

Mechanofluorochromism of difluoroboron β -ketoiminate boron complexes functionalized with benzoxazole and benzothiazole



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ARTICLE INFO

Keywords:

Difluoroboron β -ketoiminate boron complexes
Benzoxazole
Benzothiazole
Aggregation-induced emission
Mechanofluorochromism

ABSTRACT

New difluoroboron β -ketoiminate boron complexes bearing benzoxazole (CBO) and benzothiazole (CBS) have been synthesized. It was found that CBO was almost non-emissive in THF, and the emission could be intensified significantly when great amount of H₂O was added, illustrating AIE (aggregation-induced emission) property. CBS could not show AIE property in THF/H₂O system, but its emission in solid state was also strong. The single crystal structure of CBS suggested that π - π interactions and the hydrogen bonds of C(Ar)–F...H, C(Ar)–H...S and C(Ar)–H...Cl would suppress the rotation of single bonds, resulting into obvious emission enhancement. It is interesting that the as-synthesized crystals of CBO and CBS both emitted azure light, and the grinding made their emitting colors to change into cyan and green, which could be recovered under fuming with DCM or heating. The reversible mechanofluorochromism was due to the transformation between crystalline and amorphous states, which could be confirmed from the results of absorption spectra, XRD patterns and DSC curves in different solid states. Additionally, the high-contrast mechanofluorochromism of CBS compared with CBO might be originated from the loose packing in crystalline state and the better π -electron delocalization.

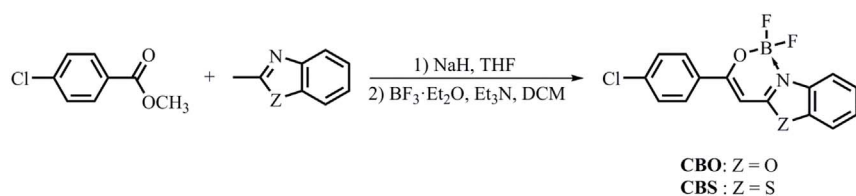
1. Introduction

Mechanofluorochromic (MFC) materials, whose emitting colors change in response to external mechanical stimuli (such as grinding crushing, and rubbing, etc) [1,2], have received much attention owing to their promising applications in data storage [3], optical switches [4], sensors [5,6], rewritable media [7], security ink [8] and optoelectronic devices [9]. Since Araki et al. reported the first organic mechanofluorochromic compound based on 1,3,6,8-tetraphenylpyrene derivative bearing four hexyl amide groups [10], a great deal of effort has been made to design novel organic mechanofluorochromic materials. For example, Weder et al. found that the emitting color of crystalline powders of cyano substituted oligo(phenylene vinylene) changed from blue to yellow upon compressed, and heating facilitated the recovery of the original luminescent color [11]. The MFC behaviors of the dendritic liquid crystalline compounds of phenylethynyl modified pyrene/anthracene were studied by Kato et al. [12] Wang and coworkers reported the MFC properties of anthrylpyrazole-based dyes [13]. It is obvious that the strong emission of the organic compounds in solid states is essential for mechanofluorochromism. However, the fluorescence efficiency of the luminescent organic dyes is often weakened in solid state or in concentrated solutions due to the aggregation-caused quenching

(ACQ) effect. In 2001, Tang et al. reported a kind of fluorescent dyes, namely aggregation-induced emission (AIE) materials, which are highly emissive in the aggregated states compared with those in isolated states [14]. In 2010, Park et al. found the first MFC behaviors of AIEE (aggregation-induced enhanced emission) compound based on (2Z,2'Z)-2,2'-(1,4-phenylene)bis(3-(4-butoxyphenyl)acrylonitrile) [16]. Xu et al. investigated MFC properties of a series of tetraphenylethylene derivatives, which are typical AIEgens [17]. Our group has found that the emitting colors of the as-synthesized crystals formed from D- π -A type conjugated compounds of benzoxazole, triphenylacrylonitrile, terephthalate, quinoxalines and phenothiazine changed obviously upon grinding, and could be recovered via fuming with organic vapors [15,18,19]. Among the luminescent materials, boron-containing complexes, especially, *N,N*-, *O,O*- and *N,O*-chelated difluoroboron complexes, are attractive fluorophores employed in sensors, bioimaging, OLED and near-infrared emitters on account of the easily tuneable structures of the ligands, high molar absorption coefficients, large Stokes shift, high fluorescence quantum yields in solutions and in solid-states, and photochemical stability [20]. Fraser et al. have reported the changes of the solid emission of a series of difluoroboron β -diketonate complexes upon stimulated by mechanical forces [21]. Matsui et al. have synthesized pyrazine- and thiazole-boron complexes exhibiting

