

Supplementary Information

Development of fluorescence sensors based on a combination of PET (photo-induced electron transfer) and FRET (Förster resonance energy transfer) for detection of water

Daisuke Jinbo, Kazuki Ohira, Keiichi Imato and Yousuke Ooyama *

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima, 739-8527, Japan.

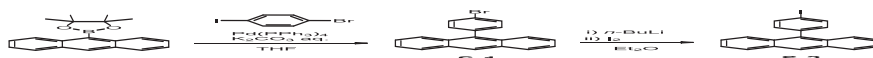
Fax: +81 82 424 5494; Tel: +81 82 424 7689; E-mail:yooyama@hiroshima-u.ac.jp

Synthesis of 9-(4-bromophenyl)anthracene (S-1)

A solution of 2-(anthracen-9-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.30 g, 7.56 mmol), 1-bromo-4-iodobenzene (2.45 g, 8.32 mmol), Pd(PPh₃)₄ (0.131 g, 0.113 mmol), and 2 M K₂CO₃ (150 mL, 302 mmol) in THF (150 mL) and water (0.44 mL) was refluxed for 24 h under a nitrogen atmosphere. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane, and washed with water. The dichloromethane extract was dried over anhydrous Na₂SO₄, filtrated, and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane as eluent) to give **S-1** (1.92 g, 56 % yield) as a white solid; m.p. 178–179 °C; FT-IR (ATR): $\tilde{\nu}$ = 3051, 1475, 1440, 1409, 1384, 1357, 1166, 1010 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 7.32 (d, *J* = 8.2 Hz, 2H), 7.35-7.39 (m, 2H), 7.45-7.49 (m, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 8.05 (d, *J* = 8.5 Hz, 2H), 8.51 (s, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 121.86, 125.32, 125.76, 126.56, 127.11, 128.56, 130.18, 131.43, 131.77, 133.10, 135.57, 137.86 ppm; HRMS (APCI): *m/z* (%): [M+H]⁺ Calcd for C₂₀H₁₄Br, 333.02734; found 333.02737.

Synthesis of 9-(4-iodophenyl)anthracene (S-2)

To a diethyl ether solution (200 mL) of **S-1** (3.33 g, 10.0 mmol) at -78 °C under a nitrogen atmosphere was added dropwise 2.8 M hexane solution of *n*-BuLi (5.00 mL, 14.0 mmol). After stirring for 1 h at -10 °C, I₂ (4.31 g, 17 mmol) was added and then the reaction mixture was stirred for 12 h at room temperature. The reaction mixture was quenched with 25% Na₂S₂O₃ aq., and then the solution was extracted with diethyl ether. The diethyl ether extract was dried over anhydrous Na₂SO₄, filtrated, and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane as eluent) to give **S-2** (3.47 g, 91 % yield) as a light yellow solid; m.p. 173–176 °C; FT-IR (ATR): $\tilde{\nu}$ = 3049, 1477, 1442, 1411, 1384, 1359, 1188, 1006 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 7.19 (d, *J* = 8.2 Hz, 2H), 7.35-7.39 (m, 2H), 7.45-7.48 (m, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.2 Hz, 2H), 8.05 (d, *J* = 8.5 Hz, 2H), 8.51 (s, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 93.46, 125.31, 125.76, 126.57, 127.10, 128.56, 130.12, 131.42, 133.37, 135.64, 137.71, 138.48 ppm; HRMS (APCI): *m/z* (%): [M+H]⁺ Calcd for C₂₀H₁₄I, 381.01347; found 381.01355.

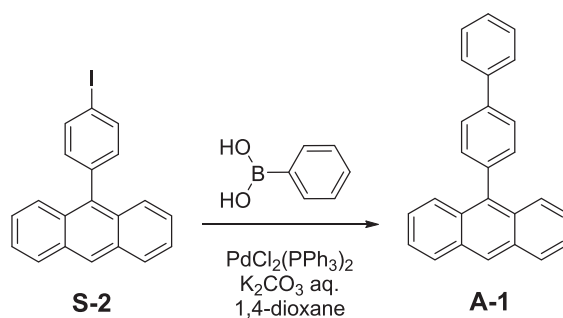


Scheme S1 Synthesis of **S-2**.

