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Boron difluoride dibenzoylmethane derivatives: Electronic structure and luminescence

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ABSTRACT

Electronic structure and optical properties of boron difluoride dibenzoylmethanate and four of its derivatives have been studied by X-ray photoelectron spectroscopy, absorption and luminescence spectroscopy and quantum chemistry (DFT, TDDFT). The relative quantum luminescence yields have been revealed to correlate with charge transfers of HOMO-LUMO transitions, energy barriers of aromatic substituents rotation and the lifetime of excited states in the investigated complexes. The bathochromic shift of intensive bands in the optical spectra has been observed to occur when the functional groups are introduced into *p*-positions of phenyl cycles due to destabilizing HOMO levels. Calculated energy intervals between electronic levels correlate well with XPS spectra structure of valence and core electrons.

1. Introduction

Boron difluoride β-diketonates possess intensive luminescence [1–6], liquid crystal properties [7–9] and are applied as laser dyes [10], organic light diodes [11,12], optical chemosensors [13], active components of sunlight collectors [14], materials for non-linear optics [15] and polymer optical materials [16,17].

Among boron difluoride β-diketonates the dibenzoylmethanate one (BF_2Dbm) is quite special. BF_2Dbm possesses high photostability, luminescent dichroism [18], bright luminescence in solution [19], crystal state [20] and in polymer matrix [21]. Electronic structure and optical properties of monomer and dimer of BF_2Dbm are studied quite well both in the ground [22] and in the first excited singlet state [22–24]. Introducing substituents into *o*-, *m*- or *p*-positions of benzene cycle allows controlling optical properties of the complexes that makes researching relationships between electronic structure and spectral properties of BF_2Dbm and its derivatives very topical [25–27]. In particular, based on BF_2Dbm derivatives the phosphorescent optical oxygen biosensors [28].

Most of the works related to investigating molecular design and optical properties of BF_2Dbm derivatives use theoretical and experimental methods in combination. To model electronic structure and optical properties the density functional theory (DFT) and time-dependent density functional theory (TDDFT) are commonly used. Dependence of orbital energies of BF_2Dbm alkoxy derivatives versus the position of OCH_3 substituent (*o*-, *m*- and *p*-positions) have been studied [29]. In [30] the results of quantum chemical modelling conducted for a variety of chelate boron complexes are reviewed with special attention paid to implicit solvent model. The influence of metoxy and alkyl groups in *p*-positions of benzene cycles of BF_2Dbm on the luminescence spectra have been investigated [31–33].

Earlier [22,34] we studied the relationship between electronic structure and optical properties of BF_2Dbm and four of its derivatives (substituents *p*-$OCH_3C_6H_4$, *p*-$NO_2C_6H_4$, *m*-$NO_2C_6H_4$, $C_{10}H_7$) by the means of X-ray photoelectron spectroscopy (XPS) data, absorption spectroscopy, luminescence spectroscopy and DFT as well as TDDFT calculations. Except [22,34] there is no experimental works related to study of electronic structure and how it impacts on luminescence properties of BF_2Dbm derivatives.

The most reliable information regarding electronic structure of the complexes can be obtained by a combined application of XPS and quantum chemistry. XPS is a direct method for studying electronic structure of valence and core levels [35]. Straightforward measuring characteristics of the certain levels in the XPS methods allows comparing obtained results with calculated electron energies (DFT approximation). Using DFT approximation despite the ab initio methods (Harthree-Fock [36], configuration interaction [37], Green's functions [38] and etc.) allows obtaining good correlation between calculated and experimental ionization energies [39] and requires much less computational resources. Good agreement between theory and experiment in case of valence ionization [40,41] is explained by similarity of Kohn-Sham equation and quasi-particle Dyson equation [42], which is one of the ways to obtain Green's

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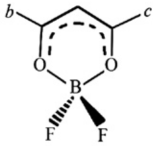
functions [38]. Using absorption and luminescence spectroscopies together with TDDFT calculations enables one to reveal the influence of substituents on the optical properties of the complexes. Revealing dependence of spectral characteristics of BF_2Dbm derivatives on their electronic structure paves the way to targeted synthesis of new luminophores.

As shown in [22,43–45], calculation results obtained in terms of DFT and TDDFT correlate well with energies of electronic levels and excited states of boron β-diketonate complexes that allows reliably interpreting XPS and absorption spectra and analyzing electron effects of substitution in a number of BF_2Dbm derivatives.

This work presents results of electronic structure investigation and optical properties study of BF_2Dbm (I) and its four derivatives (II-V) by the means of XPS, absorption spectroscopy, luminescence spectroscopy, DFT and TDDFT.



I. $b = c = C_6H_5$ (BF_2Dbm);
II. $b = c = p\text{-}CH_3C_6H_4$ (BF_2Dtm);
III. $b = p\text{-}OCH_3C_6H_4$; $c = C_6H_5$
IV. $b = p\text{-}OCH_3C_6H_4$; $c = p\text{-}BrC_6H_4$
V. $b = p\text{-}OCH_3C_6H_4$; $c = o\text{-}OHC_6H_3COOC_6H_4OCH_3$

2. Experimental and calculation methods

The electronic absorption spectra were recorded at a Shimadzu UV – 2550 apparatus (Japan) in ethanol at the concentration 10^{-5} mol/L. The luminescence and excitation spectra were registered at a Shimadzu-RF5301 spectrofluorimeter in ethanol at the concentration 10^{-5} mol/L. A solution of anthracene was used as a standard for measuring the fluorescence quantum yield ($\varphi_F = 0.27$) [46]. The measurements of fluorescence lifetime by time-correlated single-photon counting (TCSPC) were performed using a FluoTime 200 device (PicoQuant, Germany) with a 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.

