

Supplementary Information

Development of highly-sensitive fluorescence PET (photo-induced electron transfer) sensor for water: anthracene-boronic acid ester

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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 SHIMADZU IRAffinity-1 FT-IR spectrometer by ATR method. Absorption spectra were observed with a Shimadzu UV-2910 spectrophotometer. Fluorescence spectra were measured with a Hitachi F-4500 spectrophotometer. ¹H NMR spectra were recorded on a Varian-400 (400 MHz) FT NMR spectrometer. High-resolution mass spectral data by ESI were acquired on a Thermo Fisher Scientific LTQ Orbitrap XL. Elemental analyses were measured with a Perkin-Elmer 2400 II CHN analyzer. Column chromatography was performed on silica gel (KANTO CHEMICAL, 60N, spherical, neutral). The addition of water to organic solvents containing OF-1 or OF-2 was made by weight percent (wt%). The determination of water in 1,4-dioxane, THF, acetonitrile and ethanol solution 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 water) for below 1.0 wt% and volumetric titration for above 1.0 wt%, respectively.

Preparation of 1-(anthracen-9-yl)-N-(2-bromo-5-methoxybenzyl)-N-methylmethanamine (1)

A solution of 9-(methylaminomethyl)anthracene (1.00 g, 4.5 mmol), 1-bromo-2-(bromomethyl)-4-methoxybenzene (3.8 g, 13.7 mmol), Na₂CO₃ (1.9 g, 17.9 mmol) and DMF (60 ml) was stirred for 24 h at room temperature under an argon atmosphere. The water was added to the reaction mixture and the aqueous layer was extracted with dichloromethane. After concentrating under reduced pressure, the residue was chromatographed on silica gel (dichloromethane–hexane = 1 : 3) to give **1** (1.7 g, yield 90 %) as a yellow solid. m.p. 116–119 °C; IR (ATR): $\tilde{\nu}$ = 1595, 1260, 1053 cm⁻¹; ¹H NMR (400

MHz, acetone- d_6) δ = 2.28 (s, 3H), 3.68 (s, 3H), 3.77 (s, 2H), 4.66 (s, 2H), 6.73 (dd, J = 3.2 and 8.7 Hz, 1H), 7.05 (d, J = 3.2 Hz, 1H), 7.40 (d, J = 8.7 Hz, 1H), 7.48–7.52 (m, 2H), 7.54–7.58 (m, 2H), 8.07 (d, J = 8.3 Hz, 2H), 8.54 (s, 1H), 8.63 (d, J = 8.1 Hz, 2H) ppm; HRMS (ESI): m/z calcd for $C_{24}H_{23}NOBr$ [$M+H^+$] 420.09575, found 420.09546.

Preparation of 1-(anthracen-9-yl)-*N*-(5-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-*N*-methylmethanamine (OF-1)

A solution of **1** (1.0 g, 2.4 mmol), bis(pinacolato)diboron (0.61 g, 2.4 mmol), and KOAc (0.47 g, 4.8 mmol) and $PdCl_2(dppf)$ (0.06 g, 0.03 mmol) and toluene (10 ml) was stirred for 24 h at 80 °C under an argon atmosphere. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane, and washed with water. The residue was chromatographed on silica gel (dichloromethane and then ethyl acetate as eluent) to give **OF-2** (0.11 g, yield 10 %) as a yellow solid. m.p. 107–108 °C; IR (ATR): $\tilde{\nu}$ = 1603, 1346, 1130 cm^{-1} ; 1H NMR (400 MHz, acetone- d_6) δ = 1.27 (s, 12H), 2.22 (s, 3H), 3.77 (s, 3H), 3.99 (s, 2H), 4.44 (s, 2H), 6.83 (dd, J = 2.6 and 8.3 Hz, 1H), 7.07 (d, J = 2.6 Hz, 1H), 7.45–7.53 (m, 4H), 7.75 (d, J = 8.3 Hz, 1H), 8.03–8.05 (m, 2H), 8.46–8.49 (m, 3H) ppm; HRMS (APCI): m/z (%): [$M+H^+$] calcd for $C_{30}H_{35}BNO_3$, 468.27045; found 468.27066. Anal. calcd for $C_{30}H_{34}BNO_3$: C 77.09, H 7.33, N 4.00; found C 77.14, H 7.52, N 2.98.

