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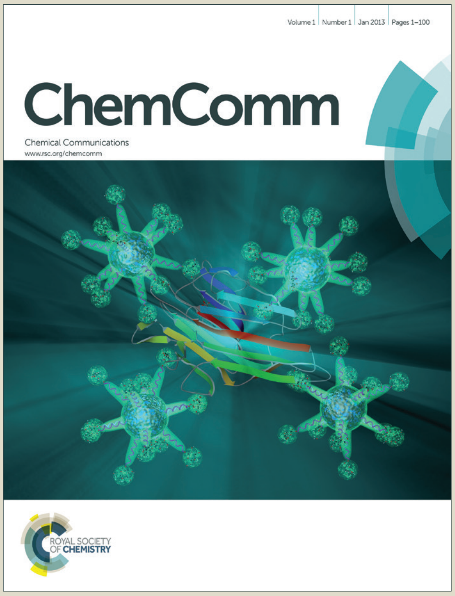

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Thermo-responsive white-light emission based on tetraphenylethylene- and rhodamine B-containing boronate nanoparticles

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Boronate nanoparticles with built-in tetraphenylethylene (TPE) have been prepared. Their emissive color tuning by altering the amount of rhodamine B grafted onto the surface gave white-light emissive nanoparticles. They showed a reversible and thermo-responsive emission in the temperature range of 5–65 ºC in water, which enabled them to serve as a bright nanothermometer.

The behavior of chemical and biological systems is affected by temperature. Thus, thermo-responsive materials are among the most fundamental indicators used for a wide range of applications from industry to medical diagnostics.[1] In this regard, luminescence materials such as quantum dots[2] and lanthanide systems[3] have been prepared and elucidated. The fluorescent organic systems, the luminescence depending on temperature, are promising candidates. Indeed, the related systems derived from organic molecules,[4] polymers (e.g. poly *N*-isopropylacrylamide (PNIPAM))[5] and triblock copolymers (e.g. poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide))[6] have been reported. These systems are capable of monitoring the temperatures of solutions by changing their fluorescence intensity due to temperature-dependent photophysical changes in the fluorophores or conformational transitions. Considering thermal imaging of local environment in fluids,[7] it is worthwhile to develop a simple technique with high color-contrast scheme for the measurement of fluid temperature. With this in mind, white-luminescence nanomaterials are valuable targets, which are made up of components that emit either the three primary colors (red, green, and blue) or two complementary colors to cover the entire visible wavelength region.[8] With the help of molecular organization modes such as supramolecular polymers,[9] gels,[10] self-assembled nanoparticles formation,[11] metal-organic frameworks,[12] vesicles,[13] micelles,[14] organic-inorganic hybrids,[15] and supramolecular cages,[16] some examples of white-luminescence nanomaterials have been fabricated. However, molecular-based nanothermometers with white-light emission have not been reported yet. The discovery of a sophisticated interplay between the thermo-responsive luminophore and the complementary emissive color unit to cover the visible region in the solid state would enable us to produce the desired binary system with white luminescence.

We have recently investigated boronate self-assemblies, which are built by sequential dehydration reactions of diboronic acids with tetraols to form highly dispersible three-dimensional particles through a nucleation process.[17] Purposeful surface functionalization of boronate particles allowed us to prepare heterogeneous catalysts[18] as well as a recyclable chemosensor for selective monitoring of Cu^{2+} in water.[19] Inspired by these results, we have envisaged that the use of aggregation-induced emission (AIE)-active luminogens, a series of propeller-shaped luminescent molecules,[20] as a component for boronate assembly would be a promising way to develop a fluorescent particle through restriction of their intramolecular rotation. In the past decade, a number of TPE-derived sensing systems have been proposed by making use of the easy synthetic modification of tetraphenylethylene (TPE). This was possible because of the existence of unique fluorescent switching in response to chemical stimulus-induced conformation transactions as well as changes in the microenvironment.[21] In the case of TPE-containing luminescent thermometers, very few examples with PNIPAM have been reported.[5b,d] This is probably responsible for the limited number of thermo-responsive polymers.

In this study, structurally defined di(boronic acid)-appended tetraphenylethylene (**DB-TPE**)[22] was used to prepare AIE-active blue-emissive boronate nanoparticles (**BP**). As described below in detail, tuning of the emission color of these particles has been achieved by varying the amount of rhodamine B grafted onto the surface, which endowed it with white-light emission. It is worth emphasizing that such a bright nanoparticle exhibited reversible and thermo-responsive emission in water; this property could be exploited to develop a white-light emissive nanothermometer that can be operated in water.

