

Tetraphenylethene-based β -diketonate boron complex: Efficient aggregation-induced emission and high contrast mechanofluorochromism

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ARTICLE INFO

Article history:

Received 16 October 2016

Received in revised form

1 December 2016

Accepted 4 December 2016

Available online 6 December 2016

Keywords:

β -Diketonate boron

Mechanofluorochromism

Aggregation induced emission

Intramolecular charge transfer

Tetraphenylethene

ABSTRACT

A new tetraphenylethene functionalized β -diketonate boron luminogen **BF₂-TPE** has been designed and successfully synthesized, and its aggregation induced emission (AIE) characteristics and the mechanofluorochromic (MFC) behaviors have been investigated in detail. The results showed that boron complex **BF₂-TPE** could emit intense yellow fluorescence in the solid state ($\lambda_{em} = 544$ nm, $\Phi_f = 92.5\%$) and exhibited obvious AIE characteristics ($\alpha_{AIE} = 231$). More interestingly, the compound showed the reversible MFC behavior between the crystalline and the amorphous states. Simple mechanical force could change the emission color of **BF₂-TPE** solid from initial yellow (544 nm) to final orange-red (606 nm), affording high contrast mechanofluorochromism with large spectral shift of up to 62 nm. The results obtained would be of great help in designing new MFC materials.

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1. Introduction

Recently, mechanofluorochromic (MFC) emissive luminogens [1] exhibiting reversible stimuli-responsive emission switching in the solid state have gained more and more attention owing to their fundamental importance and potential applications in memory devices [2], optoelectronic devices [3], security papers [4] and mechanosensors [5]. As a kind of “smart material”, their emitting colors change in response to external mechanical forces such as grinding, crushing, and pressing, and can be restored to the original states by heating, recrystallization, or exposure to solvent vapors. Till now, a good number of MFC molecules have been designed, including the derivatives of pyrene [6], anthracene [7], dibenzofulvene [8], tetraphenylethene [9], Silole [10], and cyanostilbene [5a,11], as well as some boron complexes [12,13]. High solid-state luminescence efficiency and an obvious color contrast play an important role in the applications of mechanochromic fluorescent

materials. However, the fluorescence efficiency of many traditional organic luminescent materials often becomes very weak while in the solid state through the aggregation-caused quenching (ACQ) effect caused by intermolecular π - π stacking interaction [14]. Consequently, the MFC phenomenon becomes difficult to observe. In 2001, Tang et al. reported on aggregation-induced emission (AIE) materials, an important class of anti-ACQ materials that exhibit strong emission when a molecular aggregate occurs in poor solvents or in the solid state [15]. And in 2002, Park et al. reported on aggregation-induced enhanced emission (AIEE) materials [16], which are similar to AIE materials. Since then, a large number of AIE luminogens characterized by strongly twisted skeleton bearing rotatable aryl units have been developed and most of them have been found to possess MFC nature due to their strong solid-state fluorescence and diverse aggregation morphology [17]. Indeed, AIE has been considered a key for opening a treasure chest of MFC materials. For example, in 2010, Park's group reported the cyanodistyrylbenzene derivative [11a], which has mechanofluorochromic aggregation-induced enhanced emission (AIEE) properties. Then a number of new mechanofluorochromic AIE compounds were also synthesized by Tang, Chi and their co-

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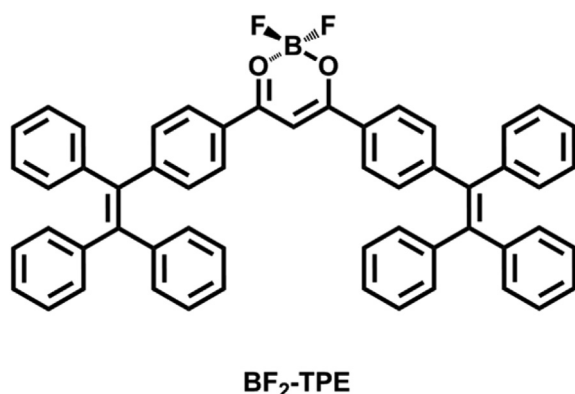
workers [1b,7a,b,8,9a–c,17d,18,19]. However, most present MFC materials based on AIE dyes show the MFC shifts within tens of nanometers under simple mechanical force, and those with very large MFC shifts (>60 nm) and well-marked colorimetric fluorescence are still scarce [1c,7c,20]. To further enlarge the family of specific mechanofluorochromic AIE compounds, it is necessary to carry out more extensive exploration of new AIE-active MFC chromophores in this field.

As one of the most important types of organoboron fluorescent dyes, boron diketonate derivatives have received much attention due to their prominent photo properties such as high fluorescence quantum yields, large molar extinction coefficients, large two-photon absorption cross sections, and sensitivity to the surrounding medium [21]. Fraser et al. reported that boron diketonate derivatives exhibited prominent fluorescence, room-temperature phosphorescence, and further intriguing reversible mechanochromic fluorescence between the solid and the melt states [12a–d,21b]. However, β -diketonate boron fluorescent dyes that exhibit strong fluorescence in dilute solutions quench or reduce the fluorescence intensity in the solid state owing to ACQ caused by intermolecular π – π stacking interaction. Although some luminescent boron complexes containing chelating N,O- and N,N-chromophores showing AIE effects have been developed [13b,22–24], it is still a challenging to rationally design β -diketonate boron complex with excellent AIE properties, especially with both MFC and AIE behaviors. Bearing these facts in mind, we designed and synthesized a new D-A conjugated β -diketonate boron complex that is functionalized with tetraphenylethene, namely **BF₂-TPE** (Scheme 1). The compound exhibits typical AIE ($\alpha_{\text{AIE}} = 231$) and intramolecular charge transfer (ICT) characteristics, remarkable mechanochromism (emission wavelength change up to 62 nm), and moreover high solid-state emission efficiency up to 92.5%, which is rarely found in ICT β -diketonate boron luminogens.