Preparation of 3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzotrile (2)

A solution of 4-bromo-3-methylbenzotrile (2.0 g, 10.2 mmol), bis(pinacolato)diboron (2.58 g, 10.2 mmol), and KOAc (2.0 g, 20.4 mmol) and $PdCl_2(dppf)$ (0.24 g, 0.3 mmol) and DMF (30 ml) was stirred for 24 h at 80 °C under an argon atmosphere. The water was added to the reaction mixture and the aqueous layer was extracted with dichloromethane. After concentrating under reduced pressure, the residue was chromatographed on silica gel (dichloromethane as eluent) to give **2** (1.85 g, yield 75 %) as a white solid. m.p. 135–137 °C; IR (ATR): $\tilde{\nu}$ = 2234, 1605, 1346, 1134 cm^{-1} ; 1H NMR (400 MHz, acetone- d_6) δ = 1.37 (s, 12H), 2.57 (s, 3H), 7.55–7.57 (m, 2H), 7.85 (d, J = 7.6 Hz, 1H) ppm; HRMS (APCI): m/z (%): [$M+H^+$] calcd for $C_{14}H_{19}BNO_2$, 244.15034; found 244.15030.

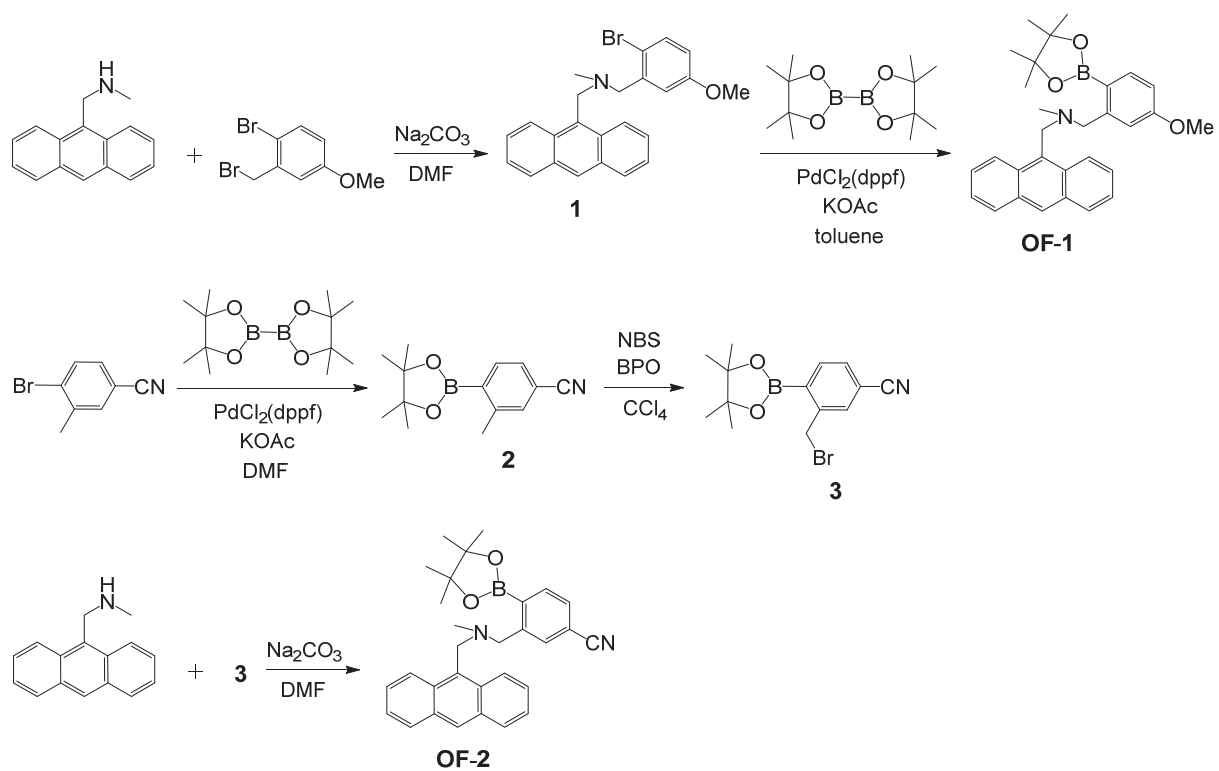
Preparation of 3-(bromomethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzotrile (3)