Synthesis of 9-([1,1'-biphenyl]-4-yl)anthracene (A-1)

A solution of **S-2** (0.10 g, 0.26 mmol), phenylboronic acid (0.038 g, 0.32 mmol), PdCl₂(PPh₃)₂ (0.041 g, 0.058 mmol), and 1 M K₂CO₃ (1.0 mL, 1.1 mmol) in 1,4-dioxane (20 mL) was refluxed for 12 h under a nitrogen atmosphere. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane, and washed with water. The dichloromethane extract was dried over anhydrous Na₂SO₄,

filtrated, and evaporated under reduced pressure. The residue was chromatographed on silica gel (dichloromethane : hexane = 1 : 9 as eluent) to give **A-1** (0.049 g, 54 % yield) as an orange solid; m.p. 219–220 °C; FT-IR (ATR): $\tilde{\nu}$ = 3059, 1489, 1438, 1413, 1359, 1105, 1006 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ = 7.36-7.43 (m, 3H), 7.46-7.49 (m, 2H), 7.51-7.54 (m, 4H), 7.75-7.78 (m, 4H), 7.81-7.83 (m, 2H), 8.07 (d, J = 8.5 Hz, 2H), 8.52 (s, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 125.28, 125.53, 126.77, 126.98, 127.20, 127.32, 127.58, 128.51, 129.05, 130.39, 131.53, 131.84, 136.81, 137.91, 140.39, 141.01 ppm; HRMS (APCI): m/z (%): $[\text{M}^+]$ Calcd for $\text{C}_{26}\text{H}_{18}$, 330.14030; found 330.14021.

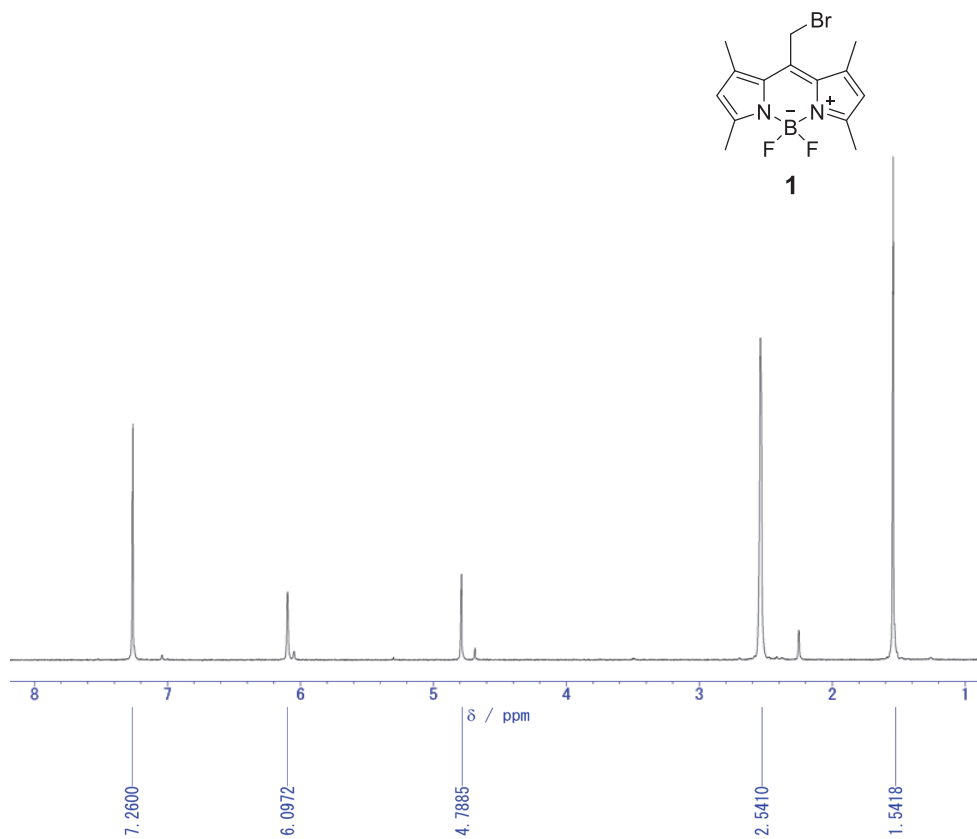


Scheme S2 Synthesis of **A-1**.

Synthesis of
1-(5,5-difluoro-1,3,7,9-tetramethyl-5H-4H,5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-10-yl)-N-methyl-N-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)methanamine (MH-2). A solution of **2** (0.050 g, 0.34 mmol), 2-(2-(bromomethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.051 g, 0.34 mmol), *N,N*-diisopropylethylamine (0.24 mL, 1.4 mmol), and acetonitrile (8 mL) was refluxed for 8 h under a nitrogen atmosphere. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The dichloromethane extract was dried over anhydrous MgSO_4 , filtrated, and evaporated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate : hexane = 1 : 3 as eluent) to give a crude product of **MH-2**. The crude product was dissolved in toluene, and HPLC was performed to give **MH-2** (0.025 g, 14 % yield) as an orange solid; m.p. 204–205 °C; FT-IR (ATR): $\tilde{\nu}$ = 2980, 1548, 1510, 1342, 1305, 1199, 1157, 1141, 1105, 1062, 974 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ = 1.32 (s, 12H), 2.23 (s, 3H), 2.52 (s, 12H), 3.90 (s, 2H), 4.02 (s, 2H), 6.06 (s, 2H), 7.17-7.24 (m, 1H), 7.31-7.32 (m, 1H), 7.34-7.37 (m, 1H), 7.76 (d, J = 7.4 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 14.71, 17.46, 25.07, 41.10, 51.85, 58.81, 83.72, 122.20, 126.20, 128.38, 129.08, 131.02, 133.39, 135.88, 141.31, 142.37, 144.99, 154.80 ppm; HRMS (ESI): m/z (%): $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{38}\text{O}_2\text{N}_3\text{B}_2\text{F}_2$, 508.31127; found 508.31059.

