Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

White-light emitting boronate microparticles for potential use as reusable bright chemosensors in water

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Materials

Boronate microparticles (**BP**) composed of polymeric 2,4,8,10-tetraoxa-3,9-diboraspiro[5.5]undecane, that provide an available surface for dye grafting were prepared from benzene-1,4-diboronic acid and pentaerythritol according to previously reported procedures (Y. Matsushima, R. Nishiyabu, N. Takanashi, M. Haruta, H. Kimura and Y. Kubo, *J. Mater. Chem.*, 2012, **22**, 24124–24131), and their final diameters were 2.4 ± 0.5 μm (Fig. a).

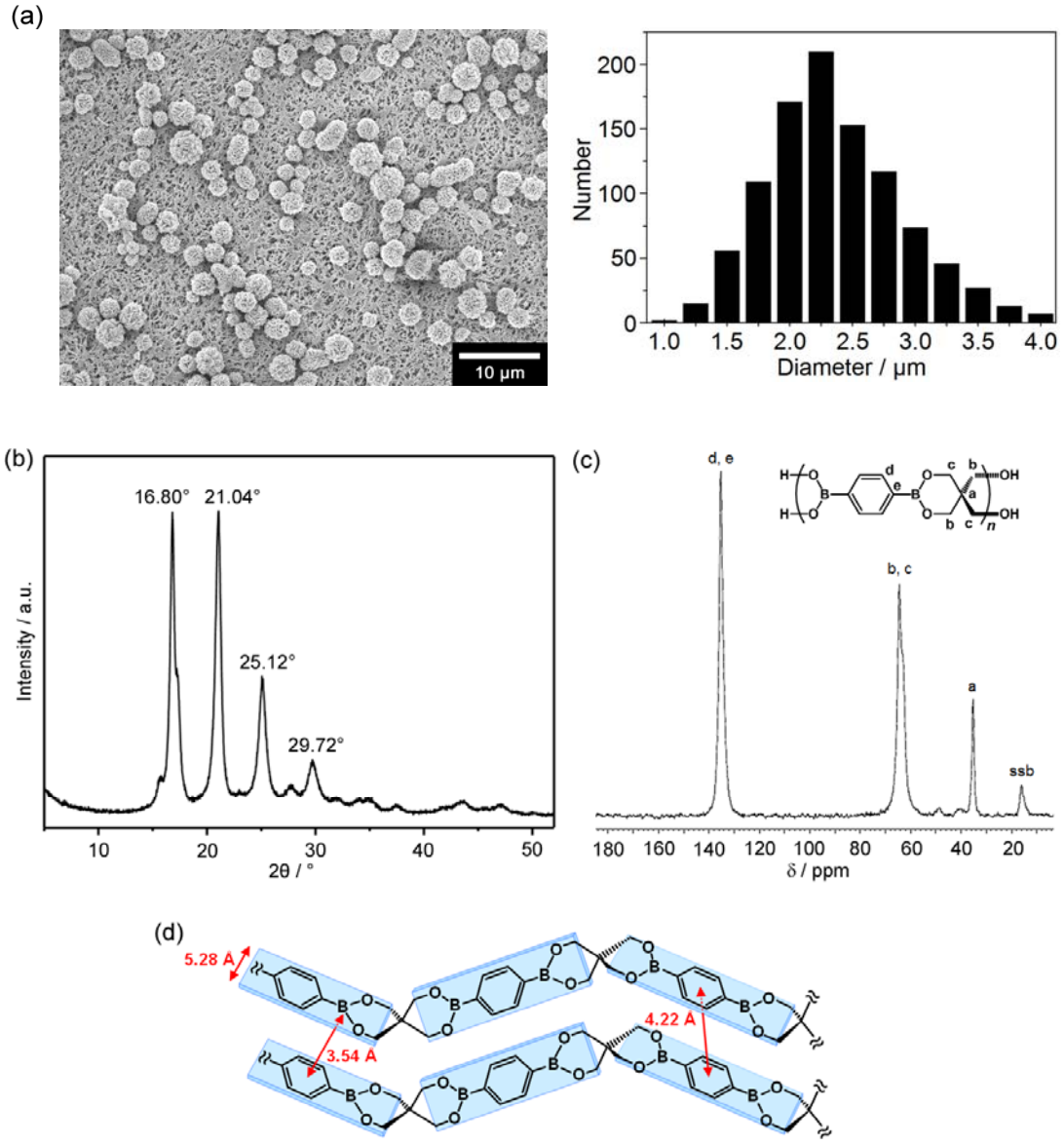

Fig. (a) The SEM image and the size distribution of boronate microparticles (**BP**), (b) PXRD pattern of **BP**, (c) ^{13}C CP-MAS NMR spectrum of **BP**, where ssb represents spinning side band and (d) plausible stacking structure of polymeric 2,4,8,10-tetraoxa-3,9-diboraspiro[5.5]undecane in **BP**.

