Supplementary Information

BODIPY sensor for water based on photo-induced electron transfer method with fluorescence enhancement and attenuation systems

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Experimental Section:

General: Melting points were measured with a Yanaco micro melting point apparatus MP model. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer by ATR method. ^{1}H and ^{13}C NMR spectra were recorded on a Varian-500 FT NMR spectrometer. High-resolution mass spectral data by ESI were acquired on a Thermo Fisher Scientific LTQ Orbitrap XL. Absorption spectra were observed with a Shimadzu UV-2910 spectrophotometer. Fluorescence spectra were measured with a Hitachi F-4500 spectrophotometer. The addition of water to organic solvents containing **MH-1** was made by weight percent (wt%). The determination of water in 1,4-dioxane, THF acetone and acetonitrile was done with a MKC-610 and MKA-610 Karl Fischer moisture titrator (Kyoto Electronics manufacturing Co., Ltd.) based on Karl Fischer coulometric titration (relative standard deviation is below 0.3% in a measurement of methanol containing 1 mg H_2O) for below 1.0 wt% and volumetric titration for above 1.0 wt%, respectively.

Preparation of 2,6-diethyl-8-(bromomethyl)-1,3,5,7-tetramethyl BODIPY (1)

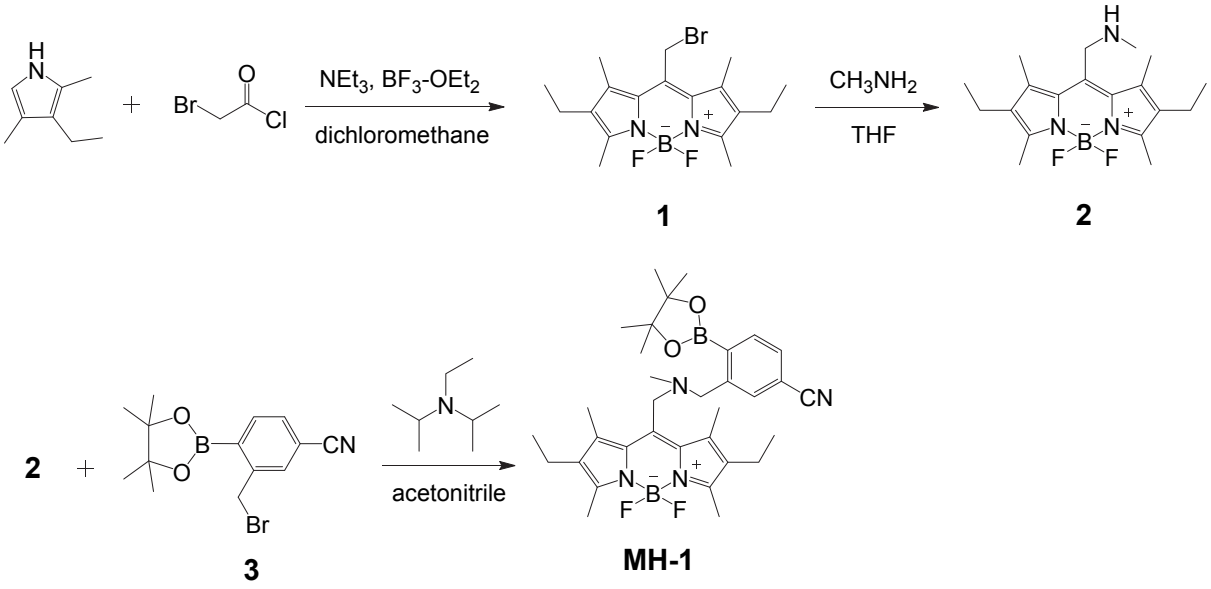
A solution of 3-ethyl-2,4-dimethylpyrrole (0.49 g, 4.0 mmol) and bromoacetyl chloride (3.12g, 20.0 mmol) in dichloromethane (20 ml) was refluxed for 3 h under an argon atmosphere. To the reaction mixture under an argon atmosphere was added triethylamine (2.80 ml, 20.0 mmol) and stirred for 10 min at room temperature. Next, $BF_3{\cdot}OEt_2$ (10 ml, 40.0 mmol) was added dropwise and the solution was refluxed for 3 h. The reaction mixture was washed with water and extracted with dichloromethane. The organic extract was dried over $MgSO_4$, filtrated, and concentrated. The residue was chromatographed on silica gel (dichloromethane–hexane = 1 : 1 as eluent) to give **1** (0.26 g, yield 33 %) as a green metallic luster solid; m.p. 198–200 °C; FT-IR (ATR): $\tilde{\nu}$ = 2964, 1551, 1188, 1041, 974 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.06 (t, J = 7.7 Hz, 6H), 2.41 (q, J = 7.7 Hz, 4H), 2.46-2.47 (s (split), 6H), 2.51 (s, 6H), 4.7-4.8 (s (split), 2H) ppm; HRMS (ESI): m/z (%):[M+Na^+] calcd for $C_{18}H_{24}N_2BBrF_2Na$, 419.10762; found 419.10754.

