

# Effects of alkyl chain length on aggregation-induced emission, self-assembly and mechanofluorochromism of tetraphenylethene modified multifunctional $\beta$ -diketonate boron complexes



Huaizhi Gao<sup>a,1</sup>, Defang Xu<sup>b,1</sup>, Yonghui Wang<sup>a</sup>, Ying Wang<sup>a</sup>, Xingliang Liu<sup>a,\*</sup>, Aixia Han<sup>a</sup>, Chao Zhang<sup>a</sup>

<sup>a</sup> Chemical Engineering College, Qinghai University, Xining 810016, China

<sup>b</sup> State Key Laboratory of Plateau Ecology and Agriculture, Qinghai University, Xining 810016, China

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## ABSTRACT

Two tetraphenylethene functionalized  $\beta$ -diketonate boron complexes **C2TPE-CAR** and **C16TPE-CAR** that were bridged by carbazole bearing alkyl chains of different lengths, have been designed and successfully synthesized. The two donor–acceptor luminogens showed typical twisted intramolecular charge-transfer (TICT) emission. In particular, they exhibited alkyl-dependent aggregation-induced emission (AIE), self-assembly and mechanofluorochromic (MFC) properties. Results showed that **C16TPE-CAR** with a long hexadecyl chain formed gels in certain solvents and also exhibited gelation-induced emission enhancement. H-aggregates were formed driven by the synergistic effect of  $\pi$ -stacking interaction and van der Waals force in the gel phase. However, **C2TPE-CAR**, which possessed the short ethyl group, exhibited no self-assembly behavior. Simple mechanical force could change the emission color of **C2TPE-CAR** and **C16TPE-CAR** powders from initial bright yellow (571 and 558 nm) to final red (617 and 610 nm), thus high contrast mechanofluorochromism with large spectral shifts of up to 46 and 52 nm, respectively, was observed. The powder XRD studies showed that the MFC behavior might be switched reversibly under the stimulus of external force because of crystalline-amorphous phase transformation.

## 1. Introduction

Mechanofluorochromic (MFC) materials [1], which sensitively respond to mechanical forces (such as grinding, shearing, stretching or pressing) with dramatic changes in their solid-state luminescence properties, have attracted much attention owing to their potential applications in mechanosensors [2], security systems [3], and memory devices [4]. In particular,  $\pi$ -conjugated molecules with aggregation-induced emission (AIE) [5], which are weakly-emissive or non-emissive in solution, but exhibit intense emission upon aggregate formation, might be potential candidates as promising MFC materials [1b,5a]. So far, much effort has been devoted to the design of new dyes with both AIE and MFC properties and a large number of AIE MFC luminogens, such as tetraphenylethene [6], 9,10-divinylanthracene [7], triphenylacrylonitrile [8] and organoboron complexes [9], have been developed. However, creating such organic AIE MFC materials, which combine high contrast mechanofluorochromism, excellent reversibility, and high fluorescence quantum yield in the solid state, is challenging. To further

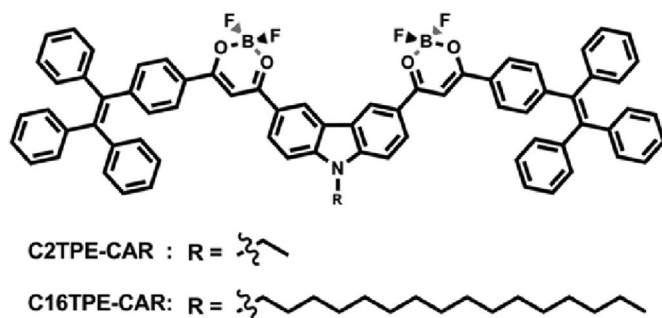
enlarge the family of specific AIE MFC compounds, it is necessary to carry out more extensive explorations on the new AIE-active MFC chromophores in this field.

Low molecular-weight gelators (LMWGs), which are colloidal matter that have an ability to trap the organic solvents or water in the network structures formed by a small quantity of gelators, have gained considerable interest in recent years [10]. LMWGs can self-assemble into nanostructures (such as fibers, sheets, tubes, and ribbons) driven by multiple weak noncovalent interactions such as  $\pi$ -stacking, hydrogen bonding, van der Waals force, and ionic interactions [11]. Gels formed by LMWGs have been used in templates of nano-scale inorganic materials [12], organic soft materials [13], and optical sensors [14]. However, the molecules with AIE, gelation, and MFC properties are still very few [15]. It is very important to rationally design and synthesize such new dyes with controllable multifunctional nature. In our previous work, we reported a  $\beta$ -diketonate boron luminogen modified with tetraphenylethene showing good AIE and MFC properties [9c]. With these results in mind, we designed and synthesized two new donor–acceptor

\* Corresponding author.