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Scheme 1. Synthetic routes for difluoroboron β -ketoiminate boron derivatives **CBO** and **CBS**.

MFC properties [22]. We have prepared carbazole-functionalized difluoroboron β -diketonate complexes with multi-colour solid-state luminescence [23] and the difluoroboron complexes bearing the ligands of salicylaldehyde with MFC activities [24]. In particular, the fluorescence of β -ketoiminate boron complexes could be easily tuned by the structures of ligands and is sensitive to external microenvironments [25,26]. It should be noted that benzoxazole and benzothiazole have numerous applications in pharmaceutical synthesis [27], CO₂ storage [28], catalytic applications [29], and luminescent dyes [30], however, they have not been introduced as the ligands in difluoroboron β -ketoiminate complexes. Herein, we synthesized new difluoroboron β -ketoiminate complexes functionalized with benzoxazole and benzothiazole (**CBO** and **CBS**, Scheme 1). It is interesting that **CBO** and **CBS** were high emissive in solid states because of the suppression of the rotation of single bonds, and they exhibited MFC properties. Interestingly, **CBS** gave high-contrast response to mechanical forces during MFC process compared with **CBO** because of the loose packing in crystalline state and the better π -electron delocalization of **CBS**. It provided a strategy for designing MFC dyes.

2. Experimental section

2.1. Materials and methods

¹H NMR spectra were recorded with Bruker Avance III 400 MHz by using DMSO-*d*₆ as the solvent. ¹³C NMR spectra were recorded on a mercury plus 100 MHz using DMSO-*d*₆ as the solvent. FT-IR spectra were measured with a Nicolet-360 FT-IR spectrometer by incorporation of samples in KBr disks. Mass spectra were obtained with Agilent 1100 MS series and AXIMA CFR MALDI-TOF (Compact) mass spectrometers. C, H, and N elemental analyses were taken on a Vario EL cube elemental analyzer. UV-vis absorption spectra were determined on a Shimadzu UV-1601PC Spectrophotometer. Fluorescent emission spectra were carried out on a Shimadzu RF-5301 Luminescence Spectrometer. The solid-state fluorescence quantum yields were measured by integrating sphere on Edinburgh Instrument FLS920. XRD patterns were obtained on Empyrean XRD equipped with graphite monochromatized Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$), employing a scanning rate of 0.00267°/s in the 2 θ range of 5° to 40°. Single crystals of **CBO** and **CBS** were selected for X-ray diffraction analysis on a Rigaku RAXIS-RAPID diffractometer using graphite-monochromatized Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$), and the crystals were kept at room temperature during data collection. The structures were solved by the direct methods and refined on F2 by full-matrix least-square using the SHELXTL-97 program. The ground powder was prepared by grinding the as-synthesized sample with a pestle in the mortar for 5 min. The fumed sample was obtained by fuming the ground powder with DCM vapor, and the ground sample was heated at 200 °C, which was lower than the melting point. Cyclic voltammetry (CV) was performed on a CHI 604C voltammetric analyzer in DCM (refluxed with CaH₂ over night) containing Bu₄NBF₄ (0.1 M) as a supporting electrolyte. Platinum button was used as a working electrode and a platinum plate as a counter electrode. All potentials were recorded versus Ag/Ag⁺ as a reference electrode (using ferrocene as internal standard). The scan rate was maintained at 50 mV/s. The optimized configurations and HOMO and LUMO molecular orbitals were calculated by the DFT (B3LYP/6-31G) method on Gaussian 09 software. Differential scanning

calorimetry (DSC) curves were obtained on a Netzsch DSC 204F1 at a heating rate of 10 °C/min.