Preparation of 2,6-diethyl-8-[(*N*-methylamino)methyl]-1,3,5,7-tetramethyl BODIPY (2)

To a solution of **1** (2.0 g, 5.0 mmol) in THF (15 ml) under an argon atmosphere was added methyl amine (5.0 ml, 10.0 mmol) and was refluxed for 3 h. The reaction mixture was washed with water and extracted with dichloromethane. The organic extract was dried over $MgSO_4$, filtrated, and concentrated. The residue was chromatographed on silica gel (dichloromethane as eluent) to give **2** (0.39 g, yield 22 %) as a green metallic luster solid; m.p. 192–195 °C; FT-IR (ATR): $\tilde{\nu}$ = 2962, 1547, 1192, 1045, 972 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.05 (t, J = 7.7 Hz, 6H), 2.37-2.42 (q, J = 7.7 Hz, 4H), 2.39 (s, 6H), 2.49 (s, 6H), 2.56 (s, 3H), 3.91 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 12.42, 12.56, 14.82, 17.21, 36.64, 46.97, 131.82, 132.92, 136.46, 138.59, 153.40 ppm; HRMS (ESI): m/z (%):[M+H^+] calcd for $C_{19}H_{29}N_3BF_2$, 348.24171; found 348.24188.

Preparation of 2,6-diethyl-8-[*N*-(5-cyano-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-*N*-methylaminomethyl]-1,3,5,7-tetramethyl BODIPY (MH-1)

A solution of **2** (0.20 g, 0.58 mmol), 2-bromomethyl-4-cyanophenylboronic acid **3**[1] (0.19 g, 0.58 mmol), *N*,*N*-diisopropylethylamine (0.40 ml, 2.32 mmol) and acetonitrile (15 ml) was stirred at 80 ºC for 24 h under an argon atmosphere. The water was added to the reaction mixture and the aqueous layer was extracted with dichloromethane. The organic extract was dried over $MgSO_4$, filtrated, and concentrated. The residue was chromatographed on silica gel (dichloromethane and then acetonitrile, as eluent) to give crude product. The crude product was dissolved in toluene, and HPLC was performed to give **MH-1** (0.15 g, yield 44 %) as a red solid; m.p. 227–229 °C; FT-IR (ATR): $\tilde{\nu}$ = 2962, 2228, 1540, 1192, 1043, 978 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 1.07 (t, J = 7.6 Hz, 6H), 1.32 (s, 12H), 2.28 (s, 3H), 2.40-2.45 (q, J = 7.6 Hz, 4H), 2.47 (s, 6H), 2.50 (s, 6H), 3.98 (s, 2H), 3.99 (s, 2H), 7.44 (d, J = 7.6 Hz, 1H), 7.54 (s, 1H), 7.79 (d, J = 7.6 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 12.70, 14.32, 14.96, 17.42, 25.06, 29.85, 42.14, 52.04, 57.37, 84.33, 114.37, 119.20, 129.22, 131.87, 132.80, 133.39, 136.08, 137.24, 138.54, 147.12, 153.57 ppm; HRMS (ESI): m/z (%):[M+H$^+$] calcd for $C_{33}H_{45}O_2N_4B_2F_2$, 589.36912; found 589.36957.



Scheme S1. Synthetic rote to fluorescent BODIPY sensor **MH-1**.

[1] a) Y. Ooyama, A. Matsugasako, K. Oka, T. Nagano, M. Sumomogi, K. Komaguchi, I. Imae, Y. Harima, *Chem. Commun*. **2011**, *47*, 4448-4450; b) Y. Ooyama, A. Matsugasako, Y. Hagiwara, J. Ohshita, Y. Harima, *RSC Adv*. **2012**, *2*, 7666-7668; c) Y. Ooyama, K. Uenaka, A. Matsugasako, Y. Harima, J. Ohshita, *RSC Adv*. **2013**, *3*, 23255-23263; d) Y. Ooyama, K. Furue, K. Uenaka, J. Ohshita, *RSC Adv*. **2014**, *4*, 25330-25333.

