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Electronic Supporting Information

Thermo-responsive white-light emission based on tetraphenylethylene- and rhodamine B-containing boronate nanoparticles

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General

NMR spectra were taken by a Bruker Avance 500 (¹H: 500 MHz, ¹³C: 125 MHz,) spectrometer. In ¹H and ¹³C NMR measurements, chemical shifts (δ) are reported downfield from the internal standard Me₄Si. Fast atom bombardment (FAB) mass spectra were obtained on a JEOL JMS-700 spectrometer where *m*-nitrobenzylalcohol was used as a matrix. The absorption and fluorescence spectra were measured using a Shimadzu UV-3600 and a JASCO FP-6300 spectrophotometers, respectively. Fluorescence quantum yield of dye-grafted BP was taken on using a JASCO FP-8500 spectrofluorometer with a substandard light source (JASCO ESC-842) and an integrating sphere (JASCO IL835). Elemental analyses were performed on an Exeter Analytical, Inc. CE-440F Elemental Analyzer. Field-emission scanning electron microscopy (FE-SEM) was performed by a JEOL JSM-7500F (acceleration voltage of 5 kV). As for FE-SEM measurements, boronate particles BP collected on a polycarbonate type membrane filter (pore size, 0.2 µm (GRADE : K020A047A), Advantec, Ltd.) by filtration was employed. Solid-state ¹³C cross-polarization-magic angle spinning (CP-MAS) NMR was measured by a JEOL ECA 400SS spectrometer. The observation frequency was 100.53 MHz for ¹³C. The spectrometer is equipped with a 3.2 mm MAS probe head capable of producing an MAS speed of 18 kHz. Spectra were obtained by using a ¹H-¹³C CP contact time of 2 ms, an acquisition time of 25.5 ms, a recycle delay of 5 s between scans, and an MAS speed of 18 kHz. The ¹³C chemical shifts were calibrated by using adamantine ($\delta = 29.5$ ppm) as an external standard relative to tetramethylsilane (TMS; $\delta = 0$ ppm).¹¹B dipolar decoupling (DD)-MAS NMR spectrum also measured by using boric acid (H₃BO₃) saturated aqueous solution ($\delta = 19.49$ ppm) as an external standard relative to boron trifluoride etherate (BF₃·O(C₂H₅)₂; $\delta = 0$ ppm). Powder X-ray diffraction (PXRD) data were collected by a Rigaku RINT-TTR III X-ray diffractometer with Cu Ka radiation. Zeta potential measurements for **BP** in MeOH (solvent) (1 g L⁻¹) were performed using an ELSZ-2 (OTSUKA ELECTRONICS) instrument. Photographic images were recorded using a NIKON D3200 digital single-lens reflex camera.

Materials

Unless otherwise indicated, reagents used for the synthesis were commercially available and were used as supplied. Synthesis of 3,5-di-*tert*-butylphenylboronic acid 2^1 and 2-(3-diethylamino-6-diethylazaniumylidene-xanthen-9-yl)-5-{[3-(dihydroxyborylphenyl)amino]sulfonyl}-benzenesulfonate **R-dye**² were conducted according to the method previously reported.

Synthesis of 4,4'-(2,2-diphenylethane-1,1-diyl)bis(dihydroxyborylbenzene) (DB-TPE)



Scheme S1 Synthesis of DB-TPE

Synthesis of **DB-TPE** was conducted from diphenylmethane as shown in Scheme. S1 where 4,4'-(2,2-Diphenylethane-1,1-diyl)bis(bromobenzene) **2Br-TPE**, was prepared according to the method previously reported.³ The detailed experimental procedure for the synthesis of **DB-TPE** and the characterization data have been below:

Preparation of DB-TPE. To a solution of **2Br-TPE** (1.86 g, 3.80 mmol) in dry THF at -78 °C was added *n*-BuLi (1.55 M in hexane, 9.8 mL, 15.2 mmol) under a N₂ atmosphere. After stirring for 1 h at the temperature, triethylborate (3.8 mL, 22.9 mmol) was added dropwise. The resultant mixture was stirred for 1 h at -78 °C, then warmed to room temperature and stirred overnight. The mixture was acidified to pH = 2 by the addition of 1 M HCl aq. (32 mL) and then poured into H₂O (200 mL). After adding aqueous NaHCO₃ into the mixture until pH = 5, the organic solvent was removed *in vacuo* and the resultant aqueous solution was extracted with ethyl acetate (250 mL). The organic layer was washed with H₂O (1000 mL) and dried with Na₂SO₄. After the removal of solvent *in*

vacuo, the residue was reprecipitated from ethyl acetate/hexane to give a crude product (0.70 g). The material was chromatographed on silica gel (Wacogel C-300) using a gradient of hexane ($50 \rightarrow 0\% \text{ v/v}$) in ethyl acetate as an eluent and the product was reprecipitated with ethyl acetate/hexane to give **1** as a pale yellow solid (0.42 g, 26%). ¹H NMR (500 MHz, DMSO-*d*₆) δ (ppm) 6.92 (d, 4H, *J* = 8.20 Hz), 6.96–6.98 (m, 4H), 7.09–7.15 (m, 6H), 7.53 (d, 4H, *J* = 8.30 Hz), 7.93 (s, 4H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ (ppm) 126.6, 127.8, 129.7, 130.6, 133.6, 140.7, 143.2, 144.8; FAB MS: *m/z* 960 [M + 4(*m*-nitrobenzylalcohol) – 4H₂O]⁺, 825 [M + 3(*m*-nitrobenzylalcohol) – 3H₂O]⁺; elemental analysis: calcd for C₂₆H₂₂B₂O₄ – 0.6H₂O: C, 76.30; H, 5.12, found: C, 76.44; H, 4.87

References

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The procedure for determination of amount of rhodamine B grafted on the boronate surface

Methanol solutions (2 mL) of **R-dye** (20, 100, 200 and 500 μ M) were set up and added to each vial where **BP**s (10.00 mg) were present. The resultant dispersed solutions were allowed to stand for 4 h at room temperature, and then centrifuged with 4500 rpm. The supernatant solutions were subject to UV-Vis absorption measurement. Compared to the absorption spectra of **BP**-free solutions of **R-dye**, the amounts of grafted **R-dye** were calculated where the changes in absorbance at 560 nm were employed. Absorption spectra of each solution were shown below.



Fig. Absorption spectra of methanol solutions of **R-dye** before and after the immersion of **BP**s. Concentration of **R-dye** before **BP**s' immersion are (a) 20 μ M, (b) 100 μ M, (c) 200 μ M, (d) 500 μ M. Each solution was diluted 50-fold with MeOH for measurement.



Fig. S1 (a) FE-SEM image and (b) DLS measurement of boronate nanoparticles (BPs).



Fig. S2 (a)¹³C-CP-MAS NMR and (b)¹¹B-DD-MAS NMR spectra of **BP**.



Fig. S3 ATR-FT-IR spectra of **DB-TPE**, **1**, and **BP**. A characteristic intense peak at 646 cm⁻¹ (*) was assignable to boronate ester.



Fig. S4 PXRD spectrum of BP.



Fig. S5¹³C-CP-MAS NMR spectra of (a) **BP** and (b) the solid obtained by aging **BP** in a MeOH solution of 2.



Fig. S6 Absorption (dashed) and fluorescence (solid) spectra of **BP** (blue, 0.1 mg mL⁻¹ in water) and **R-dye** (red, 20 μ M in MeOH) at 25 °C. $\lambda_{ex} = 365$ nm for **BP**; $\lambda_{ex} = 365$ nm for **R-dye**.



Fig. S7 (a) Fluorescence spectra and (b) fluorescence intensity at 479 nm of aqueous dispersion of **R-BP(W)** (0.1 mg mL⁻¹) at 25 °C for 60 min. $\lambda_{ex} = 365$ nm.



Fig. S8 (a) Fluorescence spectra and (b) fluorescence intensity at 479 nm of aqueous dispersions of **R-BP(W)** (0.1 mg mL⁻¹) while heating at 65 °C for 60 min. $\lambda_{ex} = 365$ nm.



Fig. S9 (a) Variable temperature ¹³C-CP-MAS NMR spectra of **BP** at 25 °C and 65 °C. (b) DLS spectra and average particle diameters of **BP** at 5 °C and 65 °C.