Scheme S3 Synthesis of **MH-2**.

(a)



(b)

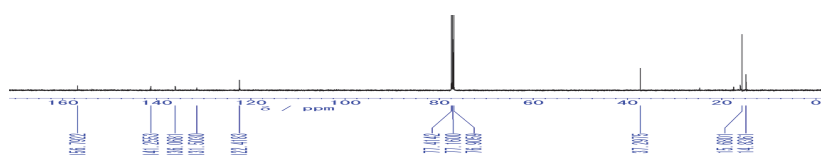
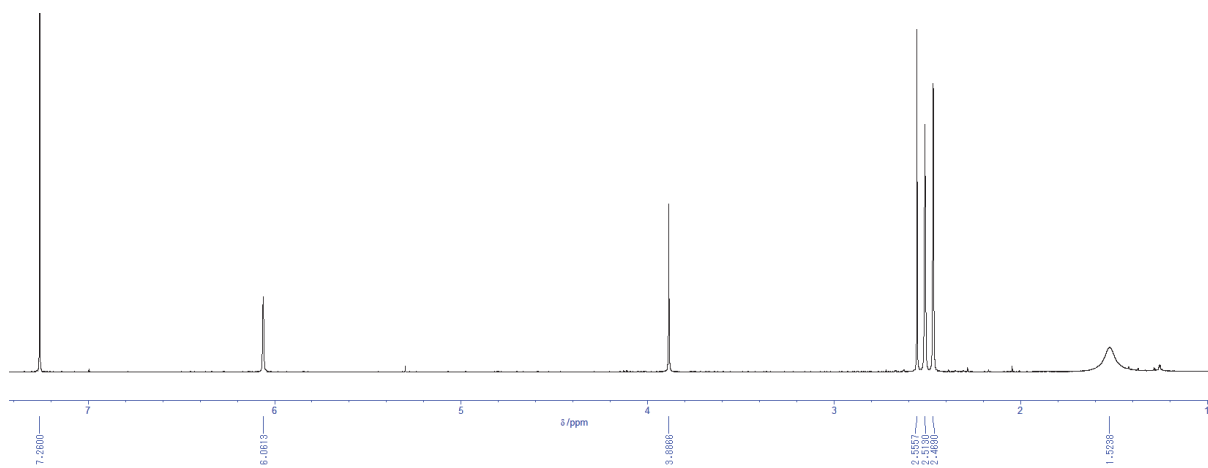
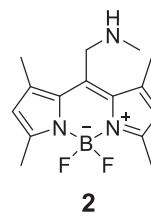


Fig. S1 (a) ¹H NMR (500 MHz) and (b) ¹³C NMR (125 MHz) spectra of **1** in CDCl₃.

(a)



(b)

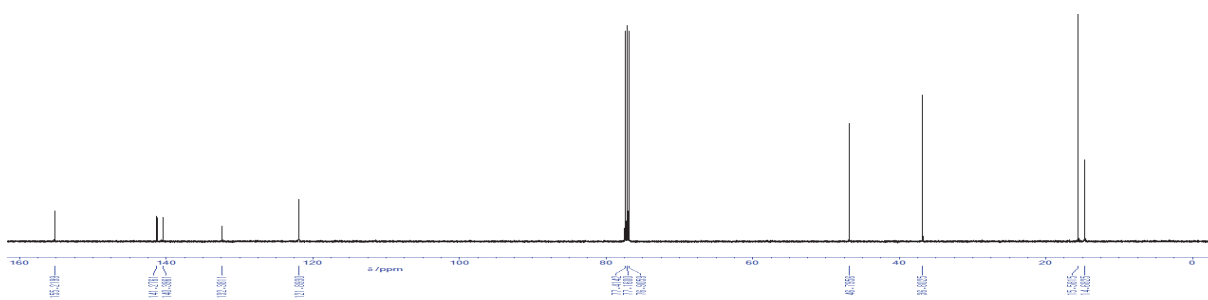


Fig. S2 (a) ¹H NMR (500 MHz) and (b) ¹³C NMR (125 MHz) spectra of **2** in CDCl₃.