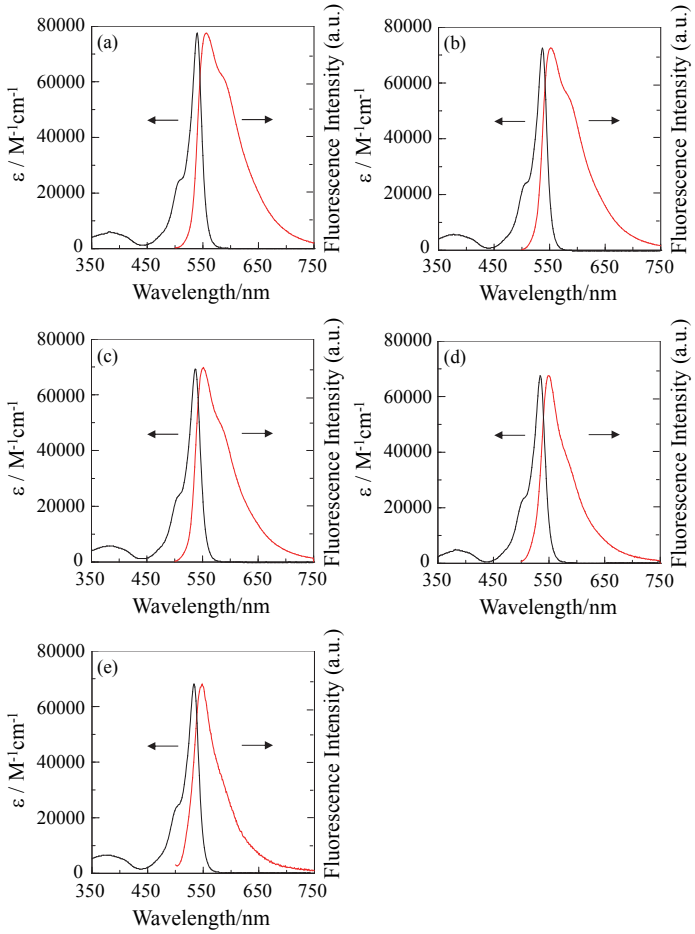


Fig. S1 Absorption and fluorescence spectra (λ_{ex} = 490 nm) of **MH-1** in (a) toluene, (b) 1,4-dioxane, (c) THF, (d) acetone and (e) acetonitrile.

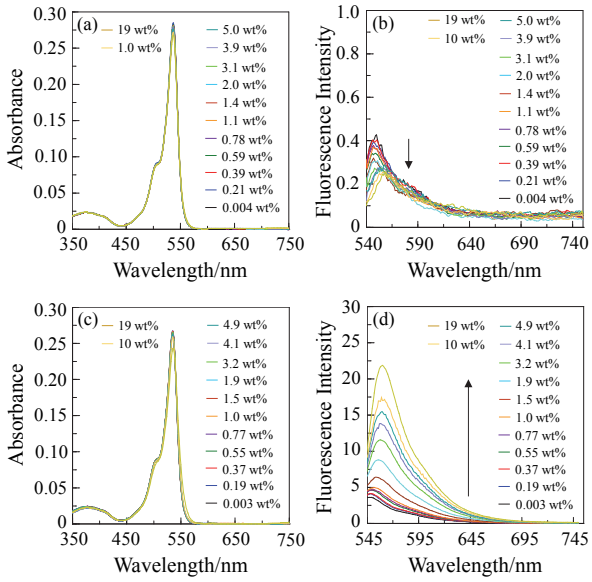


Fig. S2 (a) Absorption and (b) fluorescence spectra (λ_{ex} = 537 nm, slit: 1.0 nm) of **MH-1** (c = 4.0×10^{-6} M) in THF containing water (0.004–19 wt%). (c) Absorption and (d) fluorescence spectra (λ_{ex} = 534 nm, slit: 2.5 nm) of **MH-1** (c = 4.0×10^{-6} M) in acetone containing water (0.003–19 wt%).

