Electronic Supplementary Information

Bright solid-state red-emissive BODIPYs: facile synthesis and their high-contrast mechanochromic property

Chong Duan,[a,†] Yibin Zhou,[b,†] Guo-Gang Shan,[d] Yuncong Chen,[d] Weijun Zhao,[d] Dandan Yuan,[e] Lintao Zeng,[a,*] Xiaobo Huang,[b,*] and Guangle Niu[c,d,*]

[a] School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin 300384, P. R. China. E-mail: zlt1981@126.com (L. Zeng)

[b] College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, P. R. China. E-mail: xiaobhuang@wzu.edu.cn (X. Huang)

[c] Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China. E-mail: niugl@ust.hk (G. Niu)

[d] Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong 999077, P. R. China

[e] School of Chemistry and Chemical Engineering, Key Laboratory of Mesoscopic Chemistry of Ministry of Education, Institute of Theoretical and Computational Chemistry, Nanjing University, Nanjing 210023, P. R. China

[†] These authors contributed equally to this work.

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Materials and Methods

General

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer in deuterated chloroform ($CDCl_3$) with tetramethylsilane (TMS) as an internal standard. High-resolution mass spectra were recorded by a HP-1100 LC-MS spectrometer and were reported in units of mass to charge (m/z). Fluorescence and UV-vis absorption spectra were measured with a Hitachi FL-4500 fluorometer and a Hitachi UV-3310 spectrometer, respectively. Solid-state fluorescence quantum yield was determined by a FluoroMax-4 (Horiba Jobin Yvon) fluorometer with an integrated sphere. Powder XRD patterns were recorded on a Bruker D8 Advance X-ray diffractometer. Single-crystal X-ray diffraction measurements were performed on a Bruker-Nonius Smart Apex CCD diffractometer with graphite monochromated Mo Kα radiation. Dynamic light scattering (DLS) data were obtained at room temperature using a ZEN3690 Dynamic Light Scattering detector (Malvern, UK). Scanning electron microscope (SEM) images were taken on a Zeiss Merlin Compact High Resolution Field Emission Scanning Electron Microscope. 2,4-Dimethylpyrrole, acetyl chloride, various benzaldehyde derivatives, tetrachloro-*p*-benzoquinone (*p*-chloranil), $BF_3{\bullet}OEt_2$, NEt_3, and CF_3COOH were purchased from commercial suppliers (Sigma-Aldrich and TCI) and used as received.

Synthesis of BODIPYs with different substituents

General procedure for various aryl-substituted BODIPYs

Phenylaldehyde derivative (compound **1a**, **1b** and **1c**) (5 mmol) was dissolved in 20 mL of dry CH_2Cl_2 in a round bottom flask, and then 2,4-dimethylpyrrole (1.28 mL, 12.5 mmol) and two drops of CF_3COOH were added. The reaction mixture was stirred at room temperature for 3 h in N_2

atmosphere. After complete consumption of compound **1** monitored by TLC, *p*-chloranil (1.23 g, 5 mmol) was added to the reaction mixture. An hour later, 4 mL of NEt_3 and 5 mL of $BF_3 \cdot OEt_2$ were added, and the mixture was stirred at room temperature for another 1 h. When the reaction was completed, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography with AcOEt/petroleum ether (1/50, v/v) to give the corresponding BODIPYs. The characterization data for various aryl-substituted BODIPYs are listed as follows:

PhMe$_3$-BODIPY. Red solid (1.48 g, 80.8% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.94 (s, 2H), 5.96 (s, 2H), 2.56 (s, 6H), 2.33 (s, 3H), 2.09 (s, 6H), 1.38 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.20, 142.42, 141.79, 138.68, 135.03, 131.24, 130.73, 129.11, 120.89, 21.35, 19.64, 14.77, 13.54. HRMS (EI): m/z calcd for $[C_{22}H_{26}BF_2N_2]^+$ 367.2179 ($[M+H]^+$), found 367.2160.

PhMe-BODIPY. Red solid (1.22 g, 70.9% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.38-7.28 (m, 3H), 7.16-7.14 (d, J = 8.4 Hz, 1H), 5.97 (s, 2H), 2.56 (s, 6H), 2.20 (s, 3H), 1.36 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.55, 142.89, 141.57, 135.58, 134.67, 131.12, 130.78, 129.30, 128.07, 126.95, 121.20, 19.35, 14.73, 13.83. HRMS (EI): m/z calcd for $[C_{20}H_{22}BF_2N_2]^+$ 339.1839 ($[M+H]^+$), found 339.1836.

Ph-BODIPY. Red solid (1.31 g, 80.1% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.49-7.47 (m, 3H), 7.29-7.26 (m, 2H), 5.98 (s, 2H), 2.56 (s, 6H), 1.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.57, 143.29, 141.87, 135.14, 131.57, 129.26, 129.07, 128.08, 121.33, 14.73, 14.47. HRMS (EI): m/z calcd for $[C_{19}H_{20}BF_2N_2]^+$ 325.1709 ($[M+H]^+$), found 325.1696.

Synthesis of Me-BODIPY

To a solution of 2,4-dimethylpyrrole (1.08 mL, 10.5 mmol) in dry CH_2Cl_2 (20 mL) was dropwise added acetyl chloride (1.74 mL, 24.54 mmol) at room temperature over 30 min. After acetyl chloride

(1.74 mL, 24.54 mmol) was added, the reaction solution was heated to reflux for 1 h. Then, it was cooled down to room temperature, and n-hexane (100 mL) was added. The solvents were removed by a rotary evaporator, and the residue was dissolved in dry CH_2Cl_2 (20 mL). Then, 4 mL of NEt_3 and 5 mL of BF_3•OEt_2 were added, and the resulting mixture was stirred at room temperature for 1 h. After the reaction was completed, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography with AcOEt/petroleum ether (1/50, v/v) to give the product in red solid (1.32 g, 20.5% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.05 (s, 2H), 2.58 (s, 3H), 2.52 (s, 6H), 2.41 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.76, 141.55, 141.12, 132.21, 121.39, 17.42, 16.50, 14.54. HRMS (EI): m/z calcd for $[C_{14}H_{18}BF_2N_2]^+$ 263.1562 ($[M+H]^+$), found 263.1543.