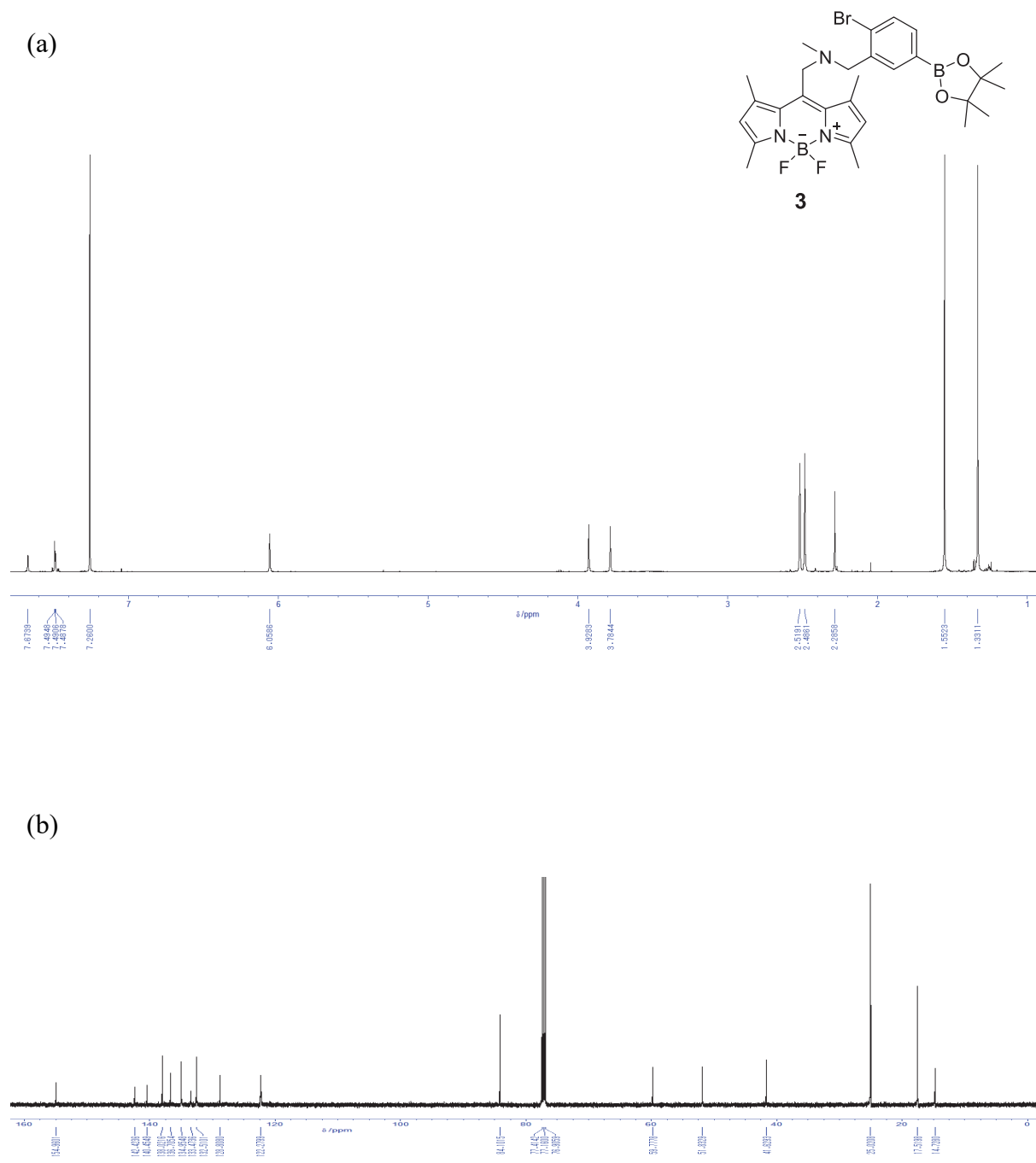
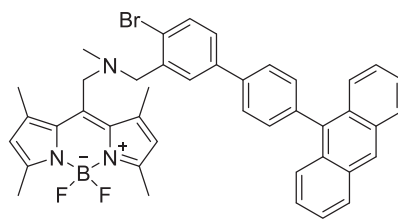
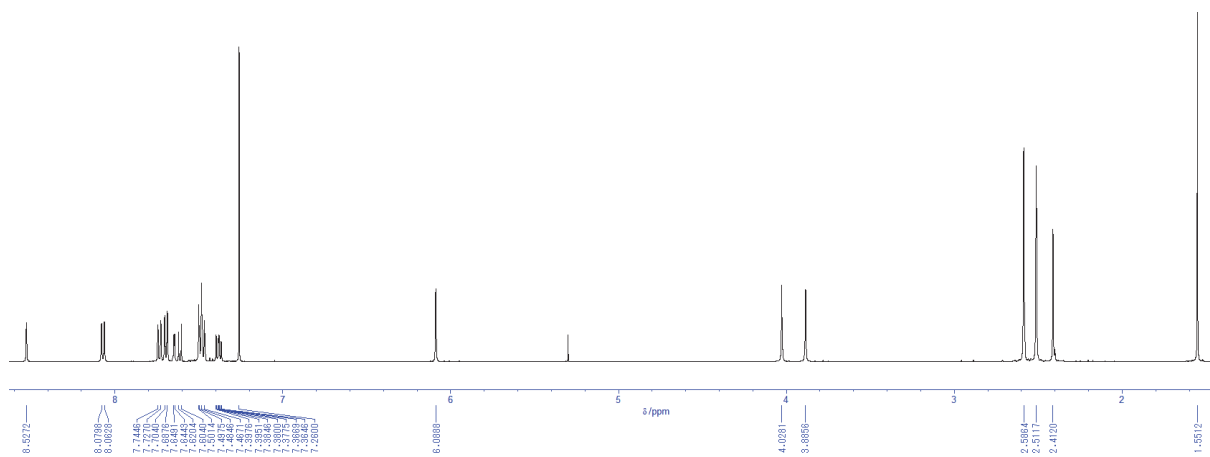


