

Supplementary Information

Development of colorimetric and fluorescent sensor based on a combination of ICT (intramolecular charge transfer) and FRET (Förster resonance energy transfer) for detection of water

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Experimental Section:

General

Melting points were measured with an AS ONE ATM-02. IR spectra were recorded on a SHIMADZU IRTracer-100 spectrometer by the ATR method. ^1H , ^{11}B and ^{13}C NMR spectra were recorded on a Varian-400 or -500 FT and Bruker AVANCE NEO400 NMR spectrometer. High-resolution mass spectral data were acquired by APCI on a Thermo Fisher Scientific LTQ Orbitrap XL. Photoabsorption spectra were observed with a SHIMADZU UV-3600 plus. Fluorescence spectra were measured with a Hitachi F-7100 spectrophotometer. The fluorescence quantum yields (Φ_f) were determined using a Hamamatsu C9920-01 equipped with CCD using calibrated integrating sphere system. Thermogravimetry-differential thermal analysis (TG-DTA) was performed by RIGAKU TG-DTA8122. The addition of water to acetonitrile or solutions containing **KOY-1-BF₃**, **KOY-1**, **D1-BF₃**, **D1** and **A1** were made by weight percent (wt%). The determination of water in solvents was done with MKC-610 and MKA-610 Karl Fischer moisture titrators (Kyoto Electronics Manufacturing Co., Ltd) based on Karl Fischer coulometric titration for below 1.0 wt% and volumetric titration for 1.0–40 wt%.

Synthesis

4-(3,6-Dibromo-9H-carbazol-9-yl)benzaldehyde (**2**)

A solution of **1** (3.256 g, 12 mmol) in DMF (50 mL) at 0°C was slowly added dropwise *N*-bromosuccinimide (NBS) (4.293 g, 24.12 mmol) dissolved in DMF (24 mL). After completion of the addition, the solution was stirred for 24 hours at room temperature under light. The reaction solution was then quenched with water. The solution was vacuum filtered and was washed by water and ethanol to give **2** (4.808 g, 93% yield) as a white solid; m.p. 156–157 °C; FT-IR (ATR): $\tilde{\nu}$ = 2893, 1695, 1597, 1435, 806, 785 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.34 (d, J = 8.76 Hz, 2H), 7.54 (dd, J = 8.76 Hz, 2H), 7.73 (d, J = 8.36 Hz, 2H), 8.15 (d, J = 8.52 Hz, 2H), 8.21 (d, J = 1.68 Hz, 2H), 10.13 (s, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 111.60, 114.07, 123.62, 124.66, 127.01, 129.91, 131.71, 135.36, 139.27, 142.49, 190.93 ppm; HRMS (ESI): m/z (%): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{12}\text{Br}_2\text{NO}$, 429.92807; found 429.92548.

4-(3,6-Bis(5-(pyridin-4-yl)thiophen-2-yl)-9H-carbazol-9-yl)benzaldehyde (**3**)

A solution of **2** (2.248 g, 5.24 mmol), **S1** (4.998 g, 11.1 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.302 g, 0.26 mmol) in DMF (60 mL) was refluxed for 2 hours at 90°C under a nitrogen atmosphere. The reaction was stopped by adding the reaction mixture to water (400 mL). The resulting precipitate was vacuum filtered and washed with methanol to give **3** (2.503 g, 81% yield) as a yellow solid; m.p. 252–257 °C; FT-IR (ATR): $\tilde{\nu}$ = 3067, 2816, 1697, 1589, 1429, 779 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ = 7.61 (d, J = 8.60 Hz, 2H), 7.71 (d, J = 6.08 Hz, 4H), 7.74 (d, J = 3.92 Hz, 2H), 7.89 (dd, J = 8.68 Hz, 2H), 7.93 (d, J = 3.84 Hz, 2H), 7.99 (d, J = 8.44 Hz, 2H), 8.25 (d, J = 8.44 Hz, 2H), 8.61 (d, J = 6.08 Hz, 4H), 8.87 (s, 2H), 10.17 (s, 1H) ppm; It was not possible to obtain the ^{13}C NMR spectrum to make assignments due to the low solubility of **3** in the solvent; HRMS (APCI): m/z (%): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{37}\text{H}_{24}\text{N}_3\text{OS}_2$, 590.13553; found 590.13556.

9-(4-(bis(3,5-dimethyl-1H-pyrrol-2-yl)methyl)phenyl)-3,6-bis(5-(pyridin-4-yl)thiophen-2-yl)-9H-carbazole (**4**)

A solution of **3** (100 mg, 0.17 mmol) and 2,4-dimethylpyrrole (60 μL , 0.58 mmol) in dichloromethane (200 mL) was refluxed at 45°C under a nitrogen atmosphere. Then, Two drops (0.03 μL) of trifluoroacetic acid were added using a syringe needle, and the mixture was stirred for 18 hours. After reaction, the mixture was dissolved in dichloromethane and washed with water. The dichloromethane extract was evaporated under reduced pressure. The residue was washed

with methanol to give **4** (82 mg, 63% yield) as a red solid ; m.p. over 300°C; FT-IR (ATR): $\tilde{\nu}$ = 2916, 1591, 1436, 793 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ = 1.97 (s, 6H), 2.15 (s, 6H), 5.51 (s, 1H), 5.53 (s, 2H), 7.33 (d, J = 8.02 Hz, 2H), 7.45 (d, J = 8.61 Hz, 2H), 7.62 (d, J = 8.17 Hz, 2H), 7.69 (m, 6H), 7.85 (d, J = 8.61 Hz, 2H), 7.91 (d, J = 3.82 Hz, 2H), 8.60 (d, J = 5.82 Hz, 4H), 8.83 (s, 2H), 9.88 (s, 2H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 11.08, 12.94, 37.86, 106.91, 110.69, 113.64, 118.15, 119.04, 123.26, 124.28, 124.68, 125.26, 125.84, 126.03, 126.21, 127.98, 129.54, 134.07, 138.17, 140.49, 140.51, 143.91, 146.31, 150.43 ppm; HRMS (APCI): m/z (%): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{49}\text{H}_{40}\text{N}_5\text{S}_2$, 762.27196; found 762.27161.

9-(4-(5,5-Difluoro-1,3,7,9-tetramethyl-5H-4/4,5/4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)phenyl)-3,6-bis(5-(pyridin-4-yl)thiophen-2-yl)-9H-carbazole (KOY-1)

A solution of **4** (129 mg, 0.17 mmol) in dichloromethane (200 mL) was refluxed at 45°C under a nitrogen atmosphere. DDQ (2,3-Dichloro-5,6-dicyano-1,4-benzoquinone) (40 mg, 0.18 mmol) in dichloromethane (20 mL) was added to the reaction mixture under a nitrogen atmosphere and stirred for 1 hour at 45°C. The reaction mixture was vacuum filtered and washed with a mixture of dichloromethane (200 mL) and triethylamine (0.3 mL) and the filtrate was collected. After drying the filtrate in an evaporator, dissolve it in a mixture of dichloromethane (300 mL) and triethylamine (0.3 mL, 2.16 mmol), and stirred for 5 minutes at room temperature under a nitrogen atmosphere. Next, 47% $\text{BF}_3\text{-Et}_2\text{O}$ (0.5 mL, 3.98 mmol) was added dropwise and the solution was stirred for 4 h. The reaction mixture was washed with water and extracted with dichloromethane. Then, the crude was purified by GPC to give **KOY-1** (36 mg, 26% yield) as a red solid; m.p. over 300°C; FT-IR (ATR): $\tilde{\nu}$ = 2922, 2852, 1593, 1433, 1047, 793 cm^{-1} ; ^1H NMR (500 MHz, Acetonitrile- d_3): δ = 1.63 (s, 6H), 2.53 (s, 6H), 6.18 (s, 2H) 7.48 (d, J = 8.55 Hz, 2H), 7.56 (d, J = 3.85, 2H), 7.63 (dd, J = 4.5 Hz, 4H), 7.68 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 3.8 Hz, 2H), 7.80 (d, J = 8.45 Hz, 2H), 7.84 (dd, J = 8.58 Hz, 2H), 8.59 (dd, J = 4.5 Hz, 4H), 8.66 (s, 2H) ppm; It was not possible to obtain the ^{13}C NMR spectrum to make assignments due to the low solubility of **KOY-1** in the solvent; ^{11}B NMR (160 MHz, Acetonitrile- d_3): δ = 1.14, 1.34, 1.54 ppm; HRMS (APCI): m/z (%): $[\text{M}+\text{H}^+]$ calcd for $\text{C}_{49}\text{H}_{38}\text{N}_5\text{BF}_2\text{S}_2$, 808.25460; found 808.25336.

9-(4-(5,5-Difluoro-1,3,7,9-tetramethyl-5H-4/4,5/4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)phenyl)-3,6-bis(5-(pyridin-4-yl)thiophen-2-yl)-9H-carbazole-boron trifluoride complex (KOY-1-BF₃)

A solution of **KOY-1** (36 mg, 0.045 mmol) in chloroform (200 mL) under a nitrogen atmosphere was added dropwise 47% $\text{BF}_3\text{-Et}_2\text{O}$ (13 μL , 0.104 mmol) diluted with chloroform (0.5 mL) for 5 min, and then the solution was stirred for 3 hour at room temperature. The resulting precipitate was filtered by membrane and was washed by chloroform to give **KOY-1-BF₃** (28 mg, 67% yield) as a red solid; m.p. over 300°C; FT-IR (ATR): $\tilde{\nu}$ = 3144, 2920, 2851, 1627, 1423, 1045, 790 cm^{-1} ; ^1H NMR (500 MHz, Acetonitrile- d_3): δ = 1.64 (s, 6H), 2.54 (s, 6H), 6.19 (s, 2H) 7.52 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 8.45, 2H), 7.74 (d, J = 4.1 Hz, 2H), 7.81 (d, J = 8.45 Hz, 2H), 7.92 (d, J = 7.45 Hz, 2H), 8.08 (d, J = 4.05 Hz, 2H), 8.12 (d, J = 7.05 Hz, 4H), 8.53 (d, J = 7.0 Hz, 4H), 8.76 (s, 2H) ppm; It was not possible to obtain the ^{13}C NMR spectrum to make assignments due to the low solubility of **KOY-1-BF₃** in the solvent; ^{11}B NMR (160 MHz, Acetonitrile- d_3): δ = -0.61, 1.07, 1.27, 1.48 ppm; HRMS (ESI): m/z (%): $[\text{M}^+]$ calcd for $\text{C}_{49}\text{H}_{36}\text{N}_5\text{B}_3\text{F}_8\text{S}_2$ 994.26363 ; found $[\text{KOY-1}+2\text{H}]^{2+}$ $\text{C}_{49}\text{H}_{38}\text{N}_5\text{BF}_2\text{S}_2$ 404.63129.