THF was dried over sodium and benzophenone. DCM was dried over calcium hydride. The other chemicals and reagents were used as received without further purification. The single crystals of **CBO** and **CBS** were gained by slow evaporation of the solutions in DCM/petroleum ether.

2.2. Synthesis

3-(4-chlorophenyl)-1,1-difluoro-1H-benzo[4,5]oxazolo[3,2-c][1,3,2]oxazaborinine (**CBO**)

NaH (60%, 0.28 g, 7.03 mmol) was added to a solution of 2-methylbenzoxazole (0.61 mL, 7.03 mmol) in dry THF (30 mL) at 0 °C. Then, methyl 4-chlorobenzoate (1.12 g, 8.44 mmol) was added and the mixture was stirred at room temperature for 30 min. After that, the mixture was refluxed under an atmosphere of nitrogen for 24 h and cooled to room temperature and acidified with HCl (0.1 mol/L). A white cotton-like solid was collected by filtration and dried under vacuum. The intermediate of β -ketoiminate was not purified and dissolved in DCM (30 mL), in which boron trifluoride ether complex (0.93 mL, 7.80 mmol) and triethylamine (1.09 mL 7.80 mmol) were added. The mixture was refluxed under an atmosphere of nitrogen for another 2 h. After that, the mixture was poured into water (200 mL), and was extracted with DCM, followed by dried over anhydrous Na₂SO₄. After removal of the solvent, the crude product was purified by column chromatography (silica gel) using petroleum ether/ethyl acetate (v/v = 5/1) as eluate to afford **CBO** (1.76 g) as a white solid in 76% yield. m.p.: 250 °C (obtained from DSC); ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.13 (d, *J* = 8.0 Hz, 2H), 7.96–7.94 (m, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.60–7.57 (m, 2H), 7.25 (s, 1H) (Fig. S10). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 169.33, 164.94, 148.50, 137.90, 131.94, 130.07, 129.57, 129.29, 127.45, 126.99, 114.94, 112.53, 82.56 (Fig. S11). FT-IR (KBr, cm⁻¹) ν 659, 697, 724, 740, 752, 786, 838, 886, 1008, 1034, 1092, 1115, 1132, 1171, 1222, 1270, 1280, 1297, 1339, 1372, 1394, 1421, 1462, 1487, 1554, 1593, 1630. MALDI-TOF MS: *m/z*: calculated for C₁₅H₉O₂NBF₂Cl: 319.5; found: 320.9 ([M + H]⁺) (Fig. S12). Elemental analysis (%): C 56.39, H 2.84, N 4.38; found: C 56.29, H 3.13, N 4.32.

3-(4-chlorophenyl)-1,1-difluoro-1H-benzo[4,5]thiazolo[3,2-c][1,3,2]oxazaborinine (**CBS**)

Following the synthetic procedure of **CBO**, the intermediate was afforded by the condensation of methyl 4-chlorobenzoate (1.20 g, 7.03 mmol) and 2-methylbenzothiazole (0.94 mL, 8.44 mmol) in THF, followed by complexed with boron trifluoride diethyl ether (1.30 mL, 10.28 mmol) in the presence of triethylamine (1.40 mL, 10.28 mmol). The crude product was purified by column chromatography (silica gel) using petroleum ether/ethyl acetate (v/v = 6/1) as eluate to afford **CBS** as a light yellowish solid (1.70 g) in 73% yield. m.p. 243 °C (obtained from DSC); ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.24 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 8.0, 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 8.0, 8.0 Hz, 1H), 7.54 (s, 1H) (Fig. S13). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 169.15, 163.52, 142.06, 137.42, 131.98, 129.64, 129.45, 129.02, 128.91, 126.64, 124.14, 117.88, 91.20 (Fig. S14). FT-IR (KBr, cm⁻¹) ν 482, 579, 632, 683, 724, 752, 785, 805, 841, 876, 933, 1013, 1046, 1097,

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