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E.V. Fedorenko, A.G. Mirochnik, A. Yu. Beloliptsev, V.V. Isakov

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($S_2 \rightarrow S_0$) and ($S_1 \rightarrow S_0$) Luminescence of Dimethylaminostyryl-β-diketonates of Boron Difluoride

Fedorenko[1] E.V., Mirochnik[1] A.G., Beloliptsev[1] A. Yu., Isakov[2] V.V.

[1] - *Institute of Chemistry, Far-Eastern Branch of the Russian Academy of Sciences,*

159, Prosp. 100-letiya Vladivostoka, Vladivostok 690022, Russian Federation.

Fax: 007(4232)311 889. E-mail: gev@ich.dvo.ru

[2] - *G.B. Elyakov Pacific Institute of Bioorganic Chemistry Far-Eastern Branch of the Russian*

Academy of Sciences,

159, Prosp. 100-letiya Vladivostoka, Vladivostok 690022, Russian Federation.

Spectral-luminescence properties of several dimethylaminostyryl-β-diketonates of boron difluoride with different α-substituents have been investigated through stationary and time-resolved spectroscopy. Quantum chemistry studies of the structure of excited states of 2,2-difluoro-4-(4′-dimethylaminostyryl)-6-phenyl-1,3,2-dioxaborine have been performed. Two luminescence centers have been revealed for the compound under study: an intensive band in the red-orange region of the spectrum caused by an S_1-S_0 transition and a short-wave luminescence in the blue region of the spectrum caused an by S_2-S_0 transition.

Introduction

Traditionally, polymethine dyes are used as photosensitizers in photography, fluorescence probes, initiators for polymerization, active and passive components for tunable lasers and non-linear optical materials [1-5]. The prospects of their further development requires more ex-

tensive studies of electron structure of different types of conjugated molecules. Recently, a significant number of papers devoted to the studies on polymethine dyes based on β-diketonates of boron difluorides have been published [6-10]. Boron-containing dyes are of interest due to their thermochromic [11], non-linear optical [12, 13] and two-photon absorption [14, 15] properties and their possible use in organic light-emitting diodes [16, 17].

It should be mentioned that in the investigation of polymethine dyes based on β-diketonates of boron difluoride the main focus was made on the effect of the structure and the length of the polymethine chain on optical properties of the dyes [7-14]. Here, the role of the second α-substituent remains almost completely unstudied. In the present paper, a series of new β-diketonates of boron difluoride with a dimethylaminostyryl substituent were synthesized, and their structures and spectral-luminescence properties have been investigated by spectral methods and quantum chemistry calculations.

Materials and Equipment

Materials

The initial β-diketonates of boron difluoride were prepared and purified according to the following papers: benzoylacetonate and acetylacetonate of boron difluorde [18], anisoylacetonate of boron difluoride [19], 2,2-difluoro-4-(9*H*-fluorene-2-yl)-6-methyl-1,3,2-dioxaborine [20], 2,2-difluoro-4-(naphth-2-yl)-6-methyl-1,3,2-dioxaborine [21], 2,2-difluoro-4-(9-anthracyl)-6-methyl-1,3,2-dioxaborine [22].

General procedure of synthesis of dimethylaminostyryl-β-diketonates of boron difluorides

The β-diketonate of boron difluoride(0.002 mol) and 4-dimethylaminobenzaldehyde [(0.002 mol (0.004 mol for compound 6)] were heated in acetic anhydride (5 mL) in a water bath for 30 min. Then, the solution was cooled, and the product was then filtered off and washed with ace-

tic acid. The products were purified by flash silica gel chromatography (eluent: chloroform) and recrystallized.

2,2-Difluoro-4-(p-dimethylaminostyryl)-6-phenyl-1,3,2-dioxaborine (**1**). Black crystals with metallic luster, yield: 0.40 g (60%), m.p. 216-217°C (acetonitrile). IR (KBr): 1582, 1558, 1494, 1373, 1172, 1132, 1101, 1055 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): 3.11 (s, 6H), 6.53 (s,1H), 6,57 (d, J= 15.5 Hz, 1H), 6.72 (d, J=9.1 Hz, 2H), 7.50 (m, 2H), 7.56 (d, J=9.1 Hz, 2H), 8.05 (m, 2H), 8.11 (d, J=15.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$): 40.2, 97.0, 112.1, 114.4, 122.2, 128.3, 128.8, 132.1, 132.7, 133.9, 149.4, 153.1, 179.0, 181.0. Anal. calc. for C$_{19}$H$_{18}$BF$_2$NO$_2$: C, 66.89; H, 5.32; N, 4.11. Found: C, 66.54; H, 5.23; N, 4.20.

2,2-Difluoro-4-(p-dimethylaminostyryl-6-(p-methoxyphenyl)-1,3,2-dioxaborine (**2**). Black solid, yield: 0.46 g (62%), m.p. 204-205°C (acetonitrile). IR (KBr): 1596, 1577, 1539, 1521, 1506, 1456, 1435, 1373, 1257, 1254, 1159, 1120, 1045, 1012 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): 3.11 (s, 6H), 3.92 (s, 3H), 6.46 (s, 1H), 6.57 (d, J=15.2 Hz, 1H), 6,79 (m, 2H), 7.00 (m, 2H), 7.56 (m, 2H), 7.56 (m, 2H), 8.05 (m, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): 40.4, 55.6, 96.1, 112.6, 114.3, 125.0, 130.8, 131.6, 147.9, 164.8, 179.6. Anal. calc. for C$_{20}$H$_{20}$BF$_2$NO$_2$: C, 64.72; H, 5.43; N, 3.77. Found: C, 64.83; H, 5.23; N, 3.56.

2,2-Difluoro-4-(p-dimethylaminostyryl-6-(9H-fluoren-2-yl)-1,3,2-dioxaborine (**3**). Black solid, yield: 0.57 g (67%), m.p. 238-239°C (acetonitrile). IR (KBr): 1600, 1517, 1479, 1365, 1324, 1286, 1163, 1126, 1045 cm^{-1}.^{1}H NMR (500 MHz, CDCl$_3$): 3.11 (s, 6H), 6.59 (s, 1H), 6.58 (d, J=15.1 Hz, 1H), 6.71 (m, 2H), 7.43 (m, 3H), 7.55 (m, 2H), 7.87 (m, 2H), 8.10 (m, 2H), 8.27 (s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$): 36.8, 40.1, 97.2, 112.1, 114.7, 120.0, 121.1, 125.0, 125.3, 127.2, 127.7, 128.5, 130.8, 131.9, 140.3, 143.7, 144.7, 147.8, 148.8, 153.1, 180.2. Anal. calc. for C$_{26}$H$_{22}$BF$_2$NO$_2$: C, 72.75; H, 5.17; N, 3.26. Found: C, 72.90; H, 5.11; N, 3.31.

2,2-Difluoro-4-(p-dimethylaminostyryl-6-(naphth-2-yl)-1,3,2-dioxaborine (**4**). Black solid, yield: 0.51 g (65%), m.p. 201-202°C (acetonitrile). IR (KBr): 1595, 1558, 1516, 1490, 1375, 1184,1157, 1132, 1043 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): 3.11 (s, 6H), 6.60 (d, J=15.1 Hz, 1H),

6.66 (s, 1H), 6.71 (m, 2H), 7.65-7.51 (m, 5H), 7.90 (m, 2H), 7.99 (m, 2H), 8.12 (d, J=15.1 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): 40.1, 97.5, 112.1, 114.4, 122.1, 123.4, 127.1, 127.9, 128.6, 129.0, 129.7, 130.4, 132.1, 136.0, 149.4, 153.2, 178.6, 180.8. Anal. calc. for C$_{23}$H$_{20}$BF$_2$NO$_2$: C, 70.61; H, 5.15; N, 3.58. Found: C, 70.43; H, 5.14; N, 3.58.

