)	72(3)	48(3)	-19(2)	-3(2)	15(3)
F(2)	59(3)	71(3)	54(3)	21(2)	12(2)	7(3)
N(1)	38(3)	39(3)	36(4)	5(2)	-1(3)	-5(3)
N(2)	35(3)	46(3)	30(3)	-3(3)	-2(2)	-2(3)
C(1)	46(5)	37(4)	60(5)	-8(4)	-10(4)	-4(4)
C(2)	57(6)	68(6)	89(8)	-18(5)	16(5)	13(5)
C(3)	52(6)	50(5)	104(8)	8(5)	-35(6)	-1(5)
C(4)	57(5)	58(5)	53(5)	7(4)	-15(5)	-15(5)
C(5)	103(8)	72(7)	70(6)	20(5)	-42(6)	8(6)
C(6)	47(5)	46(4)	55(5)	14(4)	-14(4)	-13(4)
C(7)	37(4)	73(6)	34(4)	6(4)	-3(3)	-2(4)
C(8)	36(5)	143(11)	89(9)	37(8)	17(6)	2(7)
F(3)	140(4)	129(4)	126(4)	4(3)	17(3)	-14(3)
F(4)	188(9)	111(5)	49(4)	-11(3)	-11(4)	-21(6)
F(5)	163(8)	152(7)	85(5)	-26(5)	25(5)	-9(7)
C(9)	55(5)	49(4)	26(4)	-2(3)	0(3)	-5(4)
C(10)	43(5)	48(4)	45(5)	-7(3)	11(4)	3(4)
C(11)	98(8)	88(7)	55(6)	6(5)	21(5)	20(7)
C(12)	44(5)	55(5)	71(6)	5(4)	4(4)	5(4)
C(13)	51(5)	46(5)	40(4)	2(3)	-10(4)	0(4)
C(14)	66(6)	77(6)	34(5)	10(4)	-12(4)	21(5)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for CF_3-BODIPY **1**.

	x	y	z	U(eq)
H(2A)	5727	4804	5879	107
H(2B)	7953	4639	6262	107
H(2C)	7237	5814	5987	107
H(3)	7739	4461	7779	82
H(5A)	5639	4211	9215	123
H(5B)	4672	5336	9490	123
H(5C)	7095	5240	9332	123
H(11A)	-1640	8746	8776	121
H(11B)	-2117	7509	8972	121
H(11C)	-3664	8182	8433	121
H(12)	-2863	8475	7038	68
H(14A)	682	8238	5542	89
H(14B)	-1770	8114	5576	89
H(14C)	-350	7072	5455	89

Table S7. Torsion angles [°] for CF$_3$-BODIPY **1**.

F(1)-B(1)-N(1)-C(1)	58.4(10)
F(2)-B(1)-N(1)-C(1)	-60.2(10)
N(2)-B(1)-N(1)-C(1)	178.4(6)
F(1)-B(1)-N(1)-C(6)	-122.8(8)
F(2)-B(1)-N(1)-C(6)	118.6(8)
N(2)-B(1)-N(1)-C(6)	-2.8(10)
F(1)-B(1)-N(2)-C(13)	-58.4(10)
F(2)-B(1)-N(2)-C(13)	61.7(10)
N(1)-B(1)-N(2)-C(13)	-177.9(6)
F(1)-B(1)-N(2)-C(9)	124.4(8)
F(2)-B(1)-N(2)-C(9)	-115.5(8)
N(1)-B(1)-N(2)-C(9)	4.8(11)
C(6)-N(1)-C(1)-C(3)	1.8(8)
B(1)-N(1)-C(1)-C(3)	-179.3(7)
C(6)-N(1)-C(1)-C(2)	-179.6(7)
B(1)-N(1)-C(1)-C(2)	-0.6(12)
N(1)-C(1)-C(3)-C(4)	-2.4(9)
C(2)-C(1)-C(3)-C(4)	179.1(8)
C(1)-C(3)-C(4)-C(6)	1.9(9)
C(1)-C(3)-C(4)-C(5)	178.4(8)
C(1)-N(1)-C(6)-C(7)	177.4(7)
B(1)-N(1)-C(6)-C(7)	-1.5(11)
C(1)-N(1)-C(6)-C(4)	-0.6(8)
B(1)-N(1)-C(6)-C(4)	-179.6(7)
C(3)-C(4)-C(6)-C(7)	-178.5(9)
C(5)-C(4)-C(6)-C(7)	5.5(16)
C(3)-C(4)-C(6)-N(1)	-0.8(9)
C(5)-C(4)-C(6)-N(1)	-176.8(9)
N(1)-C(6)-C(7)-C(9)	4.8(12)
C(4)-C(6)-C(7)-C(9)	-177.7(8)
N(1)-C(6)-C(7)-C(8)	-170.3(8)
C(4)-C(6)-C(7)-C(8)	7.1(14)