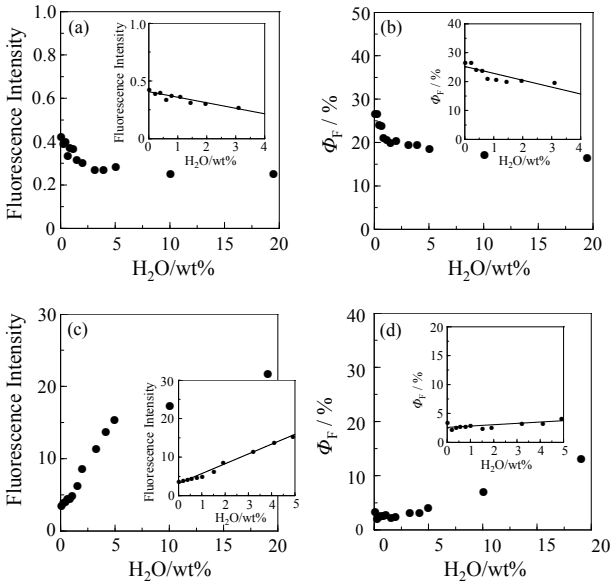


Fig. S3 (a) Fluorescence peak intensity at around 550 nm (λ_{ex} = 537 nm, slit: 1.0 nm) and (b) Φ_F of **MH-1** as a function of water content in THF in a water-content region below 20 wt%. (c) Fluorescence peak intensity at around 550 nm (λ_{ex} = 534 nm, slit: 2.5 nm) and (d) Φ_F of **MH-1** as a function of water content in acetone in a water-content region below 20 wt%; inset: the fluorescence peak intensity and Φ_F of **MH-1** in acetone in a low water-content region below 4.0 wt% for acetone and 5.0 wt% for acetone, respectively.