A solution of **2** (0.5 g, 2.1 mmol), *N*-bromosuccinimide (0.37 g, 2.1 mmol), and benzoylperoxide (0.003 g, 0.01 mmol) in CCl_4 (5 ml) was stirred for 24 h at 80 °C under an argon atmosphere. The reaction mixture was filtrated and concentrated. The resulting residue

was dissolved in ethyl acetate, and washed with 0.5 M HCl aq. and then with water. The organic extract was dried over MgSO₄, filtrated, and concentrated. The resulting residue was subjected to reprecipitation from dichloromethane–hexane to give **3** (0.34 g, yield 52 %) as a white powder. m.p. 108–110 °C; IR (ATR): $\tilde{\nu}$ = 2234, 1607, 1346, 1142 cm⁻¹; ¹H NMR (400 MHz, acetone-d₆) δ = 1.41 (s, 12H), 5.00 (s, 2H), 7.73 (dd, *J* = 1.6 and 7.7 Hz, 1H), 7.89 (d, *J* = 1.6 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 1H) ppm; HRMS (APCI): *m/z* (%):[M+H⁺] calcd for C₁₄H₁₈BNO₂Br, 322.06085; found 322.06085.

Preparation of 3-(((anthracen-9-ylmethyl)(methylamino)methyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzotrile (OF-2)

A solution of 9-(methylaminomethyl)anthracene (0.17 g, 0.62 mmol), **3** (0.2 g, 0.6 mmol), Na₂CO₃ (0.26 g, 2.5 mmol) and DMF (5 ml) was stirred for 24 h at room temperature 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 MgSO₄, filtrated, and concentrated. The residue was dissolved in toluene, and HPLC was performed to give **OF-2** (0.03 g, yield 10 %) as a yellow solid. m.p. 129–131 °C; IR (ATR): $\tilde{\nu}$ = 2228, 1605, 1342, 1136 cm⁻¹; ¹H NMR (400 MHz, acetone-d₆) δ = 1.29 (s, 12H), 2.28 (s, 3H), 4.01 (s, 2H), 4.47 (s, 2H), 7.47–7.54 (m, 4H), 7.65 (dd, *J* = 1.6 and 7.6 Hz, 1H), 7.75 (d, *J* = 1.0 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 8.04–8.06 (m, 2H), 8.39 (d, *J* = 8.8 Hz, 2H), 8.51 (s, 1H) ppm; HRMS (APCI): *m/z* calcd for C₃₀H₃₂BN₂O₂ [M+H⁺] 463.25514, found 463.25510. Anal. calcd for C₃₀H₃₁BN₂O₂: C 77.93, H 6.76, N 6.06; found C 77.67, H 6.74, N 5.92.



Scheme S1 Synthesis of fluorescence PET sensors **OF-1** and **OF-2**.

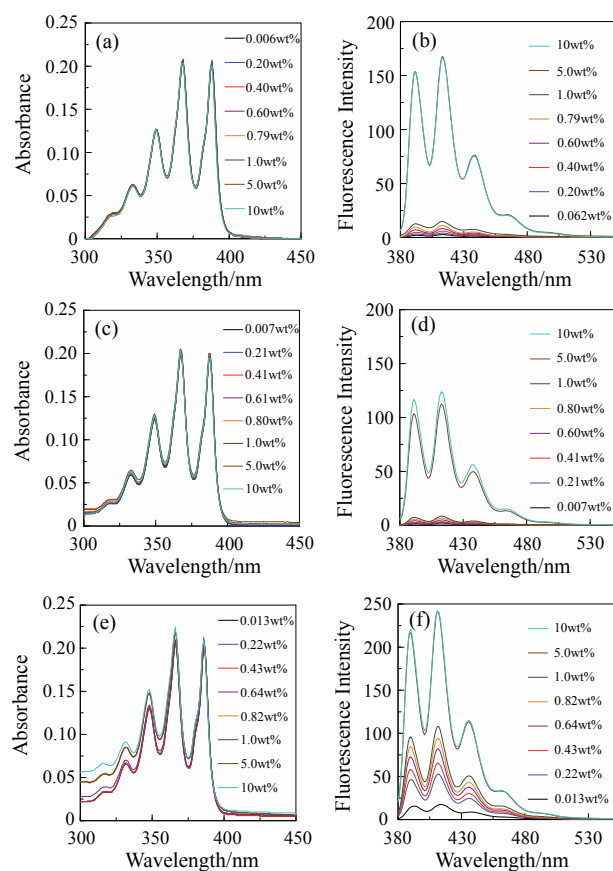


Fig. S1 (a) Absorption and (b) fluorescence spectra ($\lambda_{\text{ex}} = 366 \text{ nm}$) of **OF-1** ($c = 2.0 \times 10^{-5} \text{ M}$) in 1,4-dioxane-containing water (0.006–10 wt%). (c) Absorption and (d) fluorescence spectra ($\lambda_{\text{ex}} = 366 \text{ nm}$) of **OF-1** ($c = 2.0 \times 10^{-5} \text{ M}$) in THF-containing water (0.007–10 wt%). (e) Absorption and (f) fluorescence spectra ($\lambda_{\text{ex}} = 366 \text{ nm}$) of **OF-1** ($c = 2.0 \times 10^{-5} \text{ M}$) in ethanol-containing water (0.013–10 wt%).