2,2-Difluoro-4-(p-dimethylaminostyryl-6-(anthr-9-yl)-1,3,2-dioxaborine (**5**). Dark green solid, yield: 0.52 g (59%), m.p. 114-115°C (acetic acid). IR (KBr): 1558, 1538, 1519, 1483, 1437, 1371, 1282, 1221, 1184, 1142, 1043, 1012 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): 3.13 (s, 6H), 6.35 (s, 1H), 6.55 (d, J=15.1 Hz, 1H), 6.73 (m, 2H), 7.60-7.46 (m, 8H), 8.04 (m, 2H), 8.24 (m, 3H), 8.89 (s,1H), ^{13}C NMR (125 MHz, CDCl$_3$): 40.1, 105.6, 112.2, 113.7, 122.3, 125.2, 125.3, 125.4, 125.6, 126.6, 127.3,128.6, 129.2, 130.9, 132.5, 151.1, 153.5, 181.1, 182.0. Anal. calc. for C$_{27}$H$_{22}$BF$_2$NO$_2$: C, 73.49; H, 5.03; N, 3.17. Found: C, 73.46; H, 5.04; N, 3.15.

2,2-Difluoro-4,6-di(p-dimethylaminostyryl-1,3,2-dioxaborine (**6**). Black solid, yield: 0.49 g (60%), m.p. 220-221°C (acetonitrile). IR (KBr): 1603, 1558, 1519, 1487, 1471, 1373,1228, 1192, 1115, 1036 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): 3.09 (s, 12H), 5.90 (s, 1H), 6.47 (d, J=15.2 Hz, 2H), 6.74 (d, J=8.8 Hz, 4H), 7.52 (m, 4H), 7.97 (d, J= 15.1 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): 40.1, 100.9, 112.4, 115.4, 131.3, 140.7, 178.0. Anal. calc. for C$_{23}$H$_{25}$BF$_2$N$_2$O$_2$: C, 67.33; H, 6.14; N, 6.83. Found: C, 67.43; H, 6.24; N, 6.76.

Instrumentations and methods

The luminescence and excitation spectra were registered on a Shimadzu-RF5301 spectrometer. A solution of rhodamine 6G was used as a standard for measuring the fluorescence quantum yield (φ_F = 0.96) [23]. The measurements of fluorescence lifetime by time-correlated single-photon counting (TCSPC) were performed on a FluoTime 200 device (PicoQuant) with a PDL 800-B (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. The absorption spectra

were registered on a Shimadzu-UV2550 spectrometer in a cell of 10x10 mm size. The IR spectra were registered on an IRAffinity-1 Shimadzu spectrometer.

Computational details

The quantum chemistry simulations of electron absorption spectra of the compounds in different conformations were performed in a cluster approximation with the use of GAMESS-US program complexes [24]. 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 with the exchange-correlation potential B3LYP. The electron absorption spectra of the compound **1** with the account of excited singlet and triplet states were calculated by the TDDFT method in the 6-311G(d, p) basis with the potential B3LYP.

Results and Discussion

The dyes **1-6** were synthesized from β-diketonates of boron difluoride by aldol-crotonic condensation with *para*-N,N-dimethylaminobenzaldehyde, similarly to the method described in [25] for 2,2-difluoro-4-mehtylnaphtho-[2,1-e]-1,3,2-dioxaborine (Fig. 1).

R: 1 - C_6H_5; 2 - p-$CH_3OC_6H_4$;

3

4

5

6

Scheme 1.
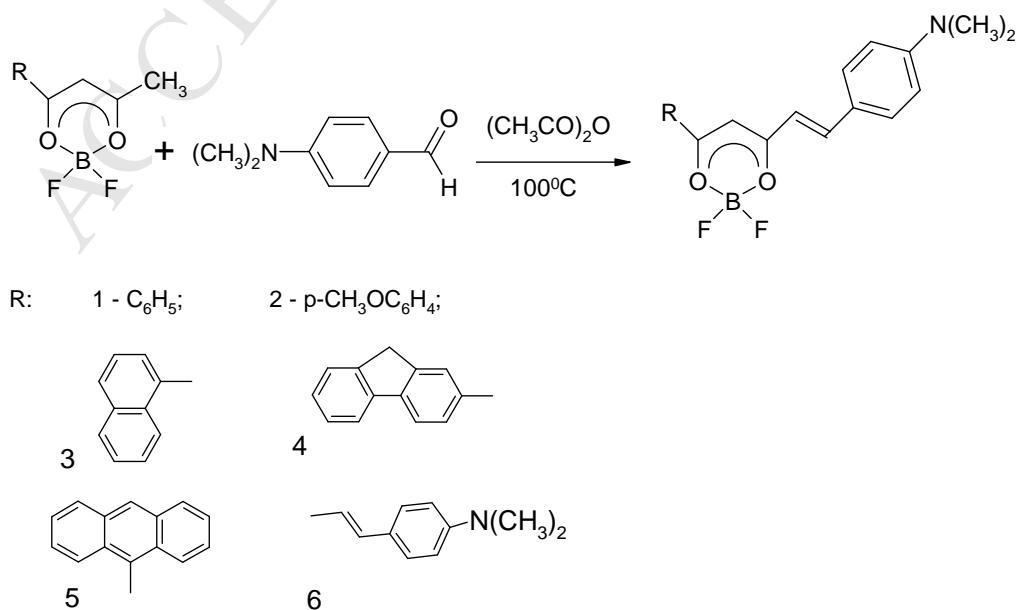
In organic solvents, the obtained compounds form solutions of either red or violet color with an intensive luminescence in the red-orange region of the spectrum. The quantum yield in non-polar solvents was in the range 0.2 - 0.8 and it decreases along the solvent polarity increases. The dye solutions are characterized with sovatochromism and luminescence solvatochromism (Table 1).

In the ground or excited states, β-diketonates of boron difluoride are known to interact with some solvents, thus forming exciplexes with aromatic compounds [26, 27] and hydrates with water [28, 29]. Upon heating in acetonitrile or dimethylformamide the decomposition of boron difluoride complexes was observed with the formation of β-diketones [30]. Therefore, to avoid the effect of specific solvatation, chlorinated hydrocarbons with different polarities were selected for the study of the solvatochromism phenomenon: dichloromethane, chloroform, and carbon tetrachloride ($\varepsilon(CH_2Cl_2) = 9.08$, $\varepsilon(CHCl_3) = 4.81$, $\varepsilon(CCl_4) = 2.24$ [31]).