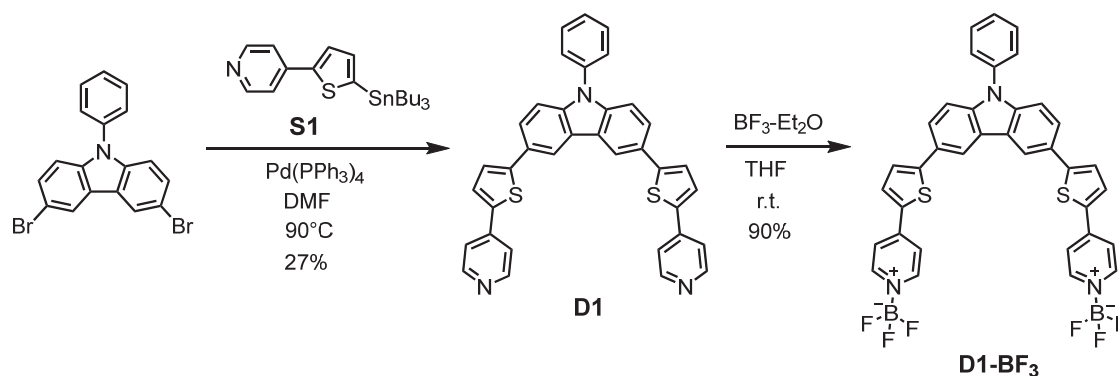
9-Phenyl-3,6-bis(5-(pyridin-4-yl)thiophen-2-yl)-9H-carbazole (D1)

A solution of 3,6-dibromo-9-phenylcarbazole (0.7 g, 1.75 mmol), **S1** (1.713 g, 3.8 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.1 g, 0.09

mmol) in DMF (70 mL) was refluxed for 3 hours at 90°C under a nitrogen atmosphere. The reaction was stopped by adding the reaction mixture to ethyl acetate (200 mL). Then, The resulting precipitate was vacuum filtered and washed with ethyl acetate to give **D1** (0.266 g, 27% yield) as a white solid; m.p. 262-263 °C; FT-IR (ATR): $\tilde{\nu}$ = 3069, 3036, 1587, 799 cm^{-1} ; ^1H NMR (500 MHz, CD_2Cl_2) δ = 7.46-7.48 (m, 4H), 7.55(dd, J = 4.53, 4H), 7.74-7.57 (t, 1H), 7.76 (d, J = 8.85 Hz, 2H), 7.62 (d, J = 7.05 Hz, 2H), 7.68 (t, J = 7.75 Hz, 2H), 7.78 (dd, J = 8.55 Hz, 2H), 8.50 (s, 2H), 8.60 (d, J = 4.55 Hz, 4H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 113.03, 118.14, 119.67, 123.97, 124.09, 125.12, 126.80, 127.00, 127.30, 128.39, 130.50, 137.36, 139.56, 141.56, 141.69, 147.47, 150.82 ppm; HRMS (APCI): m/z (%): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{36}\text{H}_{24}\text{N}_3\text{S}_2$, 562.14062; found 562.14117.

9-Phenyl-3,6-bis(5-(pyridin-4-yl)thiophen-2-yl)-9H-carbazole-boron trifluoride complex (**D1-BF₃**)

A solution of **D1** (100 mg, 0.175 mmol) in THF (200 ml) under a nitrogen atmosphere was added dropwise 47% $\text{BF}_3\text{-Et}_2\text{O}$ (120 μL , 0.96 mmol) diluted with THF (2 ml) for 10 min, and then the solution was stirred for 3 hour at room temperature. The resulting precipitate was filtered and was washed by THF to give **D1-BF₃** (111 mg, 90% yield) as a red solid; m.p. 285–290 °C; FT-IR (ATR): $\tilde{\nu}$ = 3267, 3153, 3095, 1628, 1421, 1024, 791 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ = 7.42 (d, J = 8.6 Hz, 2H), 7.58-7.62(t, 1H), 7.61 (d, J = 7.64 Hz, 2H), 7.66 (d, J = 4.04 Hz, 2H), 7.71 (t, J = 7.64 Hz, 1H), 7.78 (dd, J = 8.64 Hz, 2H), 8.02 (d, J = 4.04 Hz, 2H), 8.06 (d, J = 7.04 Hz, 4H), 8.49 (d, J = 7.04 Hz, 4H), 8.63 (s, J = 1.68 Hz, 2H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 111.03, 118.14, 119.67, 123.97, 124.09, 125.12, 126.80, 127.00, 127.30, 128.39, 130.50, 137,36, 139.56, 141.56, 141.69, 147.47, 150.82 ppm (one aromatic carbon signals was not observed owing to overlapping resonances); ^{11}B NMR (160 MHz, Acetonitrile- d_3): δ = -0.64 ppm; HRMS (ESI): m/z (%): $[\text{M}+2\text{H}]^{2+}$ calcd for $\text{C}_{36}\text{H}_{25}\text{N}_3\text{S}_2$, 281.57395; found 281.57223.



Scheme S1 Synthesis of **D1** and **D1-BF₃**.

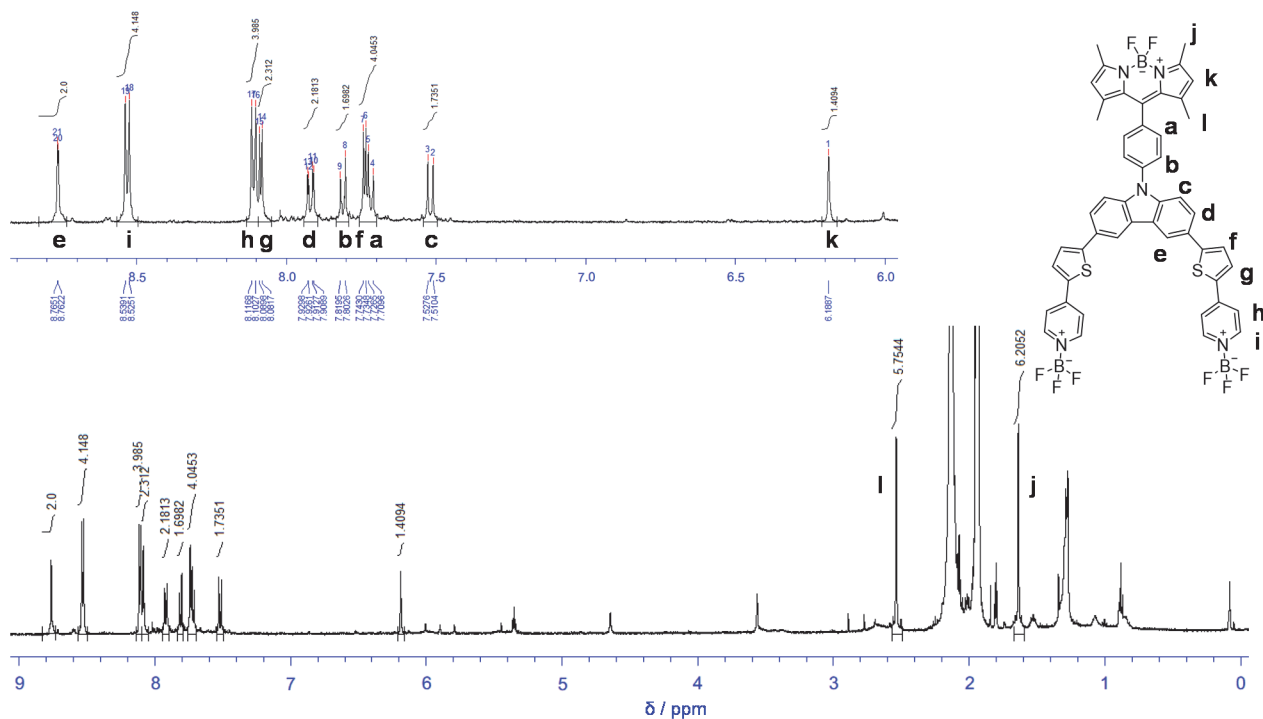
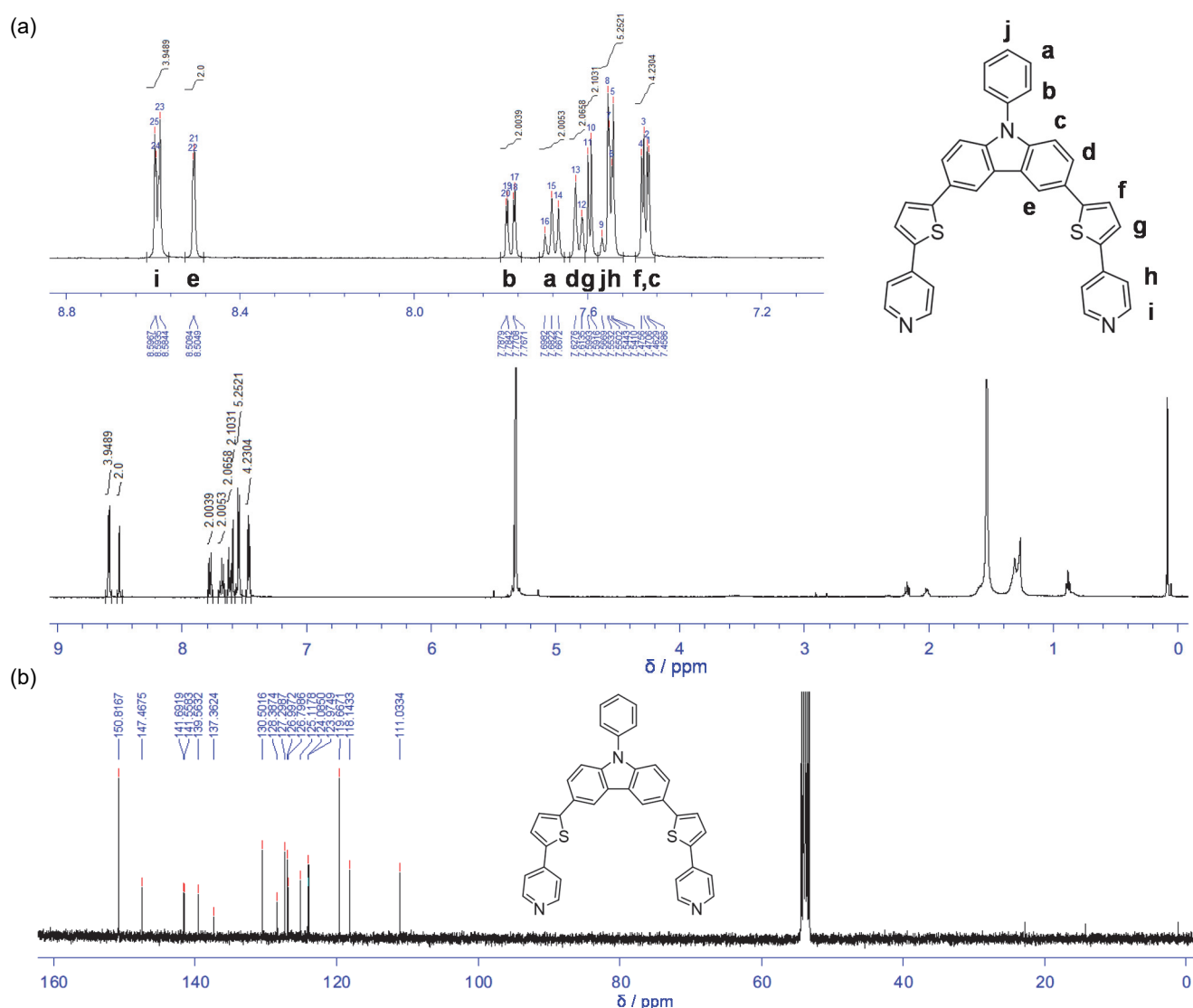


