Electronic Supplementary Information for

Synthesis and Spectroscopic Properties of BODIPY Dimer with Effective Solid State Emission

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I Experimental Section

I.1 Synthesis

Synthesis of 5,5-difluoro-1,3,7,9-tetramethyl-10-phenyl-5H-BODIPY(1)

2, 4-Dimethylpyrrole (1 mL, 9.71 mmol) and benzaldehyde (0.5mL, 4.95mmol) were dissolved in dry CH_2Cl_2 (50mL) under nitrogen. One drop of trifluoroacetic acid (TFA) was added, and the solution was stirred for 5 h at ambient temperature in the dark. 2,3-Dichloro-5,6-dicyanoquinone (DDQ, 4.95 mmol) was added, and the mixture was stirred for an additional 45 min. The reaction mixture was then treated with triethylamine (3 mL) for 5 min. Boron trifluoride etherate (3.2 mL) was added and stirred for another 40 min, and the dark-brown solution was washed with water (2 × 20 mL) and brine (30 mL), dried over anhydrous magnesium sulfate, and concentrated at reduced pressure. The crude product was purified by silica-gel flash column chromatography (elution with 10% EtOAc/hexane) to yield product as crystals Yield: 418 mg (26%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.488-7.472 (m, 3 H), 7.29-7.26 (m, 2H, phenyl), 5.98 (s, 2 H), 2.56 (s, 6 H, CH_3), 1.37 (s, 6 H, CH_3).

Synthesis of 4-bromophenyl-triphenyl silane

1,4-Dibromobenzene(4.8 g, 20.2 mmol) in anhydrous ether (40 mL) was cooleddown to –78°C, 8.08 mL of *n*-BuLi (2.5 M in hexane, 20.2 mmol) was added slowly under an argon atmosphere. After 1 h, thereaction mixture was warmed to room temperature and stirredfor an additional1 h. Then, chlorotriphenylsilane (5.0 g, 17.0 mmol) in ether (50 ml) was delivered dropwise via syringe. After 2 h, thesolution was poured into 100 mL of water and the crudeproduct was extracted with excess ether. The organic layer was washed with water and dried over $MgSO_4$, the solvent removedunder reduced pressure, recrystallizationwith THF/ MeOH gave a white powder in 69% yield (4.86 g, 11.7 mmol).^{1}HNMR($CDCl_3$, 400 MHz): δ7.56-7.51 (m, 8 H) 7.47-7.43 (m, 4 H), 7.41-7.37 (m, 7 H).

Synthesis of 4-triphenylsilylphenyl boronic acid.

To a schlenk containing the solution of 4-bromophenyltriphenyl silane(2.7 g, 6.6 mmol) in 50 mL of anhydrous THF, 4.3 mLof n-BuLi (2.5 M in hexane, 10.6 mmol) was added via syringeunder an argon atmosphere at -78 °C. After stirring for 2 h, 1.2 mL(10.6 mmol) of trimethylborate was added slowly for 10 min. Then the temperature of the reaction mixturewas raised to roomtemperature, and stirred over night. Finally the reaction mixture was poured into 50 mL of water and acidified with aqueous 2MHCl. The crudeproduct was extracted with EtOAc and purified by silica gelcolumn chromatography (hexane/EtOAc = 9: 1) to give awhite powder in 40% yield (0.53 g). ^{1}H NMR($CDCl_3$, 400 MHz): δ8.2 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz,2H), 7.6 (m, 7 H) 7.45-7.37(m, 10H). GC-MS (EI): calcd [$C_{24}H_{21}BO_2Si$]m/z = 380, found: 380 [M].

