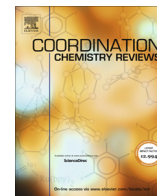




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## Review

Difluoroboron  $\beta$ -diketonate dyes: Spectroscopic properties and applicationsPeng-Zhong Chen<sup>a</sup>, Li-Ya Niu<sup>a</sup>, Yu-Zhe Chen<sup>b</sup>, Qing-Zheng Yang<sup>a,\*</sup><sup>a</sup> Key Laboratory of Radiopharmaceuticals, Ministry of Education, College of Chemistry, Beijing Normal University, Beijing 100875, China<sup>b</sup> Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

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## ABSTRACT

Difluoroboron  $\beta$ -diketonate complexes (BF<sub>2</sub>bdks) are highly luminescent organoboron complexes with several attributes such as strong fluorescence in both solution and solid state, large extinction coefficients, tunable fluorescent emission, and two-photon excited fluorescence. Some BF<sub>2</sub>bdks exhibit mechanochromic properties and room temperature phosphorescence (RTP) in solid state. Due to their rich photophysical properties, BF<sub>2</sub>bdks have shown wide applications in various areas. This review focuses on the basic chemistry and spectroscopic properties of BF<sub>2</sub>bdks in solution and solid state, as well as their self-assemblies and applications in biosensing, bioimaging and optoelectronic devices. A brief summary and outlook on BF<sub>2</sub>bdks chemistry are also included.

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**Abbreviations:** OLEDs, organic light emitting diodes; BF<sub>2</sub>bdks, difluoroboron  $\beta$ -diketonates; BF<sub>2</sub>dbm, difluoroboron dibenzoylmethane; RTP, room temperature phosphorescence; BODIPY, boron dipyrromethene; ICT, intramolecular charge transfer; TICT, twisted intramolecular charge-transfer; DCM, dichloromethane; THF, tetrahydrofuran; XRD, X-ray diffraction; SEM, scanning electron microscope; TEM, transmission electron microscope; AFM, atomic force microscope; DLS, dynamic light scattering; TADF, thermally activated delayed fluorescence; AIE, aggregation-induced emission; AIEE, aggregation-induced enhanced emission; TPA, two-photon absorption; NIR, near infrared; ML, mechanochromic luminescence; BF<sub>2</sub>AVB, difluoroboron avobenzene; PLA, poly(lactic acid); PCL, poly( $\epsilon$ -caprolactone); UPy, ureidopyrimidinone; SPNPs, supramolecular polymer nanoparticles; HOMO, highest occupied molecular orbital; LUMO, lowest occupied molecular orbital; EQE, external quantum efficiency.

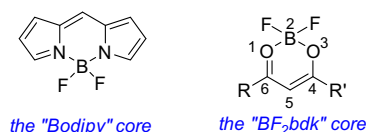
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## 1. Introduction

Organic luminescent compounds are of paramount importance in various fields such as chemsensing, biolabeling, bioimaging and organic light emitting diodes (OLEDs). Over the past decades, there have been continuous efforts to develop novel organic luminophore, among which organoboron complexes are types of dyes possessing large family members [1–8]. Boron containing organic luminophores can be classified into two categories, triarylboranes and tetra-coordinate boron dyes. Compared with tri-coordinate boron, tetra-coordinate boron dyes display higher stability [4]. To date, tetra-coordinate boron complexes mainly focused on the use of difluoroboron ( $\text{BF}_2$ ) to configurationally lock the  $\text{N}^-\text{N}$ ,  $\text{N}^-\text{O}$  and  $\text{O}^-\text{O}$  ligands, thus resulting in the formation of highly fluorescent complexes [2,9–13]. Boron dipyrromethene (BODIPY) derivatives and difluoroboron  $\beta$ -diketonate complexes ( $\text{BF}_2\text{bdks}$ ) are the most studied organoboron complexes. Bodipy dyes, with two pyrrole rings' chelation with  $\text{BF}_2$ , are the widely used tetra-coordinate boron complexes due to their large extinction coefficients, high fluorescence quantum yield in solution, tunable photophysical properties and good photostability. Numerous reviews and papers have described the successful use of BODIPY dyes in diverse research fields, such as fluorescent probes and imaging reagents [1,2,14–17].