Fig. S5 ^1H NMR (500 MHz) spectrum of **KOY-1-BF₃** in acetonitrile- d_3 .



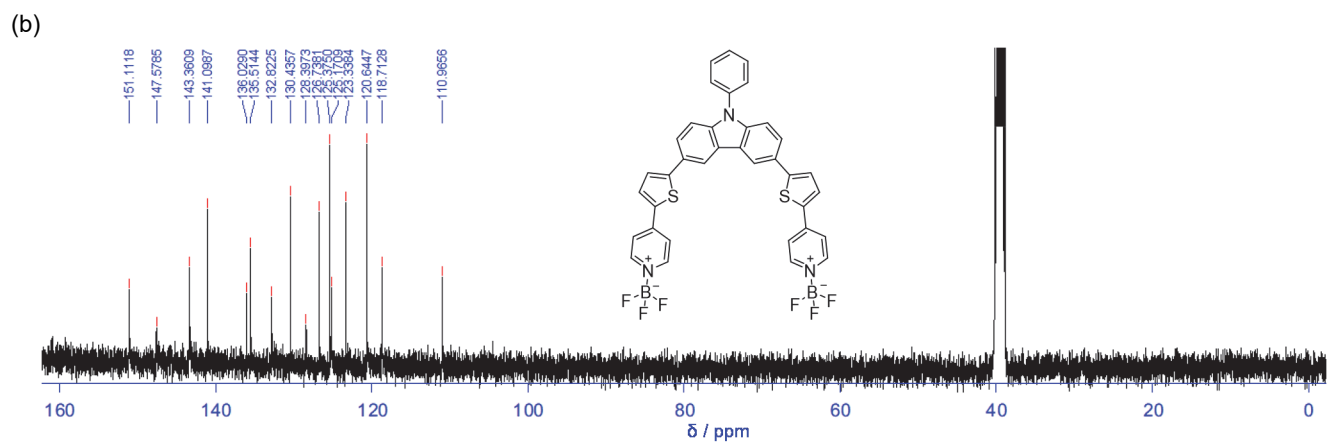
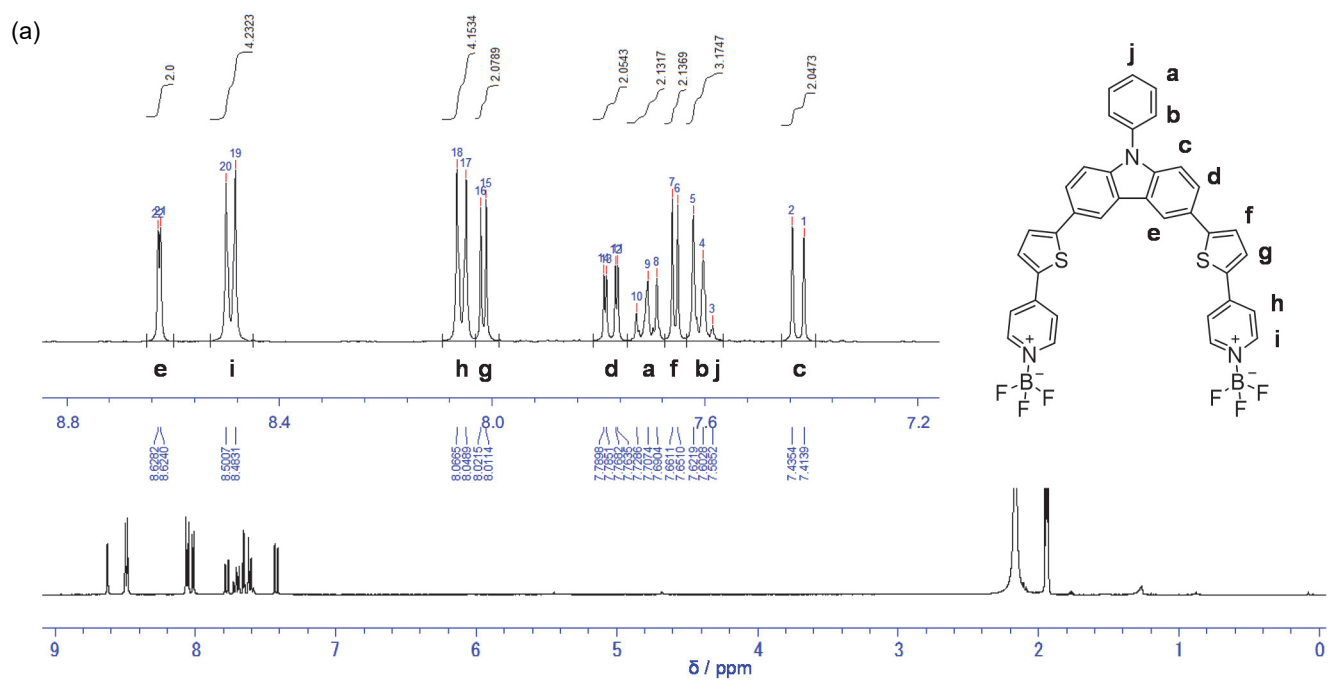


Fig. S7 (a) ¹H NMR (400 MHz) spectrum of **D1-BF₃** in acetonitrile-*d*₃. (b) ¹³C NMR (100 MHz) spectrum of **D1-BF₃** in DMSO.

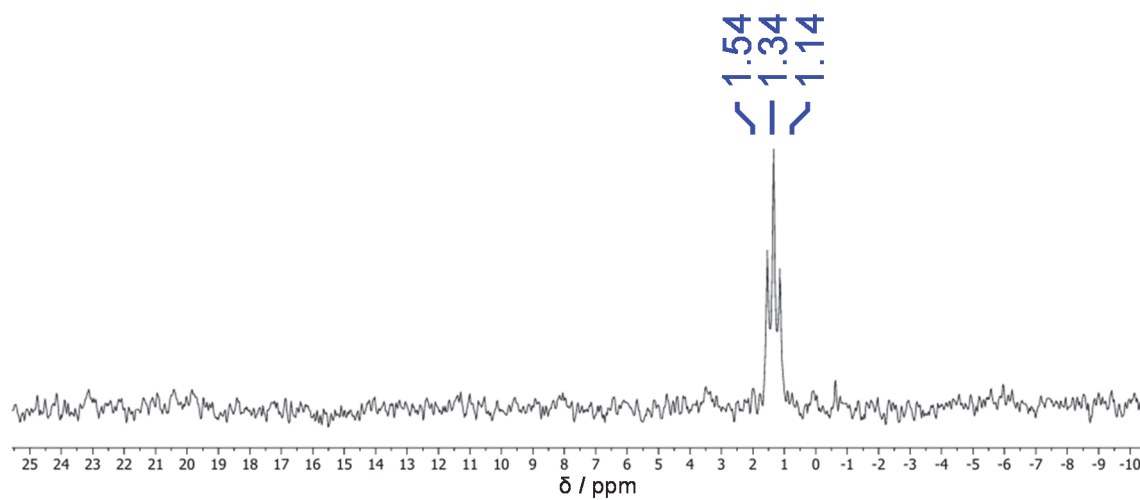


Fig. S8 ¹¹B NMR (160 MHz) spectrum of **KOY-1** in acetonitrile-*d*₆.