C(6)-C(7)-C(8)-F(3)	-99.6(11)
C(9)-C(7)-C(8)-F(3)	85.0(12)
C(6)-C(7)-C(8)-F(4)	37.6(16)
C(9)-C(7)-C(8)-F(4)	-137.9(11)
C(6)-C(7)-C(8)-F(5)	143.0(9)
C(9)-C(7)-C(8)-F(5)	-32.5(12)
C(13)-N(2)-C(9)-C(7)	-179.9(6)
B(1)-N(2)-C(9)-C(7)	-2.4(11)
C(13)-N(2)-C(9)-C(10)	0.9(8)
B(1)-N(2)-C(9)-C(10)	178.5(7)
C(6)-C(7)-C(9)-N(2)	-2.9(12)
C(8)-C(7)-C(9)-N(2)	172.4(8)
C(6)-C(7)-C(9)-C(10)	176.0(8)
C(8)-C(7)-C(9)-C(10)	-8.7(14)
N(2)-C(9)-C(10)-C(12)	-1.0(8)
C(7)-C(9)-C(10)-C(12)	180.0(9)
N(2)-C(9)-C(10)-C(11)	179.7(10)
C(7)-C(9)-C(10)-C(11)	0.8(16)
C(9)-C(10)-C(12)-C(13)	0.8(9)
C(11)-C(10)-C(12)-C(13)	-179.8(8)
C(9)-N(2)-C(13)-C(12)	-0.4(9)
B(1)-N(2)-C(13)-C(12)	-178.0(7)
C(9)-N(2)-C(13)-C(14)	178.6(8)
B(1)-N(2)-C(13)-C(14)	1.0(12)
C(10)-C(12)-C(13)-N(2)	-0.3(10)
C(10)-C(12)-C(13)-C(14)	-179.2(8)

Table S8. Crystal data and structure refinement for CH$_3$-BODIPY **2**.

Identification code	CH$_3$-BODIPY **2**
Empirical formula	$C_{14} H_{17} B F_2 N_2$
Formula weight	262.11
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pnma
Unit cell dimensions	a = 11.3274(11) Å = 90°.
	b = 7.1032(6) Å = 90°.
	c = 16.0113(15) Å = 90°.
Volume	1288.3(2) Å^3
Z	4
Density (calculated)	1.351 Mg/m^3
Absorption coefficient	0.099 mm^{-1}
F(000)	552
Crystal size	0.38 x 0.34 x 0.33 mm^3
Theta range for data collection	2.20 to 28.33°.
Index ranges	-15<=h<=11, -7<=k<=9, -21<=l<=20
Reflections collected	9171
Independent reflections	1734 [R(int) = 0.0426]
Completeness to theta = 28.33°	99.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	1734 / 0 / 117
Goodness-of-fit on F^2	1.151
Final R indices [I>2sigma(I)]	R1 = 0.0526, wR2 = 0.1253
R indices (all data)	R1 = 0.0869, wR2 = 0.1736
Largest diff. peak and hole	0.426 and -0.513 e.Å^{-3}

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for CH_3-BODIPY **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	7511(2)	2500	5910(2)	37(1)
F(1)	8003(1)	909(2)	6275(1)	57(1)
N(1)	6163(2)	2500	6029(1)	32(1)
N(2)	7741(2)	2500	4964(1)	33(1)
C(1)	5582(2)	2500	6768(1)	37(1)
C(2)	4372(2)	2500	6616(2)	40(1)
C(3)	4182(2)	2500	5764(2)	36(1)
C(4)	5320(2)	2500	5383(1)	31(1)
C(5)	6187(3)	2500	7593(2)	48(1)
C(6)	2983(2)	2500	5369(2)	45(1)
C(7)	5678(2)	2500	4544(1)	33(1)
C(8)	4762(2)	2500	3874(1)	41(1)
C(9)	6876(2)	2500	4335(1)	32(1)
C(10)	7472(2)	2500	3552(1)	38(1)
C(11)	8668(2)	2500	3734(2)	44(1)
C(12)	8816(2)	2500	4597(2)	38(1)
C(13)	6975(3)	2500	2683(2)	50(1)
C(14)	9939(2)	2500	5075(2)	49(1)

Table S10. Bond lengths [Å] and angles [°] for CH_3-BODIPY **2**.

B(1)-F(1)#1	1.3885(19)
B(1)-F(1)	1.3885(19)
B(1)-N(2)	1.536(3)
B(1)-N(1)	1.539(3)
N(1)-C(1)	1.354(3)
N(1)-C(4)	1.408(3)
N(2)-C(12)	1.352(3)
N(2)-C(9)	1.406(3)
C(1)-C(2)	1.392(3)
C(1)-C(5)	1.487(3)
C(2)-C(3)	1.382(4)
C(2)-H(2)	0.9500
C(3)-C(4)	1.425(3)
C(3)-C(6)	1.499(3)
C(4)-C(7)	1.404(3)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-C(9)	1.397(3)
C(7)-C(8)	1.492(3)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-C(10)	1.424(3)
C(10)-C(11)	1.385(4)
C(10)-C(13)	1.502(3)
C(11)-C(12)	1.393(3)
C(11)-H(11)	0.9500
C(12)-C(14)	1.485(4)

