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Dimesitylborylphenyl substituted 1,3,4-oxadiazole: Synthesis, characterization and sensitivity to F⁻

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Abstract

A new 1,3,4-oxadiazole compound with a dimesitylboryl group was synthesized and characterized by ¹H NMR, MS, element analysis and X-ray single-crystal diffraction. It exhibits good blue emission at 425 nm and high sensitivity to fluoride anion. \bigcirc 2010 Xiang Hong Li. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

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Owing to the vacant *p*-orbital of heteroatom boron, dimesitylboryl compounds containing three-coordinated organoboron groups exhibit interesting fluorescence emission. Design and synthesis of new dimesitylboryl compounds have been of interest to chemists for recent years because of their potential applications in OLEDs [1–3], fluoride ion chemo-sensors [4–6] and optical materials [7]. To explore diverse properties of dimesitylboryl compounds, thiophene [1,3b], fluorene [3b], naphthylphenylamine [2,3a], SiPh₄ group [6b] and heavy metal complexes [5,6] were introduced respectively. However, there were no reports about oxadiazole compounds containing dimesitylboryl groups.

Herein, we designed phenyl as π -bridges and synthesized a new 1,3,4-oxadiazole compound with dimesitylboryl group: 2-(4-*tert*-butylphenyl)-5-(4-(dimesitylboryl)phenyl)-1,3,4-oxadiazole (abbreviated as TBDO, Scheme 1). 4-Bromophenylterazole was synthesized according to Ref. [8]. When 4-bromophenylterazole and 4-*tert*-Butylbenzoyl chloride were refluxed in pyridine under argon, 2-(4-bromophenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (abbreviated as BTBO) was obtained with a yield of 90% [9]. Then, *n*-BuLi was added slowly into a suspension of the BTBO in anhydrous THF at -78 °C. Dimesitylboron fluoride (FB(Mes)₂) in THF was added by injection successively. The mixture was stirred overnight without a cooling bath to give TBDO as white solids (yield: 54%) [10].

From X-ray single-crystal diffraction, the colorless crystal belongs to monoclinic. As shown in Fig. 1, for compound TBDO, the central boron and its three bonded carbon atoms are also perfectly coplanar and form a trigonal BC3 plane, with the sum of the three C–B–C angles (359.99°) being very close to 360° . This indicates a sp² hybrid format for the atomic orbitals of the central boron. Around the central boron, three benzene ring planes are arranged in a propeller-like fashion, which can form a good protection to the central boron. The bond lengths of B1–C7 and

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Scheme 1. The synthetic route of the compound TBDO. Conditions and reagents: (a) NaN₃, NH₄Cl/DMF, 100 °C, 20 h; (b) 4-*tert*-butylbenzoyl chloride, pyridine, reflux 2 h; (c) *n*-BuLi, FB(Mes)₂, THF, -78 °C \rightarrow r.t., 24 h.



Fig. 1. ORTEP diagram of TBDO (CCDC 788677) with the thermal ellipsoids drawn at the 30% probability level and the H atoms removed for clarity.

B1–C18 are 1.567(5) and 1.576(5) Å, respectively. However, that of B1–C19 is reduced to 1.559(5) Å, indicating some additional π -bonding between trivalent boron and 1,3,4-oxadiazole.

In THF solution, TBDO shows strong absorption centered at 331 nm due to π - π * transitions. When excited at 330 nm, it exhibits good blue emission at 425 nm with quantum efficiency 0.37 (1 mol/L quinine sulfate as standard). TBDO stands for a fluoride sensor, which shows unique blue-shift absorptions and fluorescence quenching properties after the addition of fluoride anions (Figs. 2 and 3). As shown in Fig. 2, the addition of tetrabutylammonium fluoride (TBAF) to the TBDO solutions leads to a significant blue-shifted absorption from 330 nm to 310 nm. And the strong emission bands of TBDO centered at 425 nm gradually decrease (Fig. 3). It is worth to mention that the fluorescence was quenched immediately after the addition of isometric fluoride anions (Fig. 3, inset). The fluorescence response time of TBDO to isometric F⁻ is only a few seconds. Generally, the binding constant can be easily calculated by fitting the titration curve of both absorption and emission spectra [11]. Herein, the binding constant (*K*) of TBDO with F⁻ was determined as 3.1×10^5 mol⁻¹. All these facts indicate that TBDO can be used as a good fluoride anion sensor with high sensitivity.

The selectivity of the interaction was also investigated using a series of anions in addition to AcO^- , Cl^- , Br^- , I^- , HSO_4^- , HCO_3^- and $H_2PO_4^-$. However, very weak variations of absorption and emission spectra were observed upon addition of Cl^- , Br^- , I^- , AcO^- , HSO_4^- , HCO_3^- and $H_2PO_4^-$. Therefore, TBDO exhibited a high selectivity in sensing F⁻. Furthermore, the competition experiment was also carried out by adding F⁻ to the solutions of TBDO in the presence of other anions. As shown in Fig. 4, whether in the absence or presence of the other anions, obvious emission intensity changes were observed for TBDO only upon the addition of F⁻. The results indicate that the sensing of F⁻ by TBDO is hardly affected by these commonly coexistent anions. It is attributed to the strong affinity between



Fig. 2. The absorption changes of TBDO ($c = 2 \times 10^{-5}$ mol/L) upon addition of F⁻ in THF.



Fig. 3. The emission changes of TBDO ($c = 1 \times 10^{-5}$ mol/L) upon addition of F⁻ in THF ($\lambda_{ex} = 330$ nm). Inset: The fluorescence response time of the TBDO to isometric F⁻.



Fig. 4. Luminescent responses of TBDO ($c = 1 \times 10^{-5}$ mol/L) to various anions in THF. Bars represent the luminescent intensity I/I_0 at 425 nm. Black bars represent the addition of anions (5 equiv.) to the solutions of TBDO. White bars represent the addition of F⁻ (1 equiv.) to the above solutions.

trivalent B atom and F^- , which are typical "acid" and "base", respectively. On the other hand, the special steric structure of dimesityl group may make some unique contribution [4b]. This contribution is also supported by previously reported crystal structure data [12].

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