DB-TPE was straightforwardly synthesized from diphenylmethane, the assignment of the molecule being fully carried out using spectroscopic analysis (See ESI†). It was then allowed to react with pentaerythritol (**1**) in methanol under ambient conditions; aging the mixture for 2 h produced an opalescent solution (Fig. 1a). After filtration and drying *in vacuo*, the isolated solid was dispersed in water in which it emits blue light under UV-light irradiation (365 nm) using a handheld UV lamp. The formation of **BP** nanoparticles (see FE-SEM, Fig. S1a in ESI†) was confirmed by means of dynamic light scattering measurement, showing an average diameter of 86 ± 28 nm (Fig. S1b in ESI†). As shown in Fig. 1b, the fluorescence spectrum of **BP** has a peak at 479 nm when excited at

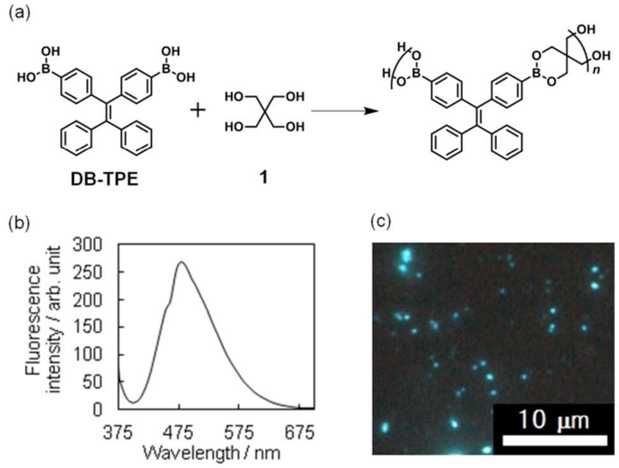

Fig. 1 (a) Sequential boronate esterification of **DB-TPE** with **1** in methanol to produce blue-emissive nanoparticle **BP**. (b) Fluorescence spectrum of **BP** in water at 25 ºC, λ_{ex} = 365 nm. (c) Fluorescence microscopic image of **BP**.

365 nm in water. Fig. 1c shows the fluorescence microscopic image of **BP**. The emission quantum yield, measured using the method of integrative spheres, was 21%. The component analysis was performed using solid-state ^{13}C-CP-MAS NMR analysis (Fig. S2a in ESI†) where not only signals ranging from 128.95 to 146.77 ppm, arising from the aromatic carbons, but also two signals of methylene carbon at 64.79 ppm and spirocarbon at 36.40 ppm were clearly observed. The use of ^{11}B-DD-MAS NMR allowed us to detect distinct peaks at 9.2 and 15.8 ppm (Fig. S2b in ESI†), which were higher field shifted than those of a typical sp^2-hybridized trigonal boron. The line shapes in a quadripolar ^{11}B spectrum have been known to be highly sensitive to the chemical and geometrical bonding environment of boron.[23] Thus, the spectrum might be interpreted on the basis of phenyl-boron π-stacking interactions between polymers in the solid state. In addition, the measurement of the infrared (IR) absorption spectrum, using equipment fitted with an attenuated total reflection (ATR) attachment, confirmed the boronate ester bond formation (Fig. S3 in ESI†). The obtained particle was found to be composed of a polymeric dehydrated compound derived from **DB-TPE** and **1**.[24] The powder X-ray diffraction (PXRD) spectrum suggests formation of a structurally ordered aggregation of TPE-containing boronate polymers (Fig. S4 in ESI†).

BP has a negative zeta potential (–12.14 mV), indicating that the hydroxyl groups at the terminal position of the component polymers are present on the surface.[11a] We were, therefore, interested in carrying out the grafting reaction using dihydroxyboryl compounds. In order to assess such a hypothesis, we investigated the reaction of **BP** with 3,5-di-*tert*-butylphenylboronic acid **2**;[25] if **2** could participate in the desired grafting reaction, then the butyl carbon could be monitored by ^{13}C-CP-MAS NMR measurement. NMR measurements of the resultant particles, obtained by aging **BP** in a MeOH solution of **2**, showed a new signal at 32.55 ppm, attributed to *tert*-butyl carbon (Fig. S5 in ESI†). This result implies that the surface functionalization is accessible through boronate esterification.