C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
F(1)#1-B(1)-F(1)	108.9(2)
F(1)#1-B(1)-N(2)	110.26(14)
F(1)-B(1)-N(2)	110.26(14)
F(1)#1-B(1)-N(1)	110.25(14)
F(1)-B(1)-N(1)	110.25(14)
N(2)-B(1)-N(1)	106.89(19)
C(1)-N(1)-C(4)	108.23(19)
C(1)-N(1)-B(1)	126.16(19)
C(4)-N(1)-B(1)	125.61(18)
C(12)-N(2)-C(9)	108.4(2)
C(12)-N(2)-B(1)	125.5(2)
C(9)-N(2)-B(1)	126.01(19)
N(1)-C(1)-C(2)	109.0(2)
N(1)-C(1)-C(5)	123.5(2)
C(2)-C(1)-C(5)	127.5(2)
C(3)-C(2)-C(1)	109.0(2)
C(3)-C(2)-H(2)	125.5
C(1)-C(2)-H(2)	125.5
C(2)-C(3)-C(4)	106.4(2)
C(2)-C(3)-C(6)	123.9(2)
C(4)-C(3)-C(6)	129.7(2)
C(7)-C(4)-N(1)	120.4(2)
C(7)-C(4)-C(3)	132.2(2)
N(1)-C(4)-C(3)	107.40(19)
C(1)-C(5)-H(5A)	109.5
C(1)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(1)-C(5)-H(5C)	109.5

H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(3)-C(6)-H(6A)	109.5
C(3)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(3)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(9)-C(7)-C(4)	120.7(2)
C(9)-C(7)-C(8)	120.2(2)
C(4)-C(7)-C(8)	119.1(2)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-N(2)	120.4(2)
C(7)-C(9)-C(10)	132.2(2)
N(2)-C(9)-C(10)	107.5(2)
C(11)-C(10)-C(9)	106.2(2)
C(11)-C(10)-C(13)	124.1(2)
C(9)-C(10)-C(13)	129.6(2)
C(10)-C(11)-C(12)	109.0(2)
C(10)-C(11)-H(11)	125.5
C(12)-C(11)-H(11)	125.5
N(2)-C(12)-C(11)	108.8(2)
N(2)-C(12)-C(14)	123.2(2)
C(11)-C(12)-C(14)	128.0(2)
C(10)-C(13)-H(13A)	109.5
C(10)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(10)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5

H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z

Table S11. Anisotropic displacement parameters ($Å^2$x 10^3) for CH_3-BODIPY **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	33(1)	45(1)	33(1)	0	-2(1)	0
F(1)	47(1)	78(1)	46(1)	22(1)	1(1)	20(1)
N(1)	31(1)	37(1)	28(1)	0	-1(1)	0
N(2)	32(1)	35(1)	32(1)	0	-3(1)	0
C(1)	39(1)	43(1)	30(1)	0	-1(1)	0
C(2)	36(1)	46(1)	36(1)	0	6(1)	0
C(3)	31(1)	37(1)	40(1)	0	-3(1)	0
C(4)	32(1)	31(1)	30(1)	0	-4(1)	0
C(5)	45(2)	65(2)	34(1)	0	-1(1)	0
C(6)	34(1)	56(2)	46(2)	0	-2(1)	0
C(7)	34(1)	30(1)	34(1)	0	-3(1)	0
C(8)	38(1)	51(1)	35(1)	0	-5(1)	0
C(9)	35(1)	30(1)	31(1)	0	-2(1)	0
C(10)	46(1)	39(1)	31(1)	0	1(1)	0
C(11)	41(1)	52(1)	39(1)	0	9(1)	0
C(12)	32(1)	41(1)	40(1)	0	3(1)	0
C(13)	55(2)	62(2)	32(1)	0	3(1)	0
C(14)	34(1)	61(2)	52(2)	0	1(1)	0

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for CH_3-BODIPY **2**.

	x	y	z	U(eq)
H(2)	3774	2500	7032	47
H(5A)	6851	1617	7579	72
H(5B)	5628	2114	8027	72
H(5C)	6479	3769	7715	72
H(6A)	2384	2243	5796	68
H(6B)	2949	1524	4937	68
H(6C)	2831	3733	5116	68
H(8A)	4523	3798	3754	62
H(8B)	4075	1776	4061	62
H(8C)	5088	1926	3368	62
H(11)	9287	2500	3334	53
H(13A)	6389	3508	2631	75
H(13B)	6598	1284	2571	75
H(13C)	7613	2707	2280	75
H(14A)	10062	1258	5327	74
H(14B)	9901	3455	5516	74
H(14C)	10596	2788	4698	74

Table S13. Torsion angles [°] for CH_3-BODIPY **2**.

F(1)#1-B(1)-N(1)-C(1)	-60.15(15)
F(1)-B(1)-N(1)-C(1)	60.15(15)
N(2)-B(1)-N(1)-C(1)	180.0
F(1)#1-B(1)-N(1)-C(4)	119.85(15)
F(1)-B(1)-N(1)-C(4)	-119.85(15)
N(2)-B(1)-N(1)-C(4)	0.0
F(1)#1-B(1)-N(2)-C(12)	60.16(15)
F(1)-B(1)-N(2)-C(12)	-60.16(15)
N(1)-B(1)-N(2)-C(12)	180.0
F(1)#1-B(1)-N(2)-C(9)	-119.84(15)
F(1)-B(1)-N(2)-C(9)	119.84(15)
N(1)-B(1)-N(2)-C(9)	0.0
C(4)-N(1)-C(1)-C(2)	0.0
B(1)-N(1)-C(1)-C(2)	180.0
C(4)-N(1)-C(1)-C(5)	180.0
B(1)-N(1)-C(1)-C(5)	0.0
N(1)-C(1)-C(2)-C(3)	0.0
C(5)-C(1)-C(2)-C(3)	180.0
C(1)-C(2)-C(3)-C(4)	0.0
C(1)-C(2)-C(3)-C(6)	180.0
C(1)-N(1)-C(4)-C(7)	180.0
B(1)-N(1)-C(4)-C(7)	0.0
C(1)-N(1)-C(4)-C(3)	0.0
B(1)-N(1)-C(4)-C(3)	180.0
C(2)-C(3)-C(4)-C(7)	180.0
C(6)-C(3)-C(4)-C(7)	0.0
C(2)-C(3)-C(4)-N(1)	0.0
C(6)-C(3)-C(4)-N(1)	180.0
N(1)-C(4)-C(7)-C(9)	0.0
C(3)-C(4)-C(7)-C(9)	180.0
N(1)-C(4)-C(7)-C(8)	180.0
C(3)-C(4)-C(7)-C(8)	0.0