II. Supplementary data.

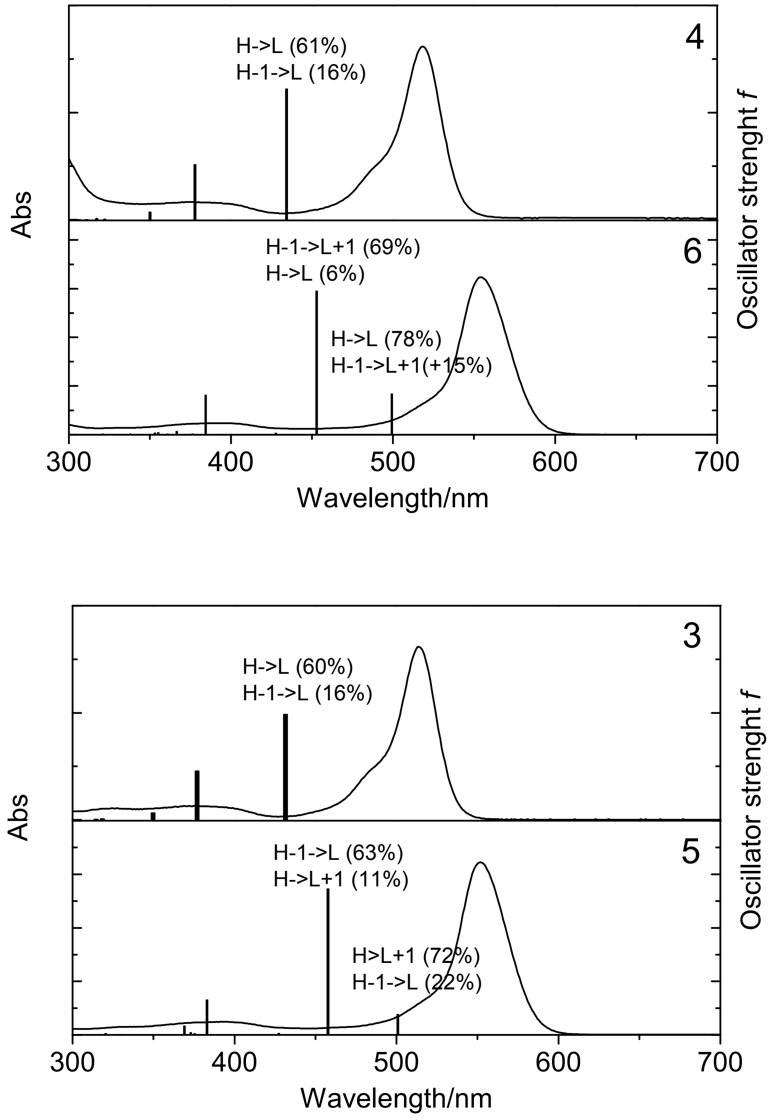


Figure S1. Observed and calculated TD–DFT spectra of **3–6** based on geometry optimizations using the B3LYP functional with 6–31G(d) basis sets.