As Table 1 shows, in β-diketonates of boron difluoride with *p*-N,N-dimethylaminostytryl groups, one observes a bathochromic shift of absorption and luminescence spectra as the solvent polarity is increased. Here, the increase of Stokes shift also takes place as well (Table 1). For compounds **1-4** in dichloromethane, the Stokes shift is about 2300-2700 cm^{-1}. In comparison to other compounds, compound **5** is characterized by an abnormally high Stokes shift of 2894 cm^{-1} (Table 1). Among primary photo-processes which cause the emergence of fluorescence with the increased Stokes shift, a prominent place is held by structural relaxation - changes in the molecule geometry resulting in the energy decrease in the electron-excited state, in comparison with its initial excited Franck-Condon state (FCS), which the molecule acquires after the light quantum absorption. The difference in the energies of excited states would constitute the in-crease of the Stokes shift, and the structurally relaxed state (SRS) is often characterized by an intramolecular charge transfer. For most of the polymethine dyes, the Stokes shift increase is re-lated to 'flattening' of the dye molecule in the excited state [32]. In dyes **1-6**, structural changes

promoting the formation of a planar structure are observed. In dyes **1-4**, **6** free rotation is of the aromatic substituent possible, and unproblematic is the location of α-substituent and β-diketonate cycle in the same plane contributing to efficient π-π conjugation. As distinct from other compounds, in **5** the anthracene group is rotated relative to the chelate cycle due to steric hindrance. The geometry of the molecule of β-diketonate of boron difluoride with an anthracene fragment is examined in detail in [22] by the example of 2,2-difluoro-4-(9-anthracyl)-6-methyl-1,3,2-dioxaborine. According to X-ray structural analysis data, the angle of the anthracene substituent planes with the chelate cycle is equal to 69°. Probably, even a slight reduction of inter-plane angle of the anthracene fragment with β-diketonate cycle from photoexcitation of **5** should involve a marked decrease of the excited state energy and larger Stokes shift than in **1-4**. By contrast, in symmetrical dye **6** observed is the lowest value of the Stokes shift in the series of compounds under study: 1907 cm^{-1} in dichloromethane. When the solvent polarity is reduced, the decrease of the Stokes shift for **6** is lower than in **1-5**.

Quantum chemistry calculations of absorption spectra of dyes for FCS and SRS geometries were performed for example **1**. Quantum chemistry calculations have been performed for a series of β-diketonates of boron difluorides [33-37]. The authors of these foregoing papers note good agreement between experimental (in nonpolar solvents and in the gas phase) and calculated absorption spectra for the Franck-Condon geometry of the excited state. For **1**, unlike the complexes described in the above papers, no correlation between the calculated and experimental spectra within the scope of the Franck-Condon geometry was observed (Table 2). In the calculated absorption spectrum for **1** in FCS first band was observed at 418.73 nm with an oscillator strength of 1.017, although the maximum of the experimental absorption spectrum of **1** in nonpolar solvents (hexane and carbon tetrachloride) equals to 509 nm. The earlier studied β-diketonates had hydrocarbon substituents with similar donor-acceptor properties, whereas the S_0-S_1 transition was accompanied by an insignificant redistribution of the electron density delocalized over the whole molecule [35, 37]. As was mentioned in [38], in the presence of α-

substituents with significantly different in electron-donor properties, one observes a predominant realization of intramolecular charge transfer (ICT) state during the excitation of a molecule of boron difluoride β-diketonate. The presence of solvatochromism in compounds **1-6** indicates that the S_0-S_1 transition is the transition with a charge transfer. The compounds under study differ from other β-diketonates of boron difluoride by the presence of a strong electron donor (dimethylamino-group) and a strong acceptor (BF_2) in the molecule. The presence of both the strong donor and the strong acceptor in the same molecule results in the fact that the highest occupied molecular orbital (HOMO) is localized mainly on the dimethylaminostyryl group, whereas the lowest unoccupied molecular orbital (LUMO) is localized mainly on the chelate cycle (see Fig. 1), i.e. the S_0-S_1 transition is the transition with a charge transfer. The optimization of the excited state geometry revealed that the LUMO SRS is substantially different from the LUMO FCS. The electron density decreases on the dimethylaminostyryl group and is homogeneously distributed between phenyl and chelate rings (see Fig. 1), which causes the increase of the charge transfer upon the molecule excitation. When the SRS geometry is used in calculations of the absorption spectrum, one observes better agreement with the experiment than for the FCS geometry (see Fig. 2, Table 2).

Figure 3 shows geometrical changes occurring in molecule **1** in the transition to the SRS state. The lengths of the phenyl ring bonds linked to the N,N-dimethylamino group (Ph1) undergoes virtually no changes. Whereas the lengths of bonds between the Ph1 ring and the double bond and between the double bond and the chelate cycle increase substantially, they decrease between the chelate cycle and Ph2. At the same time, there occur changes in the lengths of C-C bonds of the chelate cycle. As seen from Figure 3, the above changes cause the formation of a chain of alternating one-and-half and double bonds, similarly to alternation of bonds in polymethine dyes molecules [39-41].

The low-intensity bands (see Fig. 4) are present in the short-wave range of excitation and luminescence spectra for the dyes under study, and the spectra of short-wave excitation and lu-

minescence are symmetric reflection (see Fig. 4, insert). The presence of the second group of symmetric reflection bands of excitation and luminescence indicates the existence of the second luminescence center in the dye molecule. As was demonstrated in [34,42], low-intensity bands attributed to S_n-S_0 transitions can be observed in the short-wave range of the luminescence spectrum. The excitation spectrum of short-wave luminescence really corresponds to the bands of S_0-S_2 transitions in the absorption spectrum. Here, one observes the dependence of luminescence spectra on the excitation wavelength and vice versa (Fig. 5). When the luminescence of **1** is excited by a 350 nm wavelength, which belongs to the group of short-wave bands of the excitation spectrum, a short-wave band with a maximum at 406 nm emerges in the luminescence spectrum. For the SRS state of **1**, the intensity of S_0-S_2 transition in the calculated absorption spectrum becomes, as opposed to the FCS, almost equal to that of S_0-S_1 transition (Fig. 2, Table 2). Here, in the case of the SRS, the contribution of the transfer from HUMO to LUMO+1 related to the charge transfer from dimethylaminostyryl group to the whole molecule increases from 15 up to 30%, as compared to the FCS (Fig. 1, Table in Supplementary materials). In the experimental absorption spectra of **1** in all three solvents, observed are short-wave bands of S_0-S_2 transition (342 and 359 nm) corresponding to the SRS state.

Figure 6 presents the time-resolved luminescence spectrum of **1** upon excitation at 370 nm corresponding to the excitation band of S_0-S_2 transition. In the moment of excitation, bands with maxima at 463 (S_2-S_0) and 528 (S_1-S_0) nm in the luminescence spectrum are observed. Within one nanosecond, the short-wave band disappears, and the maximum of the long-wave band bathochromically shifts to 550 nm. It indicates the initial transition to the state S_2, whose deactivation includes luminescence directly from the state S_2 and S_2-S_1 transition. In the stationary spectra, unlike the time-resolved spectra, the intensity of S_2-S_0 luminescence is much lower than that for S_1-S_0. When the solvent polarity is increased, the rate of S_2-S_1 transition decreases, and the intensity of S_2-S_0 luminescence increases. In the stationary spectrum of **1** in carbon tetrachloride, the short-wave luminescence is not manifest, it can only be registered by the time-

resolved spectroscopy method. However, in the stationary spectra of the dyes in dichloromethane, the short-wave luminescence is observed, and its quantum yield is ≈ 0.002 at the quantum yield of the long-wave luminescence S_1-S_0 being 0.05-0.2. In alcohol solutions, the quantum yield of luminescence from S_2 in the stationary spectrum reaches 0.1-0.2 and becomes comparable to that from the level S_1 (Fig. 5).

The effect of the anthracene α-substituent (**5**) on the dye spectral properties should be specially considered. As was shown earlier by the X-ray structural analysis method, in the molecule 2,2-difluoro-4-(9-anthracyl)-6-methyl-1,3,2-dioxaborine [22], the dihedral angle between the planes of the anthracene fragment and the chelate ring equals to 69°. This large value of the dihedral angle between the chelate cycle and the α-substituent is indicative of weakening of the π-π interaction between the rings and allows to consideration the anthracene fragment and the chelate ring conjugated with the dimethylaminostyryl group as two practically independent chromophores. In fact, when the dependence of the luminescence spectrum on the excitation wavelength was studied, an additional luminescence center in the stationary luminescence of **5** in ethanol and dichloromethane was observed. The third group of reflection symmetrical bands of excitation and luminescence ($\lambda_{ex} = 244$, 283 nm and $\lambda_{lum} = 314$, 368 nm) was only noticed in spectra of **5** (Fig. 7). Here, the excitation band at 244 nm corresponds to the absorption band of the anthracene fragment (Fig. 7).