C(4)-C(7)-C(9)-N(2)	0.0
C(8)-C(7)-C(9)-N(2)	180.0
C(4)-C(7)-C(9)-C(10)	180.0
C(8)-C(7)-C(9)-C(10)	0.0
C(12)-N(2)-C(9)-C(7)	180.0
B(1)-N(2)-C(9)-C(7)	0.0
C(12)-N(2)-C(9)-C(10)	0.0
B(1)-N(2)-C(9)-C(10)	180.0
C(7)-C(9)-C(10)-C(11)	180.0
N(2)-C(9)-C(10)-C(11)	0.0
C(7)-C(9)-C(10)-C(13)	0.0
N(2)-C(9)-C(10)-C(13)	180.0
C(9)-C(10)-C(11)-C(12)	0.0
C(13)-C(10)-C(11)-C(12)	180.0
C(9)-N(2)-C(12)-C(11)	0.0
B(1)-N(2)-C(12)-C(11)	180.0
C(9)-N(2)-C(12)-C(14)	180.0
B(1)-N(2)-C(12)-C(14)	0.0
C(10)-C(11)-C(12)-N(2)	0.0
C(10)-C(11)-C(12)-C(14)	180.0

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+1/2,z

9. Calculations

Geometric optimizations were performed in the gas phase at the B3LYP 6-311++G(d,p) level of theory, using the Gaussian 09 software package.[5] Absolute energies in hartrees or eV are given without additional corrections.

- **CF_3-BODIPY 1**

Energy: -1175.7575132317 hartrees

Dipole Moment: 1.9674 Debye

LUMO: -0.12162 eV

HOMO: -0.21998 eV

- **CH_3-BODIPY 2**

Energy: -878.21074217 hartrees

Dipole Moment: 4.6298 Debye

LUMO: -0.09761 eV

HOMO: -0.20941 eV

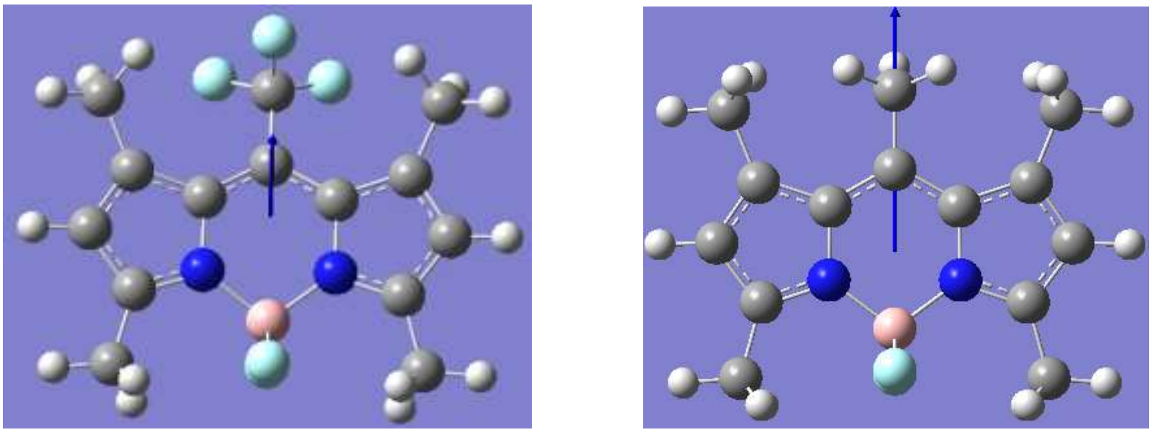


Figure S16. The calculated dipole moments of **1** (left) and **2** (right).

Cartesian Coordinates for **1** :

