Aggregation-induced emission and mechanofluorochromism of tetraphenylbutadiene modified β-ketoiminate boron complexes

Huaizhi Gao[a,1], Defang Xu[b,1], Yonghui Wang[a], Chao Zhang[a], Yan Yang[a], Xingliang Liu[a,*], Aixia Han[a], Ying Wang[a]

[a] Chemical Engineering College, Qinghai University, Xining 810016, China
[b] State Key Laboratory of Plateau Ecology and Agriculture, Qinghai University, Xining 810016, China

ARTICLE INFO

ABSTRACT

Two new benzo[d]oxazole- and benzo[d]thiazole-fused β-ketoiminate boron complexes (**BF₂-TBO** and **BF₂-TBT**) modified by tetraphenylbutadiene have been designed and successfully prepared, and their intramolecular charge-transfer (ICT), aggregation-induced emission (AIE) and mechanofluorochromic (MFC) properties were investigated. The results showed that the two D-π-A type compounds exhibited typical ICT emission, evident AIE characteristics (α_{AIE} = 89 and 33, respectively), and high state emission intensity (up to 0.445 and 0.367, respectively). More importantly, **BF₂-TBO** and **BF₂-TBT** showed the reversible MFC behavior with their emitting colors changing from yellowish green (located at 528 and 530 nm) to yellow and orange (located at 552 and 572 nm) upon grinding, respectively, with red-shifts of 24 and 42 nm were obtained. The X-ray diffraction analyses confirmed that the MFC properties of **BF₂-TBO** and **BF₂-TBT** should be derived from a phase transition between crystalline and amorphous states. It was noticed that benzo[d]thiazole-fused **BF₂-TBT** showed more contrasting MFC behavior relative to benzo[d]oxazole-fused **BF₂-TBO**. The reason is that the existence of sulfur atom in **BF₂-TBT** could lead to a larger degree of ICT in the excited state than that of **BF₂-TBO**, which endowed it with greater planar intramolecular charge transfer (PICT) after grinding, resulting in a larger red-shift in the PL spectrum.

1. Introduction

The design and synthesis of solid-state emissive π-conjugated luminophores has attracted tremendous interest because of their extensive application in various fields, such as organic light emitting diodes (OLEDs) [1], photoelectric conversion [2], and solid-state fluorescent sensors [3]. One of the main challenges in the field is the fact that many traditional fluorescent dyes become weakly emissive when they are either in the solid or aggregated states despite being strongly emissive in dilute solutions as a result of the notorious photophysical effect of "aggregation-induced emission quenching" (ACQ) [4], which has greatly limited the practical applications of the dyes as optoelectronic materials. To overcome the ACQ effect and concentration quenching, a more successful approach is to create emissive luminophores exhibiting aggregation-induced emission (AIE). AIE luminophores, which were first discovered by Tang and co-workers in 2001 [5], are nonluminescent in the dilute solutions, but become highly emissive in the aggregate states. Thus, great attention has been paid to

the design and synthesis of new luminophores exhibiting AIE behavior and a number of new AIE-active compounds were reported [6]. In fact, many AIE-active fluorophores have been found to be promising mechanofluorochromic (MFC) materials [6,7], which change their solid-state emission color in response to external mechanical stimuli (such as grinding, pressing, shearing, deformation, etc.). Since the report by Park et al., concerning the cyano-distyrylbenzene derivative that exhibits both AIE activity and MFC behavior in 2010 [8], a number of new AIE MFC compounds including tetraphenylethene [9,10], 9,10-divinylanthracene [11], triphenylacrylonitrile [12] and organoboron complexes [13,14], have been developed. However, even using the AIE strategy, the number of AIE MFC luminophores that exhibit both high solid-state luminescence efficiency and an obvious color contrast are still relatively rare. Therefore, the development of new AIE MFC luminophores will contribute to a better understanding of the phenomenon and lead to novel applications.