Fig. S3 (a) ¹H HMR (500 MHz) and (b) ¹³C HMR (125 MHz) spectra of **3** in CDCl₃.

(a)



4



(b)

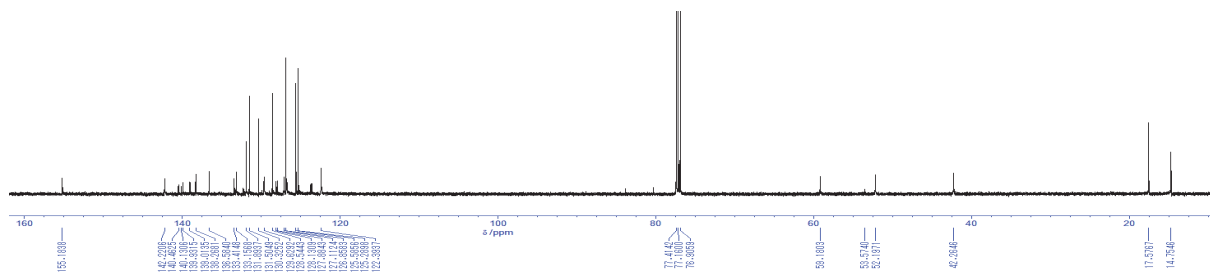
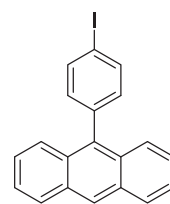
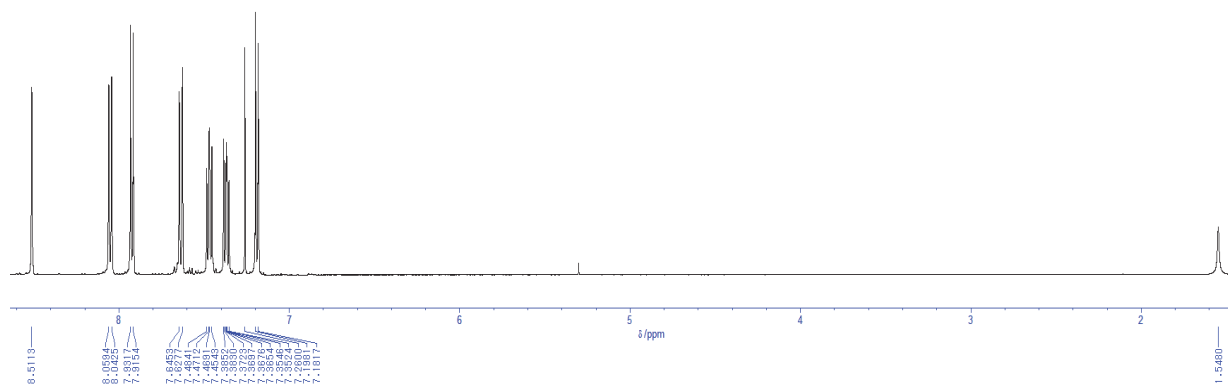


Fig. S4 (a) ¹H NMR (500 MHz) and (b) ¹³C NMR (125 MHz) spectra of **4** in CDCl₃.