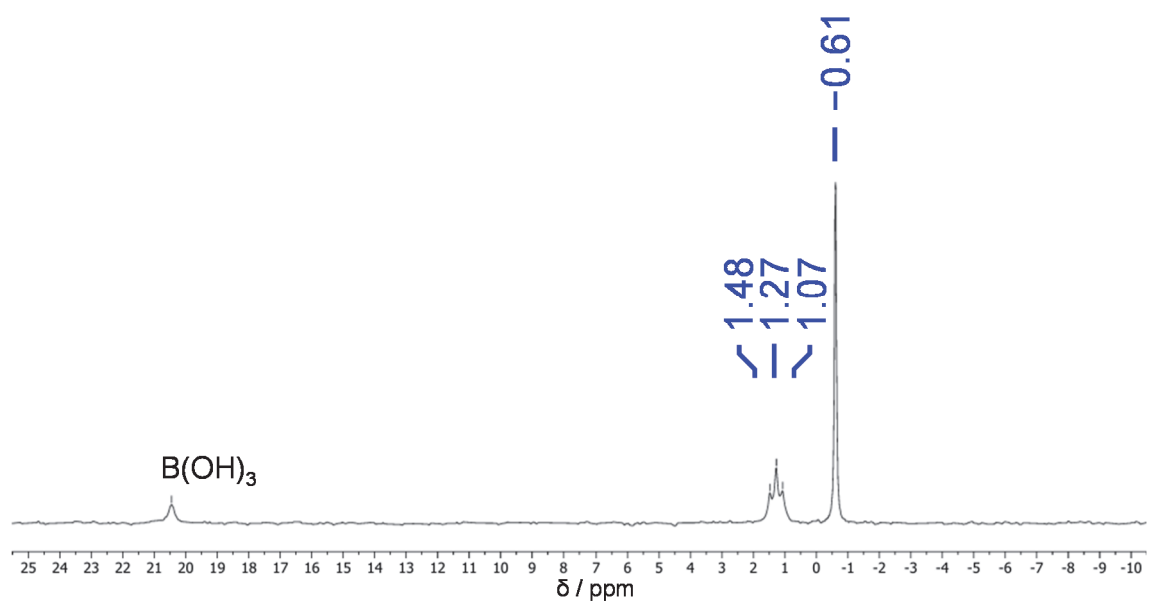


Fig. S9 ¹¹B NMR (160 MHz) spectrum of **KOY-1-BF₃** in Acetonitrile-*d*₆.

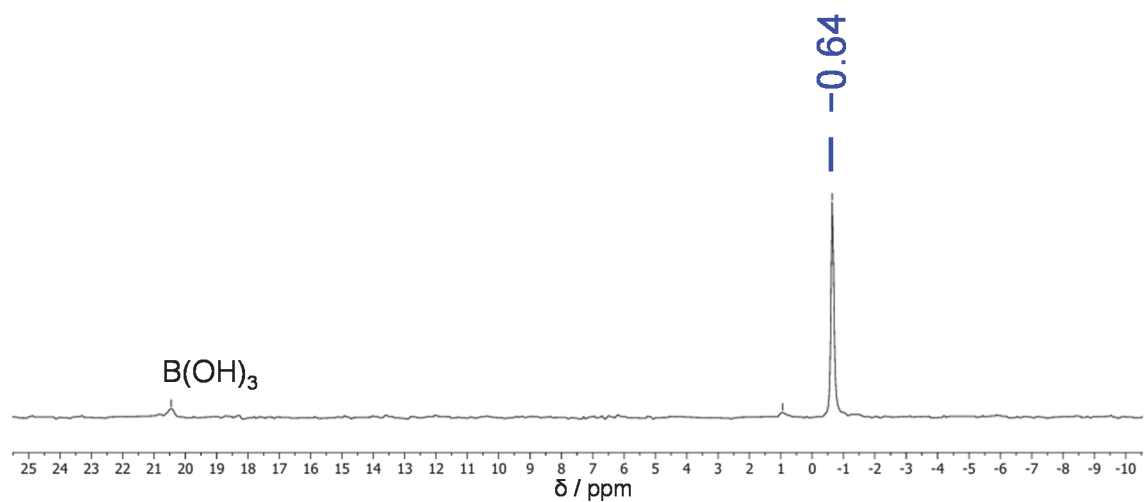


Fig. S10 ¹¹B NMR (160 MHz) spectrum of **D1-BF₃** in Acetonitrile-*d*₆.

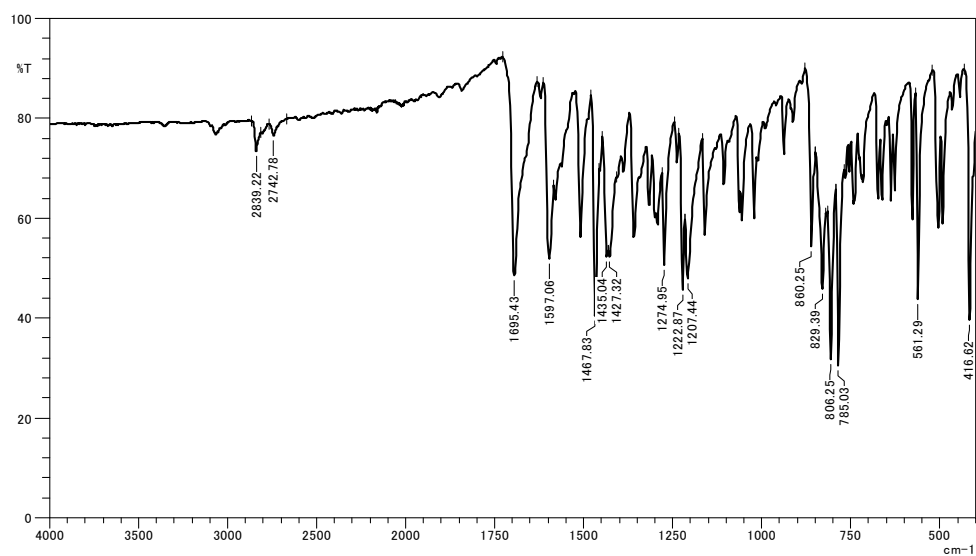


Fig. S11 FTIR (ATR) spectrum of **2**.

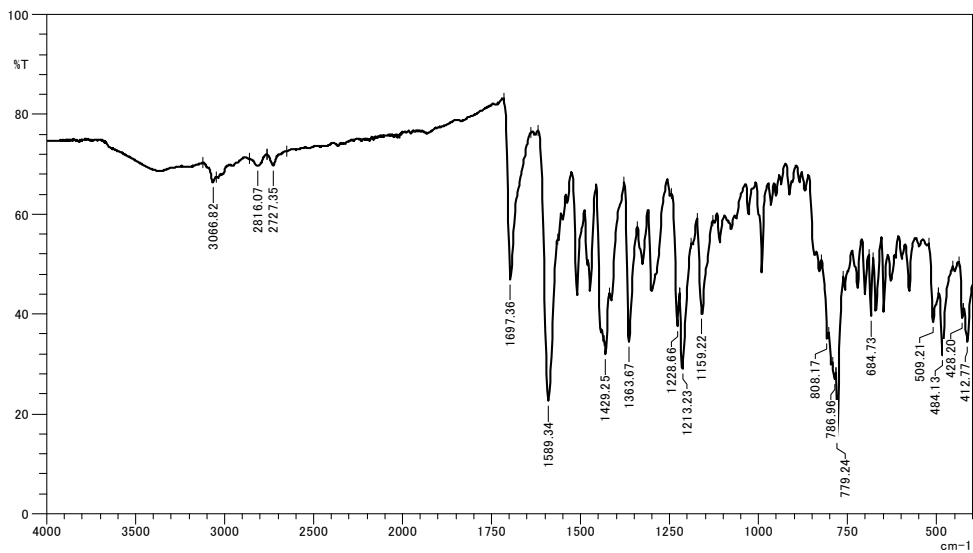


Fig. S12 FTIR (ATR) spectrum of **3**.

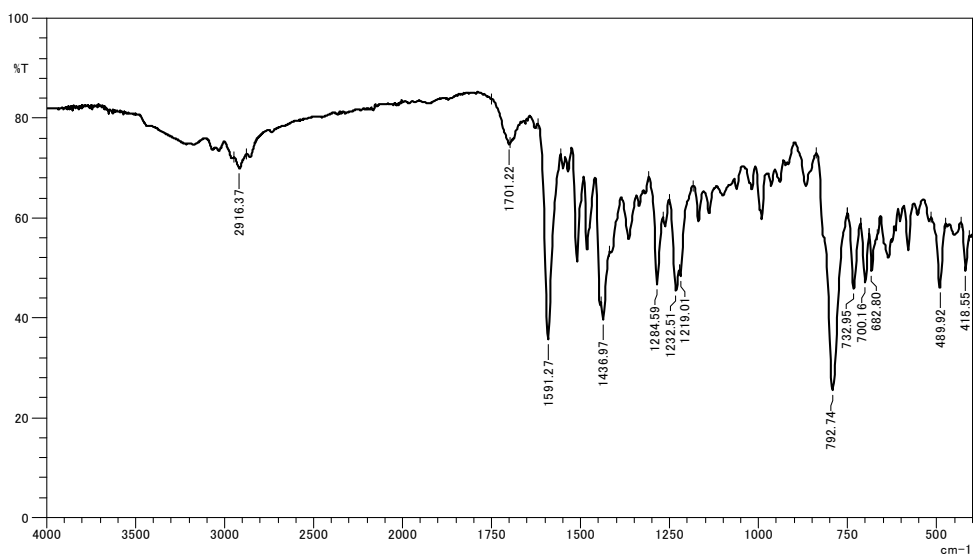


Fig. S13 FTIR (ATR) spectrum of **4**.