Recently, organoboron solid-emissive fluorescent dyes have attracted considerable attention because of their excellent photophysical

---

* Corresponding author.
 E-mail address: liuxl1219@163.com (X. Liu).
 [1] These authors contributed equally to this work.
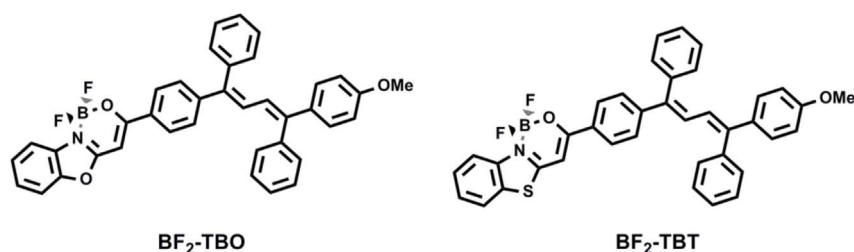
Scheme 1. The molecular structures of **BF₂-TBO** and **BF₂-TBT**.

properties and potential use in OLEDs [1a,15], fluorescent sensors [3b,16] and organic solid-state lasers [17]. However, most organoboron compounds quench or reduce the fluorescence intensity in the solid state due to ACQ effect. Although some luminescent boron complexes containing chelating *N,O*- and *N,N*-chromophores showing AIE effects have been developed [18], it is still challenging to rationally design organoboron complexes with excellent AIE properties, especially with both MFC and AIE behavior [13,14]. Herein, we present the synthesis and properties of two new D–π–A type benzo[*d*]oxazole- and benzo[*d*]thiazole-fused β-ketoiminate boron complexes with tetraphenylbutadiene units, namely **BF₂-TBO** and **BF₂-TBT** (Scheme 1). The two compounds exhibit typical ICT and significant AIE characteristics, remarkable MFC behavior, and high solid-state emission efficiency. Moreover, **BF₂-TBT** shows more contrasting MFC behavior relative to **BF₂-TBO**, which is attributed to the existence of sulfur atom in **BF₂-TBT** resulting in better π-electron delocalization.

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. Mass spectra were recorded on an Agilent Technologies 6224 spectrometer and MALDI-TOF MS Performance (Shimadzu, Japan). IR spectra were measured with a Nicolet-360 FTIR spectrometer by incorporation of samples in KBr disks. 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 yields for **BF₂-TBO** and **BF₂-TBT** were measured on an Edinburgh FLS920 steady state spectrometer using an integrating sphere. The calculations for **BF₂-TBO** and **BF₂-TBT** were based on the density functional theory (DFT) and performed at the B3LYP/6-31G(d) level, employing the Gaussian 09W suit of programs. XRD patterns were obtained on a Bruker D8 Focus Powder X-ray diffraction instrument.

2.2. Synthesis

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. Compound **1** was synthesized according to the literature [19].

The synthetic routes for boron complexes **BF₂-TBO** and **BF₂-TBT** were shown in Scheme 2. The tetraphenylbutadiene derivative **3** was obtained through the two-step Suzuki coupling reaction by using **1** as the starting material with a total yield of 52%. The target molecules of **BF₂-TBO** and **BF₂-TBT** were prepared from **3** and the corresponding compounds 2-methylbenzooxazole **4a** and 2-methylbenzothiazole **4b** in the presence of sodium hydride in anhydrous THF followed by complexation with boron trifluoride diethyl etherate, to give yields of 60% and 63%, respectively. All the intermediates and target molecules were purified by column chromatography on silica gel, and unambiguously

characterized by ¹H and ¹³C NMR, MALDI-TOF mass spectrometry, and C, H, N elemental analyses. **BF₂-TBO** and **BF₂-TBT** are soluble in common organic solvents, such as CHCl₃, CH₂Cl₂, benzene, toluene, THF and DMSO, but show poor solubility in alcohols and aliphatic hydrocarbon solvents, such as methanol, ethanol, cyclohexane and *n*-hexane.