For **OF-1**, the calibration equations for the determination of water in organic solvents were obtained from Fig. 2c as follows:

$$\begin{aligned} \text{1,4-Dioxane: } F &= 12.3[\text{H}_2\text{O}] + 1.6 \\ (R^2 &= 0.971, [\text{H}_2\text{O}] = 0.006\text{--}1.0 \text{ wt}\%) \end{aligned} \quad (1)$$

$$\begin{aligned} \text{THF: } F &= 6.7[\text{H}_2\text{O}] + 1.3 \\ (R^2 &= 0.951, [\text{H}_2\text{O}] = 0.007\text{--}1.0 \text{ wt}\%) \end{aligned} \quad (2)$$

$$\begin{aligned} \text{Acetonitrile: } F &= 55.9[\text{H}_2\text{O}] + 5.9 \\ (R^2 &= 0.938, [\text{H}_2\text{O}] = 0.014\text{--}1.0 \text{ wt}\%) \end{aligned} \quad (3)$$

$$\begin{aligned} \text{Ethanol: } F &= 86.4[\text{H}_2\text{O}] + 24.7 \\ (R^2 &= 0.964, [\text{H}_2\text{O}] = 0.013\text{--}1.0 \text{ wt}\%) \end{aligned} \quad (4)$$

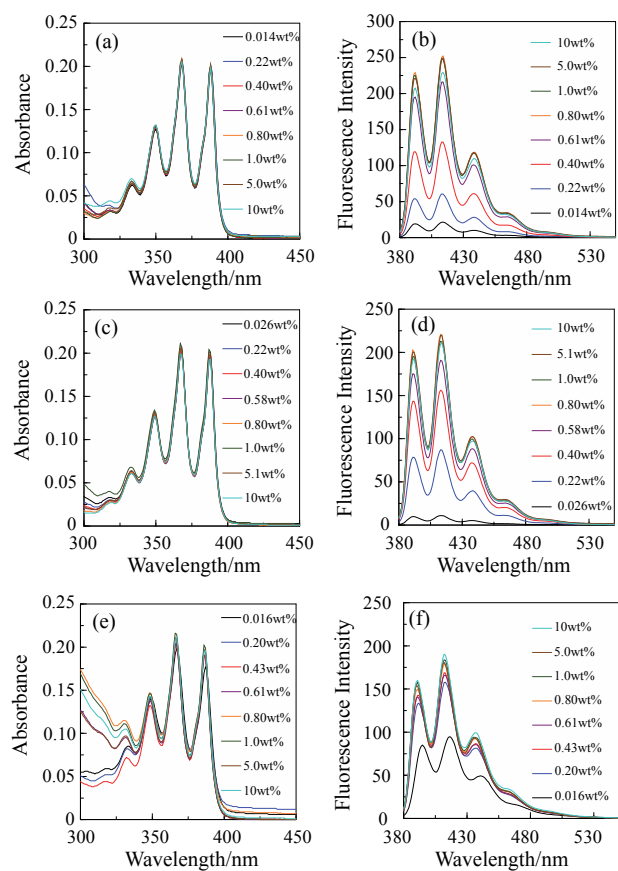


Fig. S2 (a) Absorption and (b) fluorescence spectra ($\lambda_{\text{ex}} = 366 \text{ nm}$) of **OF-2** ($c = 2.0 \times 10^{-5} \text{ M}$) in 1,4-dioxane-containing water (0.014–10 wt%). (c) Absorption and (d) fluorescence spectra ($\lambda_{\text{ex}} = 366 \text{ nm}$) of **OF-2** ($c = 2.0 \times 10^{-5} \text{ M}$) in THF-containing water (0.026–10 wt%). (e) Absorption and (f) fluorescence spectra ($\lambda_{\text{ex}} = 366 \text{ nm}$) of **OF-2** ($c = 2.0 \times 10^{-5} \text{ M}$) in ethanol-containing water (0.016–10 wt%).