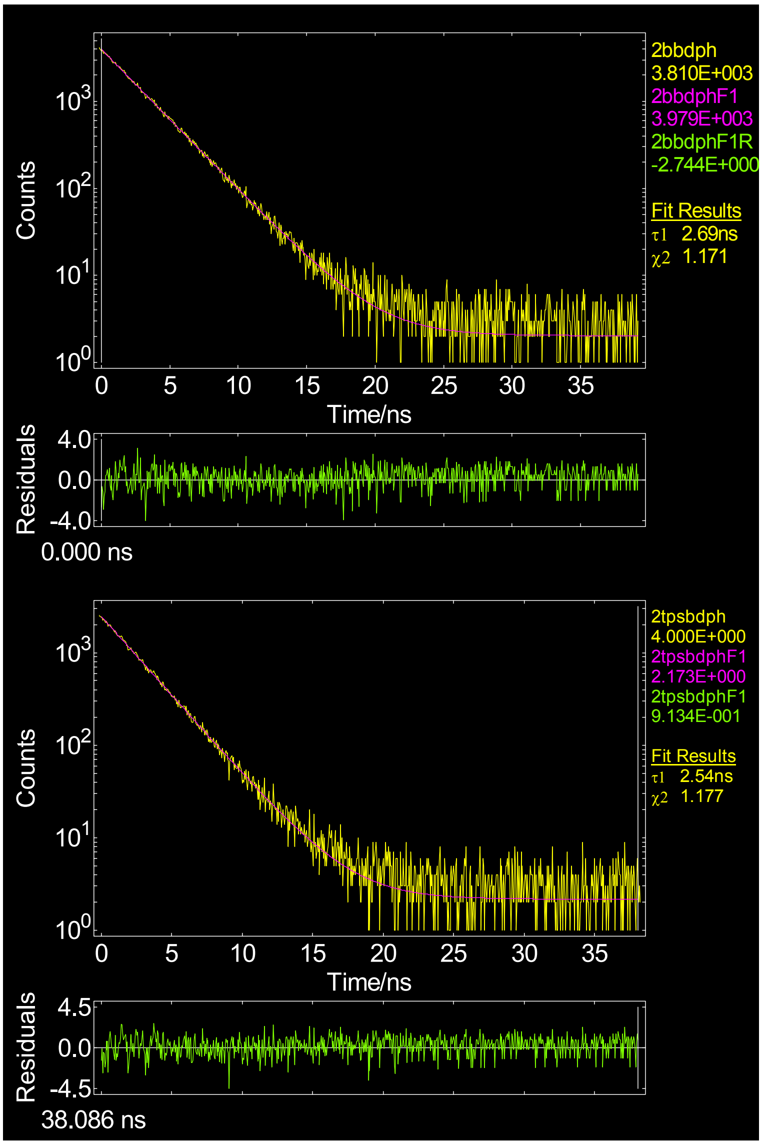
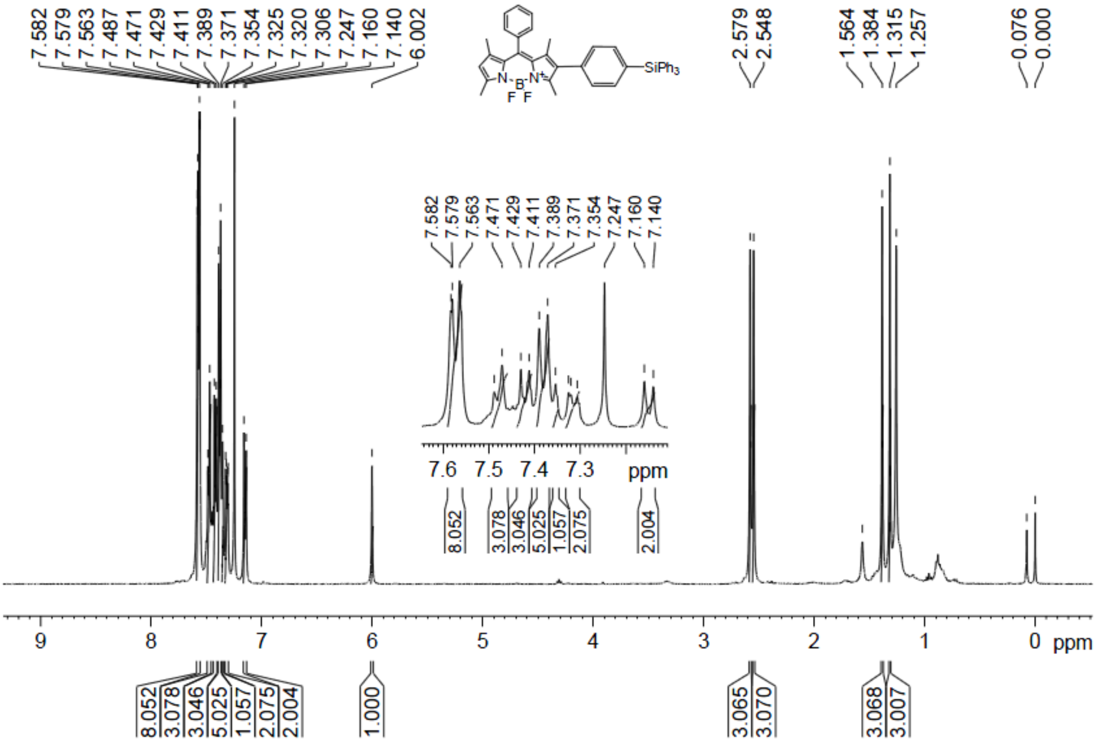