1-Pyreneboronic acid **1**, pyrene, lissaminerhodamine B sulfonyl chloride and 3-aminophenylboronic acid monohydrate were purchased from Tokyo Chemical Industry, Sigma-Aldrich, Acros Organics and Wako Chemicals, respectively. 3-[({(*N*-Dansylamino)ethylamino}ethylamino)methyl]phenylboronic acid **2** was prepared previously; see, R. Nishiyabu, H. Kobayashi and Y. Kubo, *RSC Adv.*, 2012, **2**, 6555–6561.

General Experimental Procedure

Solution-state NMR spectra were recorded on a Bruker AVANCE-500 spectrometer using tetramethylsilane (TMS) as an internal standard (0 ppm) for ^{1}H and ^{13}C NMR analysis and $BF_3 \cdot OEt_2$ as an external standard (0 ppm) for ^{11}B NMR analysis. All solution-state NMR spectra were recorded at 298 K. Solid-state ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR spectrum was measured by a JEOL JNM-ECA 500 spectrometer. The observation frequency was 125 MHz. The spectrometer is equipped with a 4 mm MAS probehead capable of producing an MAS speed of 15 kHz. Spectra were obtained by using a ^{1}H-^{13}C CP contact time of 2 ms, an acquisition time of 40.7 ms, a recycle delay of 5 s between scans. The ^{13}C chemical shifts were calibrated by using adamantane (δ = 29.5 ppm) as an external standard relative to tetramethylsilane (TMS; δ = 0 ppm). The solid-state NMR spectra was recorded at 291 K. Fast atom bombardment (FAB) mass spectrum was obtained on a JEOL JMS-700 spectrometer where 3-nitrobenzyl alcohol was used as a matrix. Elemental analysis was performed on a Yanaco CHNcoder MT-5 analyzer. Field-emission scanning electron microscopy (FE-SEM) was performed on a JEOL JSM-7500F (acceleration voltage of 5 kV). For FE-SEM measurement, particles were coated with Au on an EIKO IB3ION COATER. Nitrogen gas adsorption isotherm was recorded by a Micrometrics Trister. The sample (20.8 mg) was degassed at 150 ºC under vacuum for 5 h and the measurement was performed at 77 K. The surface area was calculated by BET method. Zeta potential measurement was performed using an OTSUKA ELECTRONICS ELSZ-2 instrument. UV-vis absorption spectra were measured on a Shimadzu UV-3600 spectrophotometer. Fluorescence spectra and quantum yields of dye-grafted **BP** were taken on using a JASCO FP-8500 spectrofluorometer with a substandard light source (JASCO ESC-846) and an integrating sphere. In addition, changes in fluorescence spectra upon adding metal ions were monitored by JASCO FP-6300Q spectrofluorometer. Quartz cell with 1-cm path length was used for UV-vis and fluorescence measurements. Fluorescence microscopic images were taken using a TS100 LED-F (λ_{ex}: 330–380 nm, λ_{em}: 420 nm~) equipped with a Plan APO 60X Oil objective lens. Photographed images of aqueous dispersions of particles were taken by a PENTAX *K-m* digital camera with a PENTAX DA 18-55mm lens (shutter speed: 0.25 s, f-number: 6.7) under UV irradiation using a handy lamp (365 nm).