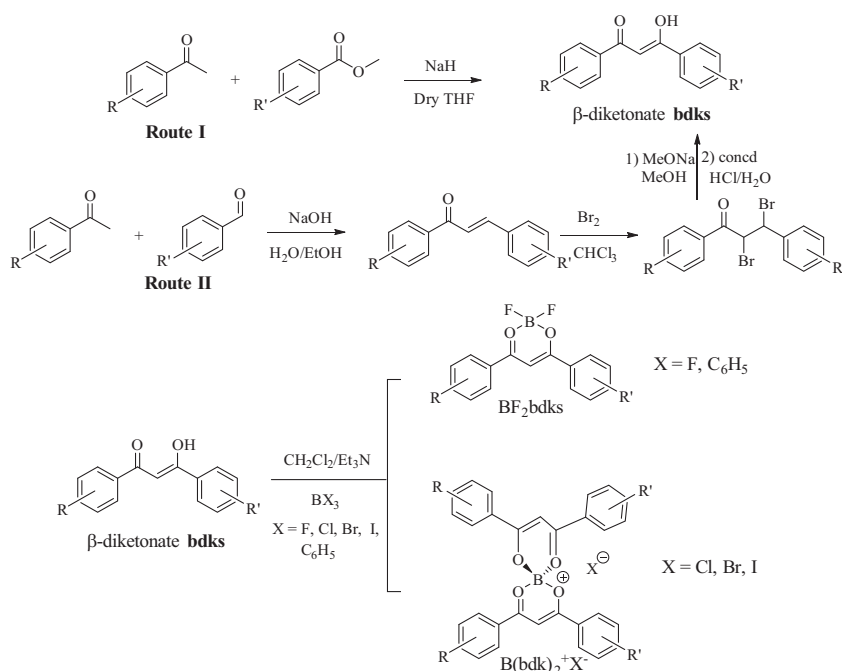


$\text{BF}_2\text{bdks}$  are another class of highly fluorescent organoboron complexes with rich photophysical properties. The first member of  $\text{BF}_2\text{bdks}$  was reported in 1924 by Morgan and Tunstall, but it has not attracted much attention until recently [18]. The readily accessible  $\beta$ -diketonates by the Claisen condensation between ester and carbonyl compound bring the  $\text{BF}_2\text{bdks}$  with tremendous varieties in structures. The photophysical properties of  $\text{BF}_2\text{bdks}$  are determined by the nature of their substitutions at 4,6-positions.

$\text{BF}_2\text{bdks}$  bearing aliphatic groups at both 4,6-positions are non-fluorescent in visible region due to the limited molecular conjugation, while  $\text{BF}_2\text{bdks}$  with aryl groups at 4,6-positions are usually emissive and show tunable emission spectra from visible to near infrared (NIR) region by modulation of structural properties of ligands. Most  $\text{BF}_2\text{bdks}$  show strong luminescence in solid state, which is quite different from the most reported BODIPY dyes. The solid state luminescent properties of  $\text{BF}_2\text{bdks}$  are related with not only the intrinsic molecular components but also the molecular packing modes associated with multiple intermolecular interactions such as  $\pi$ - $\pi$  stacking, hydrogen bonding and dipole-dipole interactions. Changes in molecular conformation and packing modes cause significant variation in the emission spectra of solid state. Thus,  $\text{BF}_2\text{bdks}$  exhibit mechanochromic properties. Interestingly, RTP is observed for some  $\text{BF}_2\text{bdks}$  in solid state. This property is rarely found in other organoboron complexes. Due to their rich photophysical properties,  $\text{BF}_2\text{bdks}$  have showed wide applications in various areas. In this review, we intend to comprehensively summarize the basic chemistry and spectroscopic properties of common  $\text{BF}_2\text{bdks}$  in solution and solid state, as well as their self-assembly and applications in biosensing, bioimaging and optoelectronic devices.

## 2. Synthetic methods

In general, both symmetrical and asymmetrical  $\beta$ -diketonate ligands are easily prepared through the Claisen condensation reaction from one ester and the corresponding carbonyl compound in the presence of a strong base such as sodium hydride, sodium *tert*-butoxide (route I, Scheme 1). An alternative approach to obtain  $\beta$ -diketonate is illustrated as route II. Condensation of benzaldehyde derivatives and acetyl containing compounds using the Claisen–Schmidt reaction gives  $\beta$ -enone, which is treated with bromine to afford the addition product. Reaction of the brominated product with sodium methanoate followed by acidolysis affords the  $\beta$ -diketonate ligands [19,20]. Certain ligands such as pentanedione, 1,3-diphenyl-1,3-propanedione, 1,3-bis(4-methoxyphenyl)-1,3-propanedione are commercially available.



Scheme 1. Synthesis of  $\beta$ -diketonate ligands,  $\text{BF}_2\text{bdks}$  and  $\text{B}(\text{bdk})_2\text{X}^-$ .

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