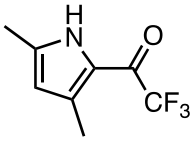
B	1.98779155	-0.00000031	0.22983628
F	3.03665389	-0.00001185	-0.70077081
F	2.50200573	-0.00003763	1.53335296
N	1.08548573	-1.24173017	-0.00260034
N	1.08548455	1.24176346	-0.00249974
C	1.52341573	-2.50980343	-0.13408611
C	2.96377381	-2.89706426	-0.08065846
H	3.51114264	-2.48542937	-0.93449335
H	3.05688751	-3.98520231	-0.08815754
H	3.44197333	-2.50401512	0.82211380
C	0.41159557	-3.35745198	-0.31795518
H	0.46549059	-4.42369366	-0.49355099
C	-0.74914458	-2.59692578	-0.26542453
C	-2.11114594	-3.18162253	-0.51391137
H	-1.99740717	-4.13359164	-1.03970623
H	-2.74441413	-2.53512740	-1.12538121
H	-2.64879313	-3.37882454	0.41833742
C	-0.31696125	-1.23486846	-0.04437233
C	-0.99140972	-0.00001109	0.04430151
C	-2.49143339	0.00001466	0.29588387
F	-3.21243871	0.00000608	-0.85945507
F	-2.88896828	-1.07203997	1.01368988
F	-2.88891381	1.07210908	1.01364934
C	-0.31696264	1.23484717	-0.04445660
C	-0.74917194	2.59687200	-0.26562594
C	-2.11116912	3.18145191	-0.51442704
H	-2.64903287	3.37868216	0.41768220
H	-2.74425194	2.53485695	-1.12598972
H	-1.99739620	4.13338658	-1.04027745
C	0.41153787	3.35745252	-0.31799680
H	0.46541805	4.42369340	-0.49360230
C	1.52337179	2.50985717	-0.13396297
C	2.96368610	2.89720673	-0.08006912
H	3.44093434	2.50612315	0.82409235
H	3.05684365	3.98531832	-0.08978987
H	3.51191227	2.48363294	-0.93238825

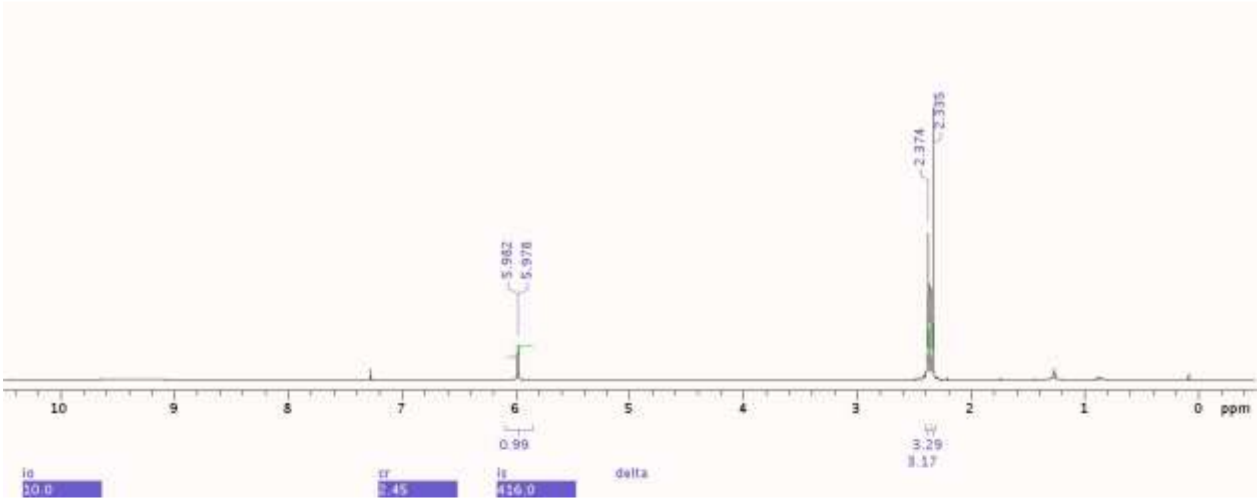
Cartesian Coordinates for **2** :

B	-0.00005564	-1.49657455	0.04479541
F	-0.00026579	-2.34634319	-1.07450773
N	-1.24490493	-0.57262628	0.00918592
N	1.24481870	-0.57256621	0.00882463
C	-2.52374172	-0.99117112	-0.02908004
C	-3.36839020	0.13365697	-0.05534886
H	-4.44708782	0.09984409	-0.09995714
C	-2.58153364	1.27845647	-0.02305222
C	-1.22146453	0.82761768	0.02255521
C	-2.91639760	-2.43045448	-0.03781490
H	-2.49624221	-2.94258790	-0.90682358
H	-4.00280302	-2.52242840	-0.05931815
H	-2.53286229	-2.94216550	0.84862850
C	-3.14188512	2.67022956	-0.06311749
H	-4.21976995	2.62401211	-0.22948410
H	-2.70841239	3.27277117	-0.86523272
H	-2.98270818	3.21017987	0.87614983
C	0.00000324	1.52272982	0.05565246
C	-0.00047421	3.02819613	0.12061927
C	1.22152154	0.82774789	0.02254275
C	2.58172291	1.27838752	-0.02299095
C	3.36837323	0.13348246	-0.05546872
H	4.44706013	0.09953415	-0.10022309
C	2.52357428	-0.99125271	-0.02946043
C	3.14275706	2.66993391	-0.06290688
H	2.98340343	3.21003760	0.87624973
H	2.71015894	3.27259678	-0.86539973
H	4.22071472	2.62309163	-0.22863933
C	2.91613162	-2.43056184	-0.03786920
F	0.00023066	-2.26789153	1.21874643
H	-0.00565765	3.46300737	-0.88528867
H	-0.87474941	3.40179636	0.64528230
H	0.87794694	3.40315116	0.63706175
H	2.53780452	-2.94047030	0.85190164
H	2.49082771	-2.94440250	-0.90329607
H	4.00239345	-2.52262455	-0.06537047