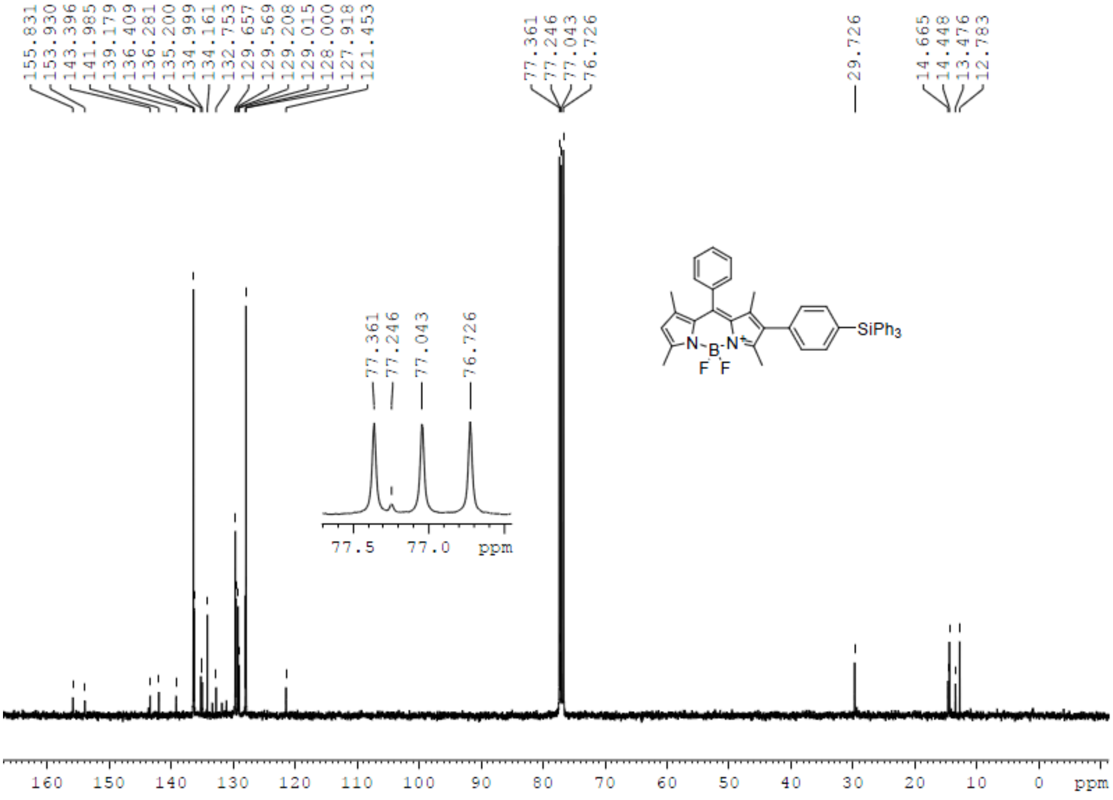