Table 1 presents the data on the effect of the structure of the second α-substituent in dimethylaminostyryl β-diketonates of boron difluoride on complex spectral-luminescence properties. The introduction of an electron-donor substituent into the *para*-position of the phenyl ring, for instance, of the methoxy-group (**2**), causes an insignificant hypsochromic shift of the maxima of luminescence and absorption spectra relative to **1** (see Table 1), as opposed to a strong bathochromic shift in the spectra in the transition from dibenzoylmethanate of boron difluoride to its methoxy-derivatives [43]. The reason of this, as was demonstrated by quantum chemistry calculations, consists in the localization of HOMO on the chelate ring and the dimethylaminostyryl

group (Fig. 1), and the second α-substituent being not included in the molecule π-system. This is why the effect of a donor group in the *para*-position of the phenyl ring on the position of the luminescence spectrum maximum is not manifest. During the excitation, the electron density is transferred from the aminostytryl group to the whole molecule. Therefore, the increase of the charge transfer efficiency must be aided by the presence in the *para*-position of the phenyl ring of an acceptor substituent, rather than a donor substituent. Really, as was shown in [44] for a similar boron chelate, the introduction of chlorine into the *para*-position of the phenyl ring resulted in the bathochromic shift of the absorption spectrum maximum by 10 nm, in the case of a nitro-group – by 30 nm. Along the π-system of an aromatic substituent is increased, one observes a bathochromic shift of absorption and luminescence spectra. Thus, upon the substitution of phenyl radical 2-fluoryl (**3**) by 1-naphthyl (**4**), there occurs a bathochromic shift of absorption and luminescence spectra by approximately 10 nm (Table 1). At further increase of the π-system, when, for instance, the second dimethylaminostyryl substituent is introduced (**6**), the shift of absorption and luminescence spectra maxima attains as much as 50-60 nm relative to **1**.

When hydrochloric acid is added to solutions **1**-**6**, the solution decolorized and a change in the luminescence color from red to either blue or green was observed (see Table 3, Fig. 8, 9). Thus, β-diketonates of boron difluoride containing the N,N-dimethylamino-group participate in the reactions characteristic for amines: they form a hydrochloride in the reactions with hydrochloric acid (Scheme 2). The reaction with hydrochloric acid occurs in water miscible solvent, such as ethanol, acetone, dioxane and hydrochloric acid vapors.
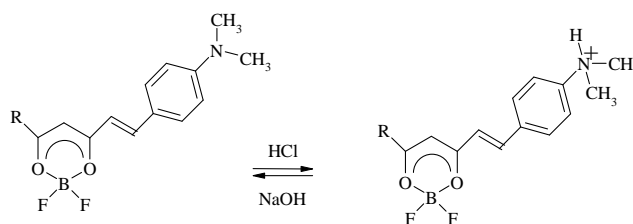
Scheme 2.

The donor amino-group is transformed into an acceptor ammonium cation, and the redistribution of electron density of the dye molecule takes place. The optimization of geometry of the cation obtained through protonation of dimethylamino-group **1** (cation **1**) demonstrates the increase of the length of C-N bond between the dimethylamino-group and the phenyl ring from 1.374 up to 1.477 Å and the disruption of the molecule coplanarity takes place: the torsion angle between the plane of the aromatic ring by the amino-group and the plane encompassing the molecule main part is equal to 25°. The disruption of coplanarity of molecule **1** upon protonation results in the reduction of π-conjugation in cation **1**. The structures of the HOMO and LUMO undergo significant changes in the transformation of the dye from the neutral form to its cation (Fig. 10). As distinct from molecule **1**, in cation **1** HOMO is localized on the second aromatic α-substituent, β-diketonate ring, and the double bond rather than on the aminostyryl group. Due to this fact, in the hydrochloride series **1-5** the positions of luminescence spectra maxima are bathochromically shifted in accordance with the increase of π-donor capacity of the second α-substituent in the same manner as in the series of benzoylacetonates and dibenzoylmethanates [30]. The lowest donor capacity is characteristic for the anthracene group rotated relative to the chelate cycle. In accordance with the increase of donor capacity, substituents can be grouped as follows: 9-anthracyl <methoxyphenyl<fluoryl<naphthyl (Table 3).

The cation HOMO is located on the β-diketonate ring, double ring, and aromatic ring by the amino-group (Fig. 10). The localization of the major part of HOMO and LUMO electron density on the chelate ring and the double bond promotes the reduction of CT character of S_0-S_1 transition. The latter results in the hypsochromic shift of the cation absorption and luminescence spectra, as compared to those of the dye neutral form. The calculated absorption spectrum for cation **1** is shown in Fig. 11, the assignment of absorption bands is presented in Supplementary Materials.

Conclusions

A series of N,N-dimethylaminostyryl β-diketonates of boron difluoride with different α-substituents have been synthesized. Spectral-luminescent properties of the obtained dyes have been investigated through stationary and time-resolved spectroscopy methods. It has been demonstrated that the introduction of an electron-donor substituent into the *para*-position of the phenyl α-substituent results in an insignificant hypsochromic shift of the luminescence and absorption spectra maxima. The bathochromic shift of the luminescence and absorption spectra maxima is observed upon introduction of the electron-acceptor substituent into the *para*-position of the phenyl ring and upon the increase of π-system of the aromatic α-substituent. For the compounds under study, two luminescence processes are observed: an intensive band in the red-orange range of the spectrum caused by S_1-S_0 transition and the short-wave luminescence in the blue range of the spectrum caused by S_2-S_0 transition. As is demonstrated by quantum chemistry simulations, the molecule geometry in the S_1 state corresponds to the geometry of the structurally relaxed state.

Supplemental Materials

Supplemental Materials include excitation and luminescence spectra for compounds **1-6** and the results of quantum chemistry calculations for compound **1** and its cation (energies, types, and compositions of some molecular orbitals; energies and oscillator strengths of singlet-singlet transitions in the electron absorption spectrum).

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Table 1.

Spectral-luminescence properties of dimethylaminostyryl β-diketonates boron difluoride.

Com-pound	CH_2Cl_2				$CHCl_3$				CCl_4			
	λ_{abs}, nm (lg ε)	λ_{fl}, nm	φ	$\Delta\upsilon_{ST}$, cm^{-1}	λ_{abs}, nm (lg ε)	λ_{fl}, nm	φ	$\Delta\upsilon_{ST}$, cm^{-1}	λ_{abs}, nm (lg ε)	λ_{fl}, nm	φ	$\Delta\upsilon_{ST}$, cm^{-1}
1	348 (4.19), 362 (4.19), 537 (4.87)	430, 627	0.026	2673	348 (4.15), 362 (4.16), 528 (4.83)	406, 427, 598	0.44	2216	342 (4.13) , 359 (4.10), 509 (4.81)	394, 416, 566	0.53	1978
2	358 (4.43), 376 (4.32), 534 (4.92)	396, 612	0.15	2386	358 (4.43), 376 (4.32), 528 (4.93)	386, 594	0.38	2104	354 (4.43), 370(4.27), 506 (4.84)	370, 388, 560	0.44	1905
3	482 (3.42), 549 (4.81)	450, 638	0.20	2540	482 (3.42), 549 (4.92)	442, 612	0.54	2213	353 (4.46), 520 (4.92)	399, 418, 576	0.56	1869
4	276 (4.23), 374 (4.23), 393 (4.37), 549 (4.92)	435, 637	0.05	2516	274 (4.38), 374 (4.23), 393 (4.37), 543 (4.83)	406, 612	0.37	2076	276 (4.23), 366 (4.29), 385 (4.46), 520 (5.10)	435, 544	0.64	848
5	254 (5.09), 283 (4.24), 330 (4.01), 346 (3.98), 380 (3.60), 540 (4.82)	415, 641	0.008	2894	254 (5.09), 283(4.24), 330 (4.01), 346(3.98), 380 (3.60), 533 (4.80)	436, 627	0.06	2812	254 (5.09),326 (4.25), 342(4.22), 503 (4.93)	308, 366, 407, 570	0.19	2336
6	309 (4.02), 337 (4.02), 460 (4.33), 598 (5.13)	430, 675	0.54	1907	278 (3.75), 340 (3.23), 460 (4.17), 590 (4.96)	440, 656	0.79	1705	273(3.92),334 (3.67), 448 (3.89), 481(4.14), 556 (4.46)	398, 415, 613	0.74	1672

