

Supplementary Information

Fluorescence PET (Photo-induced Electron Transfer) sensor for water based on anthracene-boronic acid ester

Yousuke Ooyama, Ai Matsugasako, Kazuyuki Oka, Tomoya Nagano, Minako Sumomogi, Kenji Komaguchi, Ichiro Imae, 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 6534; E-mail: harima@mls.ias.hiroshima-u.ac.jp

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. 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 APPI were acquired on a Thermo Fisher Scientific LTQ Orbitrap XL. ¹H NMR spectra were recorded on a JNM-LA-400 (400 MHz) FT NMR spectrometer with tetramethylsilane as an internal standard. 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

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

A solution of 9-(methylaminomethyl)anthracene (0.19 g, 0.84 mmol) in DMF (70 ml) was treated with sodium hydride (60%, 0.08 g, 2.1 mmol) and stirred for 1 h at room temperature. 2-bromomethylphenylboronic acid pinacol ester (1.0 g, 3.37 mmol) was added dropwise over 20 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 **2** (0.08 g, yield 22 %) as a light yellow solid. M.p. 52–55 °C; IR (ATR): $\tilde{\nu}$ =

2976 (m), 1343 (s), 1142 (m) cm^{-1} ; ^1H NMR (400 MHz, $[\text{D}_2]$ dichloromethane, 25 °C, TMS) δ = 1.27 (s, 12H, $\text{CH}_3 \times 4$), 2.17 (s, 3H, CH_3), 4.0 (s, 2H, CH_2), 4.36 (s, 2H, CH_2), 7.26–7.30 (m, 1H), 7.38–7.47 (m, 6H), 7.8 (d, $J = 8.2$ Hz, 1H), 7.96–7.99 (m, 2H), 8.34 (dd, $J = 1.9$ and 8.9 Hz, 2H), 8.38 (s, 1H); HRMS (APPI): m/z (%): $[\text{M}+\text{H}^+]$ calcd 438.25989; found 438.25970.