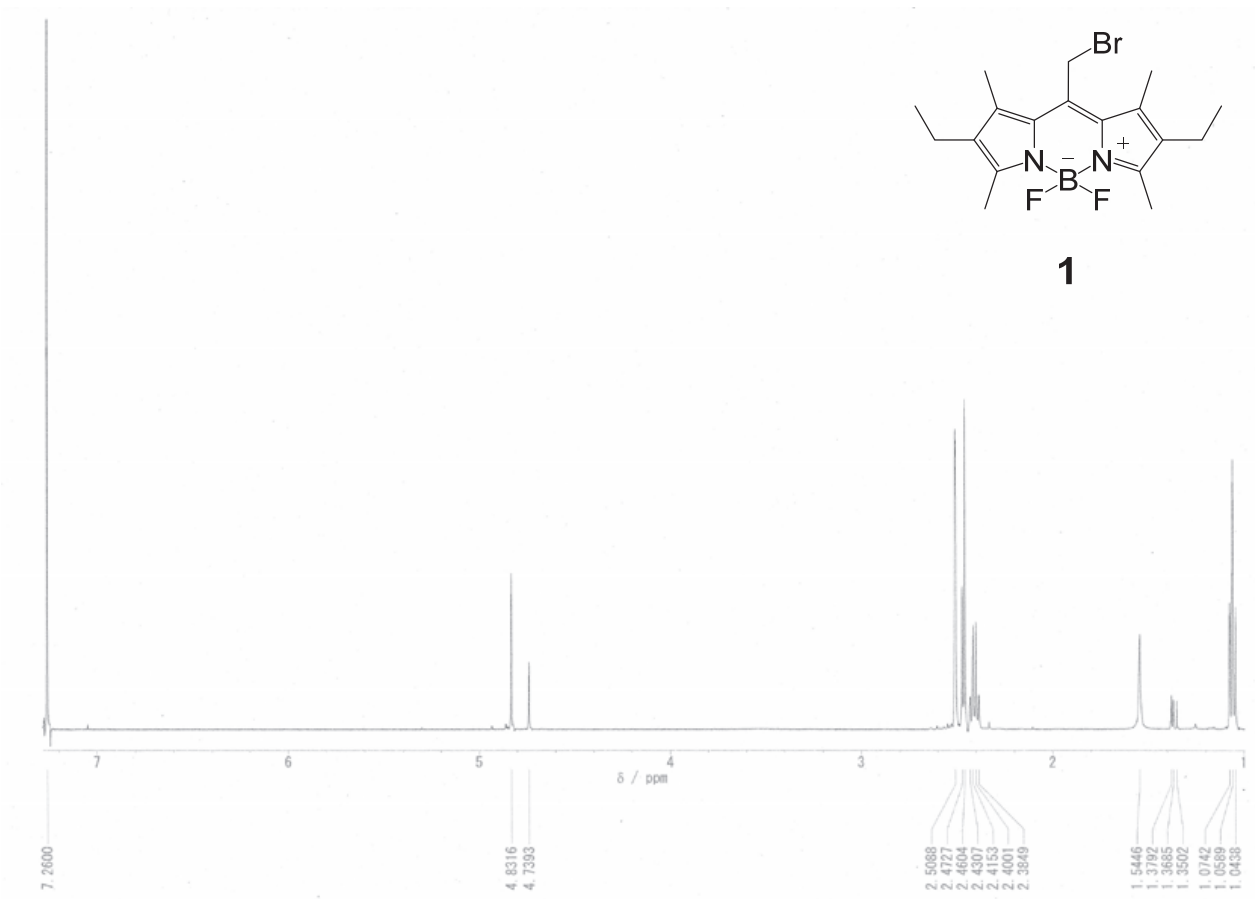


Fig. S4 ^{1}H HMR (500 MHz) of **1** in $CDCl_3$.

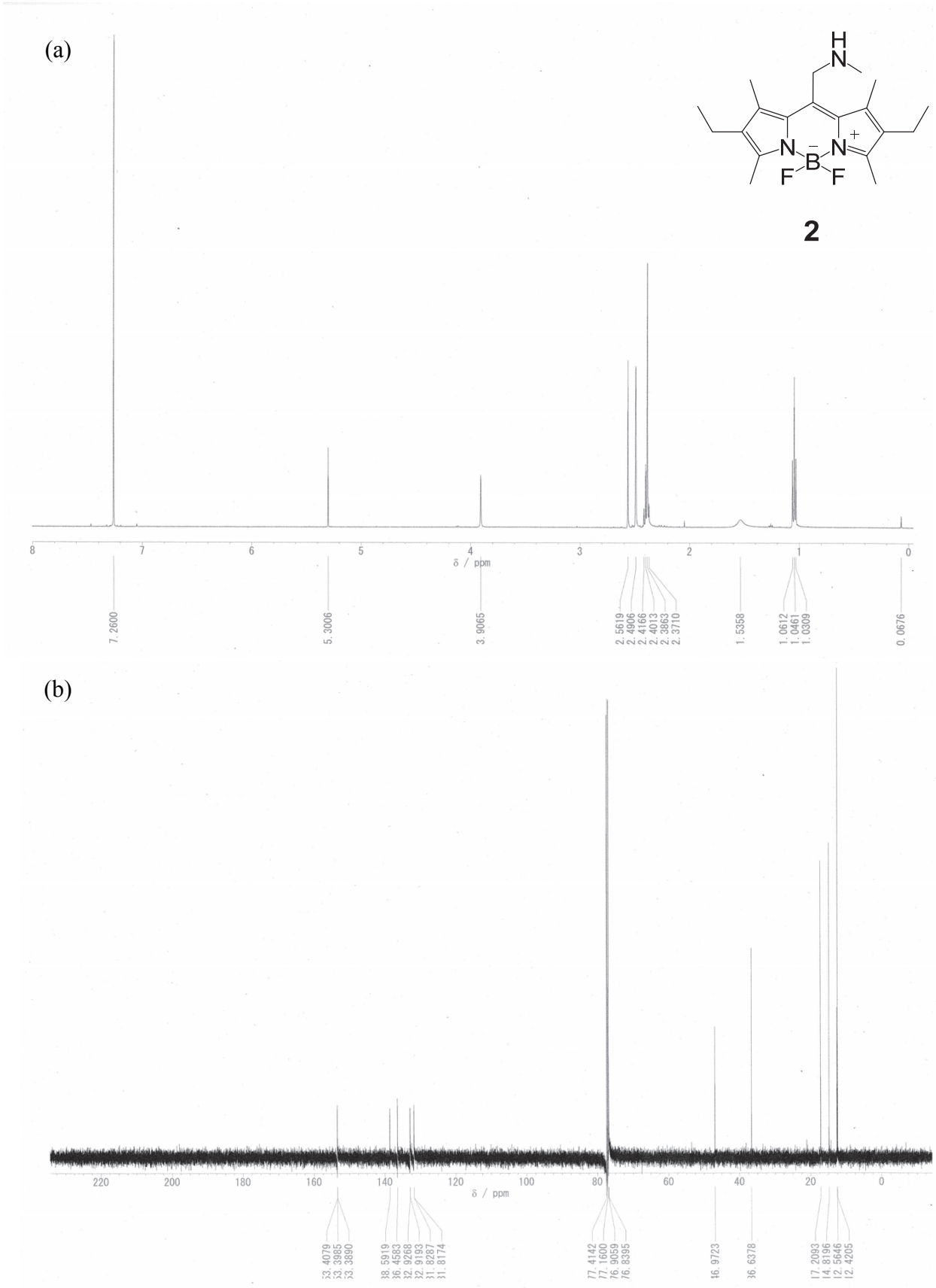


Fig. S5 (a) ^{1}H HMR (500 MHz) and (b) ^{13}C NMR (125 MHz) of **2** in $CDCl_3$.

