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## LETTER

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# Colour-Tunable Aggregation-Induced Emission of Trifunctional *o*-Carborane Dye<sup>†</sup>

Cite this: DOI: 10.1039/x0xx00000x

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Received ooth January 2012, Accepted ooth January 2012

DOI: 10.1039/x0xx00000x

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o-Carborane compounds possessing emissive  $\pi$ -electron systems at the C1 and B9 (and/or B12) positions exhibit dual emission, *i.e.*, normal emission and aggregation-induced emission (AIE). Appropriate control of the emission intensity ratio for these dyes results in colour-tunable emission from blue to orange via white.

 $\pi$ -Conjugated compounds have attracted growing attention in recent years owing to their potential applications in sensors, molecular wires, light-emitting diodes (LEDs), photovoltaic cells, and fieldeffect transistors;<sup>1</sup> hence, there is a strong need to develop versatile methods for tuning the optical properties of such compounds. Generally, conjugated organic compounds exhibit strong photoluminescence in dilute solutions; however, the emission intensity decreases drastically when they form aggregates. This phenomenon is known as aggregation-caused quenching (ACQ) or concentration quenching. On the other hand, non-emissive molecules have recently been found to aggregate in solution and thus show strong emission; this phenomenon, known as aggregationinduced emission (AIE),<sup>2</sup> is attributed to the restricted molecular motion, which results in radiative decay. Organic emissive dyes such as silole,<sup>3</sup> tetraphenylethene,<sup>4</sup> and boron ketoiminate<sup>5</sup> derivatives exhibit AIE, because their aggregates exhibit more efficient emission than their dilute solutions.



Fig. 1 Structure of o-carborane.

o-Carborane  $(C_2H_{12}B_{10})$  is a polyhedral boron cluster containing two adjacent carbon atoms in the cluster cage (Figure 1), which has unique features such as neutron capture ability, hydrophobicity, and

thermal/chemical stability.<sup>6</sup> Following the recent reports that *o*-carborane-based conjugated compounds exhibit AIE, there have been extensive studies on their optoelectronic properties.<sup>7</sup> Intramolecular charge transfer (ICT) from the  $\pi$ -conjugated moieties to the C1–C2 bond<sup>8</sup> of *o*-carborane quenches the emission in solution, whereas the freezing of the C1–C2 bond vibration causes emission in aggregates (AIE).<sup>9</sup>

o-Carborane substituted with  $\pi$ -conjugated systems at the B9 and B12 positions behaves as a common emissive molecule that exhibits ACQ.<sup>10-12</sup> Thus, o-carborane-based  $\pi$ -conjugated compounds can adopt various radiative and non-radiative decay routes, depending on the substituted positions. In this study, we constructed 1,9,12-trifunctional o-carborane-based  $\pi$ -conjugated systems to control the emission behaviours by varying the substituent groups, substitution position, and aggregates. The ratio of the emission intensities of normal emission from a  $\pi$ -conjugated substituent at B9 (and/or B12) position and AIE from a  $\pi$ -conjugated substituent at C1 (and/or C2) position was controlled by adjusting the volume fraction of H<sub>2</sub>O in the THF solution, which led to the emission colour tuning from blue to orange via white.

Figure 2 outlines the synthetic route to C1,B9,B12-trifunctional *o*-carborane **5**. The treatment of B9,B12-bifunctional *o*-carborane, which was previously prepared,<sup>10,11</sup> with *n*-BuLi and the subsequent Ullmann-type coupling reaction<sup>13</sup> with 9-iodophenanthrene **2** afforded the trifunctional *o*-carborane **3** in 27% isolated yield. Desilylation with K<sub>2</sub>CO<sub>3</sub>/MeOH formed diyne **4** in 93% isolated yield, which was then allowed to react with **2** via Sonogashira-Hagihara coupling<sup>14</sup> to obtain the target compound **5** in 28% isolated yield. Monofunctional *o*-carborane **6** and B9,B12-bifunctional *o*-carborane **7** were also prepared as model compounds (Figure 1). The structures of the obtained compounds were characterized by <sup>1H</sup>, <sup>13</sup>C, and <sup>11</sup>B NMR spectroscopy; the spectra are shown in Supporting Information.