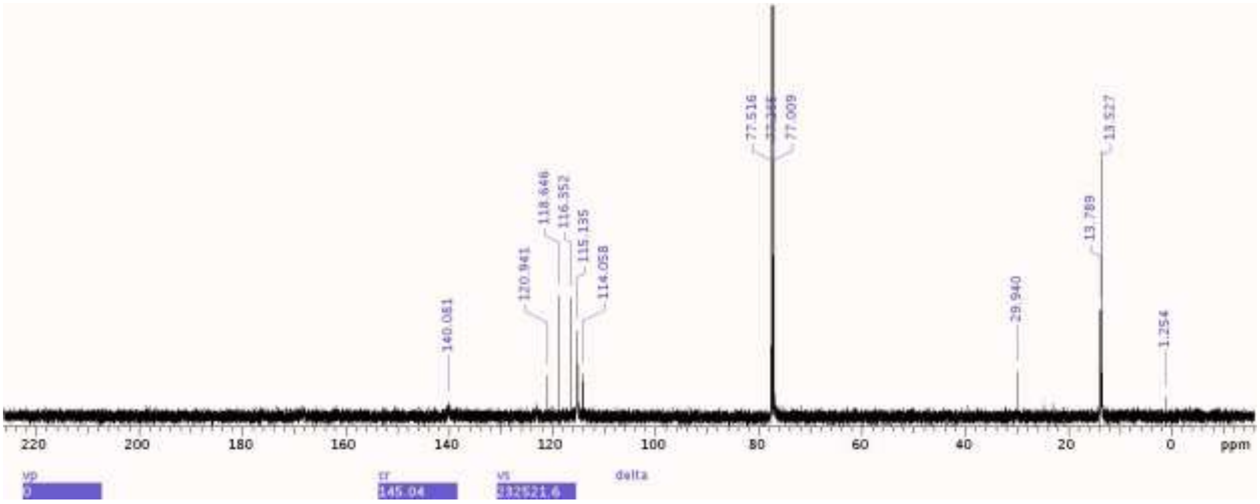
10. ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR Spectra

^{1}H-NMR Spectrum of Compound **4** in $CDCl_3$ (500 MHz):