Figure S2. Fluorescence decay curves of **5** (top) and **6** (bottom) in hexane as a example.

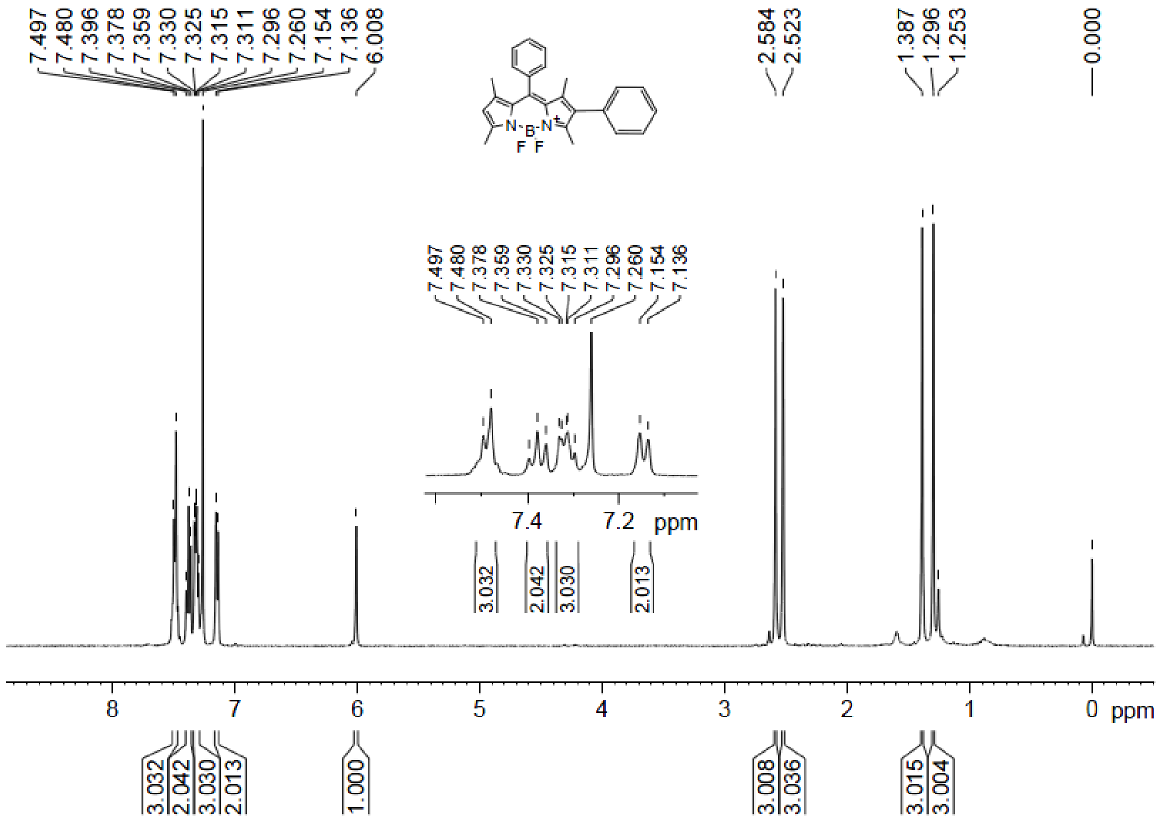
^{1}H NMR (400 MHz, CDCl$_3$)



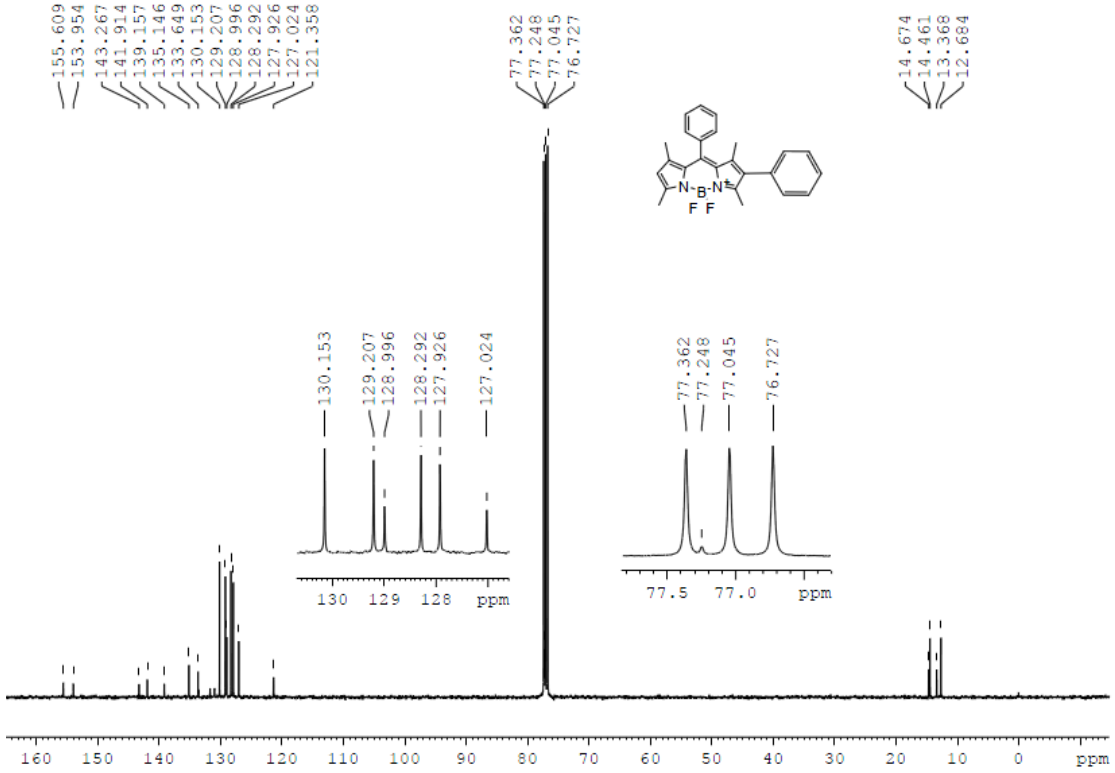
^{13}CNMR (100 MHz, CDCl$_3$)