We employed boronic acid-appended rhodamine B (**R-dye**)[19] for dye grafting because the dye emits at a longer wavelength region; this enabled us to tune emission colors from blue to red by changing the amount of the dye grafted onto the surface. As shown in Fig. S6 in the ESI†, the absorption band of **R-dye** shows a good overlap with the fluorescence band of **BP** ranging from 460 to 600 nm, thus resulting in fluorescence resonance energy transfer (FRET). The grafting of **R-dye** onto **BP** was carried out by soaking **BP** (10.00 mg) in a MeOH solution of **R-dye** (20–500 μM) at room temperature for 4 h to yield emissive boronate nanoparticle (**R-BP**). All the particles exhibited two peaks at 479 and 590 nm in the fluorescence spectrum when excited at 365 nm in water; these peaks were assignable to the components TPE and rhodamine B, respectively (Fig. 2a). As the amount of grafted **R-dye** increased, the emission color clearly changed from blue to red (Fig. 2b). A plausible partial structure where FRET occurs is shown in Fig. 2c. Interestingly, the subsequent trajectory of the Commission Internationale de l'Éclairage (CIE) coordinates in the chromaticity diagram (Fig. 2d) indicates the production of white-light emissive particles **R-BP(W)**, where the CIE chromaticity coordinates were (0.336, 0.354). The fluorescence microscopic image of **R-BP(W)** is shown in Fig. 2e; the amount of the dye grafted was calculated to be 2.7×10^{-6} mol g^{-1}.[26]

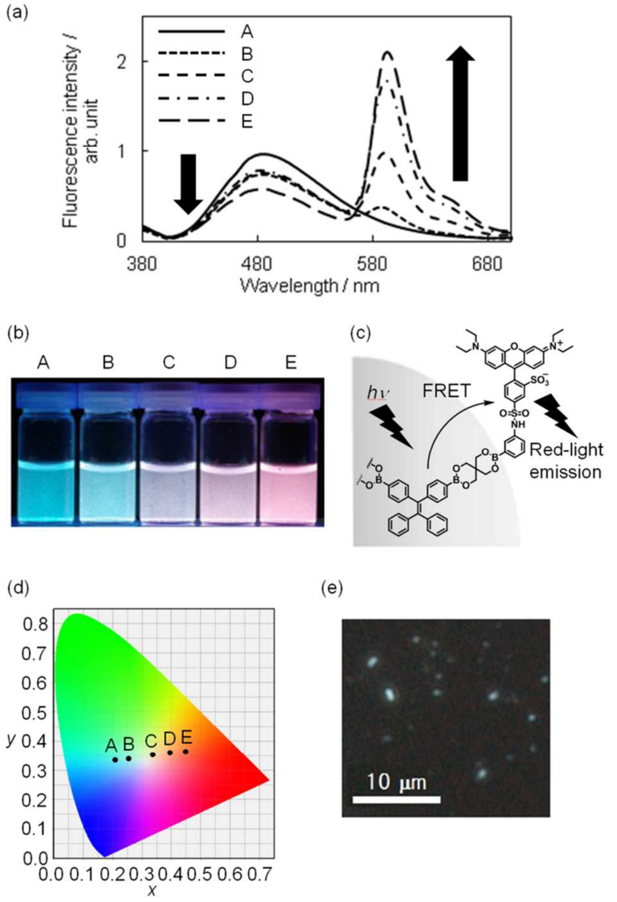

Fig. 2 (a) Fluorescence spectra of boronate nanoparticles with binary emissive units (**R-BP**) in water. λ_{ex} = 365 nm. The amount of grafted rhodamine B: A, 0.0 mol g^{-1}; B, 8.0×10^{-7} mol g^{-1}; C, 2.7×10^{-6} mol g^{-1}; D, 3.9×10^{-6} mol g^{-1}; E, 16×10^{-6} mol g^{-1}. The amount of grafted dye was assessed by UV/vis absorption spectroscopy. The procedure has been described in ESI. (b) Photographs of the corresponding boronate nanoparticles dispersion in aqueous media. (c) A plausible partial structure where FRET occurs in **R-BP**. (d) Composition trajectory to tune color through changing the amount of rhodamine B on the CIE coordinate diagram (λ_{ex} = 365 nm). (e) Fluorescence microscopic image of white-light emissive particles **R-BP(W)**.