NMR spectra

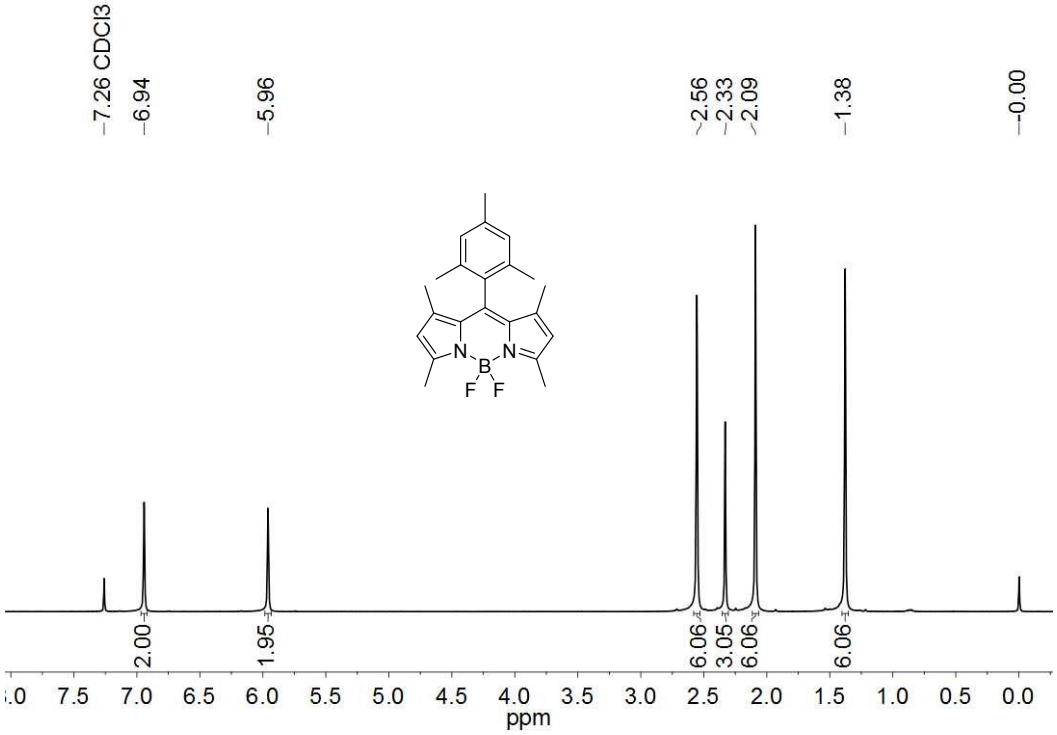

Fig. S1 ^{1}H NMR spectrum of **PhMe$_3$-BODIPY** in $CDCl_3$.

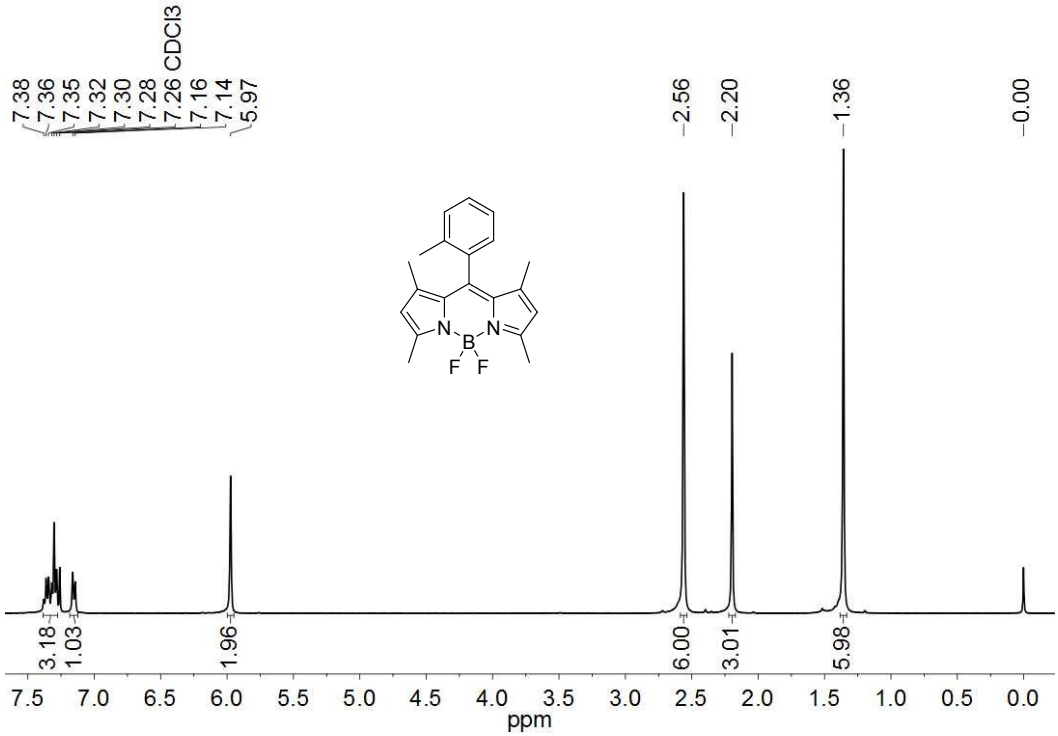

Fig. S2 ^{1}H NMR spectrum of **PhMe-BODIPY** in $CDCl_3$.

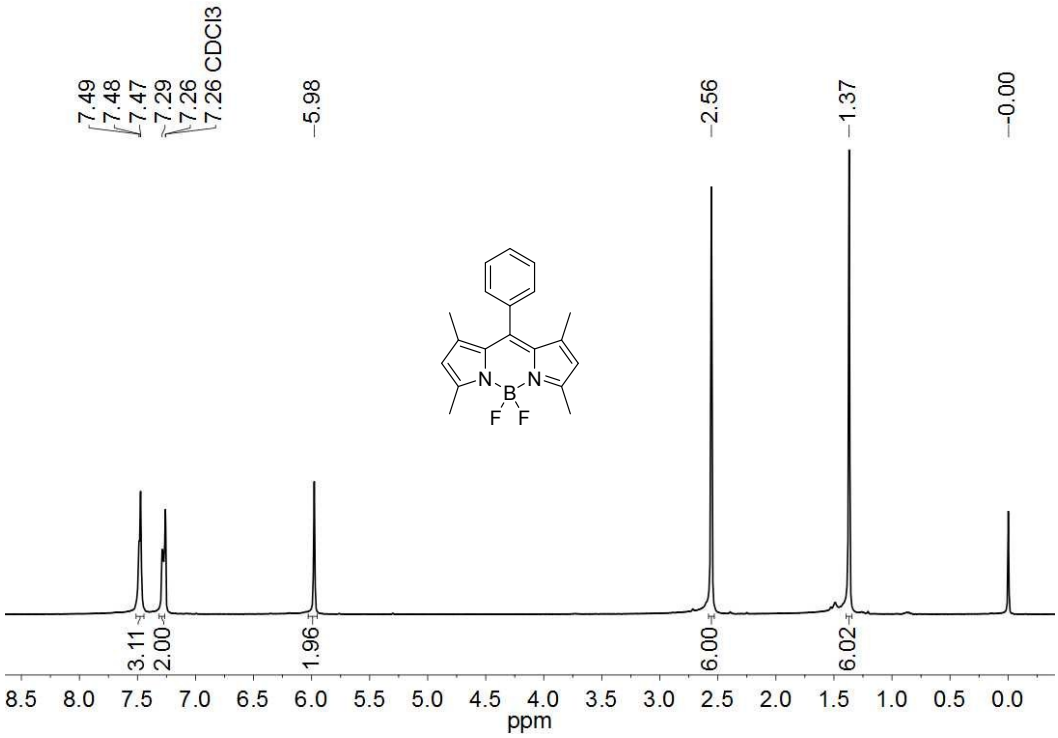

Fig. S3 ^{1}H NMR spectrum of **Ph-BODIPY** in $CDCl_3$.