The UV-vis absorption and fluorescence spectra of **5** in the THF solution  $(1.0 \times 10^{-5} \text{ M})$  and THF/H<sub>2</sub>O solution  $(v/v = 1/99, 1.0 \times 10^{-5} \text{ M})$  are shown in Figures 3A and 3B, respectively. In Figure 3A, the absorption peaks of **5** are assigned to the  $\pi$ - $\pi$ \* transition band of phenanthrene and 9-(phenylethynyl)phenanthrene moieties; these can be related to the spectra of compounds **6** and **7** (Figure S13 in Supporting Information). Figure 3B shows that the absorption spectrum of **5** in THF/H<sub>2</sub>O solution (v/v = 1/99) is red-shifted and

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becomes broad compared to that in the THF solution, indicating the presence of intermolecular interaction in the aggregates.



**Fig. 2** (A) Synthesis of 1,9,12-tifunctional *o*-carborane compound **5**. (B) Structures of model compounds 6 and 7.

The fluorescence spectrum of **5** in THF  $(1.0 \times 10^{-5} \text{ M})$  was obtained by photo-excitation at 281 nm, as shown in Figure 3A; both C1-substituted phenanthrene and B9,B12-disubstituted 9-(phenylethynyl)phenanthrene moieties were excited at this

wavelength. The emission peak was observed at around 360 nm with a clear vibrational structure. The absolute fluorescence quantum efficiency ( $\Phi_{FL}$ ) was determined to be 0.05. In the dilute THF solution, the emission of the C1-substituted phenanthrene moiety was quenched effectively by ICT; therefore, only the emission peak from the B9,B12-disubstituted 9-(phenylethynyl)phenanthrene moiety was observed (refer to the fluorescence spectra of 6 and 7 in dilute THF in Figure S13).



**Fig. 3** UV-vis absorption and fluorescence spectra of **5**: (A) in THF (excited at 281 nm) and (B) THF/H<sub>2</sub>O = 1/99 (v/v) (excited at 340 nm) ( $1.0 \times 10^{-5}$  M). Asterisk denotes that scattered light was deleted.

As shown in Figure 3B, the THF/H<sub>2</sub>O solution of 5 exhibited dual-emission behaviour, and two broad peaks at 403 nm and 579 nm were observed. The emission peak at 403 nm was assigned to the emission from the B9,B12-disubstituted 9-(phenylethynyl)phenanthrene moieties. The peak was slightly red-shifted and broadened; in addition, the emission intensity decreased.

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Figure S16 in Supporting Information shows the fluorescence spectrum of 5 in frozen 2-MeTHF ( $1.0 \times 10^{-5}$  M at 77 K). The intense emission peak of 9-(phenylethynyl)phenanthrene unit was observed at around 360 nm with a vibrational structure, similar to that observed in the spectrum in THF at room temperature. This result suggests that the red-shift and broadening of the spectrum of 5 in THF/H<sub>2</sub>O solution arose from the ACQ. In the fluorescence spectrum of 5 in frozen 2-MeTHF ( $1.0 \times 10^{-5}$  M at 77 K), the relatively weak emission peak at around 580 nm was also observed due to the suppression of the C1-C2 bond vibration. Therefore, the peak at 579 nm in THF/H<sub>2</sub>O solution of 5 could be attributed to the AIE of the C1-substituted phenanthrene moiety due to the suppression of the C1-C2 bond vibration in the aggregation. As a result, the aggregates of 5 exhibited whitish orange fluorescence due to the dual emission, with absolute  $\Phi_{FL}$  of 0.12. The emission spectrum of 5 in the solid state was also measured; it was almost identical to the spectrum obtained in the THF/H<sub>2</sub>O solution (v/v =1/99), as shown in Figure S15.