(a)



S-2



(b)

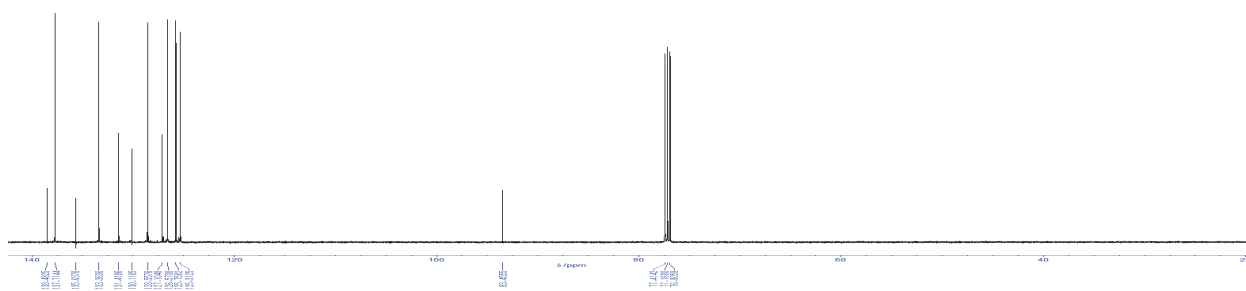
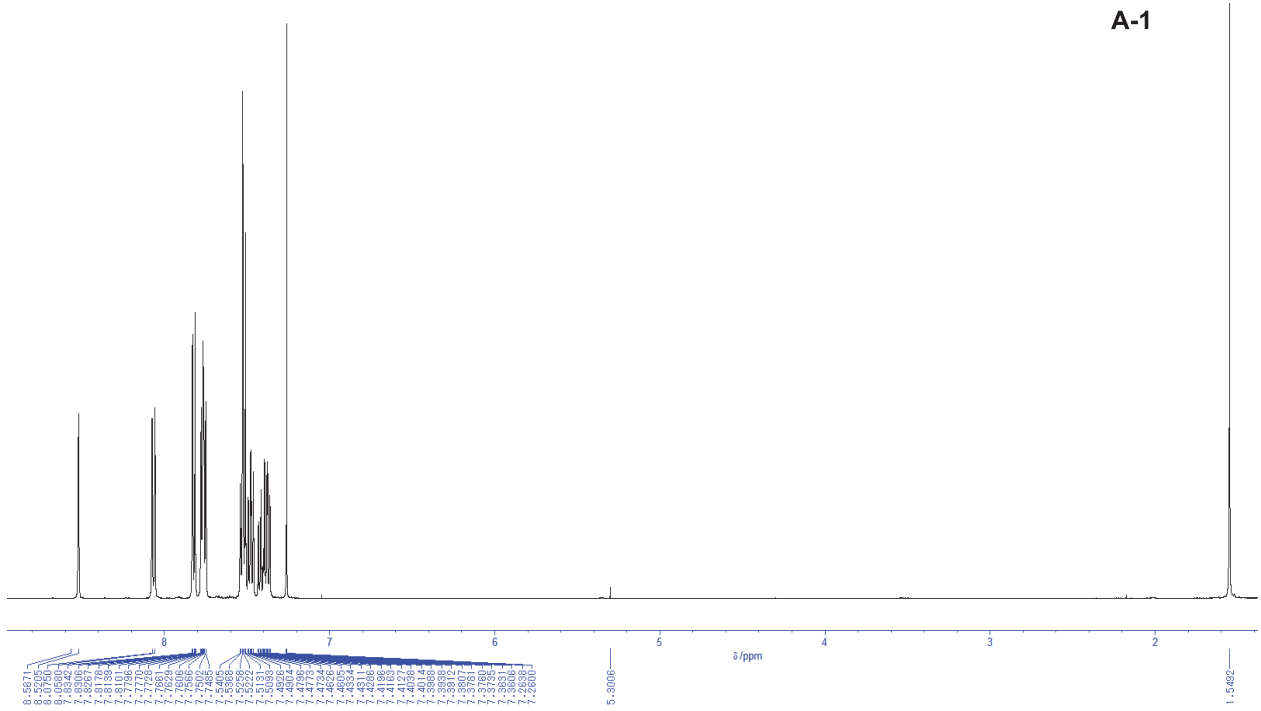
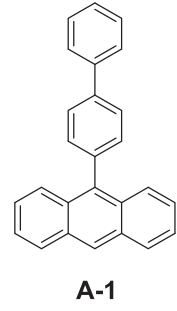


Fig. S7 (a) ^1H NMR (500 MHz) and (b) ^{13}C NMR (125 MHz) spectra of S-2 in CDCl_3 .