Table 2.

Experimental and calculated absorption spectra compound **1** .

Exp. spectra λ_{max}, nm (lg ε)	Franck-Condon exited state			Structurally relaxed state		
	λ, nm	f	Transition	λ, nm	f	Transition
509 (4.81)	418.73	1.017	89-90 (98.7)	499.74	0.613	89-90 (99.9)
342 (4.13) , 359 (4.10)	325.76	0.212	88-90 (83.8) 89-91 (15.5)	347.49	0.604	88-90 (27.7) 89-91 (65.3)

Table 3.

Absorption and luminescence maxima of ethanol solution N,N-dimethylamino-styryl β-diketonates boron difluoride and their hydrochlorides

Compound	Neutral form		Hydrochloride	
	λ_{abs}, нм	λ_{lum}, нм	λ_{abs}, нм	λ_{lum}, нм
1	530	635	387	452
2	530	631	412	483
3	545	650	443	522
4	542	625	425	531
5	251, 538	640	251, 368	401
6	591	691	413	461

a　　　　　　　　　　　　　　　　　　　　　　　　　**b**
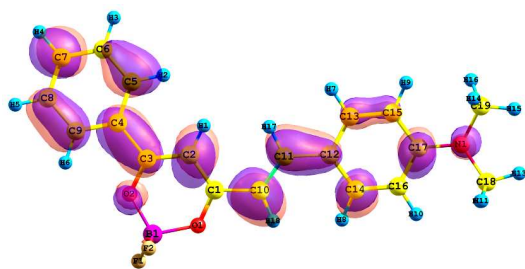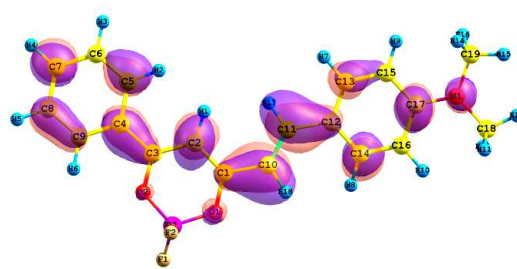
(91)　HCMO+1　-0.0449　　　　　　　　　　　-0,0507
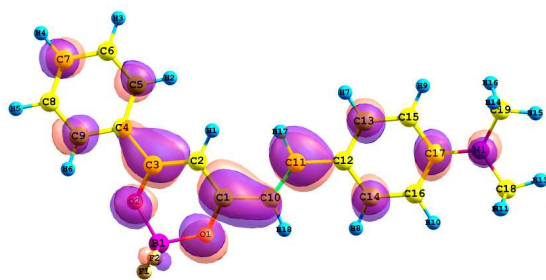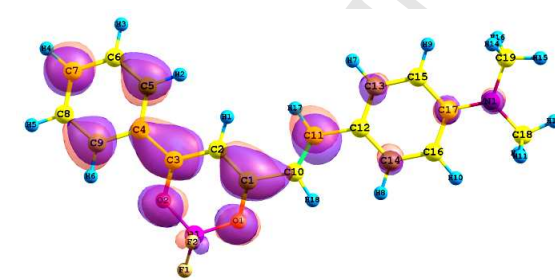
(90) HCMO　-0.0908　　　　　　　　　　　　　-0,1016
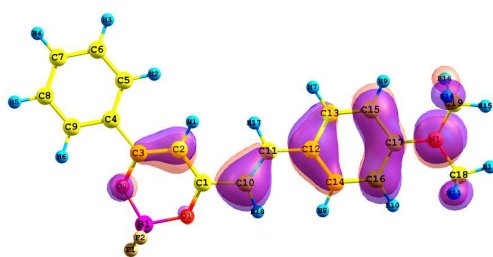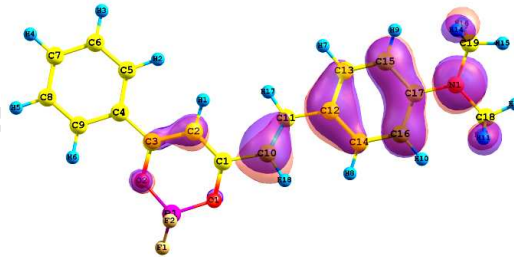
(89) B3MO　-0.2081　　　　　　　　　　　　　-0,2015
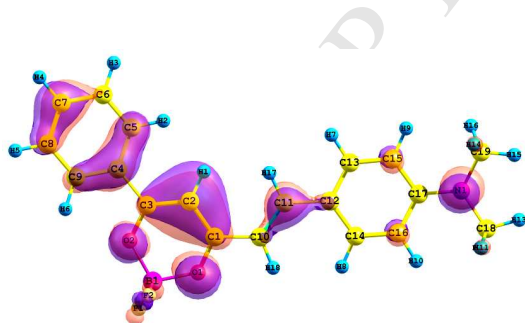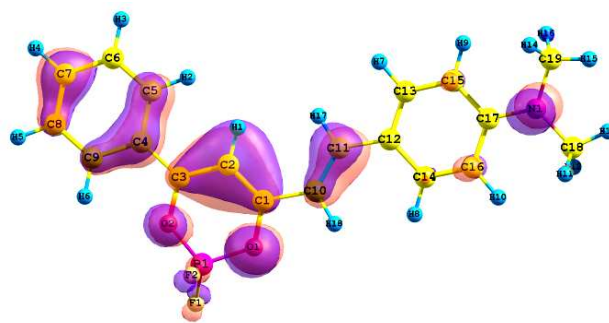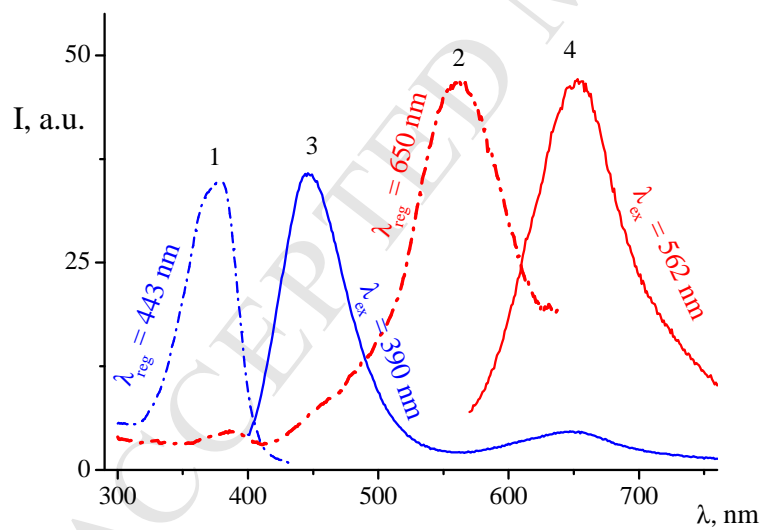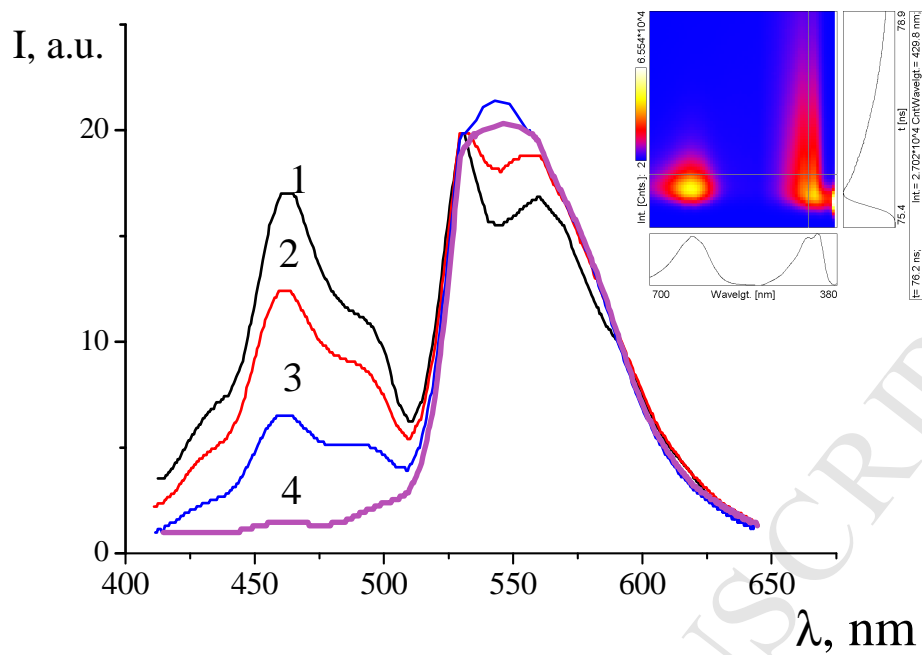