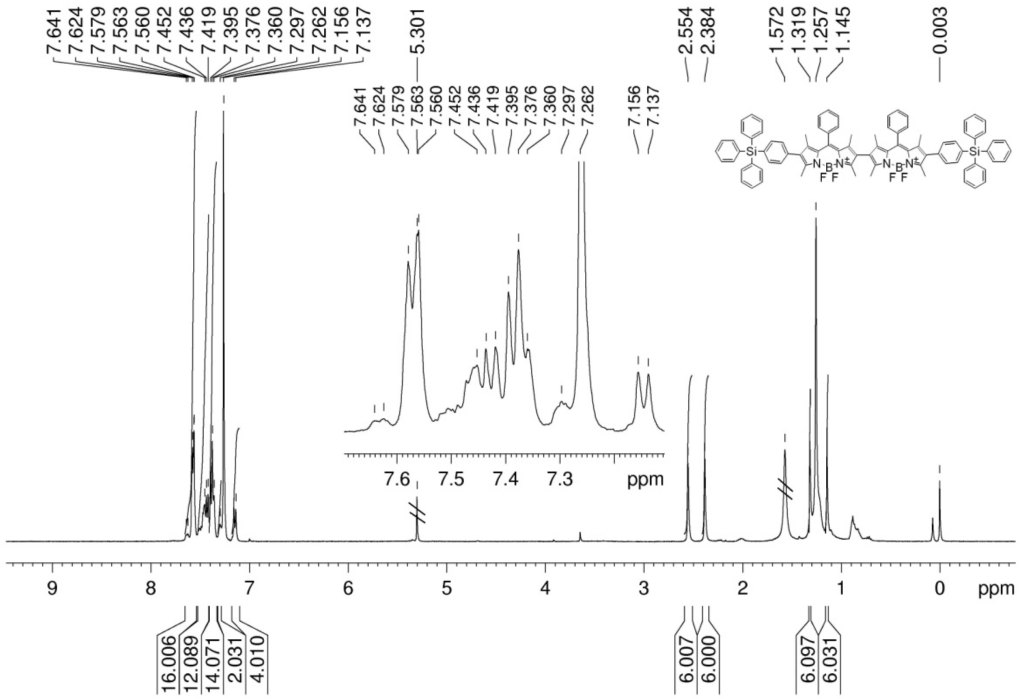
^{1}H NMR (400 MHz, $CDCl_3$)



