Electronic Supporting Information

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

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Table of Contents

1. General S2
2. Materials S2
3. Synthesis of 4,4’-(2,2-diphenylethane-1,1-diyl)bis(dihydroxyborylbenzene) (DB-TPE) S2-3
4. References S3
5. The procedure for determination of amount of rhodamine B grafted on the boronate surface S3
6. Fig. S1 FE-SEM image and DLS measurement of boronate nanoparticles (BPs) S4
7. Fig. S2 13C-CP-MAS NMR and 11B-DD-MAS NMR spectra of BP S4
8. Fig. S3 ATR-FT-IR spectra of DB-TPE, 1, and BP S4
9. Fig. S4 PXRD spectrum of BP S5
10. Fig. S5 13C-CP-MAS NMR spectra of BP and the solid obtained by aging BP in a MeOH solution of 2 S5
11. Fig. S6 Absorption and fluorescence spectra of BP and R-dye S6
12. Fig. S7 Fluorescence spectra of R-BP(W) in water at 25 °C S6
13. Fig. S8 Fluorescence spectra of R-BP(W) in water at 65 °C S6
14. Fig. S9 Variable temperature 13C-CP-MAS NMR spectra and DLS spectra of BP at 5 °C and 65 °C S7
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 Me_4Si. 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 spectrophotometer 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 adamantane (δ = 29.5 ppm) as an external standard relative to tetramethylsilane (TMS; δ = 0 ppm). 11B dipolar decoupling (DD)-MAS NMR spectrum also measured by using boric acid (H_3BO_3) saturated aqueous solution (δ = 19.49 ppm) as an external standard relative to boron trifluoride etherate (BF_3·O(C_2H_5)_2; δ = 0 ppm). Powder X-ray diffraction (PXRD) data were collected by a Rigaku RINT-TTR III X-ray diffractometer with Cu Kα 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 and 2-(3-diethylamino-6-diethylazaniumylidene-xanthen-9-yl)-5-[[3-(dihydroxyborylphenyl)amino]sulfonyl]-benzenesulfonate R-dye were conducted according to the method previously reported.3 The detailed experimental procedure for the synthesis of DB-TPE and the characterization data have been below:

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 → 0% 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%).

\[ ^{1}\text{H} \text{NMR (500 MHz, DMSO-}d_{6}) \delta \text{ (ppm) } 6.92 \text{ (d, 4H, } J = 8.20 \text{ Hz), 6.96} - 6.98 \text{ (m, 4H), 7.09} - 7.15 \text{ (m, 6H), 7.53 (d, 4H, } J = 8.30 \text{ Hz), 7.93 (s, 4H)} \]

\[ ^{13}\text{C} \text{NMR (125 MHz, DMSO-}d_{6}) \delta \text{ (ppm) } 126.6, 127.8, 129.7, 130.6, 133.6, 140.7, 143.2, 144.8; \text{ FAB MS: } m/z 960 \text{ [M + 4}(m\text{-nitrobenzylalcohol}) - 4\text{H}_2\text{O}]^+, 825 \text{ [M + 3}(m\text{-nitrobenzylalcohol}) - 3\text{H}_2\text{O}]^+; \text{ elemental analysis: } \text{calcd for C}_{26}\text{H}_{22}\text{B}_{2}\text{O}_4 - 0.6\text{H}_2\text{O: C, 76.30; H, 5.12, found: C, 76.44; H, 4.87} \]

References

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 μM) were set up and added to each vial where BPs (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 BPs. Concentration of R-dye before BPs’ immersion are (a) 20 μM, (b) 100 μM, (c) 200 μM, (d) 500 μM. 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) $^{13}$C-CP-MAS NMR and (b) $^{11}$B-DD-MAS NMR spectra of BP.

Fig. S3 AT-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. S5** $^{13}$C-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 μM in MeOH) at 25 ºC. $\lambda_{ex} = 365$ 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 ºC 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 ºC for 60 min. $\lambda_{ex} = 365$ nm.
Fig. S9 (a) Variable temperature $^{13}$C-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.