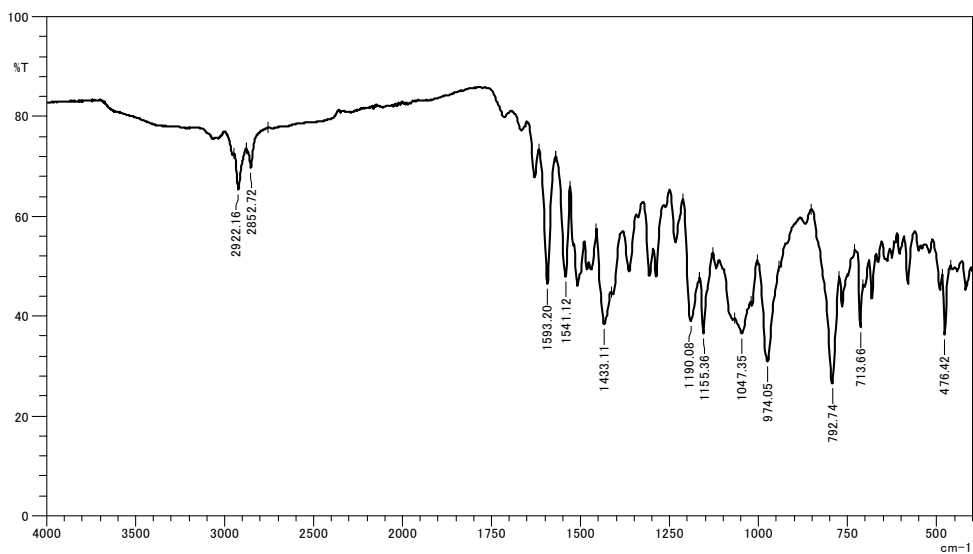


Fig. S14 FTIR (ATR) spectrum of **KOY-1**.

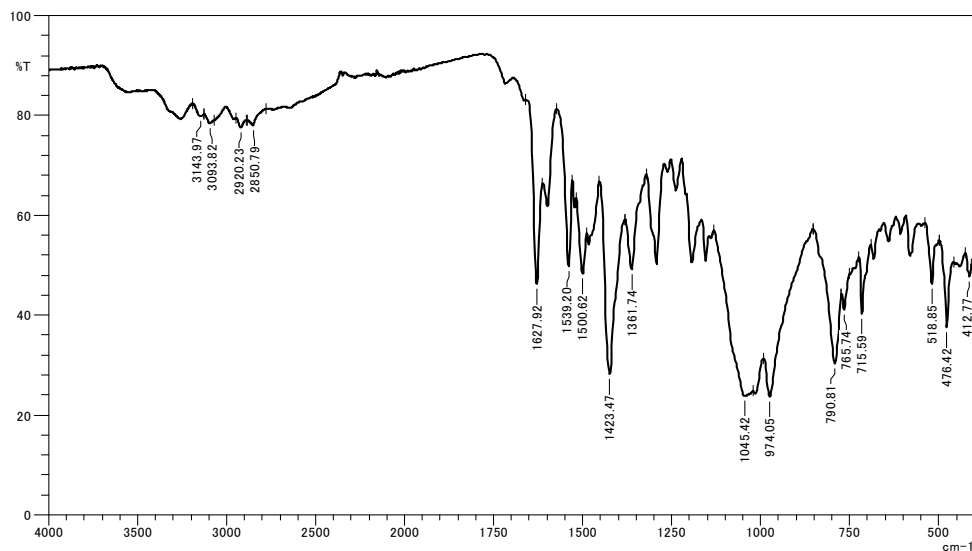


Fig. S15 FTIR (ATR) spectrum of KOY-1-BF₃.

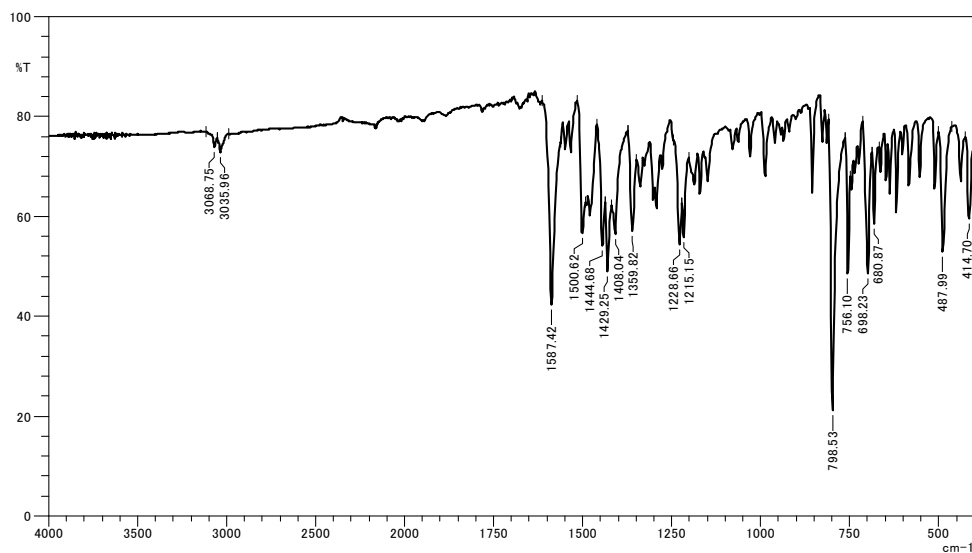


Fig. S16 FTIR (ATR) spectrum of D1.

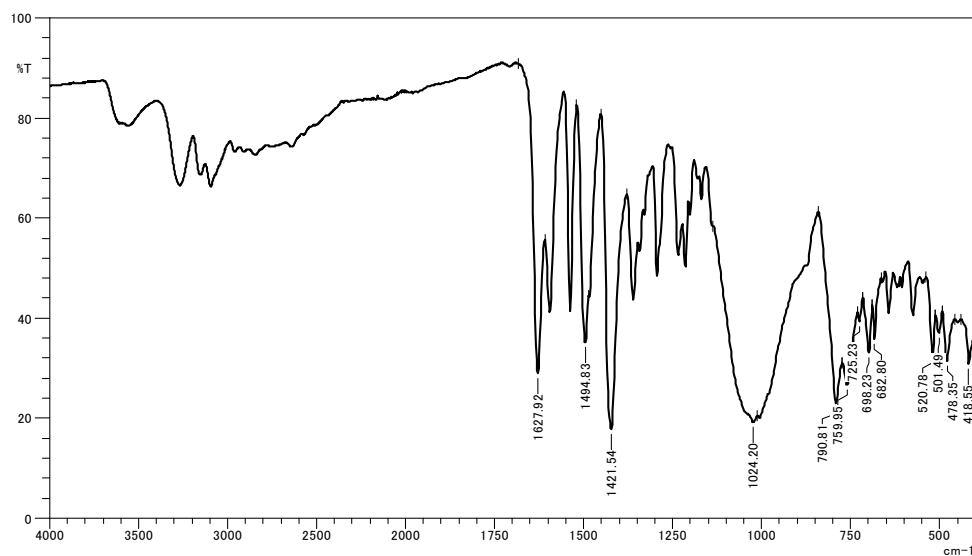


Fig. S17 FTIR (ATR) spectrum of D1-BF₃.

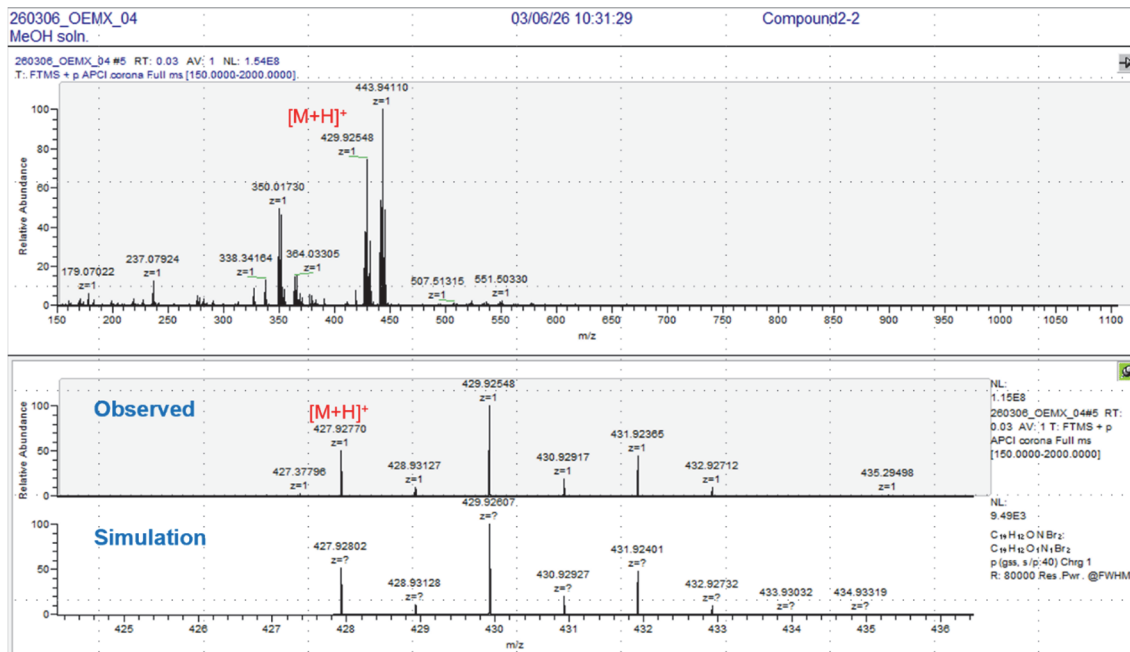


Fig. S18 HRMS spectrum of 2.