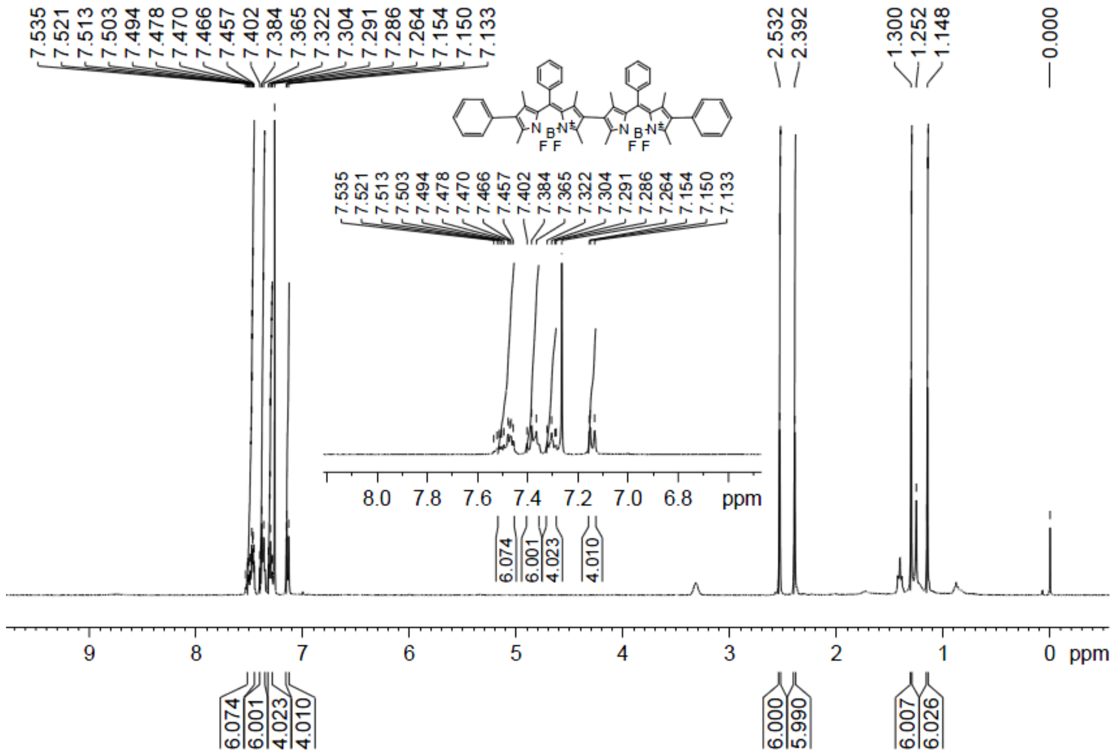
^{13}CNMR (100 MHz, $CDCl_3$)



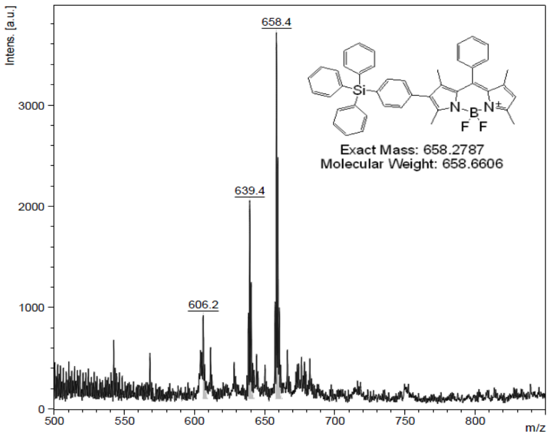
^{1}H NMR (400 MHz, CDCl$_3$)

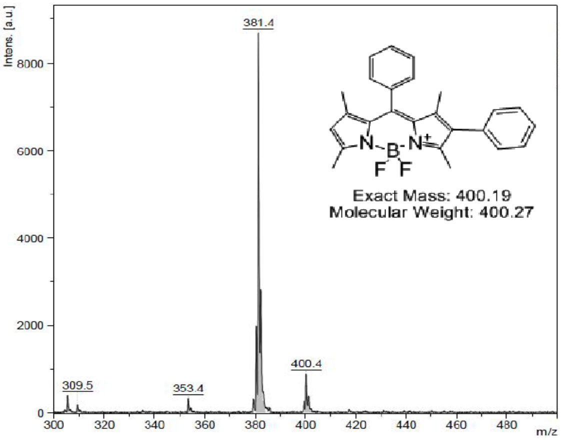


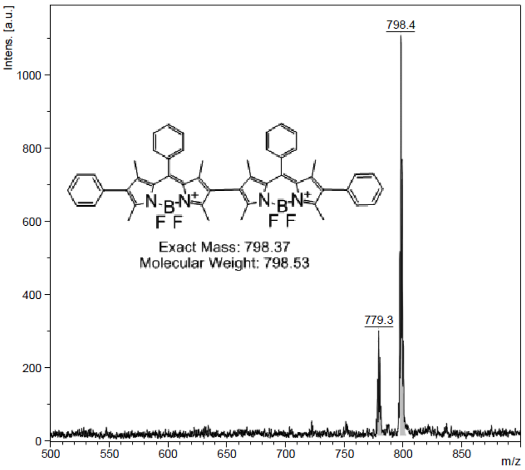
^{1}H NMR (400 MHz, CDCl$_3$)