(88) B3MO-1　-0.2454　　　　　　　　　　　　-0,2480

Fig. 1.
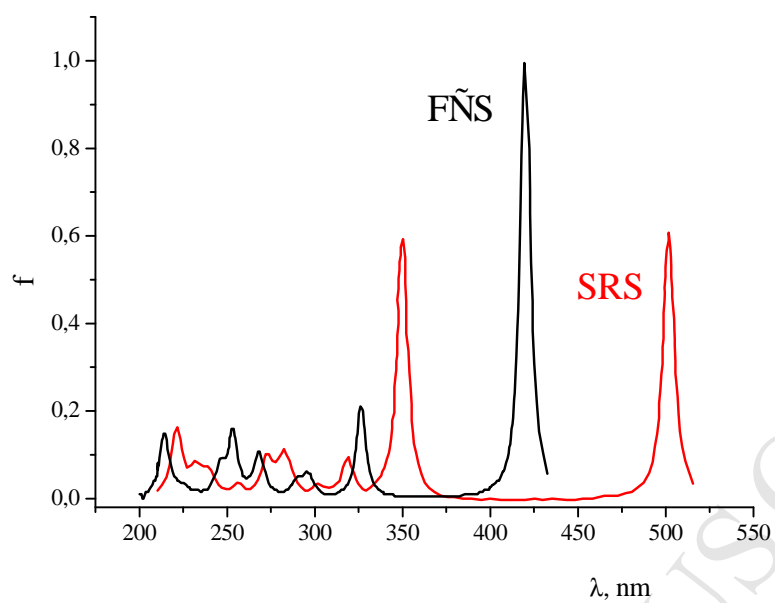
Fig. 2.
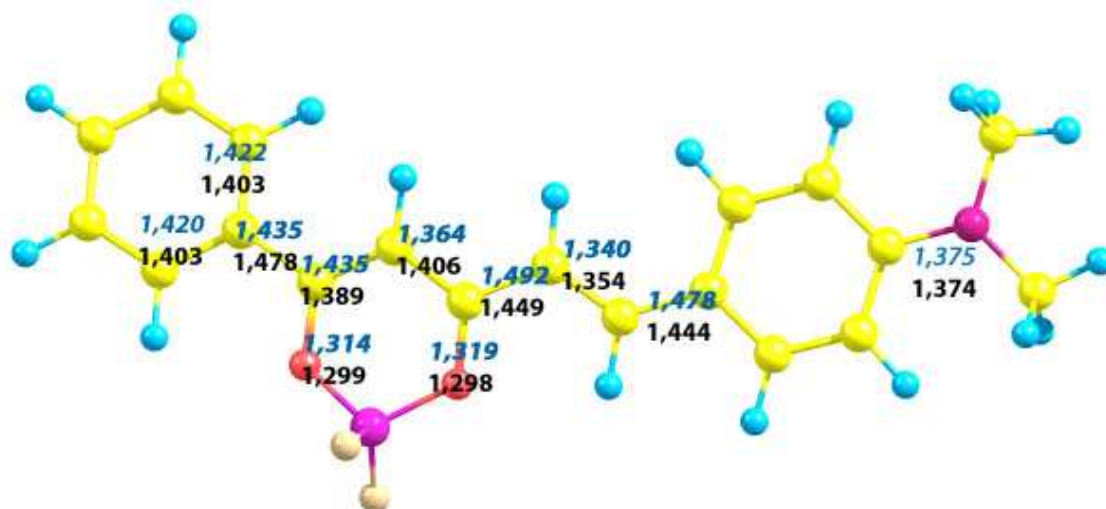
Fig. 3.
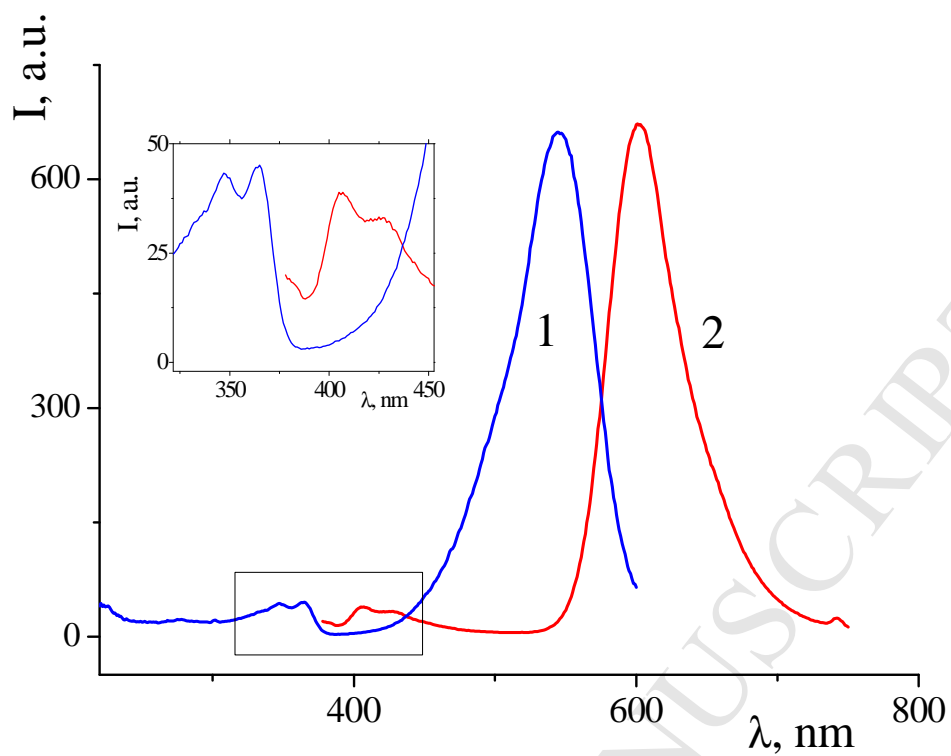
Fig. 4.

