

## Supplementary Information

### Highly-sensitive fluorescence PET (Photo-induced Electron Transfer) sensor for water based on anthracene-bisboronic acid ester

Yousuke Ooyama,\* Ai Matsugasako, Yuta Hagiwara, Joji Ohshita and Yutaka Harima\*

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

*Fax: +81 824 24 5494; Tel: +81 824 24 7689; E-mail:yooyama@hiroshima-u.ac.jp*

*harima@mls.ias.hiroshima-u.ac.jp*

#### Experimental Section:

**General:** IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer by ATR method. Absorption spectra were observed with a Shimadzu UV-3150 spectrophotometer and fluorescence spectra were measured with a Hitachi F-4500 spectrophotometer. High-resolution mass spectral data by ESI were acquired on a Thermo Fisher Scientific LTQ Orbitrap XL. <sup>1</sup>H NMR spectra were recorded on a Varian-500 (500 MHz) FT NMR spectrometer. Column chromatography was performed on silica gel (KANTO CHEMICAL, 60N, spherical, neutral). 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 for below 1.5 wt% and volumetric titration for above 1.5 wt%, respectively.

#### Preparation of 2,2'-(2-methyl-1,4-phenylene)bis[4,4,5,5-tetramethyl-1,3,2-dioxaborolane] (1)

A solution of 2,5-dibromotoluene (6.5 g, 24.6 mmol), bis(pinacolato)diboron (12.5g, 49.2 mmol), PdCl<sub>2</sub>(dppf) (0.20g, 0.62 mmol), and KOAc (4.8g, 48.9 mmol) in DMF (50 ml) was stirred for 24 h at 80 °C. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane, and washed with water. The residue was chromatographed on silica gel (dichloromethane–hexane = 3 : 1 as eluent) to give **1** (3.00 g, yield 35 %) as a white solid. M.p. 210–212 °C; IR (ATR):  $\tilde{\nu}$  = 2976 (m), 1312 (s), 1141 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.34 (s, 24H, CH<sub>3</sub>×8), 2.53 (s, 3H, CH<sub>3</sub>), 7.57–7.62 (m, 2H), 7.74 (d, *J* = 7.1 Hz, 1H); HRMS (ESI): *m/z* (%):[M+H<sup>+</sup>] Calcd for C<sub>19</sub>H<sub>31</sub>O<sub>4</sub>B<sub>2</sub>, 345.24030; found 345.24091.

### Preparation

of

#### **2,2'-(2-bromomethyl-1,4-phenylene)bis[4,4,5,5-tetramethyl-1,3,2-dioxaborolane] (2)**

A solution of **1** (2.7 g, 7.85 mmol), 1,3-dibromo-5,5-dimethylhydantoin (1.32 g, 4.62 mmol), and ZrCl<sub>2</sub> (0.91g, 3.91 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (80 ml) was stirred for 10 h at room temperature under ambient light. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane, and washed with water. The residue was recrystallized from *n*-hexane to give **2** (2.47 g, yield 74 %) as a white solid. M.p. 159–161 °C; IR (ATR):  $\tilde{\nu}$  = 2976 (m), 1324 (s), 1139 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.35 (s, 12H, CH<sub>3</sub>×4), 1.37 (s, 12H, CH<sub>3</sub>×4), 4.91 (s, 2H, CH<sub>2</sub>), 7.70 (dd, *J* = 1.2 and 7.3 Hz, 1H), 7.78–7.83 (m, 2H); HRMS (ESI): *m/z* (%):[M+Na<sup>+</sup>] Calcd for C<sub>19</sub>H<sub>29</sub>O<sub>4</sub>B<sub>2</sub>BrNa, 445.13275; found 445.13260.

### Preparation

of

#### **9-[[N-Methyl-N-(2,5-bis--(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-benzyl)amino]methyl]-anthracene (OM-2)**

A solution of 9-(methylaminomethyl)anthracene (0.48 g, 2.17 mmol) in acetonitrile (90 ml) was treated with sodium hydride (60%, 0.22 g, 5.5 mmol) and stirred for 1 h at room temperature. Compound **2** (2.3 g, 5.43 mmol) was added dropwise over 30 min and the solution was stirred at room temperature for 1 h. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane, and washed with water. The residue was chromatographed on silica gel (dichloromethane–methanol = 10 : 1 as eluent) to give a crude solid, which was then recrystallized from *n*-hexane to give **OM-2** (0.8 g, yield 65 %) as a light yellow solid. M.p. 106–108 °C; IR (ATR):  $\tilde{\nu}$  = 2976 (m), 1336 (s), 1139 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.23 (s, 12H, CH<sub>3</sub>×4), 1.35 (s, 12H, CH<sub>3</sub>×4), 2.19 (s, 3H, CH<sub>3</sub>), 4.00 (s, 2H, CH<sub>2</sub>), 4.30 (s, 2H, CH<sub>2</sub>), 7.39–7.48 (m, 4H), 7.77 (d, *J* = 7.3 Hz, 1H), 7.86–7.89 (m, 2H), 7.91–7.95 (m, 2H), 8.21–8.24 (m, 2H), 8.34 (s, 1H); HRMS (ESI): *m/z* (%):[M+H<sup>+</sup>] Calcd for C<sub>35</sub>H<sub>44</sub>O<sub>4</sub>NB<sub>2</sub>, 564.34510; found 564.34497. Anal. calcd for C<sub>35</sub>H<sub>43</sub>O<sub>4</sub>NB<sub>2</sub>: C 74.62, H 7.69, N 2.49; found C 74.49, H 7.83, N 2.46.