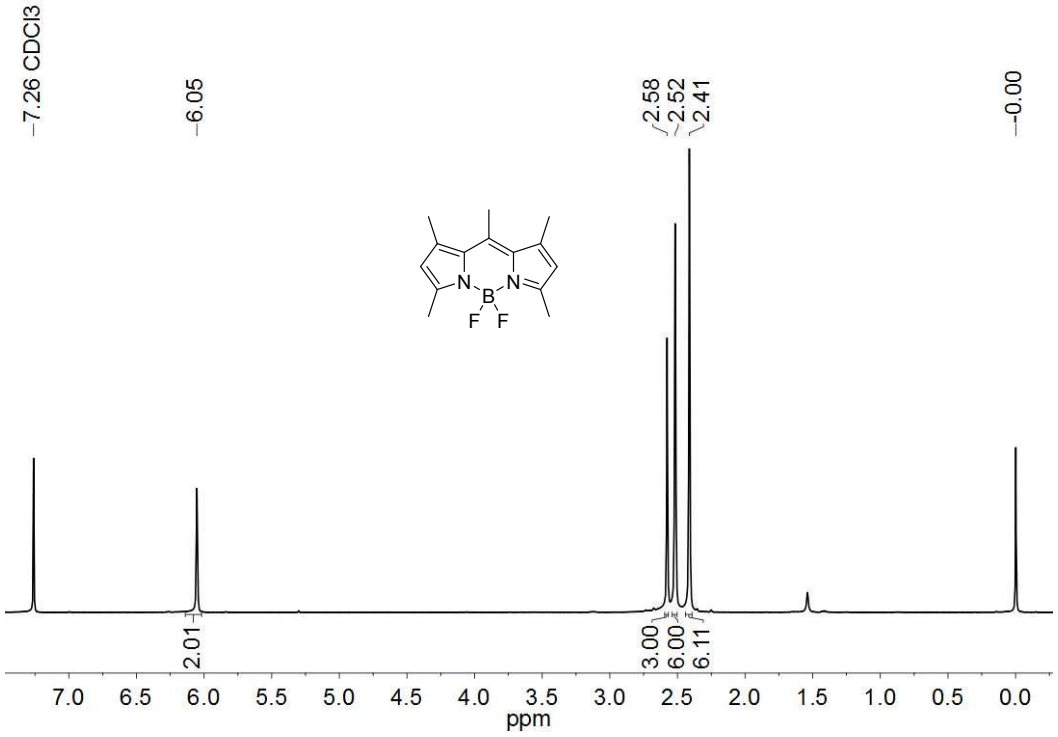

Fig. S4 ^{1}H NMR spectrum of **Me-BODIPY** in $CDCl_3$.