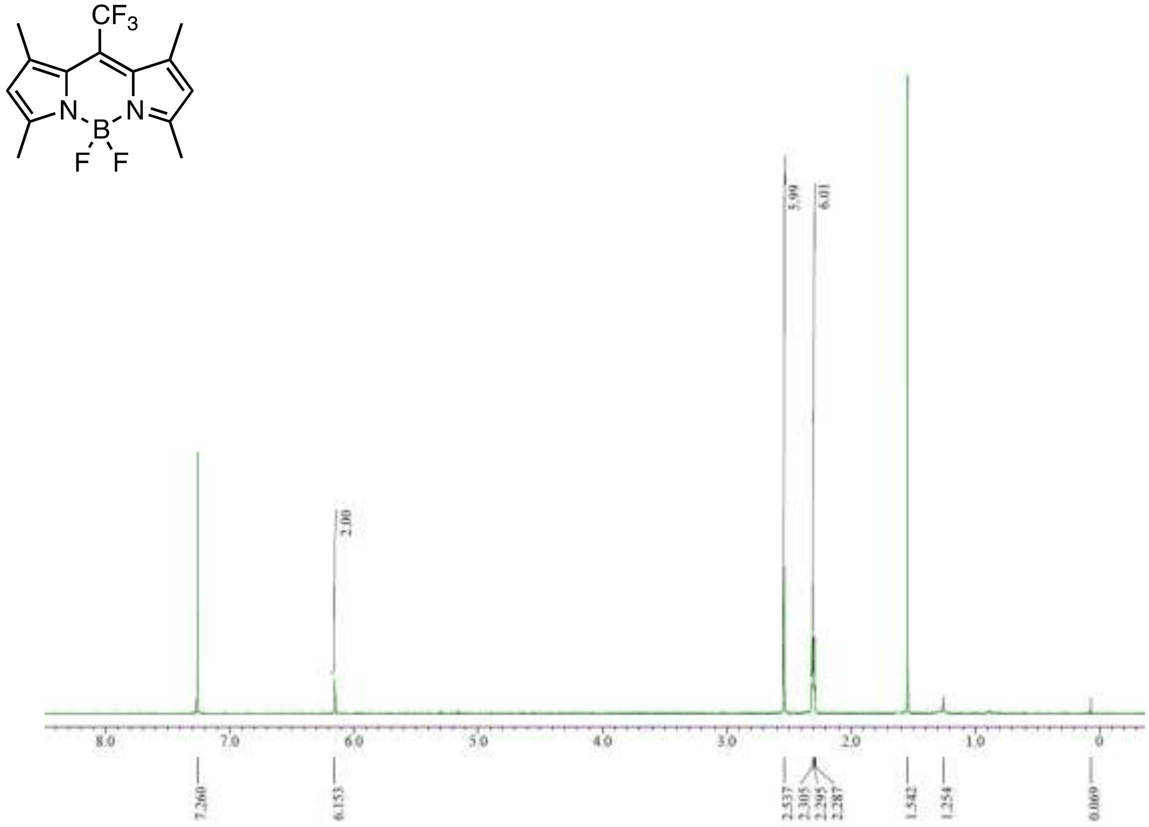




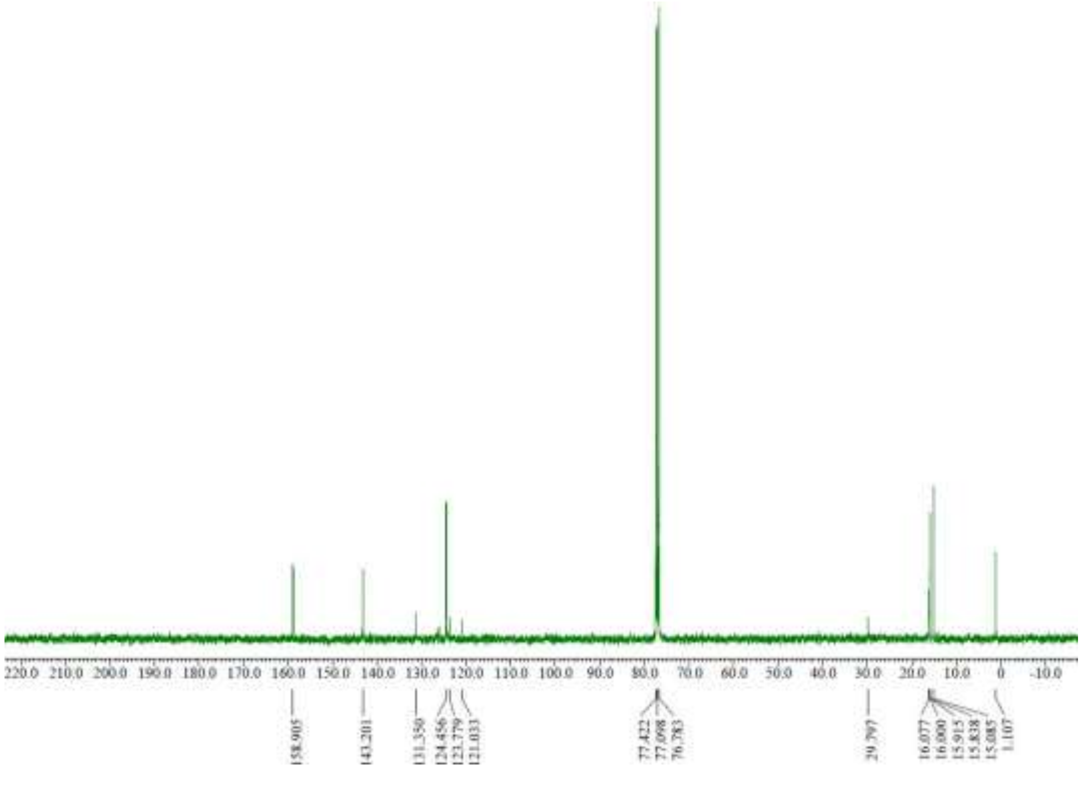
^{13}C-NMR Spectrum of Compound **4** in $CDCl_3$ (125 MHz):



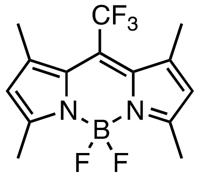
^{1}H-NMR Spectrum of CF$_3$-BODIPY **1** in CDCl$_3$ (400 MHz):

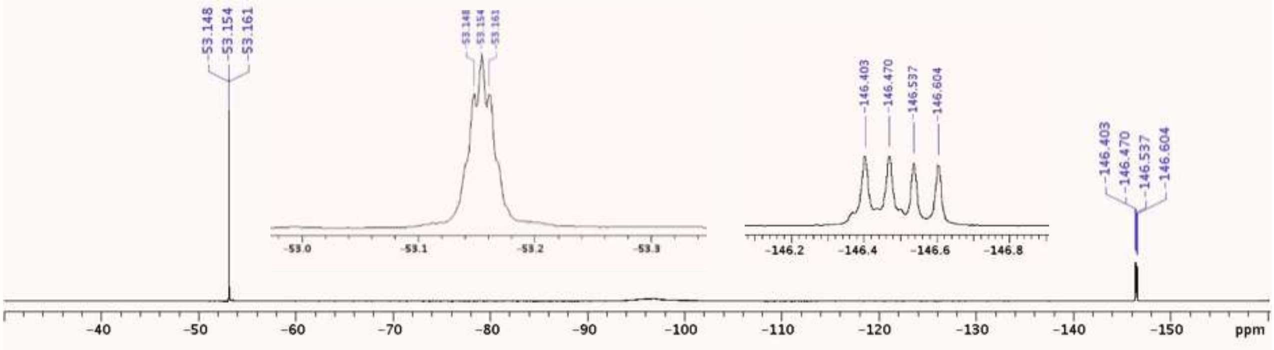


^{13}C-NMR Spectrum of CF$_3$-BODIPY **1** in CDCl$_3$ (100 MHz):