(a)

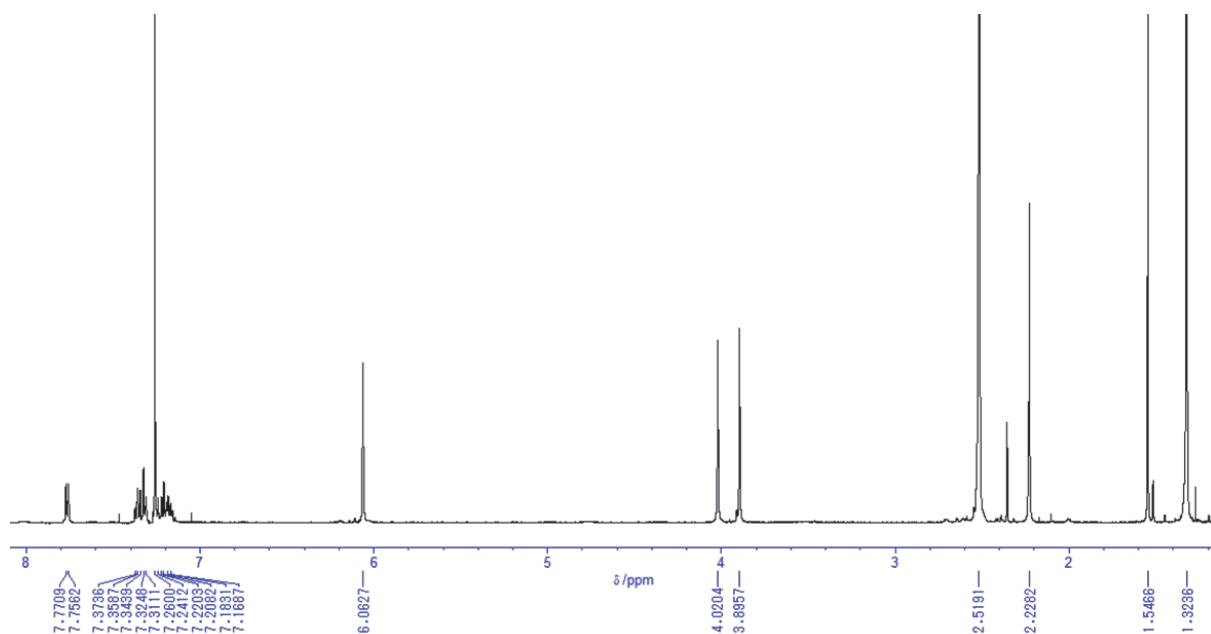
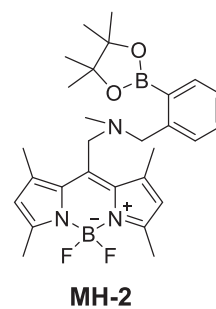


(b)



Fig. S8 (a) ^1H NMR (500 MHz) and (b) ^{13}C NMR (125 MHz) spectra of **A-1** in CDCl_3 .

(a)



(b)

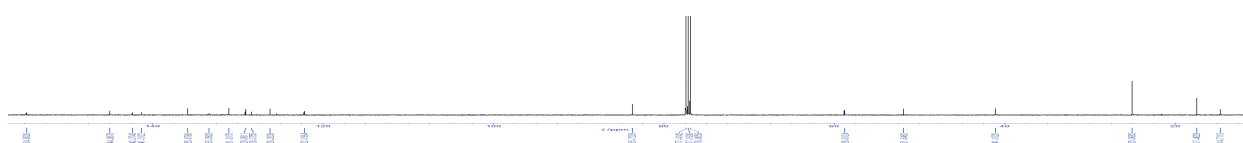


Fig. S9 (a) ¹H NMR (500 MHz) and (b) ¹³C NMR (125 MHz) spectra of **MH-2** in CDCl₃.

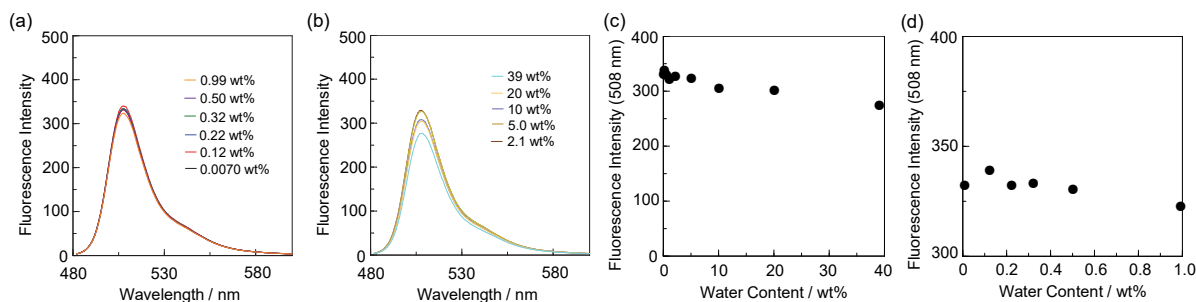


Fig. S10 Fluorescence spectra ($\lambda^{\text{ex}} = 472 \text{ nm}$) of **DJ-1** ($c = 4.0 \times 10^{-6} \text{ M}$) in acetonitrile containing (a) 0.007–0.99 wt% and (b) 2.1–39 wt% of water. Fluorescence peak intensity at 508 nm of **DJ-1** ($\lambda^{\text{ex}} = 472 \text{ nm}$) as a function of water content (c) below 40 wt% and (d) 1.0 wt% in acetonitrile.