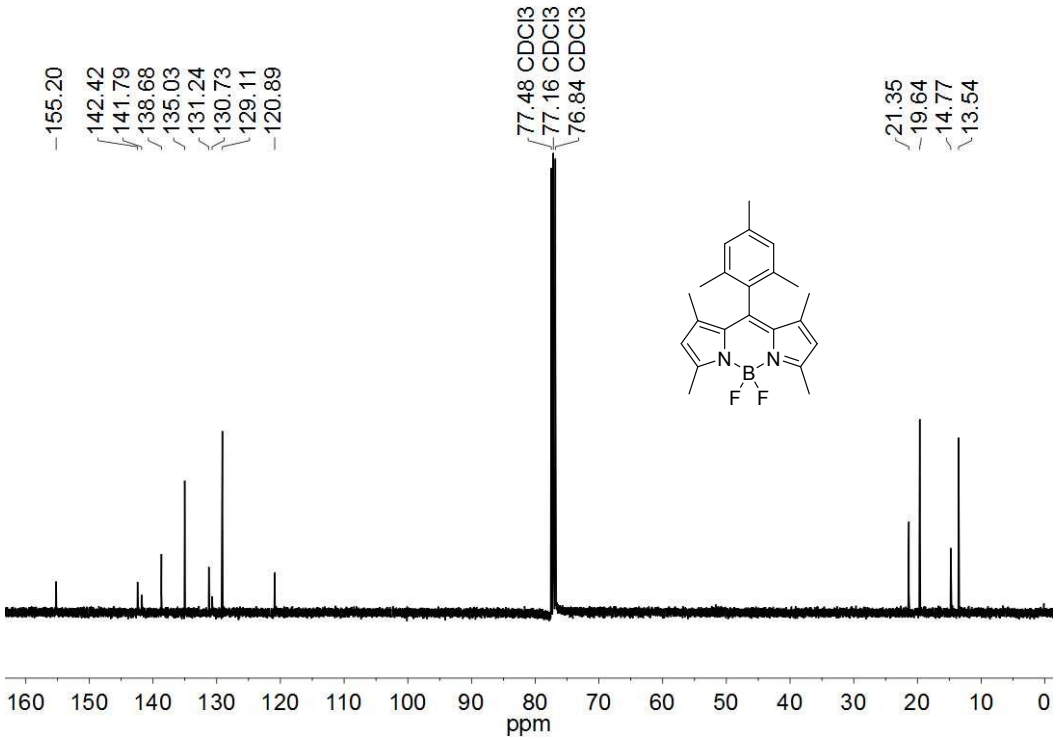

Fig. S5 ^{13}C NMR spectrum of **PhMe$_3$-BODIPY** in $CDCl_3$

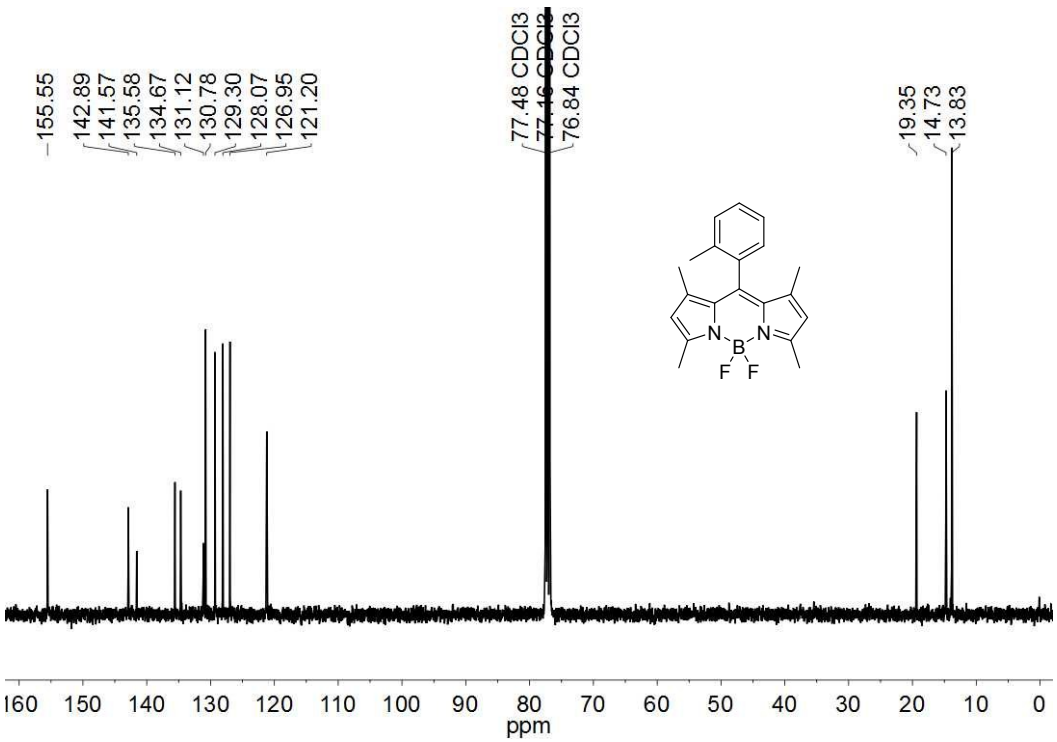

Fig. S6 ^{13}C NMR spectrum of **PhMe-BODIPY** in $CDCl_3$

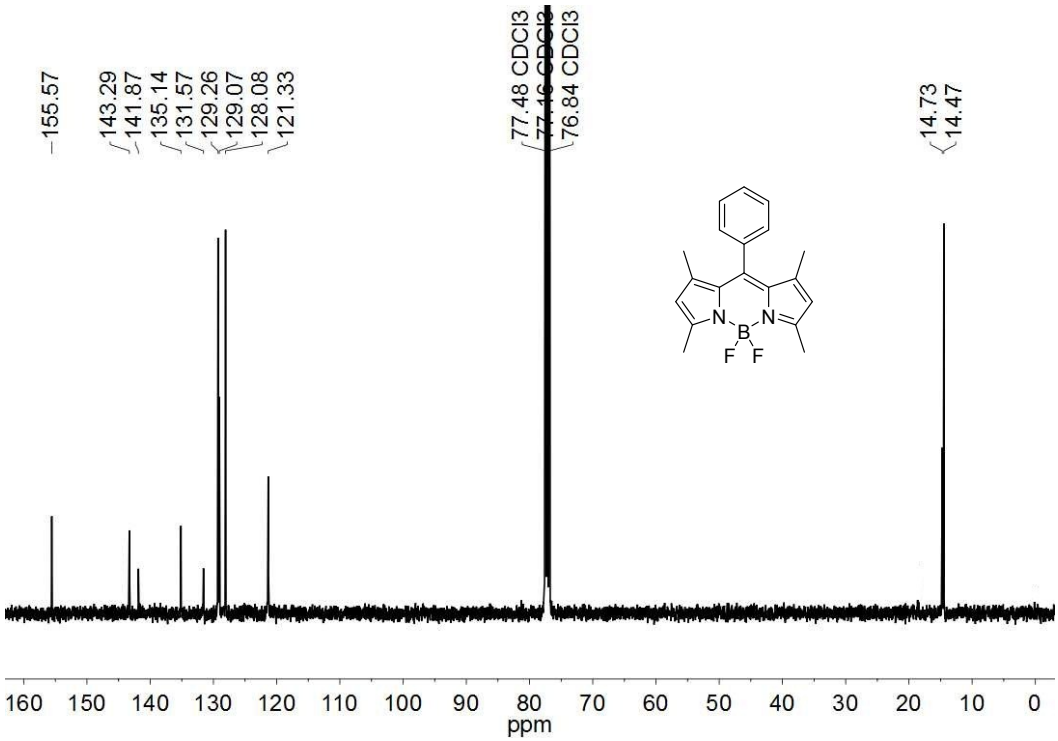

Fig. S7 ^{13}C NMR spectrum of **Ph-BODIPY** in $CDCl_3$

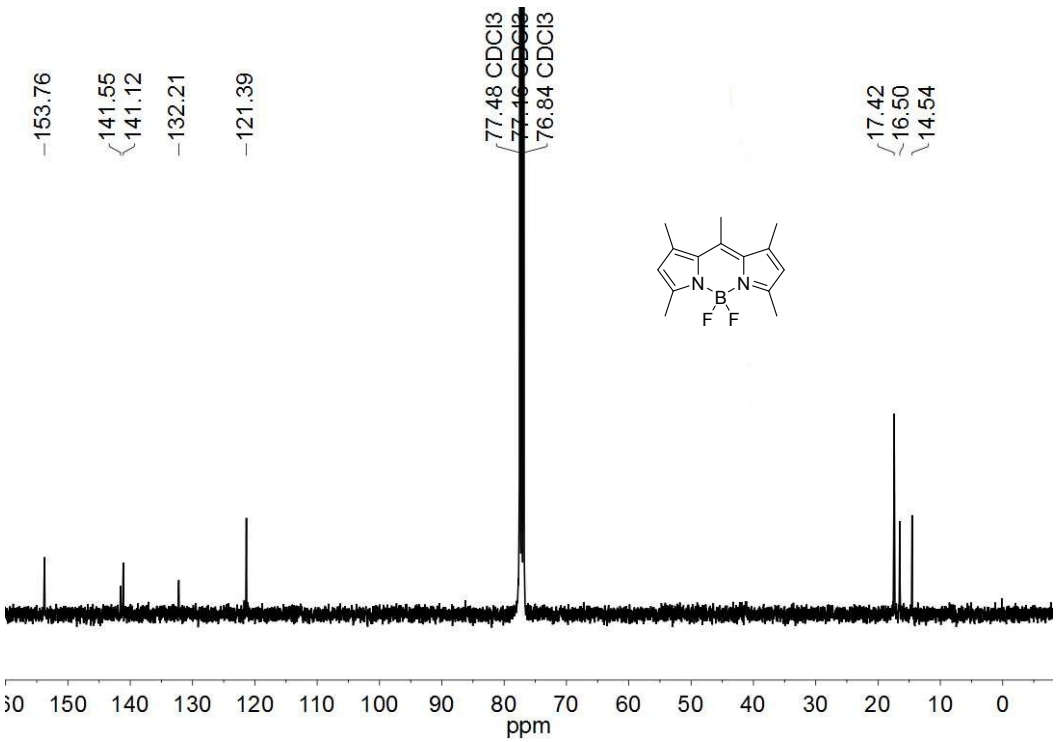

Fig. S8 ^{13}C NMR spectrum of **Me-BODIPY** in $CDCl_3$

HRMS spectra

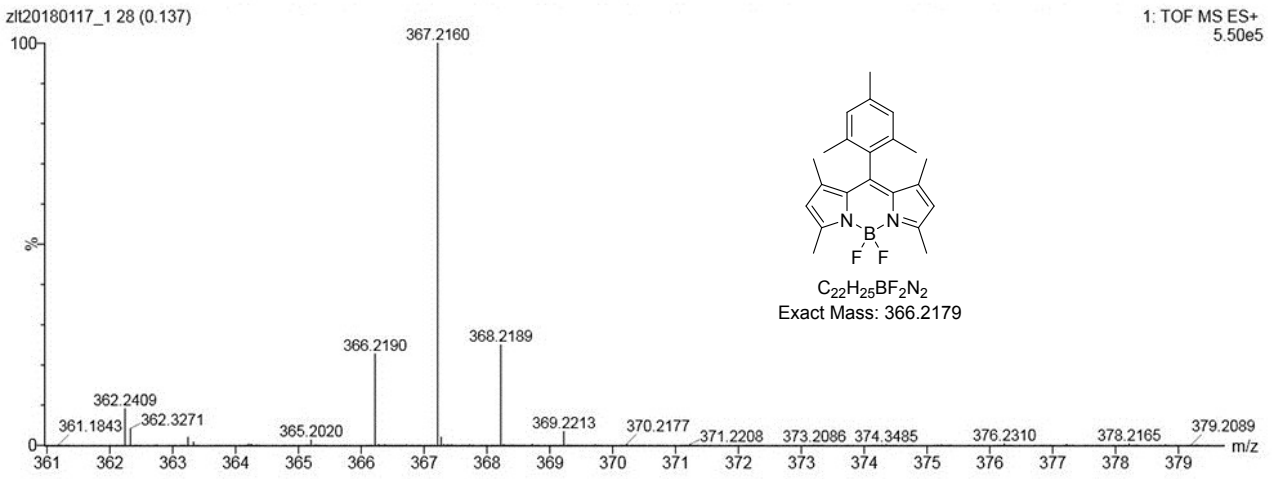

Fig. S9 HRMS spectrum of **PhMe$_3$-BODIPY**.

