



# Molecular design and luminescence of boron difluoride benzoylacetates

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## ABSTRACT

Two groups of compounds differing in the crystal supramolecular architecture and luminescence properties have been identified in a series of boron difluoride benzoylacetates. In the case of the first group, the luminescence spectra of saturated solutions are bathochromically shifted relative to those of crystals. Molecules of the compounds of the first group are organized into infinite stacks with just one type of overlapping. The quantum-chemistry simulation demonstrates that the geometry of dimers in a crystal, unlike that in saturated solutions is not optimal. J-aggregates composed of dimers of the geometry similar to the optimal one are formed in crystals of the compounds of the second group. The luminescence spectra of saturated solutions and crystals of the second group compounds are identical.

## 1. Introduction

Recently, a substantial increase of the number of publications devoted to studies of physical–chemical properties of boron difluoride  $\beta$ -diketonates [1–7] has been observed. First of all, this fact is related to unique luminescence and photochemistry properties of the above rather interesting class of compounds: intensive luminescence of solutions and crystals over the whole visible and near-IR spectral range, the ability to form excimers [8–10] and exciplexes [11,12], size-dependent [13] and mechanochromic [14,15] properties. Boron difluoride  $\beta$ -diketonates are characterized by an intensive luminescence in the both solutions and crystals. In saturated solutions and a most of crystals of these compounds, one observes an excimer luminescence, which allows producing different emission color combinations using just one luminophor. For example, a solution containing monomer and excimer forms of boron difluoride dibenzoylmethanate is characterized by white luminescence [8]. In view of this, an urgent task consists in studies of the effect of aggregation processes on luminescence properties of boron difluoride  $\beta$ -diketonates.

Presently, a substantial volume of X-ray structural studies allows revealing the effect of supramolecular architecture on optical properties [16–24]. In particular, the effect of the crystal structure on mechanochromic properties [25] and luminescence [26] of crystals was revealed for boron difluoride dibenzoylmethanates.

The present work was devoted to comparative studies of luminescence properties of concentrated solutions of a series of boron difluoride benzoylacetates (Scheme 1).

## 2. Experimental

### 2.1. Measurements

Absorption spectra of solutions were registered using a Shimadzu UV2550 spectrometer. The excitation and luminescence spectra were registered using a Shimadzu-RF5301 spectrofluorimeter. The concentrated solutions spectra were registered at a frontal cell positioning in a cell of a size of  $10 \times 1$  mm. The measurements of fluorescence lifetime by time-correlated single-photon counting (TCSPC) were performed using a FluoTime 200 device (PicoQuant) with an LDH-P-C-375 (370 nm) excitation source and a TimeHarp device as the SPC controller. The lifetime data were analyzed using the FluorFit 4.0 software from PicoQuant.

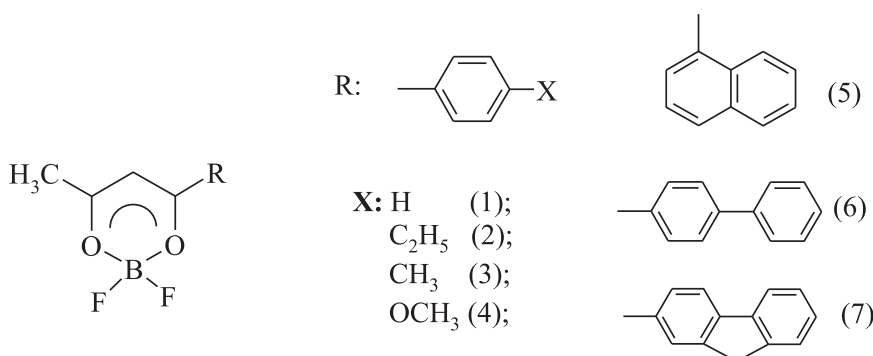
### 2.2. Materials

Chloroform, dichloromethane, and 1,2-dichloroethane were purchased from Roskhimreaktiv and used as received. Polyethylene (PE) powder (low density, 500  $\mu$ m) was purchased from Alfa Aesar. Benzoylacetates of boron difluoride were prepared and purified according to: **1** – [27], **2–6** – [28], **7** – [29] (SM 1).

PE films doped with the compound **1** were prepared according to [30]. PE powder and the complex **1** were mixed thoroughly and compacted using a hydraulic press ( $p = 8$  MPa,  $T = 130$  °C).

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Scheme 1. Structures of benzoylacetones of boron difluoride.

### 2.3. X-ray Crystallography

The X-ray diffraction diagrams of the samples were recorded on a D8 ADVANCE by Bregg-Bretanomet method with rotation of the samples in Cu K $\alpha$ -radiation ( $V = 35$  kV,  $I = 40$  mA). Identification of the experimental data was carried out taking into account all the diffraction reflections.