E-mail address: [liuxl1219@163.com](mailto:liuxl1219@163.com) (X. Liu).

<sup>1</sup> These authors contributed equally to this work.



Scheme 1. The molecular structures of C2TPE-CAR and C16TPE-CAR.

conjugated  $\beta$ -diketonate boron complexes bridged by carbazole, namely C2TPE-CAR and C16TPE-CAR, which are functionalized with tetraphenylethene and possess alkyl chains of different lengths (Scheme 1). Their alkyl-dependent AIE, self-assemblies and MFC behavior were investigated. Results illustrated that both C2TPE-CAR and C16TPE-CAR exhibited evident AIE characteristics and MFC properties, however, the length of alkyl chains can indeed make molecules to achieve distinct emission wavelength and different capability of fluorescence emission in the aggregate state. Particularly, the self-assembly behavior of the two compounds are different. C16TPE-CAR with a long hexadecyl chain formed gels in certain solvents and exhibited gelation-induced emission enhancement. By contrast, its analogue C2TPE-CAR, which possessed the short ethyl group, exhibited no self-assembly behavior.

## 2. Experimental section

### 2.1. Materials and measurements

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a Varian Mercury plus instrument at 400 and 100 MHz by using  $\text{CDCl}_3$  as the solvents. UV-visible spectra were collected on a Shimadzu UV-2550 spectrophotometer. Fluorescence measurements were performed on a Cary Eclipse Fluorescence Spectrophotometer. The absolute fluorescence quantum yields for C2TPE-CAR and C16TPE-CAR were measured on an Edinburgh FLS920 steady state spectrometer using an integrating sphere. The calculation for C2TPE-CAR was based on the density functional theory (DFT) and performed at the B3LYP/6-31G(d) level, employing the Gaussian 09W suit of programs. MS spectra were recorded on MALDI-TOF MS Performance (Shimadzu, Japan). Elemental analyses were performed with a Perkin-Elmer 240C elemental analyzer by investigation of C, H, and N. XRD patterns were obtained on a Bruker D8 Focus Powder X-ray diffraction instrument. The water/THF mixtures with different water fractions were prepared by slowly adding distilled water into solutions of the target molecules in THF under sonication at room temperature, the concentration was maintained at  $1.0 \times 10^{-5}$  M. The fluorescence emission spectral measurement of the mixture was performed immediately. The grinding powders were prepared by grinding the prepared powder with a pestle and mortar. The fumed samples were obtained by fuming the ground powder with DCM for 30 s. THF was distilled from sodium and benzophenone under nitrogen immediately prior to use. Dichloromethane (DCM) was distilled under normal pressure over calcium hydride under nitrogen before use. The other chemicals were used as received without further purification. Compounds 3, 5 and 6 were synthesized according to the reported procedures [9c,11c].

### 2.2. Synthesis

#### 2.2.1. 6,6'-(9-ethyl-9H-carbazole-3,6-diyl)bis(2,2-difluoro-4-(4-(1,2,2-triphenylvinyl)phenyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide) (C2TPE-CAR)

A mixture of 3 (4.61 g, 11.81 mmol) and 6a (1.50 g, 5.37 mmol)

was dissolved in dry THF (100 mL), and then NaH (60%, 2.15 g, 53.75 mmol) was added quickly. The mixture was refluxed with stirring for 24 h under an atmosphere of nitrogen. After cooling to room temperature, the mixture was acidified with dilute HCl and extracted with  $\text{CH}_2\text{Cl}_2$ . After solvent removal, the solid residue was dried under vacuum. The obtained solid was dissolved in dry  $\text{CH}_2\text{Cl}_2$  (120 mL), and then boron trifluoride diethyl etherate (6.78 mL, 7.62 g, 53.70 mmol) was added slowly to the solution. The mixture was refluxed for 24 h under an atmosphere of nitrogen. Then the mixture was poured into the water, and extracted with  $\text{CH}_2\text{Cl}_2$ . After solvent removal, the crude product was purified by column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$ /petroleum ether, v/v = 5/2), affording a saffron yellow solid (4.10 g). Yield 55%. Mp: 305–307 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.91 (s, 2H), 8.30 (d,  $J$  = 8.8 Hz, 2H), 7.98 (d,  $J$  = 8.4 Hz, 4H), 7.54 (d,  $J$  = 8.8 Hz, 2H), 7.26 (t,  $J$  = 9.2 Hz,  $J$  = 7.2 Hz, 4H), 7.18–7.14 (m, 18H), 7.09–7.04 (m, 14H), 4.49–4.44 (m, 2H), 1.55 (t,  $J$  = 7.2 Hz,  $J$  = 7.2 Hz, 3H) (Figs. S3 and S4);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  181.07, 151.47, 144.83, 143.68, 142.97, 142.93, 142.75, 139.61, 132.12, 131.32, 131.25, 129.90, 128.32, 128.07, 128.01, 127.74, 127.28, 126.99, 124.34, 123.41, 122.85, 109.82, 92.78, 38.66, 13.93 (Fig. S5). IR (KBr,  $\text{cm}^{-1}$ ): 699, 747, 763, 775, 797, 859, 890, 964, 1039, 1091, 1123, 1156, 1189, 1231, 1307, 1374, 1444, 1474, 1638, 1601, 1630. HRMS (MALDI-TOF)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{72}\text{H}_{51}\text{B}_2\text{F}_4\text{NO}_4$  1091.3940; Found 1091.3956 (Fig. S6). Anal. Calcd (%) for  $\text{C}_{72}\text{H}_{51}\text{B}_2\text{F}_4\text{NO}_4$ : C 79.21, H 4.71, N 1.28; Found: C 79.35, H 4.63, N 1.35.