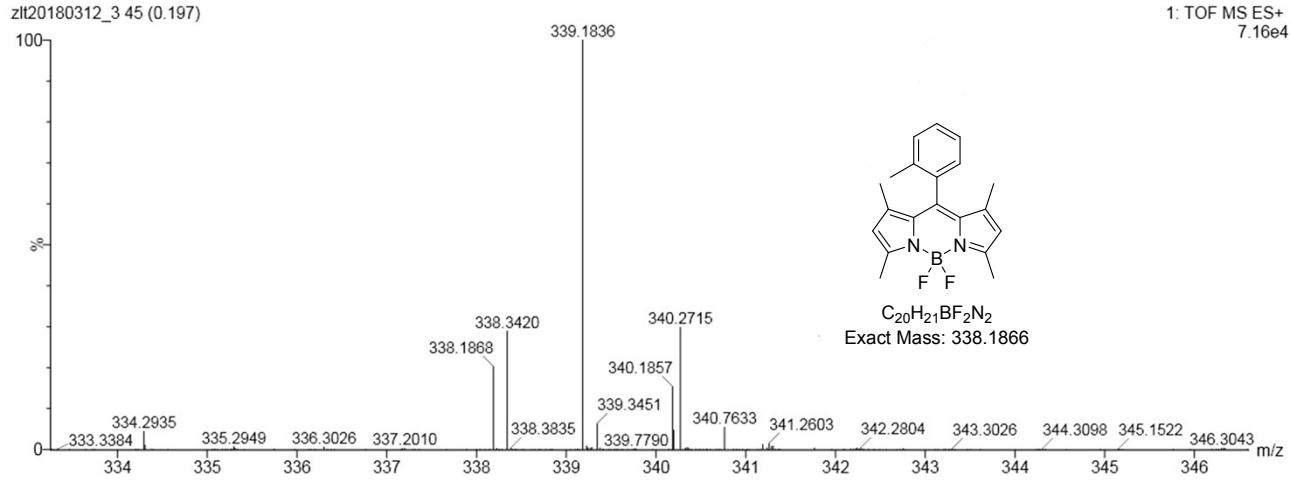

Fig. S10 HRMS spectrum of **PhMe-BODIPY**.

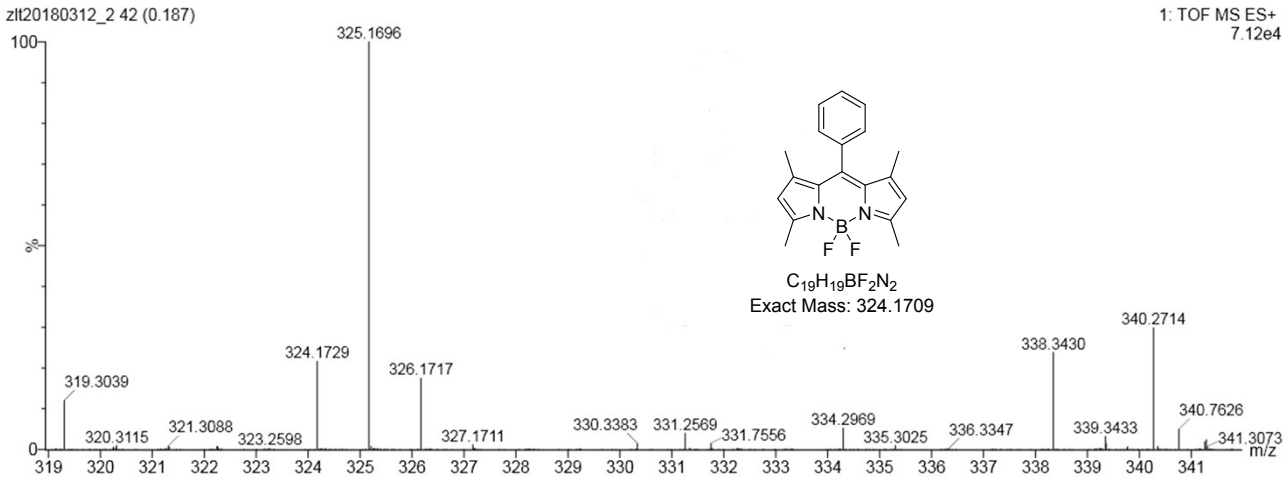

Fig. S11 HRMS spectrum of **Ph-BODIPY**.

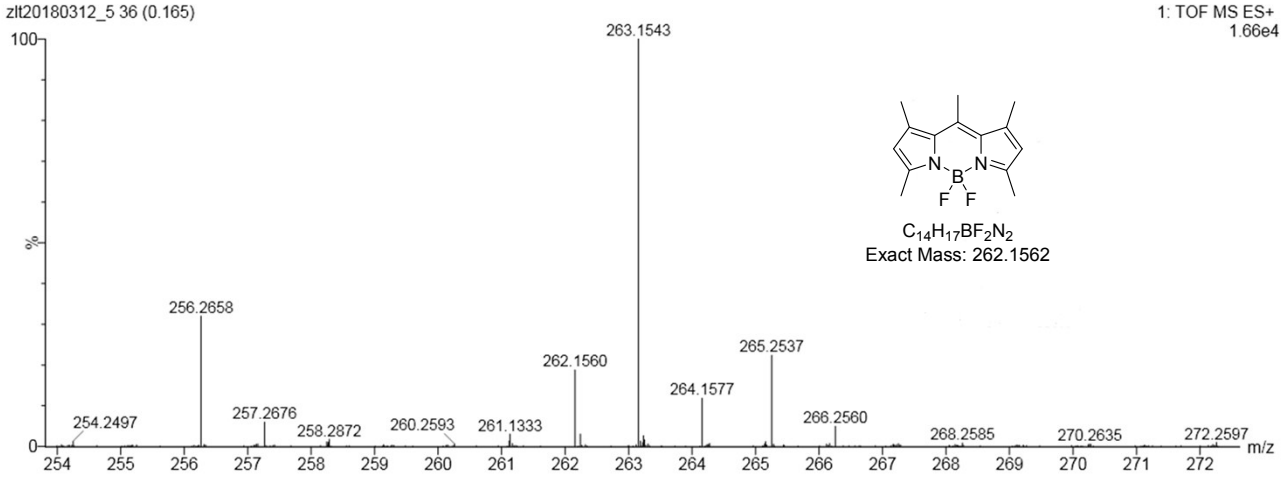

Fig. S12 HRMS spectrum of **Me-BODIPY**.