Fig. 5.

Fig. 6.
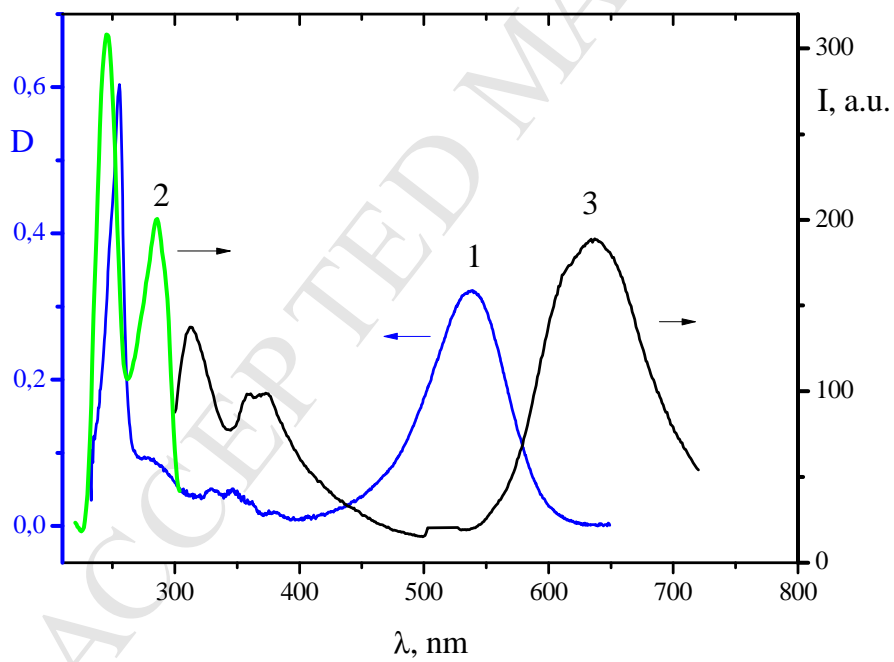
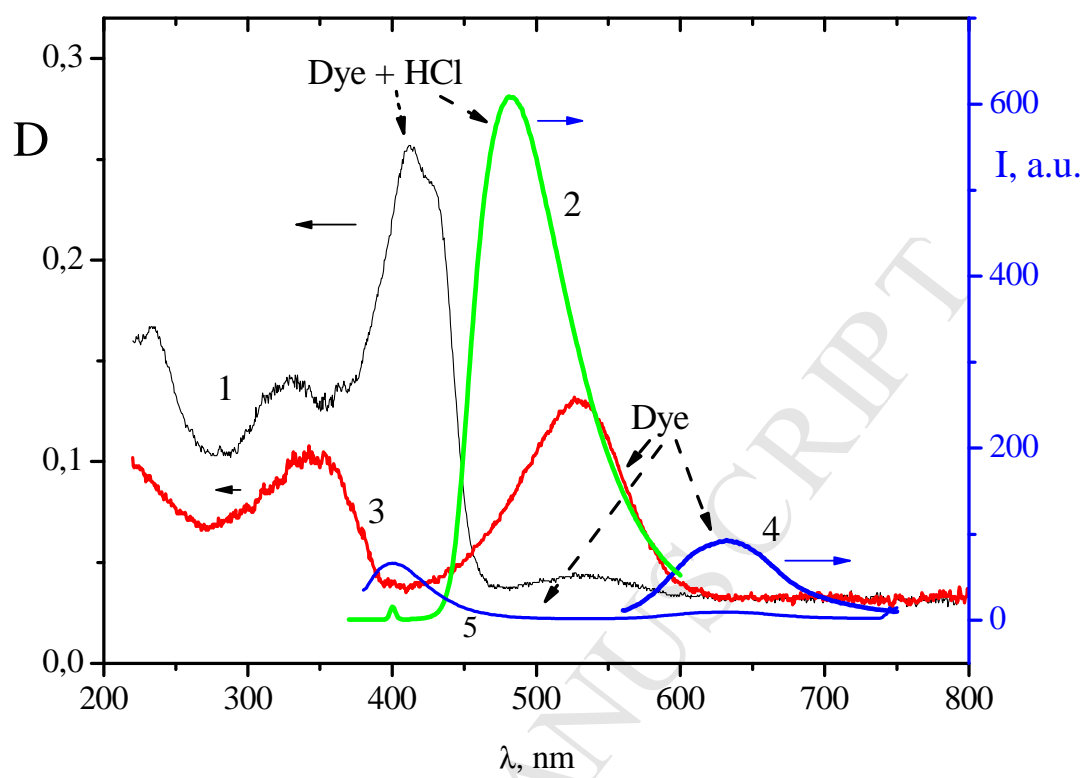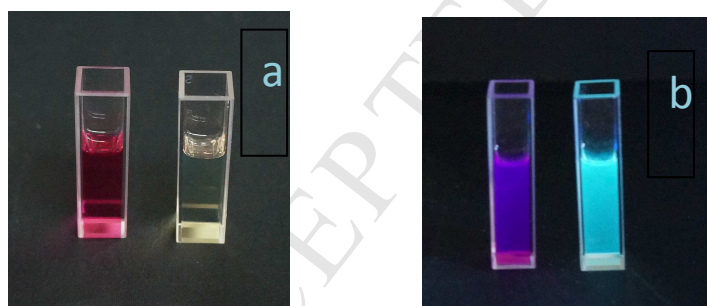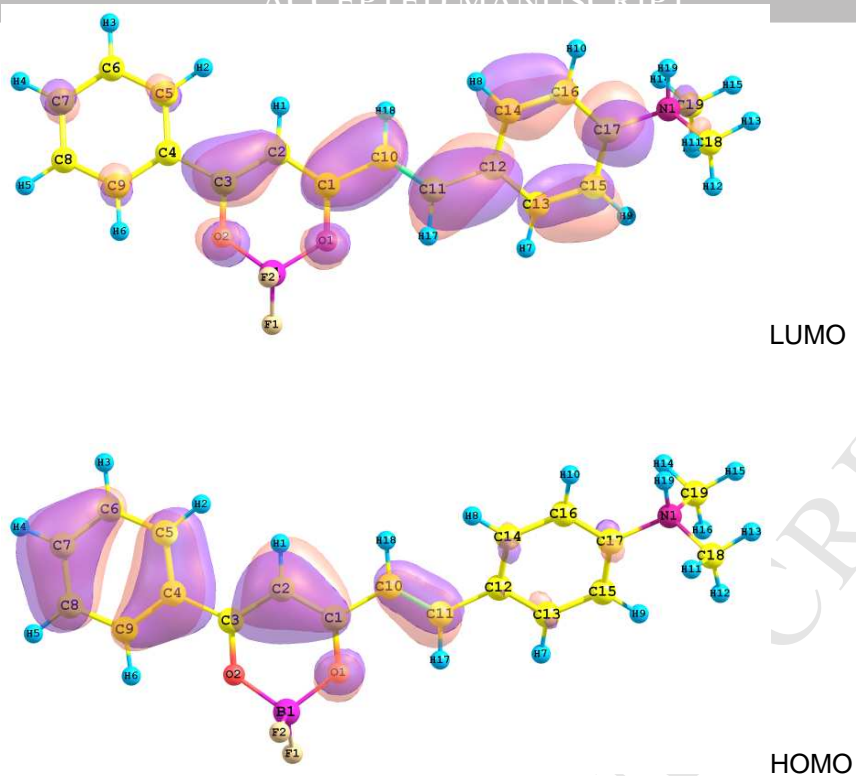Fig. 7.