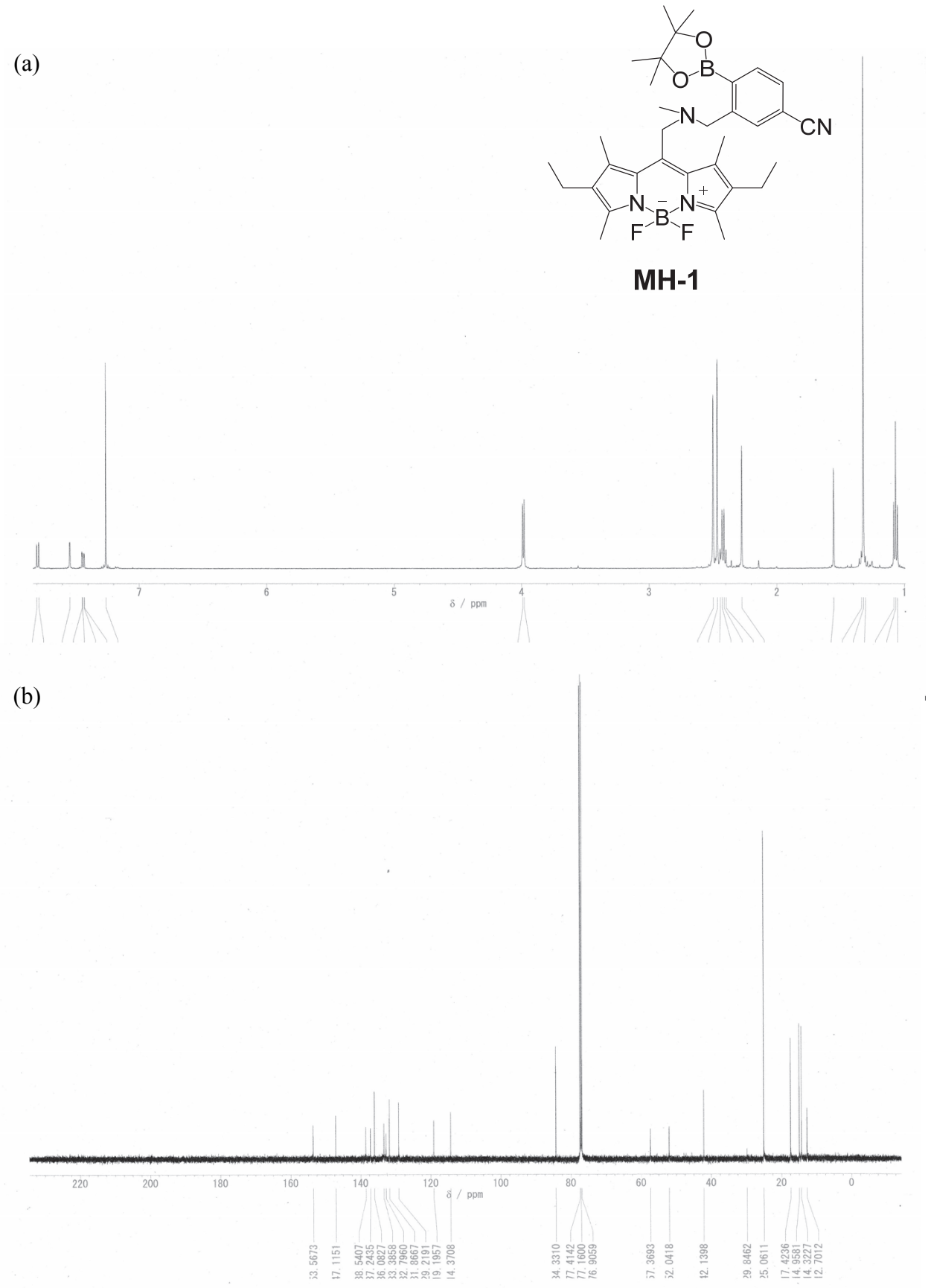


Fig. S6 (a) ^{1}H HMR (500 MHz) and (b) ^{13}C NMR (125 MHz) of **MH-1** in $CDCl_3$.