Photophysical data

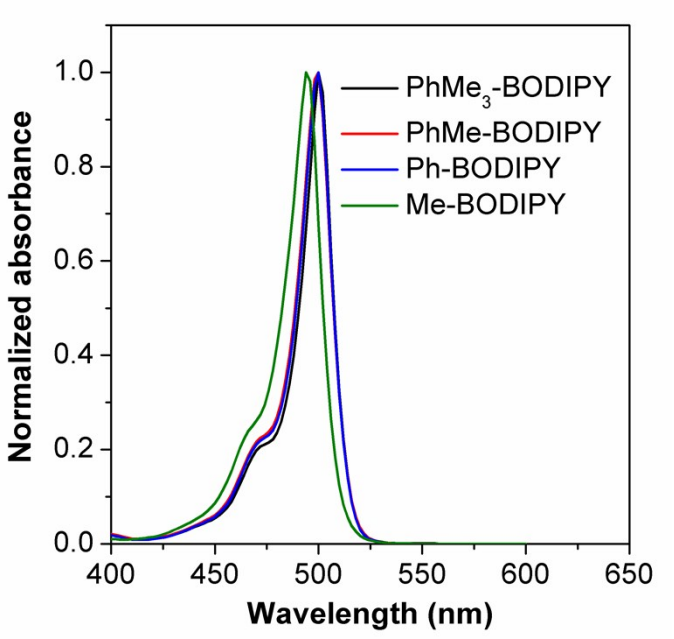

Fig. S13 Normalized UV-vis absorption spectra of **PhMe$_3$-BODIPY**, **PhMe-BODIPY**, **Ph-BODIPY** and **Me-BODIPY** in THF (10 μM).

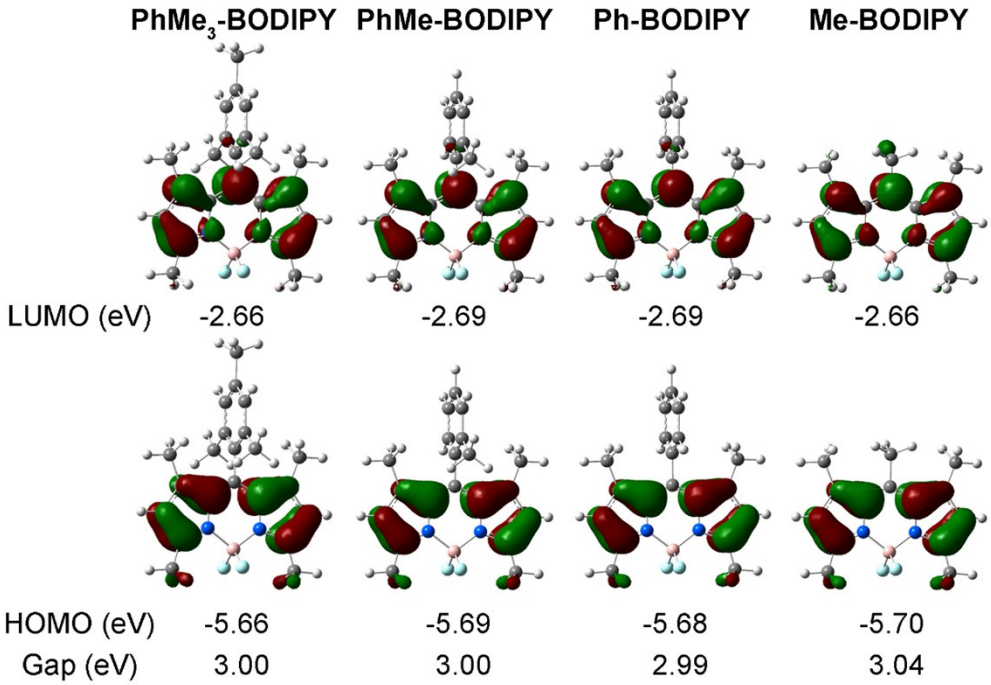

Fig. S14 Spatial orbital distributions of HOMOs and LUMOs of **PhMe$_3$-BODIPY**, **PhMe-BODIPY**, **Ph-BODIPY**, and **Me-BODIPY** calculated at the B3LYP/6-31G level of theory.

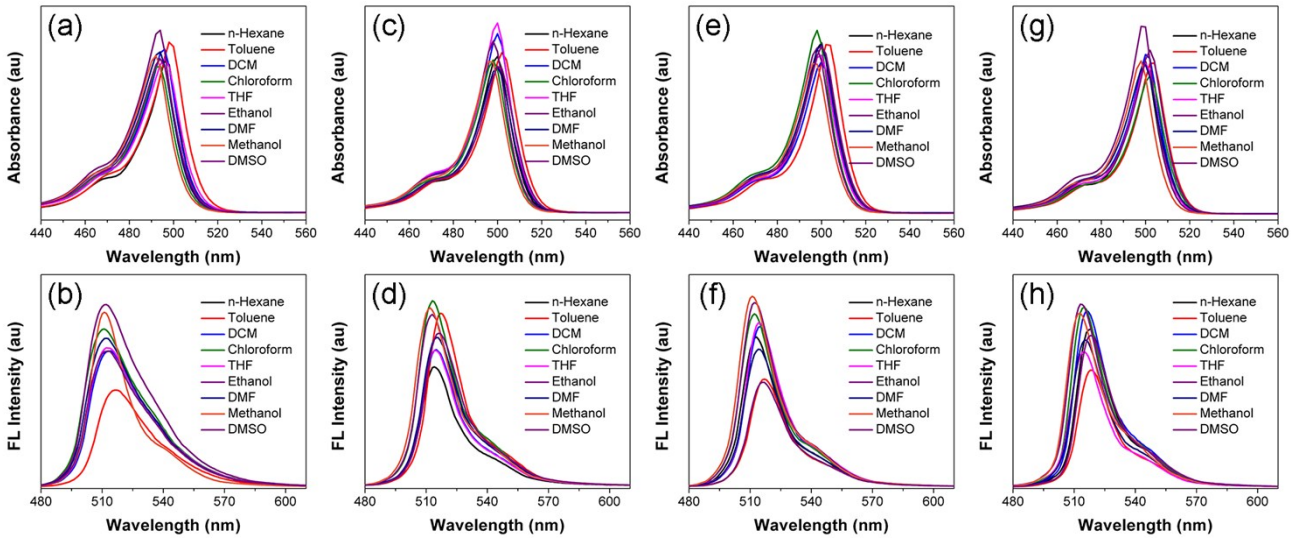

Fig. S15 Absorption and fluorescence spectra of **PhMe$_3$-BODIPY** (a, b), **PhMe-BODIPY** (c, d)**, Ph-BODIPY** (e, f), **Me-BODIPY** (g, h) in different solvents (n-Hexane, Toluene, DCM, Chloroform, THF, Ethanol, DMF, Methanol and DMSO).