Figure 4A shows the change in the fluorescence spectrum of 5 in varying concentrations of THF/H<sub>2</sub>O solution; the spectra are normalized with respect to the emission peaks of the 9-(phenylethynyl)phenanthrene unit.<sup>15</sup> The intensity ratio of the emission peak of 9-(phenylethynyl)phenanthrene at around 380 nm and the AIE peak at around 580 nm was gradually changed depending on the H<sub>2</sub>O volume fractions. For H<sub>2</sub>O volume fractions exceeding 70%, the AIE intensity increased drastically even with small changes in the dilution. Generally, the intensity of the AIE peaks depends strongly on the volume fraction of poor solvents.<sup>16</sup> We have previously reported that the AIE intensity of o-carborane dyes is remarkably enhanced above a threshold volume fraction of H<sub>2</sub>O.<sup>9</sup> The Commission Internationale de L'Eclairage (CIE) 1931 (x,y) chromaticity diagram of this fluorescence study (Figures 4B and S18) indicates the transition of emission colours. Two chromaticity transitions were observed between 0~70 and 70~99 H<sub>2</sub>O volume fractions. The earlier change was due to the of intermolecular interaction and ACQ 9\_ (phenylethynyl)phenanthrene moieties, whereas the later change was caused by the increasing contribution of orange AIE.<sup>16</sup> According to the CIE diagram, white emission, (x,y) = (0.33,0.28), was obtained from the aggregate in THF/H<sub>2</sub>O solution (v/v = 21/79).<sup>17</sup> Thus, the emission intensities of dual emission could be precisely controlled by change in the state of aggregates of a single molecule.

To understand the electronic structures of compounds **5**, **6**, and **7**, their density functional theory (DFT) calculations were performed at the B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) level of theory (Figure S19 in Supporting Information). The molecular orbital of **5** consisted of those of **6** and **7**; in addition, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **5** corresponded to the HOMO of **7** and the LUMO of **6**, respectively. The HOMO of **5** lies on the degenerate 9-(phenylethynyl)phenanthrene moieties. The HOMO did not overlap with any orbital of phenanthrene and was not electronically perturbed by the *o*-carborane unit. The LUMO of **5** overlapped with the  $\pi^*$ -orbital of phenanthrene and the anti-bonding orbital of the C1–C2 bond in the *o*-carborane cage, which thereby caused AIE.

In conclusion, *o*-carborane derivative containing  $\pi$ -electron systems at C1, B9, and B12 positions was synthesized and characterized. The obtained compound showed a dual-emission property; normal emission and AIE were observed in the B9- (and/or B12) and C1-substituted  $\pi$ -electron systems, respectively. The emission intensities could be precisely controlled depending on the aggregates formed in the THF and H<sub>2</sub>O solution, resulting in multi-coloured emission from blue to orange via white. This would be used as a new method to obtain solid materials that emit a range of

colours, tuned by varying the emissive  $\pi$ -electron systems on the *o*-carborane cage scaffold.



Fig. 4 (A) Fluorescence spectral change in THF/H<sub>2</sub>O. (B) Emission colours in a CIE 1931 chromaticity diagram of 5; table shows the ratio of THF/H<sub>2</sub>O (v/v) and the spectral chromaticity coordinates  $(1.0 \times 10^{-5} \text{ M})$ .

#### Acknowledgements

This work was supported by Grant-in-Aid for Exploratory Research (No. 24655102) and Grant-in-Aid for Scientific Research on Innovative Areas "Element-Blocks" (No. 24102013) from the Japan Society for the Promotion of Science. Financial support from The Shorai Foundation for Science and Technology is also gratefully acknowledged. M.T. appreciates Research Fellowships (No. 12J03404) from the Japan Society for the Promotion of Science for Young Scientists.

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- 17 Pictures of emission colours of 5 in THF/H<sub>2</sub>O are shown in Figure S18 in Supporting Information.
- 18 Recently, multiple emission system using 1,2-dinaphtyl-*o*-carborane was achieved, in which the orbital overlap between the aromatic

units and the C1–C2 orbital was controlled to form a new type of CT state; see reference 7m.

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Colour-Tunable Aggregation-Induced Emission of Trifunctional o-Carborane Dye

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o-Carborane compound showed a dual-emission property (normal emission and AIE), and the emission intensities could be precisely controlled, resulting in colour-tunable emission from blue to orange via white.