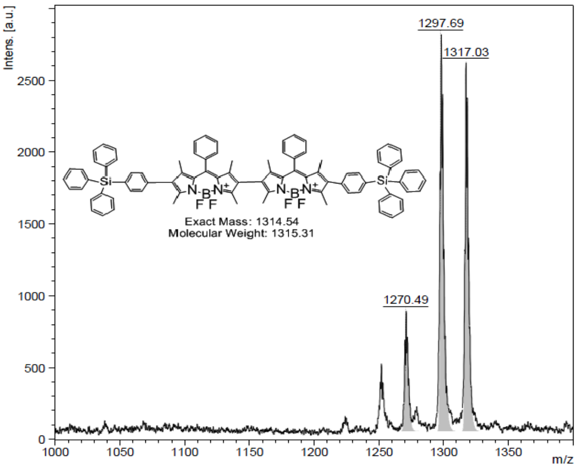


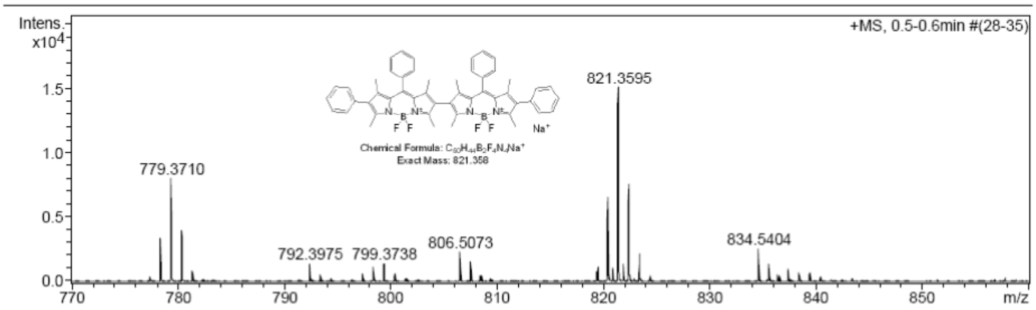
MALDI-TOF and High-resolution mass spectrometry



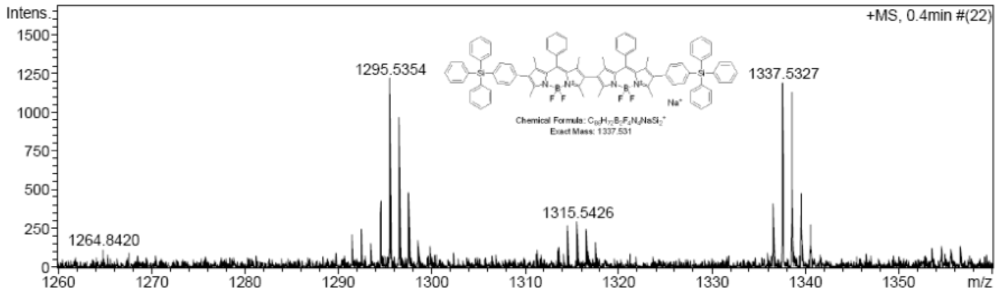








Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
779.3710	1	C 50 H 44 B 2 F 3 N 4	100.00	779.3714	0.4	0.5	10.2	30.5	even	ok
799.3738	1	C 50 H 45 B 2 F 4 N 4	9.86	799.3777	3.8	4.8	231.9	29.5	even	ok
821.3595	1	C 50 H 44 B 2 F 4 N 4 Na	100.00	821.3596	0.1	0.1	10.7	29.5	even	ok



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