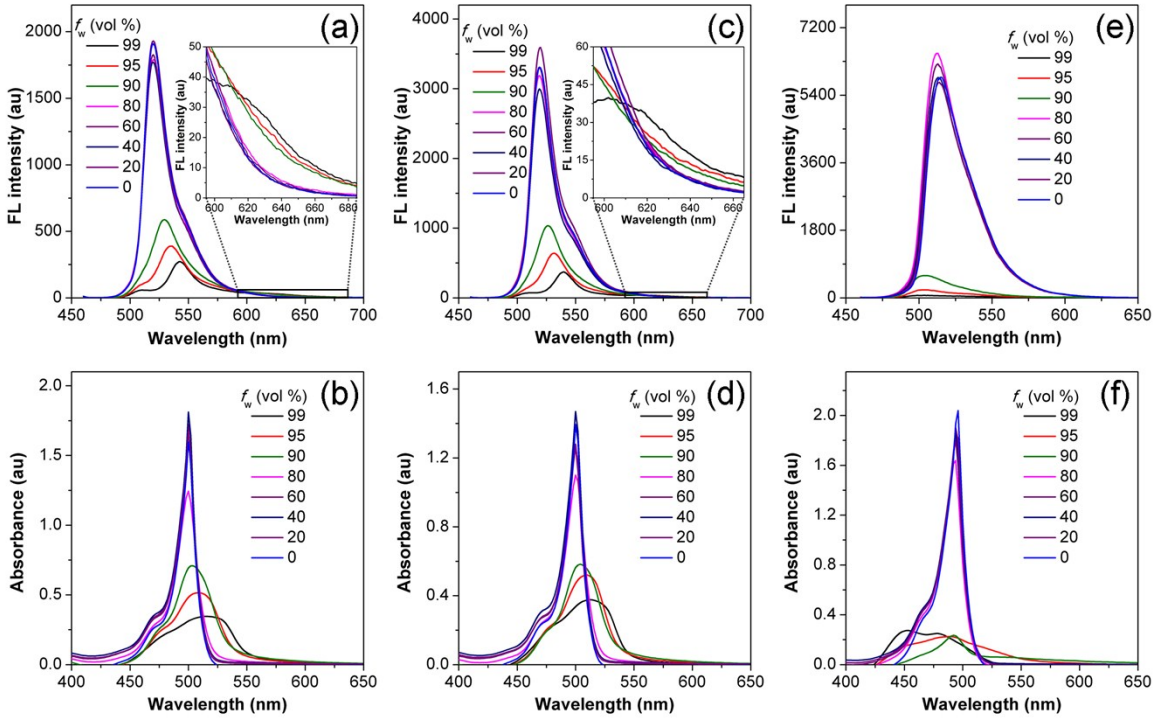

Fig. S16 (a) Fluorescence and (b) absorption spectra of **PhMe-BODIPY** (20 μM) in THF/water mixtures with different water fractions (f_w). (c) Fluorescence and (d) absorption spectra of **Ph-BODIPY** (20 μM) in THF/water mixtures with different water fractions (f_w). (e) Fluorescence and (f) absorption spectra of **Me-BODIPY** (20 μM) in THF/water mixtures with different water fractions (f_w).

Table S1. Hydrated diameter data of **PhMe$_3$-BODIPY**, **PhMe-BODIPY**, **Ph-BODIPY** and **Me-BODIPY** measured by dynamic light scattering (DLS) in THF with different water fraction (f_w).

f_w / Compound	0%	20%	90%	99%
PhMe$_3$-BODIPY	/	/	119.3 nm	135.8 nm
PhMe-BODIPY	/	/	/	133.4 nm
Ph-BODIPY	/	/	/	361.4 nm
Me-BODIPY	/	/	403.9 nm	372.1 nm

Crystallographic data

Table S2 Crystal data and details of collection and refinement for BODIPYs.

	$PhMe_3$-BODIPY	**PhMe-BODIPY**	**Ph-BODIPY**	**Me-BODIPY**
CCDC	1858004	1858005	1858006	1858007
Empirical formula	$C_{22}H_{25}BF_2N_2$	$C_{20}H_{21}BF_2N_2$	$C_{19}H_{19}BF_2N_2$	$C_{14}H_{17}BF_2N_2$
Formula weight	366.25	338.20	324.17	262.10
Temperature (K)	296(2)	296(2)	296(2)	296(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	*P*bca	*P*nma
Z	4	12	8	4
D_{calcd} [Mg/m^3]	1.178	1.205	1.280	1.327
F (000)	776	2136	1360	552
θ range [°]	2.584-26.000	1.548-24.999	2.455-25.996	3.101-25.999
R_1 [I>2σ(I)]	0.0388	0.1362	0.0455	0.0407
wR_2 [I>2σ(I)]	0.0896	0.3491	0.1189	0.0999
a [Å]	7.8705(3)	14.031(3)	13.0734(4)	11.3643(6)
b [Å]	13.5120(6)	15.207(3)	12.6281(3)	7.1999(3)
c [Å]	19.4137(10)	26.212(6)	20.3826(5)	16.0342(7)
α [deg]	90	90	90	90
β [deg]	90	90	90	90
γ [deg]	90	90	90	90
V [Å^3]	2064.57(16)	5593(2)	3365.01(15)	1311.95(11)
GOF	1.056	1.315	1.055	1.041
R(int)	0.0408	0.1179	0.0470	0.0306
No. of reflcns collected	20361	54950	32696	6975
No. of unique reflcns	4056	9827	3296	1391
R_1 (all data)	0.0513	0.1945	0.0623	0.0528
wR_2 (all data)	0.0983	0.3920	0.1327	0.1091

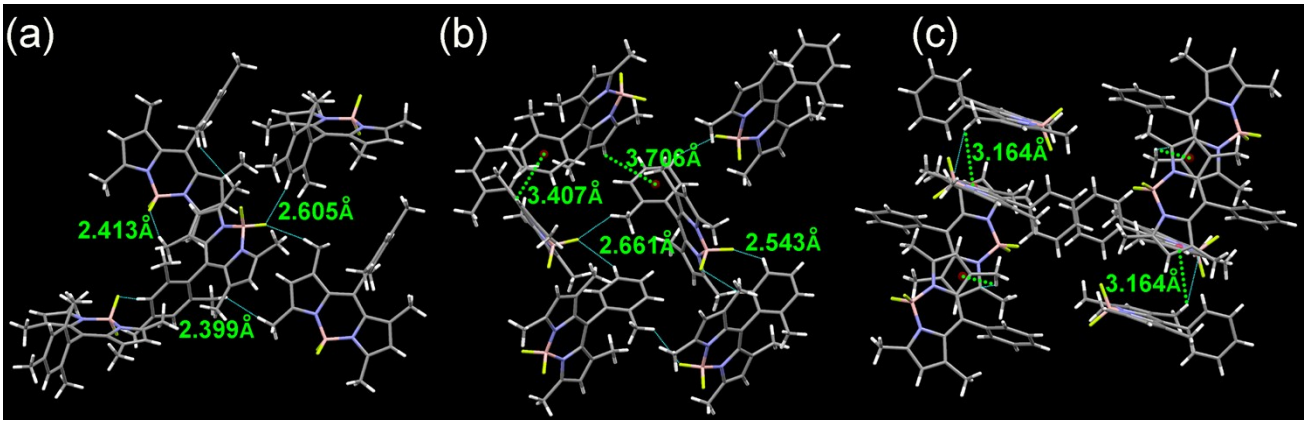

Fig. S17 Intermolecular interactions in crystals of (a) **PhMe$_3$-BODIPY**, (b) **PhMe-BODIPY**, and (c) **Ph-BODIPY**.