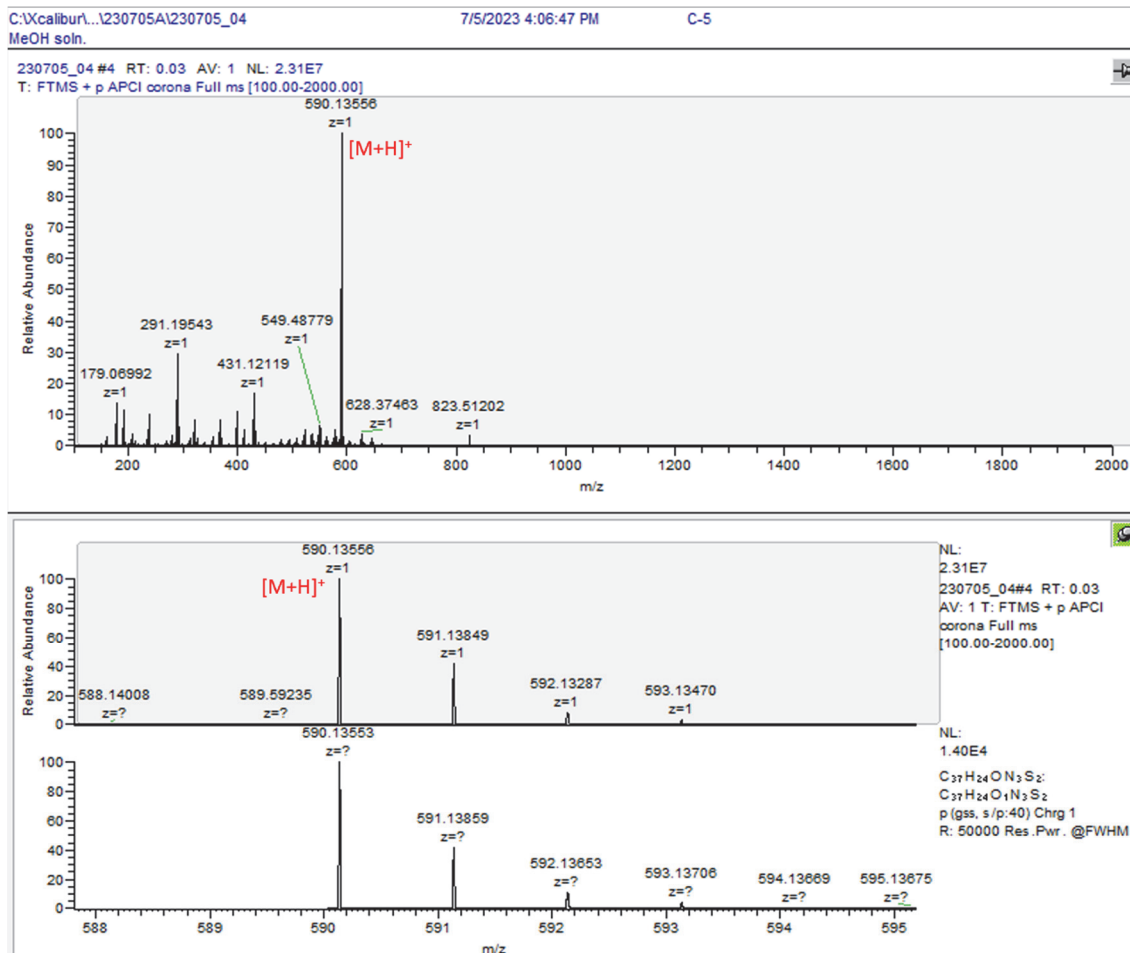


Fig. S19 HRMS spectrum of 3.

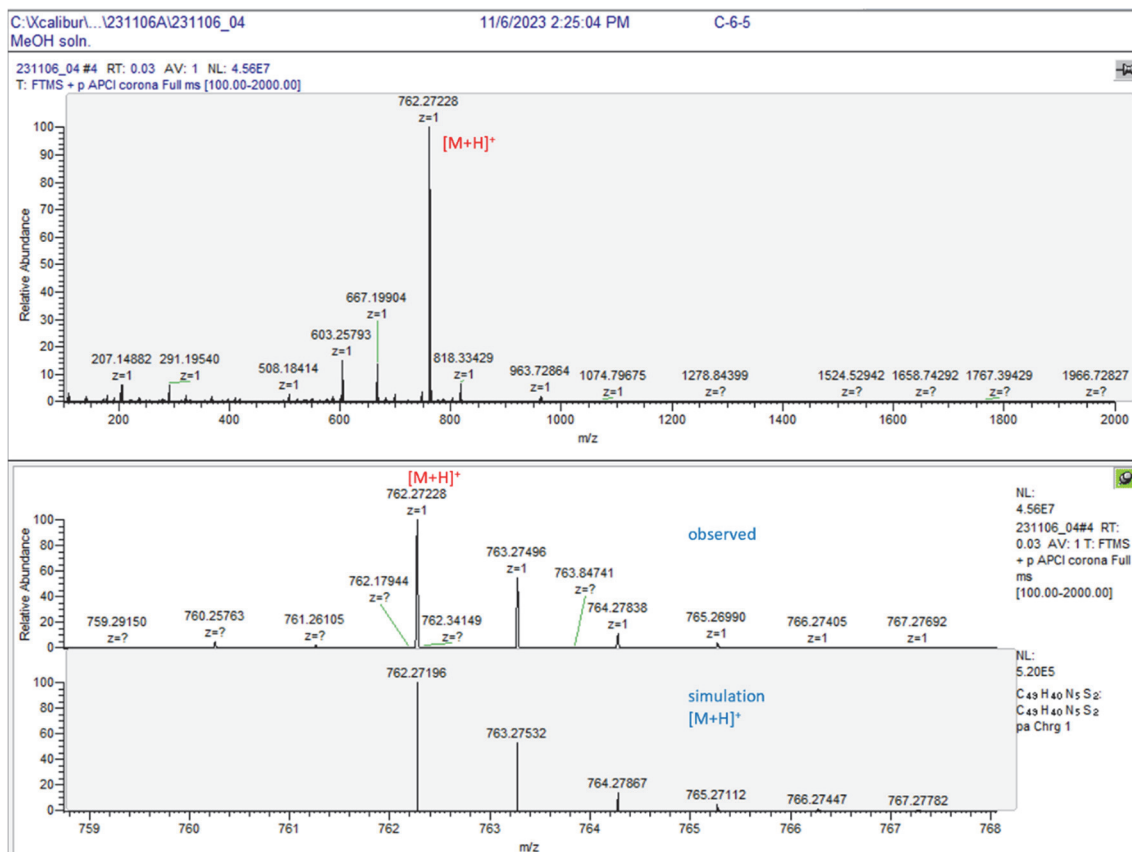


Fig. S20 HRMS spectrum of 4.

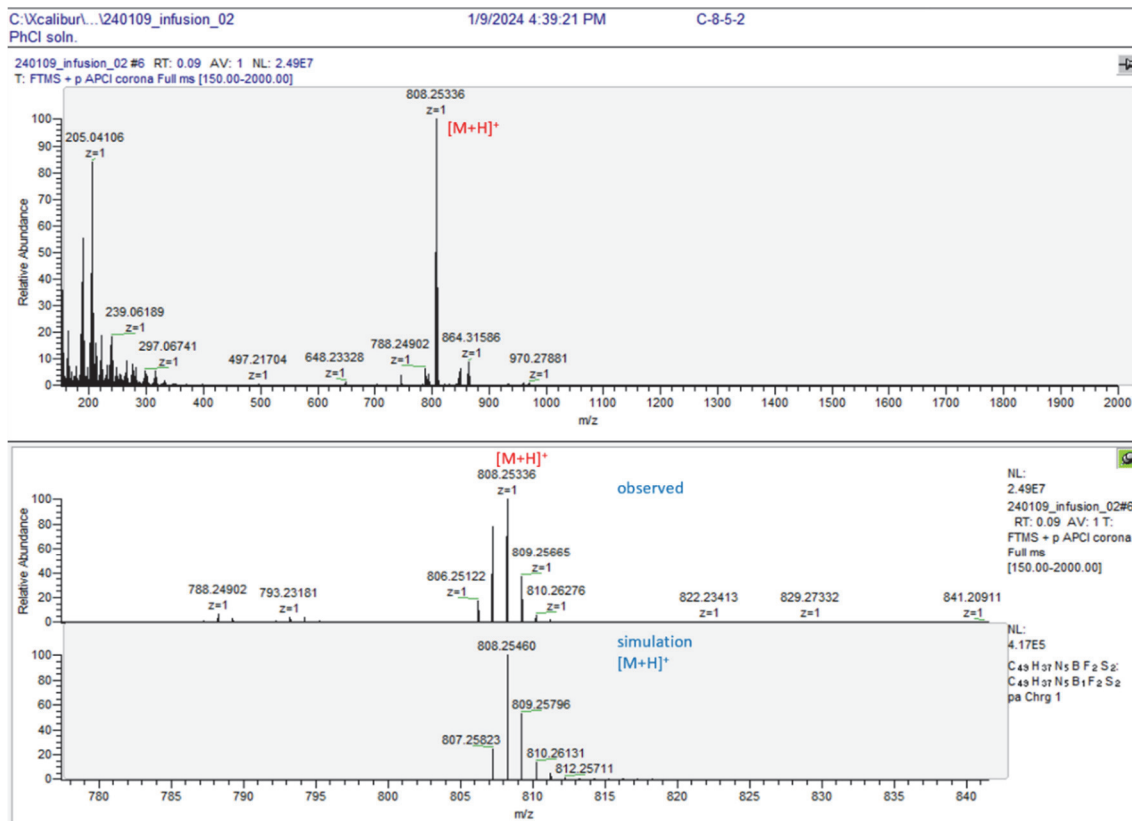


Fig. S21 HRMS spectrum of KOY-1.