#### 2.2.2. 6,6'-(9-hexadecyl-9H-carbazole-3,6-diyl)bis(2,2-difluoro-4-(4-(1,2,2-triphenylvinyl)phenyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide) (C16TPE-CAR)

By following the synthetic procedure for C2TPE-CAR, C16TPE-CAR was synthesized by using 3 (2.71 g, 6.94 mmol), 6b (1.50 g, 3.15 mmol) and NaH (60%, 1.26 g, 31.53 mmol) as the reagents. The mixture was refluxed with stirring for 24 h under an atmosphere of nitrogen. Then the intermediate was reacted with boron trifluoride diethyl etherate (3.98 mL, 4.47 g, 31.5 mmol) in  $\text{CH}_2\text{Cl}_2$ . The crude product was purified by column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$ /petroleum ether, v/v = 3/2), affording a saffron yellow solid (2.92 g). Yield 51%. Mp: 253–255 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.91 (s, 1H), 8.85 (s, 1H), 8.28 (t,  $J$  = 9.2 Hz,  $J$  = 9.2 Hz, 2H), 7.98–7.95 (m, 4H), 7.51 (t,  $J$  = 8.4 Hz,  $J$  = 8.4 Hz, 2H), 7.26 (t,  $J$  = 6.4 Hz,  $J$  = 7.2 Hz, 4H), 7.18–7.14 (m, 18H), 7.08–7.06 (m, 14H), 4.39–4.31 (m, 2H), 1.92 (s, 2H), 1.37–1.25 (m, 26H), 0.89 (t,  $J$  = 6.4 Hz,  $J$  = 6.8 Hz, 3H) (Figs. S7 and S8);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  181.74, 181.03, 151.45, 145.25, 143.67, 142.98, 142.94, 142.75, 139.62, 132.12, 131.32, 131.25, 129.90, 128.32, 128.07, 128.01, 127.91, 127.75, 127.28, 126.99, 124.28, 123.27, 122.74, 110.05, 92.78, 44.04, 31.89, 29.65, 29.62, 29.56, 29.51, 29.43, 29.32, 29.27, 28.97, 27.18, 22.66, 14.08 (Fig. S9). IR (KBr,  $\text{cm}^{-1}$ ): 699, 745, 755, 763, 775, 797, 859, 909, 964, 1037, 1073, 1092, 1123, 1141, 1189, 1231, 1308, 1369, 1410, 1444, 1474, 1538, 1599, 1630, 2852, 2924. HRMS (MALDI-TOF)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{86}\text{H}_{79}\text{B}_2\text{F}_4\text{NO}_4$  1287.6131; Found 1287.6143 (Fig. S10). Anal. Calcd. (%) for  $\text{C}_{86}\text{H}_{79}\text{B}_2\text{F}_4\text{NO}_4$ : C 80.19, H 6.18, N 1.09; Found: C 80.34, H 6.33, N 1.14.

## 3. Result and discussion

### 3.1. Synthesis of C2TPE-CAR and C16TPE-CAR

The synthetic routes for  $\beta$ -diketonate boron complexes C2TPE-CAR and C16TPE-CAR are depicted in Scheme 2. Firstly, the precursor tetraphenylethene derivative 3 was prepared by Suzuki-Miyaura coupling reaction between 1 and boric acid 2 [9c]. Then the 3,6-diacetyl carbazoles 6a-b [11c] were synthesized by Friedel-Crafts reactions of *N*-alkyl-substituted carbazoles 5a-b, respectively, which were obtained by the alkylation of carbazole 4 with alkyl halide [11c]. Finally, C2TPE-

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