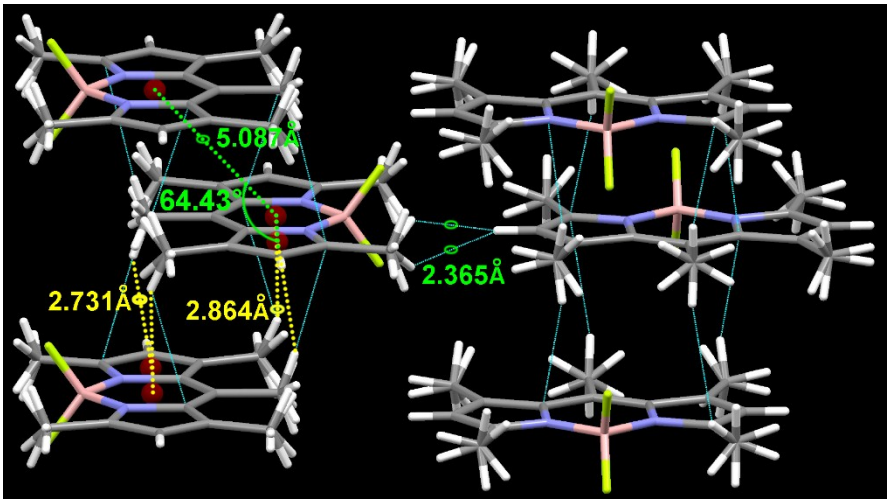

Fig. S18 Intermolecular interactions and molecular packing in the crystal structure of **Me-BODIPY**.

Mechanochromism data

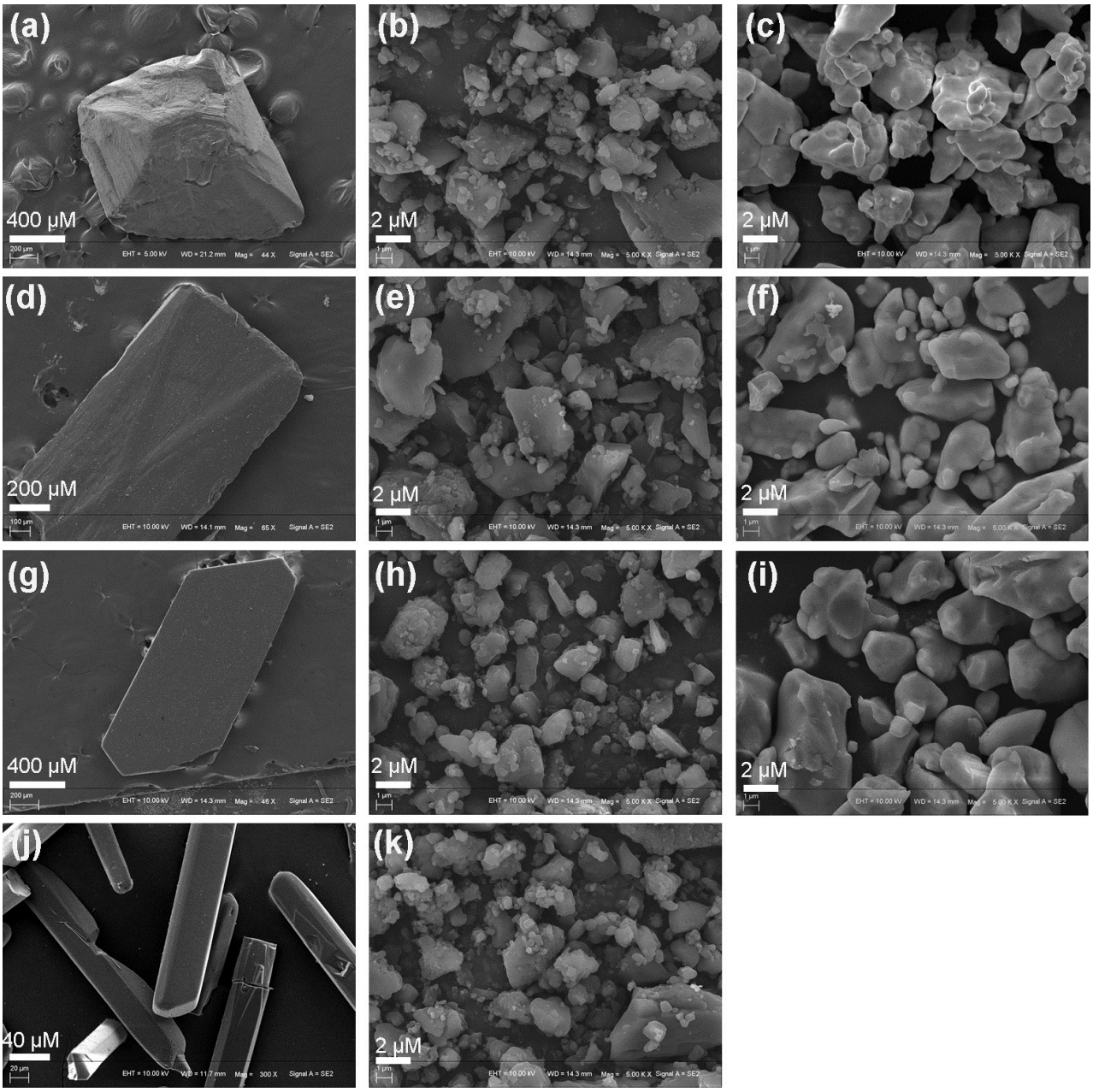

Fig. S19 SEM images of **PhMe$_3$-BODIPY** (a-c), **PhMe-BODIPY** (d-f), **Ph-BODIPY** (g-i), and **Me-BODIPY** (j and k) before and after strong grinding. (a), (d), (g), and (j): original sample; (b), (e), and (h): gently ground sample; (c), (f), and (i): strongly ground sample including large amounts of KBr; (k): strongly ground sample.

Table S3. Decay parameters and fluorescence quantum yields of BODIPYs at different solid states.

Compound	Type	τ_1 [a] (ns)	τ_2 [a] (ns)	A_1 [b]	A_2 [b]	$\langle\tau\rangle$ [c] (ns)	Φ_F (%)	k_f (s^{-1})	k_{nr} (s^{-1})
PhMe$_3$-BODIPY	Single crystals	0.60	3.42	0.05	0.95	3.28	32.2	9.8×10^7	2.1×10^8
	Gently Ground	0.62	2.26	0.48	0.52	1.33	43.5	3.3×10^8	4.2×10^8
	Strongly Ground	0.06	2.58	0.82	0.18	0.47	26.8	5.7×10^8	1.6×10^9
PhMe-BODIPY	Single crystals	0.05	2.27	0.48	0.52	1.19	9.2	7.7×10^7	7.6×10^8
	Gently Ground	0.14	1.29	0.63	0.37	0.51	24.7	4.8×10^8	1.5×10^9
	Strongly Ground	0.14	2.30	0.90	0.10	0.24	22.9	9.5×10^8	3.2×10^9
Ph-BODIPY	Single crystals	0.61	3.32	0.01	0.99	3.29	13.0	4.0×10^7	2.6×10^8
	Gently Ground	0.72	2.08	0.66	0.34	0.87	46.4	5.3×10^8	6.2×10^8
	Strongly Ground	0.22	1.77	0.91	0.09	0.36	20.2	5.6×10^8	2.2×10^9
Me-BODIPY	Single crystals	0.99	2.84	0.22	0.78	2.39	5.2	2.2×10^7	4.0×10^8
	Ground	1.12	2.96	0.39	0.61	2.07	6.0	2.9×10^7	4.5×10^8

[a] Fluorescence lifetime. [b] Fractional contribution. [c] Weighted mean lifetime.