2. Experimental section

2.1. Materials and measurements

¹H and ¹³C NMR spectra were recorded with a Mercury plus instrument at 400 and 100 MHz by using CDCl₃ as the solvents. 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. 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 yield for **BF₂-TPE** was measured on an Edinburgh FLS920



Scheme 1. The molecular structure of **BF₂-TPE**.

steady state spectrometer using an integrating sphere. The calculation for **BF₂-TPE** was based on the density functional theory (DFT) and performed at the B3LYP/6-31G(d) level, employing the Gaussian 09W suit of programs. Differential scanning calorimetry (DSC) curves were carried out using a DSC/DTA-TG instrument (STA 449F3 Jupiter Netzsch, Germany) at a heating rate of 10 °C min^{−1} under N₂ atmosphere. XRD patterns were obtained on a Bruker D8 Focus Powder X-ray diffraction instrument. Dynamic light scattering (DLS) measurements were performed on the BI-200SM Laser Light Scattering System (Brookhaven). The THF/H₂O 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 1.0×10^{-5} M. The fluorescence emission spectral measurement of the mixture was performed immediately. The grinding powders were prepared by grinding the as-prepared powder with a pestle in the mortar. The fumed samples were obtained by fuming the grinding powder with CH₂Cl₂ for 1 min. THF was distilled over sodium and benzophenone. CH₂Cl₂ was dried with sodium hydride. The other chemicals were used as received without further purification. Column chromatography was performed on silica (silica gel, 200–300 mesh).

2.2. Synthesis

2.2.1. 1-(4-(1,2,2-triphenylvinyl)phenyl)ethanone (**3**)

A solution of **1** (15.00 g, 44.74 mmol), **2** (7.50 g, 45.74 mmol), Pd(PPh₃)₄ (100 mg, 0.087 mmol), K₂CO₃ (11.0 g, 79.59 mmol) in toluene/H₂O (200 mL, v/v = 4/1) was heated to reflux under nitrogen atmosphere for 24 h. Then the mixture was cooled to room temperature and the organic layer was separated, the aqueous layer extracted with CH₂Cl₂ (2 × 100 mL), the combined organic layer dried over anhydrous Na₂SO₄, and evaporated to dryness. The crude product was purified by column chromatography (silica gel; petroleum ether/CH₂Cl₂, v/v = 1/1) to give a light yellow solid (16.25 g), yield 97%. M.p. 112.0–114.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.17–7.14 (m, 11H), 7.07–7.06 (m, 6H), 2.55 (s, 3H) (Fig. S10); ¹³C NMR (100 MHz, CDCl₃) δ 197.72, 149.05, 143.22, 143.16, 143.09, 142.62, 139.89, 134.97, 131.52, 131.29, 127.90, 127.82, 127.75, 126.95, 126.79, 26.56 (Fig. S11); HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₈H₂₃O 375.1749; Found 375.1746 (Fig. S12). Anal. Calcd for C₂₈H₂₂O: C 89.81, H 5.92; Found: C 89.65, H 6.04.

2.2.2. Methyl 4-(1,2,2-triphenylvinyl)benzoate (**5**)

By following the synthetic procedure for compound **3**, **5** was synthesized by using **1** (10.00 g, 29.83 mmol) and **4** (6.50 g, 36.12 mmol) as the reagents. The crude product was purified by column chromatography (silica gel; petroleum ether/CH₂Cl₂, v/v = 1/1) to give a light yellow solid (11.40 g), yield 98%. M.p. 144.0–146.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.81–7.78 (m, 2H), 7.13 (s, 11H), 7.05–7.03 (m, 6H), 3.88 (s, 3H) (Fig. S13); ¹³C NMR (100 MHz, CDCl₃) δ 166.99, 148.81, 143.23, 143.14, 143.08, 142.45, 139.95, 131.32, 131.27, 128.99, 127.91, 127.84, 127.71, 126.87, 126.73, 51.97 (Fig. S14). HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₈H₂₃O₂ 391.1698; Found 391.1694 (Fig. S15). Anal. Calcd for C₂₈H₂₂O₂: C 86.13, H 5.68; Found: C 86.25, H 5.49.

2.2.3. 3-Hydroxy-1,3-bis(4-(1,2,2-triphenylvinyl)phenyl)prop-2-en-1-one (**6**)

A mixture of **3** (1.92 g, 5.13 mmol) and **5** (2.00 g, 5.12 mmol) was dissolved in dry THF (60 mL), and then NaH (60%, 2.00 g, 50.00 mmol) was added. 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 CH₂Cl₂. After solvent removal, the solid residue was

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