2.2.1. ((1E,3E)-1-bromo-4-(4-methoxyphenyl)buta-1,3-diene-1,4-diyl)dibenzene (2)

Compound **1** (3.00 g, 8.24 mmol), (4-methoxyphenyl)boronic acid (1.25 g, 8.23 mmol), Pd(PPh₃)₄ (150 mg, 0.130 mmol), K₂CO₃ (3.40 g, 24.60 mmol) were added to the mixed solvents of toluene (180 mL), methanol (20 mL) and water (25 mL). The mixture was heated to reflux under a nitrogen atmosphere for 24 h. After cooling to room temperature and the organic layer was separated, the aqueous layer extracted with CH₂Cl₂ (2 × 50 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 = 1/4) to give a light yellow solid (2.10 g), yield 65%. Mp: 91–93 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 6.8 Hz, 2H), 7.41–7.29 (m, 8H), 7.23 (d, J = 8.8 Hz, 2H), 7.12 (d, J = 10.4 Hz, 1H), 7.02–6.95 (m, 3H), 3.88 (s, 3H) (Fig. S8); ¹³C NMR (100 MHz, CDCl₃) δ 159.35, 146.71, 142.39, 139.74, 132.07, 131.82, 128.59, 128.49, 128.32, 128.16, 128.05, 127.62, 127.52, 126.65, 126.43, 126.10, 113.70, 55.30 (Fig. S9). IR (KBr, cm⁻¹): 650, 697, 740, 760, 766, 800, 816, 836, 873, 881, 894, 914, 970, 1030, 1077, 1109, 1131, 1157, 1176, 1216, 1245, 1273, 1299, 1365, 1442, 1458, 1486, 1509, 1600, 1906, 1954, 2834, 2948. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₂₃H₁₉⁷⁹BrO 390.0619; Found 390.0627 (Fig. S10). Anal. Calcd for C₂₃H₁₉BrO: C 70.60, H 4.89; Found: C 70.69, H 4.82.

2.2.2. Methyl 4-((1E,3E)-4-(4-methoxyphenyl)-1,4-diphenylbuta-1,3-dien-1-yl)benzoate (3)

By following the synthetic procedure for **2**, **3** was synthesized by using **2** (2.80 g, 7.16 mmol), (4-(methoxycarbonyl)phenyl)boronic acid (2.60 g, 14.45 mmol), Pd(PPh₃)₄ (100 mg, 0.087 mmol), K₂CO₃ (2.97 g, 21.49 mmol) as the reagents. The crude product was purified by column chromatography (silica gel, CH₂Cl₂/petroleum ether, v/v = 1/1), affording a yellowish green solid (2.55 g). Yield 80%. Mp: 180–182 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.27–7.24 (m, 8H), 7.19–7.16 (m, 4H), 6.97 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 11.2 Hz, 1H), 6.67 (d, J = 11.2 Hz, 1H), 3.97 (s, 3H), 3.87 (s, 3H) (Fig. S11); ¹³C NMR (100 MHz, CDCl₃) δ 167.00, 159.17, 145.00, 144.91, 142.63, 142.38, 141.94, 131.96, 130.77, 129.57, 129.16, 128.29, 128.17, 127.89, 127.65, 127.60, 127.54, 127.14, 125.06, 113.66, 55.28, 52.15 (Fig. S12). IR (KBr, cm⁻¹): 667, 692, 710, 736, 767, 778, 812, 836, 844, 901, 910, 968, 1019, 1030, 1103, 1112, 1128, 1175, 1245, 1276, 1346, 1402, 1440, 1462, 1489, 1509, 1605, 1723, 2338, 2359, 2828, 2949. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₃₁H₂₆O₃ 446.1882; Found 446.1891 (Fig. S13). Anal. Calcd for C₃₁H₂₆O₃: C 83.38, H 5.87; Found: C 83.27, H 5.92.