Synthesis of 2-(3-diethylamino-6-diethylazaniumylidene-xanthen-9-yl)-5-{[3-(dihydroxyborylphenyl) amino]sulfonyl}-benzenesulfonate (3)

To lissaminerhodamine B sulfonyl chloride (150 mg, 0.26 mmol) in dry pyridine (5 mL) was added 3-aminophenylboronic acid monohydrate (40 mg, 0.26 mmol) under a N_2 atmosphere at room temperature. The mixture was stirred at room temperature for 24 h and then the solvent was removed *in vacuo*. The crude product was chromatographed on silica gel (wako gel C-300) using MeOH (3% (v/v)) in $CHCl_3$ as an eluent. In this way, 30 mg of **3** was obtained as a purple solid (17% yield). UV-vis absorption: λ_{max} = 563 nm ($\varepsilon = 1.1 \times 10^5$ M^{-1} cm^{-1}) in DMSO; Fluorescence: λ_{em} = 589 nm (λ_{ex} = 520 nm) in DMSO; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.33 (*s*, 1H, NH), 8.44 (*d*, *J* = 1.8 Hz, 1H, Ar-H), 8.07 (*s*, 2H, $B(OH)_2$), 7.73 (*dd*, *J* = 8.0 Hz, 1.9 Hz, 1H, Ar-H), 7.54 (*d*, *J* = 6.9 Hz, 1H, Ar-H), 7.48 (s, 1H, Ar-H), 7.36 (*d*, *J* = 8.0 Hz, 1H, Ar-H), 7.28 (*dd*, *J* = 7.6 Hz, 7.6 Hz, 1H, Ar-H), 7.21 (*d*, *J* = 8.2 Hz, 1H, Ar-H), 7.02 (*dd,* *J* = 9.6 Hz, 2.4 Hz, 2H, Ar-H), 6.91 (*d*, *J* = 2.4 Hz, 2H, Ar-H), 6.85 (*d*, *J* = 9.6 Hz, 2H, Ar-H), 3.64 (*q*, *J* = 8.0 Hz, 8H, CH_2), 1.20 (*t*, *J* = 7.0 Hz, 12H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6): δ 157.2, 157.1, 155.0, 148.0, 140.7, 136.6, 135.6, 133.4, 132.5, 130.6, 130.4, 128.2, 127.6, 126.7, 125.9, 123.4, 113.7, 113.4, 95.4, 45.3, 12.5; ^{11}B NMR (160 MHz, DMSO-d_6): δ 30.2; FABMS: *m/z* 947 ([M + 2(3-nitrobenzyl alcohol) – $2H_2O$]$^+$); elemental analysis: anal. calcd for $C_{33}H_{36}BN_3O_8S_2 \cdot 0.1CHCl_3$: C 57.66; H 5.28; N 6.09, found: C 57.67; H 5.03; N 5.72%.

Surface functionalization of BP with fluorescent dyes

Methanol solution of fluorescent dye (1.0×10^{-5} M, 10 mL) was added to a vial where **BP** (10.0 mg) was present and was allowed to stand for 24 h at room temperature (25 ºC). The resultant solid was collected by filtration and rinsed with methanol (10 mL), then dried *in vacuo* for 1 h.

Quantitative evaluation of dye grafting onto the surface of BP using Langmuir isotherm model

Methanol solutions of dye **1** at varied concentration ($0 – 2.5 \times 10^{-3}$ M, 5 mL) were added to vials where **BP** (5.0 mg) was present. The resultant suspensions were allowed to stand for 24 h at room temperature (25 ºC) and then centrifuged with 4500 rpm. UV-vis absorption spectra of the supernatant solutions were measured to determine equilibrium concentrations and amounts of dye **1** grafted. The obtained data were analyzed by the Langmuir equation expressed in the following equation.

$$q = \frac{q_{\max} \times K \times C}{1 + K \times C}$$

where q, $q_{\max}$, K and C are adsorbed amount, maximum adsorption capacity, Langmuir adsorption constant and equilibrium concentration, respectively. The values of $q_{\max}$ and K were evaluated by a nonlinear least-squares method.

Preparation of white-light emissive BP

A methanol solution (10 mL) of **1** (3.8×10^{-6} M), **2** (6.0×10^{-6} M) and **3** (2.0×10^{-7} M) was added to avail where **BP** (10.0 mg) was present. The resultant suspension was allowed to stand for 24 h at room temperature (25 ºC). The solid was collected by filtration and rinsed with methanol (10 mL). The obtained solid was dried *in vacuo* for 1 h and was used for further experiments.