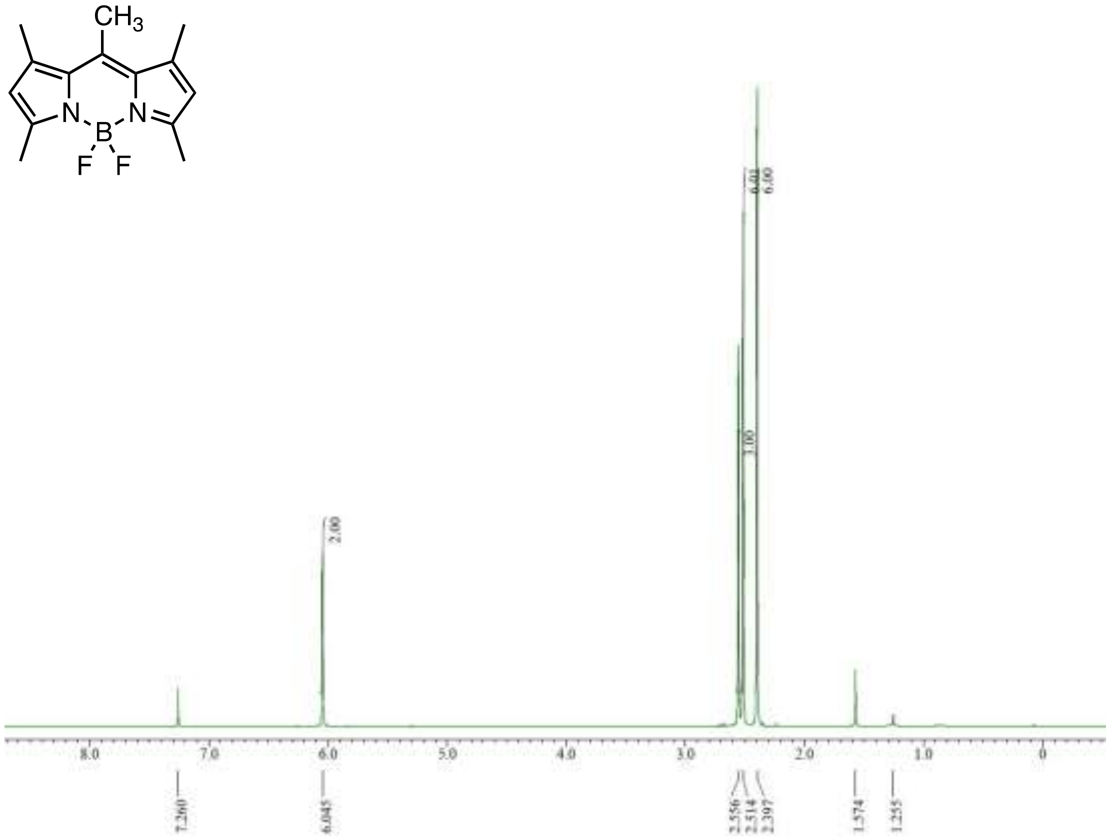


^{19}F-NMR Spectrum of CF$_3$-BODIPY **1** in CDCl$_3$ (470 MHz):

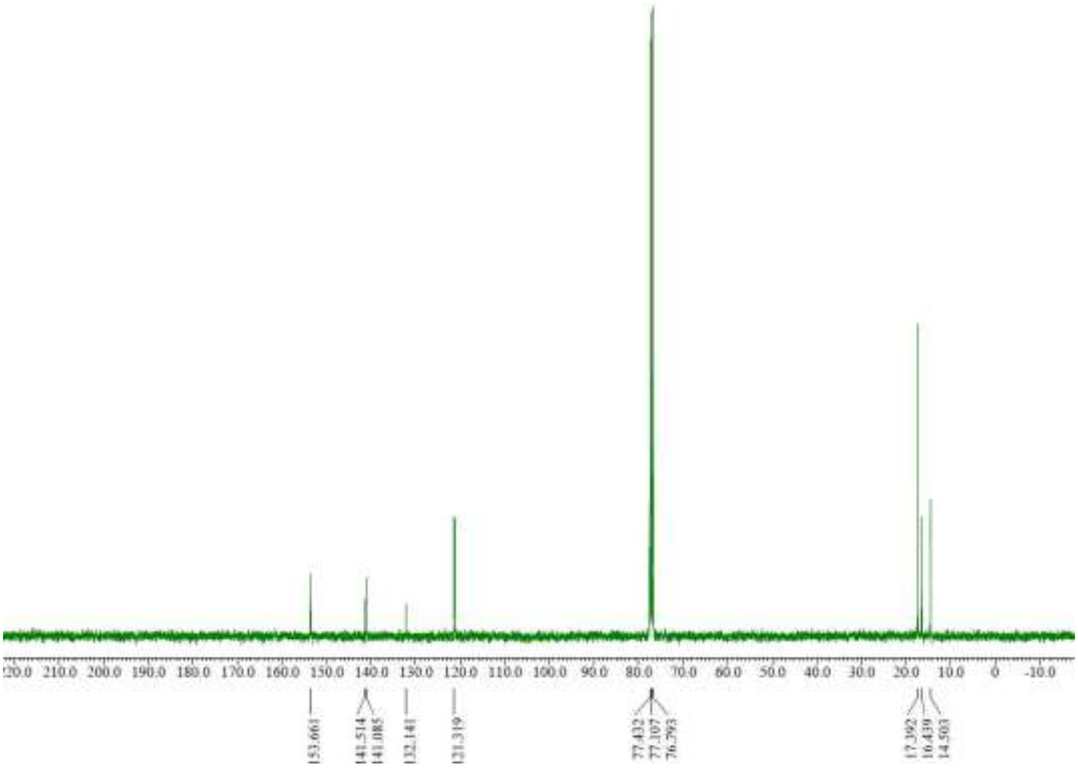




^{1}H-NMR Spectrum of CH_3-BODIPY **2** in $CDCl_3$ (400 MHz):



^{13}C-NMR Spectrum of CH_3-BODIPY **2** in $CDCl_3$ (100 MHz):



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