240510_infusion_04#23 RT: 0.41 AV: 1 NL: 2.75E7
T: FTMS + p ESI Full ms [150.00-2000.00]

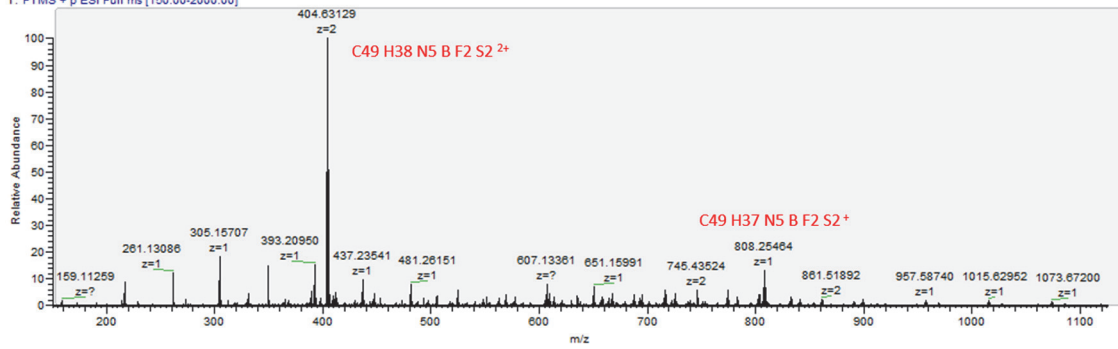


Fig. S22 HRMS spectrum of KOY-1-BF₃.

240608_27#4 RT: 0.04 AV: 1 NL: 1.89E8
T: FTMS + p APCI corona Full ms [100.00-2000.00]

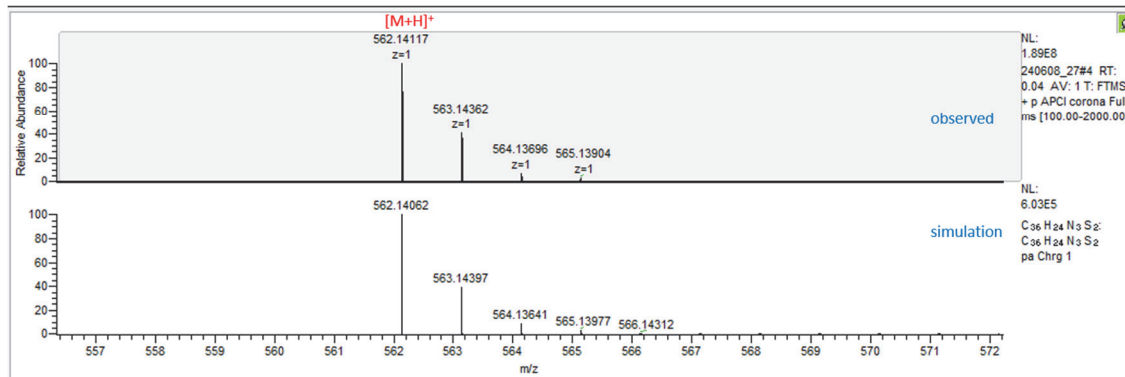
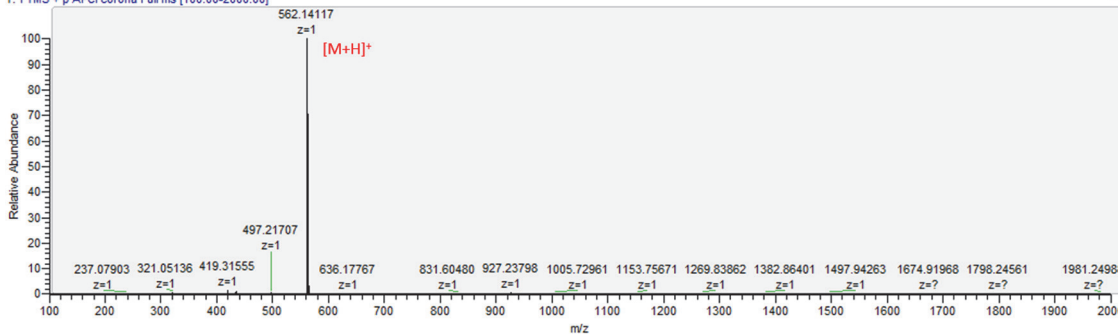


Fig. S23 HRMS spectrum of D1.

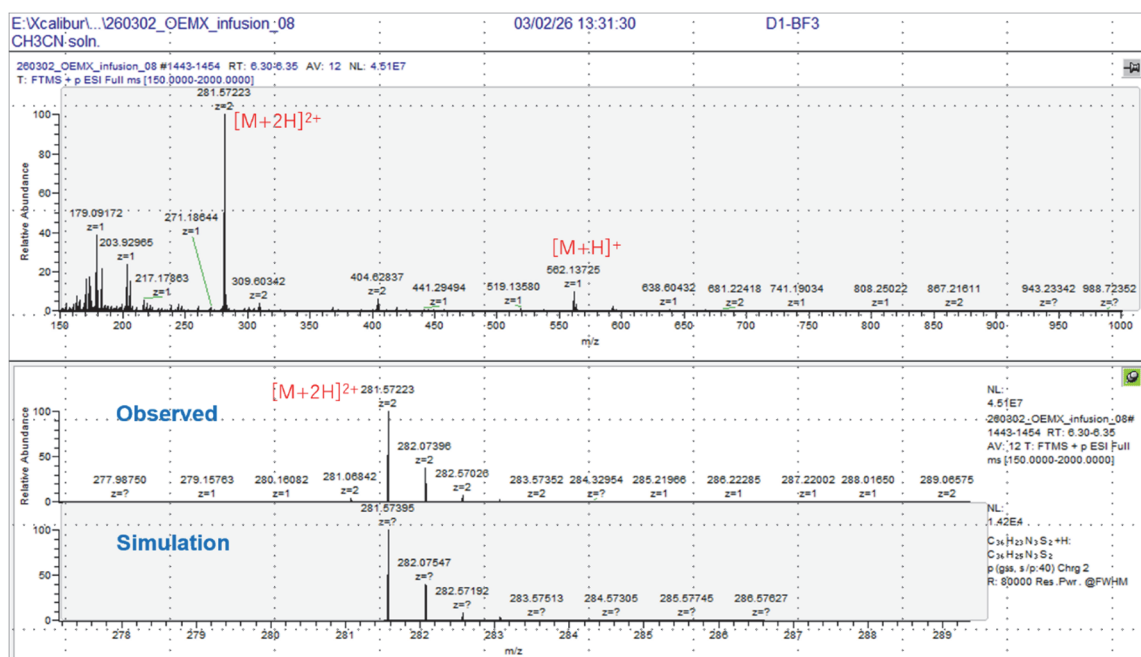


Fig. S24 HRMS spectrum of **D1-BF₃**.

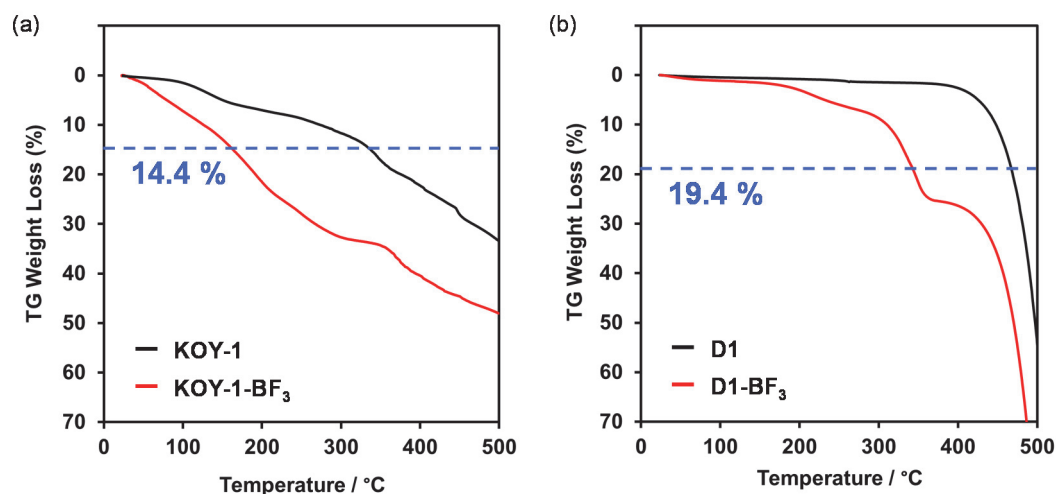


Fig. S25 (a) TG curves for **KOY-1** and **KOY-1-BF₃** at a heating rate 5 °C min⁻¹. Calculated weight loss for the release of two BF₃ units and BODIPY skeleton from **KOY-1-BF₃** to form **KOY-1** is 14.4 %. (b) TG curves for **D1** and **D1-BF₃** at a heating rate 5 °C min⁻¹. Calculated weight loss for the release of two BF₃ units from **D1-BF₃** to form **D1** is 19.4 %.