Next, we tried to harness the changes in the white emission as a readily detectable output signal. Therefore, we examined whether **R-BP(W)** could serve as a bright nanothermometer. Upon heating from 5 to 65 ºC, we observed a significant quenching of the white-light emission (Fig. 3a). The change can be seen by the naked eye (Fig. 3b), and the intensities of the fluorescence bands at 479 and 590 nm decreased upon heating. In addition, a representative heating/cooling cycle showed that the particle responded linearly to the range of temperatures studied, with a small hysteresis being observed (Fig. 3c).[27] Thus, the temperature sensitivity (S) over the temperature range was defined according to the following equation:[1a] $S = \Delta Q/Q_{\mathrm{T}}\Delta T \times 100\%$ in which Q_{T} is the fluorescence intensity at low temperature, ΔQ corresponds to the quenching of fluorescence and is equal to the change in the fluorescence intensity, ΔT is the temperature range, and S is given in % K^{-1}. The value of S for **R-BP**(**W**) was determined to be 1.1% K^{-1}, being almost consistent with that of CdTe luminescence thermometry.[28]

The successful implementation of **R-BP(W)** for use as a nanothermometer motivated us to examine reversibility of the luminescence spectra between 5 and 65 ºC. Fig. 3d shows five heating/cooling cycle experiments for the fluorescence response to temperature variation, indicating a repeatability for such cycles of heating and cooling where the fluorescence intensity at 5 ºC reached a similar state but needed 2 additional cycles. Taken together, linear sensitivity and reversible thermo-responsive switching in fluorescence have been successfully achieved by the interplay between TPE immobilized in the particle and rhodamine B grafted onto the surface. Temperature-dependent ring flipping of the unsubstituted phenyl rings in the TPE segments[29] plays a significant role in the thermo-responsive function, being followed by the change in emission of the rhodamine B through FRET from TPE to the rhodamine B units. In order to strengthen the argument, variable temperature ^{13}C-CP-MAS NMR and DLS measurements of **BP** were carried out. In the former case, the shape of signals assignable to methylene carbon and spirocarbon was significantly altered during the increase of temperature from 25 to 65 ºC (Fig. S9a in ESI), possibly due to dynamics in thermo-responsive of the particle. Such a speculation has been supported by DLS measurement which allowed us to detect change in particle sizes at different temperature (Fig. S9b in ESI). At 5 ºC, the averaged diameter of **BP** was estimated to be 79 nm, whereas the diameter at 65 ºC was 2.8 times larger than that at 5 ºC. A synergistic quenching of those emissive units under heating led to a notable change in the emission color, which was detected by the naked eye.

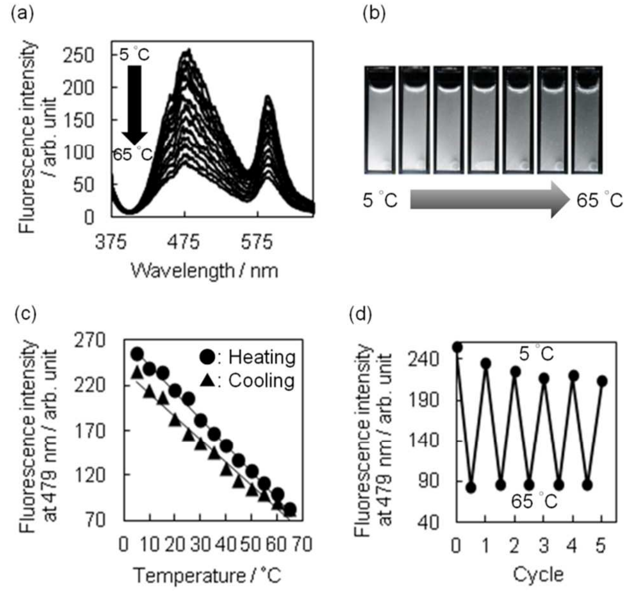

Fig. 3 (a) Overall fluorescence spectra of **R-BP**(**W**) (0.1 mg mL^{-1}) in water at various temperatures. The data acquisition interval was 10 min. (b) Temperature dependence of fluorescence intensity at 479 nm of **R-BP**(**W**) (0.1 mg mL^{-1}) under heating/cooling cycle from 5 to 65 ºC. (c) Consecutive heating-cooling cycle experiment conducted under similar conditions.

In conclusion, to the best of our knowledge, **R-BP(W)** represents the first white-light emissive nanothermometer with a temperature sensitivity of 1.1% K^{-1}, which can be operated at physiological temperatures in water. We believe that the proposed boronate-based organization would be a feasible methodology to engineer nanomaterials that can be sensitive to external stimuli.

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† Electronic Supplementary Information (ESI) available: Detailed experimental procedures and data (**Fig. S1**–**S9**). See DOI: 10.1039/b000000x/

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