Chloroform was purchased from Roshimreaktiv and used as received. Compound I was prepared and purified according to [47], II - [48], III and IV - [49], V - (Supplementary Material).

XPS spectra of compounds II-V in condensed phase were obtained on a high-vacuum photoelectron spectrometer (Omicron, Germany) with hemispherical electrostatic analyzer. The photon energy was 1253.6 eV (MgKα). The spectrometer's half-height band width determined under operating conditions using Ag3d$_{5/2}$ band was 1.2 eV. Electron energy scale (E_b) was calibrated using F 1s level as an internal standard. Atomic content (in at.%) was calculated taking into account relative ionization cross-section and depth of photoelectron emission. Relative element concentration obtained from 1s–electron band intensities was consistent with the calculated one within the error limits of the method (10%). Valence and core electron bands in the XPS spectra were related to the calculated energies taking into account the quantity of electronic levels, energy gaps between them and ionization cross-section values.

DFT and TDDFT computations were performed using Firefly 8.1. G quantum chemical software package [50] using TZVP basis set [51,52]. The calculation results depend on type of exchange-correlation functional. At the present time the hybrid functionals [53], double-hybrid functionals [54], Minnesota functionals [55] and range-separated functionals [56,57] are used for DFT calculations. The method of dispersion correction as an add-on to standard Kohn-Sham density functional theory [58] is also used. The hybrid three-parameter functional B3LYP are successfully used for DFT calculations of boron complexes [59–66]. In our review [39] it was shown that hybrid B3LYP functional [67–69] gives good results for investigation of electronic structure of boron complexes by XPS method. That's why in present work all the calculations were carried out using B3LYP functional.

Optical spectra interpretation was carried out based on TDDFT approximation. To cover excited states up to vacuum ultraviolet energy (~8 eV), there were calculated 50 transitions for every studied molecule. While modelling absorption spectra the optimized geometry of molecules I–V in the ground state was used. This allowed estimating energies of the vertical transitions between electronic levels in the ground and excited states. Calculated spectra were obtained from the energies and oscillator strengths (E_i,f_i) by summation of Gaussian curves $G_i(E) = a(f_i/d)\exp(-{}^1/_2(E-E_i)^2/d^2)$, where E is the energy, f is the oscillator strength, a is the coefficient to obtain units of molar extinction, i is the ordinal number, d is the half-width parameter (0.25 eV). Present work analyzed electronic effects of substitution and how they are connected with optical properties, therefore, solvent influence on the absorbance spectra was not taken into account.

3. Results and discussion

3.1. Modelling of electronic structure

Geometry optimization of complexes I–II and III–V has led to C_s and C_1 symmetry groups, respectively. Symmetry of molecules I–IV decreases due to small (about degrees) rotation of phenyl groups and bend of the chelate cycle plane along the O-O line. In the compound V

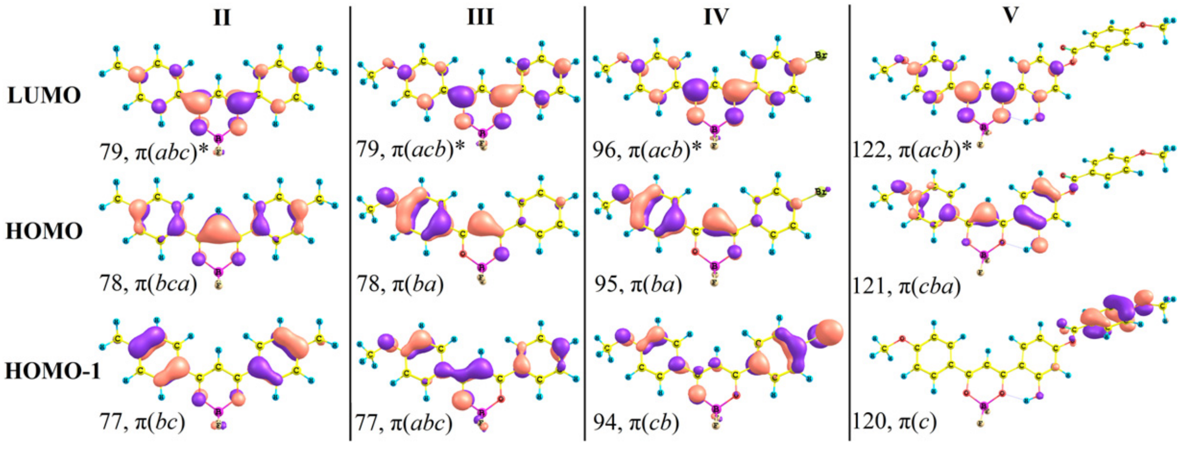


Fig. 1. Some molecular orbitals of compounds II — V.