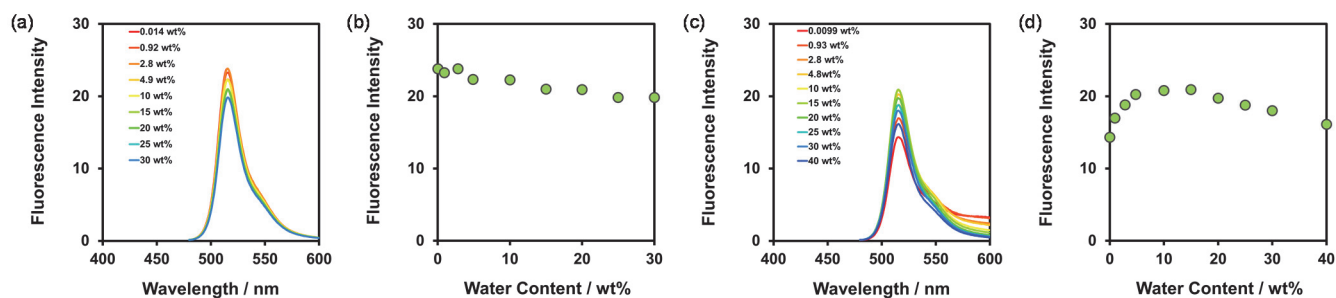


Fig. S26 (a) Fluorescence ($\lambda^{\text{ex}} = 470 \text{ nm}$) spectra of **KOY-1** ($c = 2.0 \times 10^{-5} \text{ M}$) in acetonitrile (0.014–30 wt%). (b) Fluorescence peak intensity at 515 nm of **KOY-1** ($\lambda^{\text{ex}} = 470 \text{ nm}$) as a function of water content (0.014–40 wt%) in acetonitrile. (c) Fluorescence ($\lambda^{\text{ex}} = 470 \text{ nm}$) spectra of **KOY-1-BF₃** ($c = 2.0 \times 10^{-5} \text{ M}$) in acetonitrile (0.014–40 wt%). (d) Fluorescence peak intensity at 515 nm of **KOY-1-BF₃** ($\lambda^{\text{ex}} = 470 \text{ nm}$) as a function of water content (0.0099–40 wt%) in acetonitrile.

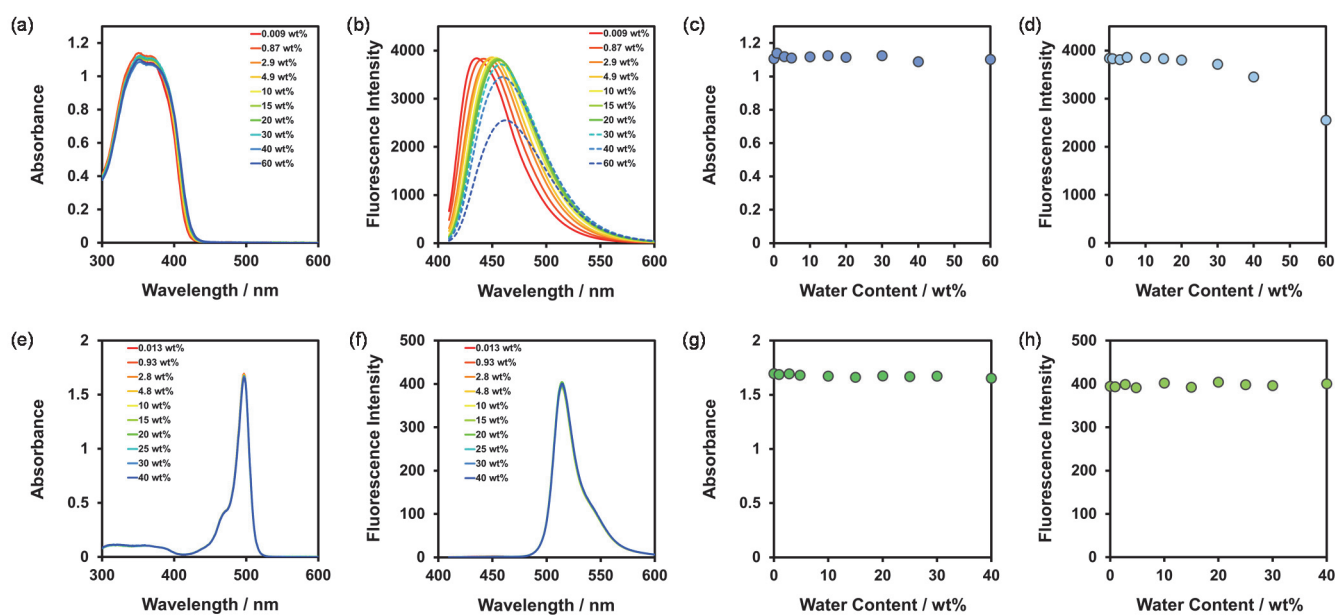


Fig. S27 (a) Photoabsorption and (b) fluorescence spectra ($\lambda^{\text{ex}} = 400 \text{ nm}$) of **D1** ($c = 2.0 \times 10^{-5} \text{ M}$) in THF containing water (0.009–60 wt%). (c) Absorbance at 352 nm of **D1** as a function of water content (0.009–60 wt%) in THF. (d) Fluorescence peak intensity at about 440 nm of **D1** ($\lambda^{\text{ex}} = 400 \text{ nm}$) as a function of water content (0.009–60 wt%) in THF. (e) Photoabsorption and (f) fluorescence spectra ($\lambda^{\text{ex}} = 400 \text{ nm}$) of **A1** ($c = 2.0 \times 10^{-5} \text{ M}$) in acetonitrile containing water (0.013–40 wt%). (g) Absorbance at 497 nm of **A1** as a function of water content (0.013–40 wt%) in acetonitrile. (h) Fluorescence peak intensity at 515 nm of **A1** ($\lambda^{\text{ex}} = 400 \text{ nm}$) as a function of water content (0.013–40 wt%) in acetonitrile.

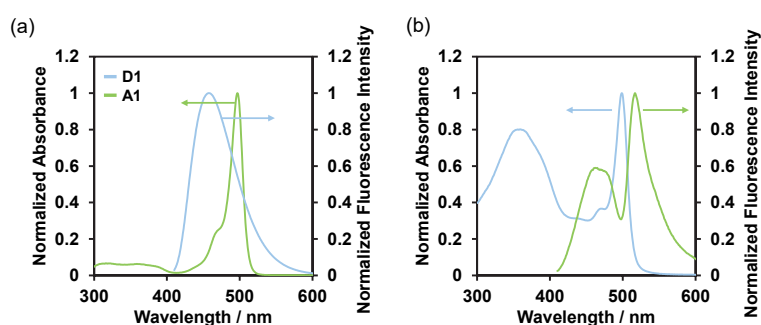


Fig. S28 (a) Photoabsorption spectrum of **A1** ($c = 2.0 \times 10^{-5} \text{ M}$) in acetonitrile and fluorescence spectrum ($\lambda^{\text{ex}} = 400 \text{ nm}$) of **D1** ($c = 2.0 \times 10^{-5} \text{ M}$) in THF. (b) Photoabsorption and fluorescence spectra ($\lambda^{\text{ex}} = 400 \text{ nm}$) of **KOY-1-BF₃** ($c = 2.0 \times 10^{-5} \text{ M}$) in acetonitrile solution containing water content of 25 wt%.

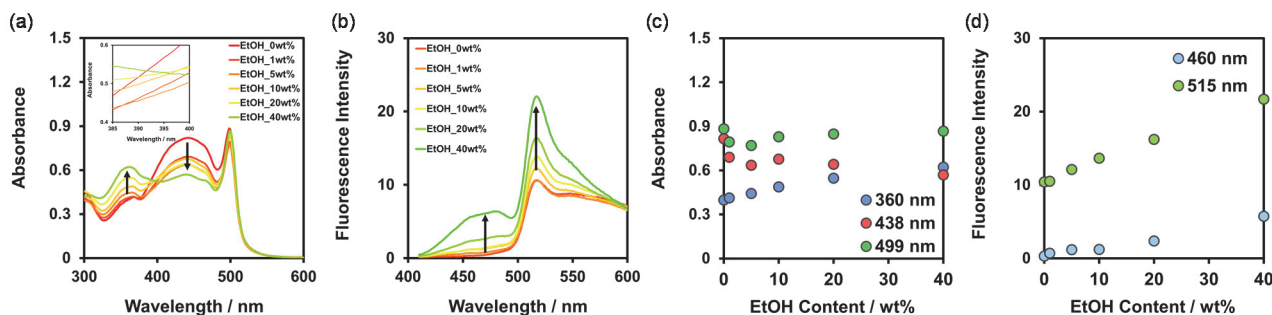


Fig. S29 (a) Photoabsorption and (b) fluorescence spectra ($\lambda^{\text{ex}} = 400 \text{ nm}$) of **KOY-1-BF₃** ($c = 2.0 \times 10^{-5} \text{ M}$) in acetonitrile containing ethanol (0–40 wt%). (c) Absorbance at 360 nm, 438 nm and 499 nm of **KOY-1-BF₃** as a function of ethanol content (0–40 wt%) in acetonitrile. (d) Fluorescence peak intensity at 460 nm and 515 nm of **KOY-1-BF₃** ($\lambda^{\text{ex}} = 400 \text{ nm}$) as a function of ethanol content (0–40 wt%) in acetonitrile.

Table S1 DL values of recently reported fluorescent sensors for water in various organic solvents

Ref.	Solvent	DL	Mechanism
22	THF	0.75 vol%	ICT
	DMSO	0.50 vol%	
24	THF	0.060 vol%	ESIPT
	Acetonitrile	0.026 wt%	
43	THF	0.018 wt%	PET
	Acetonitrile	0.020 wt%	
45	THF	0.058 wt%	PRET
	Acetonitrile	0.063 wt%	
35	Acetonitrile	0.25 wt%	PET/FRET
This work	Acetonitrile	7.56 wt%	ICT/FRET

^a Detection limit (DL) of sensor for water.