Fluorescence measurements for the detection of Cu^{2+}

For the measurements, nitrate salts of metal ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, Al^{3+}, and Pb^{2+}) were used. Each aqueous solution of the metal ion was added to aqueous dispersions of **BP** (1.0 mg·mL^{-1}, 5 mM HEPES buffer, pH 7.0)at room temperature (25 ºC). The resultant suspensions were measured by fluorometry. Association constant (K_a) for complexation of dansyldiethylenetriamine moiety with Cu^{2+} was determined from the titration curve of normalized changes in fluorescence intensities $(I - I_0) / I_0$ of **Sen-BP** at 510 nm upon the addition of incremental amounts of Cu^{2+}. The normalized change in fluorescence intensity was expressed in the following equations.

$$(I - I_0)/I_0 = \frac{(\Delta I_{\lim}/I_0) \times (\mathrm{A} - \sqrt{\mathrm{A}^2 - 4 \times K_a^{\,2} \times \mathrm{S}_0 \times \mathrm{M}_0}}{2 \times K_a \times \mathrm{S}_0}$$

$$\mathrm{A} = K_a \times \mathrm{M}_0 + K_a \times \mathrm{S}_0 + 1$$

where I, I_0 and $\Delta I_{\lim}$ are the observed fluorescence intensity, the fluorescence intensity in the absence of metal ion, and the saturation value of change in fluorescence intensity of **Sen-BP**, respectively. In the equation, K, S_0 and M_0 are the binding constant, the initial concentrations of dansyldiethylenetriamine moiety and Cu^{2+} added, respectively. The values of K_a, S_0 and $\Delta I_{\lim} / I_0$ were determined to be $(5.9 \pm 0.6) \times 10^6$ M^{-1}, $(9.6 \pm 0.4) \times 10^{-7}$ M and -0.73 ± 0.01 by a nonlinear least-squares method, respectively.

Determination of the detection limit for Cu^{2+}

The detection limit for Cu^{2+} was determined from the point of intersection between the regression line obtained from fluorescence intensities (*I*) of **Sen-BP** at 510 nm in dynamic range of the titration curve and the line given by following equation.

$$Y = I_{avg} - 3 \times \sigma$$

where I_{avg} and σ are the average value and the standard deviation of fluorescence intensity of **Sen-BP** at 510 nm in the absence of metal ion measured by five times, respectively.

Reusability test of Sen-BP for Cu^{2+} detection

Initially, fluorescence spectrum of aqueous dispersion of **Sen-BP** (1 $mg \cdot mL^{-1}$) in the presence of Cu^{2+} (3.0×10^{-5} M) was measured in 5 mM HEPES buffer (pH 7.0). After that aqueous EDTA (5.0×10^{-2} M) in 5 mM HEPES buffer (pH 7.0) was added to the dispersion at room temperature (25 ºC). The resultant dispersion containing 1.0×10^{-3} M EDTA was allowed to stand for 5 min at room temperature (25 ºC). Then, **Sen-BP** was collected by filtration, rinsed with water and dried *in vacuo* for 1 h. Such are cycled **Sen-BP** was again dispersed in 5 mM HEPES buffer (pH 7.0).

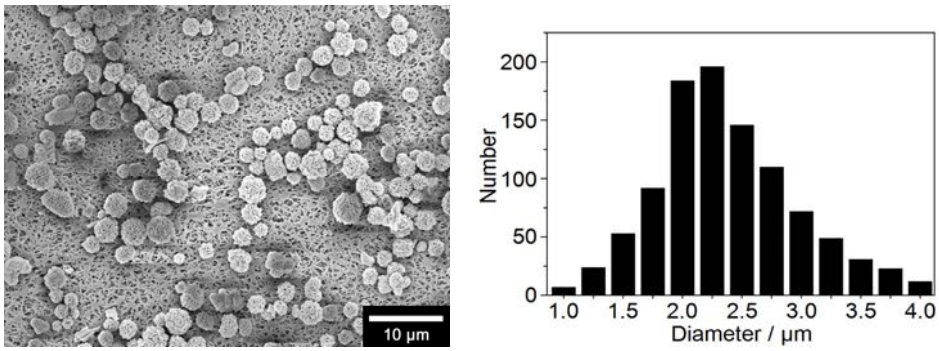

Fig. S1 SEM image and the size distribution of **BP** immersed in a MeOH solution of dye **1**.