Data were collected on SMART-1000 CCD instrument (Bruker) for **2**, **3**, **5–7** refined by full-matrix least-squares procedures with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were calculated in ideal positions. CIF files (CCDC-184217 for **2**, 184216 for **3**, 721686 for **5**, 735612 for **6**, 751758 for **7**) can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

The CCDC data were used for the compounds **1** and **3**: codes BZACBF02 and NOLDOH for **3** [31]. The compliance of these structures (**1** and **3**) with the codes above was corroborated by the method of XRD (SM 3).

### 2.4. Computation details

All of the computational work in this paper was performed in a cluster approximation with the use of GAMESS-US program complexes [32]. The structural parameters, energy characteristics, and electron structures of the compounds were determined at full geometry optimization in the 6–311G(d, p) basis by the non-empirical (ab initio) method and the density functional method (DFT and TDDFT) with the exchange-correlation potential B3LYP [33] using the Grimme's D3 dispersion correction (DFT-D3) with the Becke-Johnson damping (DFT-D V4) [34,35].

## 3. Results and discussion

### 3.1. Excimer formation in saturated solution of boron difluoride benzoylacetone

An anomalous bathochromic shift of the maximum of luminescence spectra of solutions relative to crystals was found at studies of luminescence properties of the saturated solution of boron difluoride benzoylacetone. As a rule, the luminescence spectra of solutions of organic luminophors and, in particular, boron difluoride  $\beta$ -diketonates [8,36,37] are hypsochromically shifted relative to the spectra of crystals. Among organic luminophors, one can single out the substance **1**, for which the spectrum of luminescence of the saturated solution ( $C = 0.6$  mol L<sup>-1</sup>) is bathochromically shifted relatively to that of crystals by 25 nm (Fig. 1). In the excitation spectrum of the solution of **1**, one observes a single narrow band with a maximum at 380 nm, whereas the excitation spectrum of crystals has a more complex structure: aside from the band at 380 nm, the bands at 345, 281, and 244 nm are present in the spectrum short-wavelength range (Fig. 1).

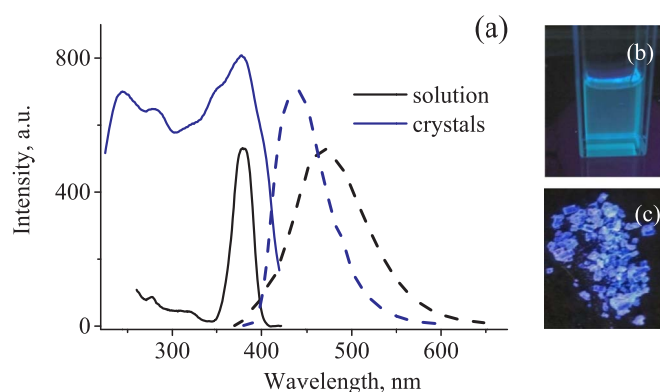


Fig. 1. (a) Excitation spectra (continuous lines) and luminescence spectra (dashed lines) of crystals and the concentrated solution of **1** in dichloromethane ( $C = 0.6$  mol L<sup>-1</sup>). (b) Fluorescence image of solution of **1** in dichloromethane ( $C = 0.6$  mol L<sup>-1</sup>). (c) Fluorescence image of crystals of **1**.

To examine the reason of the anomalous spectral behavior of **1**, the luminescence of its solutions and crystals was studied by the stationary and time-resolved spectroscopy methods. The maximum of the spectrum of monomer luminescence of the diluted solution ( $10^{-5}$  mol L<sup>-1</sup>) was observed at 395 nm,  $\tau = 0.5$  ns. At the concentration increase up to  $10^{-3}$  mol L<sup>-1</sup>, the maximum of the luminescence spectrum shifts to 428 nm and the luminescence decay becomes two-exponential (Table 1), whereas at further increase of the concentration of **1** one observes the intensity increase and bathochromic shift of the long-wavelength band in the luminescence spectrum to 470 nm. In the time-resolved spectrum, the contribution of the short-lived component (0.5–1 ns) decreases while the one of the long-lived component increases, that indicates to excimer formation. For the saturated solution ( $0.6$  mol L<sup>-1</sup>), the luminescence kinetics is two-exponential, whereas lifetimes (10.0 and 23.1 ns) correspond to excimer luminescence. Assumingly, the formation of excimers of different structures occurs in the concentrated solution of **1**.

The data of time-resolved spectroscopy corroborate the formation of the two types of excimers in the concentrated solution of **1**. As seen

Table 1  
Lifetimes of **1** in solutions in chloroform.

C, mol L <sup>-1</sup>	$\lambda_{lum}$ , nm	$\tau$ , ns ( $I^a$ , %)
$10^{-5}$	395	0.5 (100)
$10^{-3}$	428	0.8 (75.18), 7.3 (24.82)
$10^{-1}$	470	1.0 (13.18), 13.9 (86.98)
$2 \cdot 10^{-1}$	470	0.9 (15.38), 14.3 (84.62)
$6 \cdot 10^{-1}$	470	10.0 (33.18), 23.1 (66.82)
Crystal	440	10.5 (100)

<sup>a</sup> Fractional intensities of the positive decay components.

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