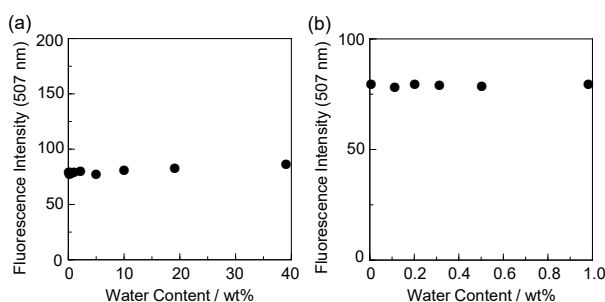


Fig. S11 Fluorescence peak intensity at 507 nm of **B-1** ($\lambda^{\text{ex}} = 367 \text{ nm}$) as a function of water content (a) below 40 wt% and (b) 1.0 wt% in acetonitrile.

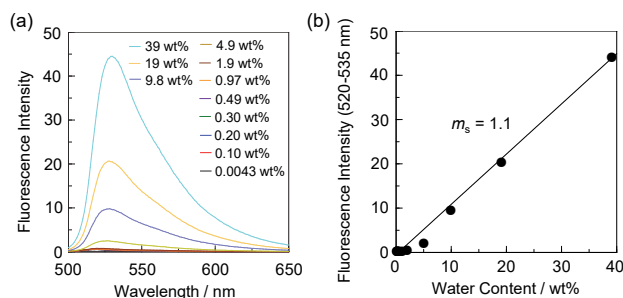


Fig. S12 (a) Fluorescence spectra ($\lambda^{\text{ex}} = 485 \text{ nm}$) of **MH-2** ($c = 4.0 \times 10^{-6} \text{ M}$) in acetonitrile containing 0.0043–39 wt% of water. (c) Fluorescence peak intensity at 520–535 nm of **MH-2** ($\lambda^{\text{ex}} = 485 \text{ nm}$) as a function of water content below 40 wt% in acetonitrile.

Fig. S13 Fluorescence peak intensity at around 405 nm of **A-1** ($\lambda^{\text{ex}} = 366 \text{ nm}$) as a function of water content below 40 wt% in acetonitrile.

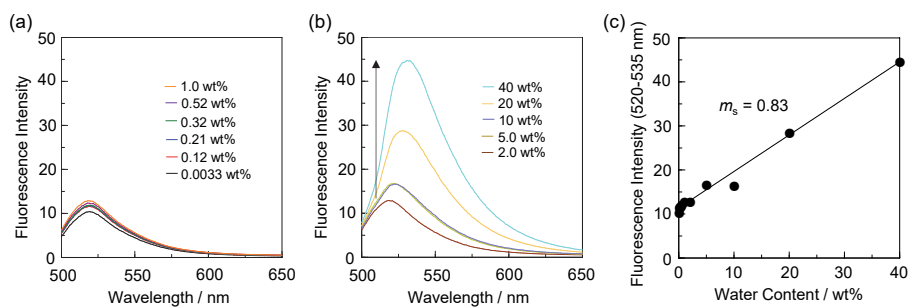


Fig. S14 Fluorescence spectra ($\lambda^{\text{ex}} = 486 \text{ nm}$) of **DJ-2** ($c = 4.0 \times 10^{-6} \text{ M}$) in acetonitrile containing (a) 0.0033–1.0 wt% and (b) 2.0–40 wt% of water. (c) Fluorescence peak intensity at 520–535 nm of **DJ-2** ($\lambda^{\text{ex}} = 486 \text{ nm}$) as a function of water content below 40 wt% in acetonitrile.

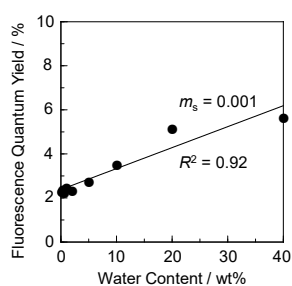


Fig. S15 Fluorescence quantum yield of **DJ-2** by photoexcitation at 367 nm as a function of water content below 40 wt% in acetonitrile.