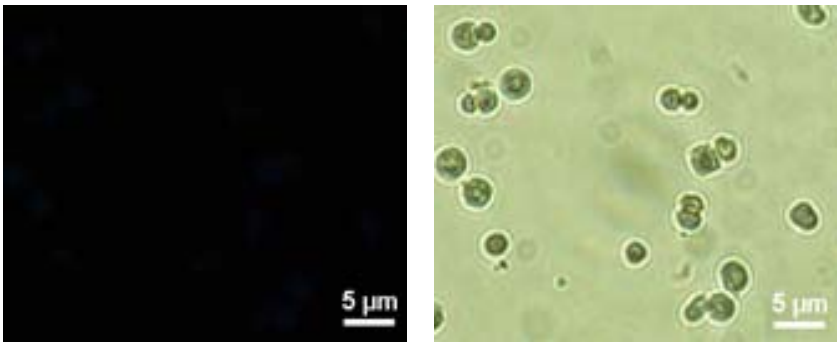

Fig. S2 Fluorescence microscopic image (left) and the corresponding optical microscopic image (right) of aqueous dispersion of **BP** (5 mM HEPES buffer, pH 7.0) after immersion in a MeOH solution of pyrene.

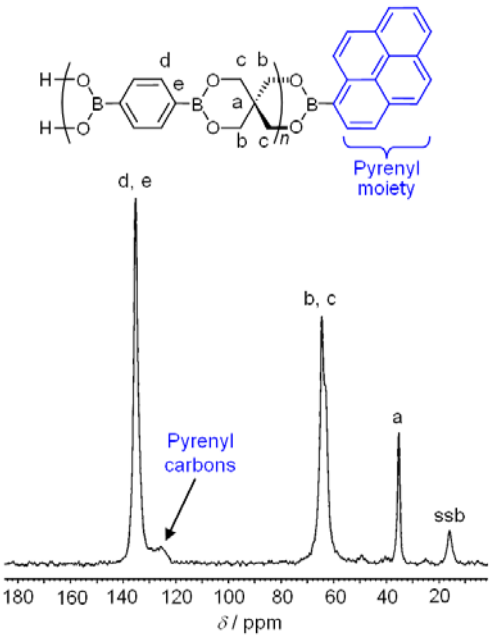

Fig. S3 ^{13}C-CP-MAS NMR spectrum of **1-BP**, where ssb represents spinning side band.

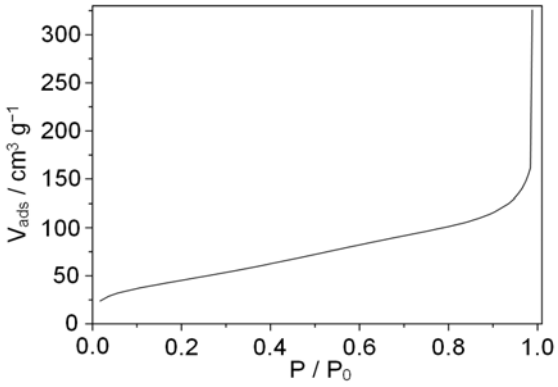

Fig. S4 Nitrogen adsorption isotherm of **BP**.

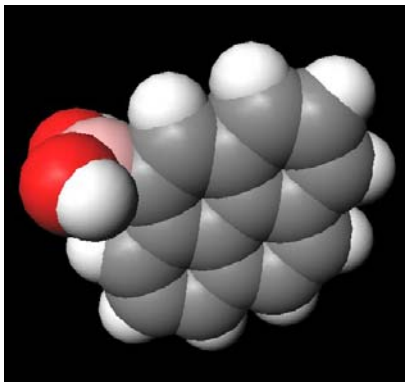

Fig. S5 Optimized structure of **1** using DFT calculation (B3LYP/6-31G*).

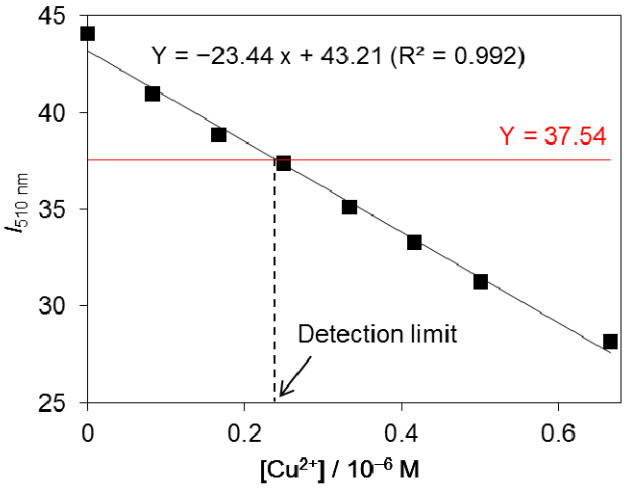

Fig. S6 Determination of the detection limit for Cu^{2+}.