Fig. 8.

Fig. 9.

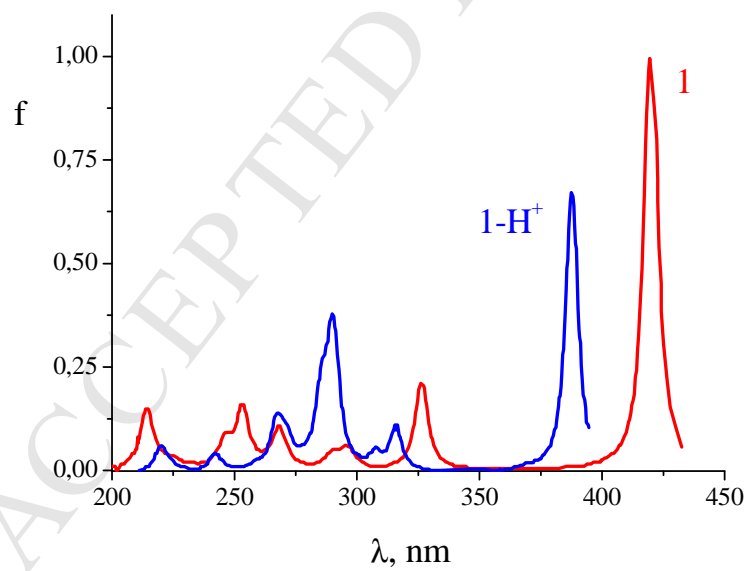LUMO

HOMO

Fig. 10. HOMO and LUMO for cation 1.

Fig. 11. Theoretical absorption spectra compound **1** and it's cation (1-H$^+$) for Franck-Condon state.

Figure captions

Fig. 1. Orbitals involved in the absorption spectra for **1** (a) - Franck-Condon state, (b) - structurally relaxed state.

Fig. 2. Theoretical absorption spectra of **1** Franck-Condon state (FCS) and structurally relaxed state (SRS).

Fig. 3. Bond length in ground (bottom) and excited structurally relaxed (top) states.

Fig. 4. Spectra of solution **1** in chloroform C = $5 \cdot 10^{-6}$ mol/l: 1 – excitation; 2 – luminescence; in insert shown expanded short-wave part of spectra.

Fig. 5. Spectra of solution **4** in ethanol C = $5 \cdot 10^{-6}$ mol/l: excitation: 1 - λ_{reg} = 443 nm, 2 - λ_{reg} = 650 nm; luminescence: 3 - λ_{ex} = 390 nm, 4 - λ_{ex} = 562 nm.

Fig. 6. Time-resolved emission spectra of solution **1** in carbon tetrachloride C = $5 \cdot 10^{-5}$ mol/l: 1 - 75.7 ns, 2 -75.8 ns, 3 – 76 ns, 4 – 76.4 ns. Time is the time after the laser pulse. λ_{ex} = 370 nm.

Fig. 7. Spectra of solution **5** in dichloromethane C = $5 \cdot 10^{-6}$ mol/l: 1 – absorption; 2 - excitation, λ_{reg} = 313 nm; 3 - luminescence, λ_{ex} = 256 nm.

Fig. 8. Spectra of solution in ethanol C = $5 \cdot 10^{-6}$ mol/l: 1 - absorption of **2**; 2 – absorption of hydrochloride **2**; 3 – luminescence of **2**, λ_{ex} = 550 nm; 4 – luminescence of hydrochloride **2**, λ_{ex} = 420 nm; 5 – luminescence of hydrochloride **2**, λ_{ex} = 365 nm.

Fig. 9. The pictures of 2 (left) and 2–H$^+$ (right) on a solution in ethanol under day light (a) and UV light (b).

Fig. 10. HOMO and LUMO for cation 1.

Fig. 11. Theoretical absorption spectra compound **1** and it's cation (1-H$^+$) for Franck-Condon state.

N,N-dimethylaminostyryl-β-diketonates of boron difluoride were synthesized.
Two luminescent processes were revealed for the compounds.
The quantum chemistry simulation of absorption spectra was calculated.
These compounds form hydrochloride with a bright luminescence.

Supplementary Material for

Luminescence of Dimethylaminostyryl-β-diketonates of Boron Difluoride

Fedorenko*[1] E.V., Mirochnik[1] A.G., Beloliptsev[1] A. Yu., Isakov[2] V.V.

[1] - Institute of Chemistry, Far-Eastern Branch of the Russian Academy of Sciences,
159, Prosp. 100-letiya Vladivostoka, Vladivostok 690022, Russian Federation.
Fax: 007(4232)311 889. E-mail: gev@ich.dvo.ru
[2] - G.B. Elyakov Pacific Institute of Bioorganic Chemistry Far-Eastern Branch of the Russian Academy of Sciences,
159, Prosp. 100-letiya Vladivostoka, Vladivostok 690022, Russian Federation.

Table 1

Energies, types, and compositions of some molecular orbitals **1** for excited Franck-Condon state

N	E, a.e.	Type	Composition
88	-0.2454	HOMO -1	π Ch[a] (57,58%)+π Ph[b]1(21,31%)+π N-Me2 (9,66%)+ π Ph2(4,70%)+ π -CH=CH-(4,62%)
89	-0.2081	HOMO	π Ph2 (37,19%)+ π N-Me2 (12,67%)+π -CH=CH-(11,44%)+π Ch (9,56%)+π Ph1(2,77%)
90	-0.0908	LUMO	π Ch (47,37%)+ π -CH=CH-(18,99%)+ π Ph1(16,70%)+ π Ph2 (11,93%)+π N-Me2 (4,43%)
91	-0.0449	LUMO 1	πPh1(37,53%)+π -CH=CH-(20,94%)+π Ch (19,81%)+π Ph2 (17,26%)+π N-Me2 (4,04%)

(a) – Ch-orbitals localized predominantly on chelate ring and (b) – Ph-orbitals localized predominantly on substituents.

Table 2

The parameters of calculated **1** absorption spectrum (S_0- S^*-transitions) for excited Franck-Condon state

N	E, a.e.	Type	Composition
1 A	418,73	1,017	89-90 (98)
2 A	325,76	0,212	88-90 (84),89-91(16)
3 A	295,98	0,051	86-90 (10), 88-98 (12), 89-91 (62), 89-92(12)
5 A	289,08	0,032	86-90(53), 89-91 (19), 89-92 (22)
6 A	270,30	0,013	83-90 (10), 85-90 (73)
7 A	268,02	0,089	86-90 (30), 89-92 (53)
10 A	253,24	0,143	84-90 (63), 88-91 (29)
11 A	246,34	0,064	84-90 (25), 88-91 (63)
13 A	226,00	0,017	89-94 (63), 89-95 (28)
16 A	215,59	0,045	86-91(88)
17 A	214,51	0,077	87-91 (21), 88-93 (57)
18 A	213,80	0,030	85-91 (76), 88-93 (10)

Table 3

Energies, types, and compositions of some molecular orbitals **1** for structurally relaxed excited state.

N	E, a.e.	Type	Composition
88	-0,248	HOMO -1	π Ch[a] (56,53%)+π Ph[b]1(17,85%)+ π -CH=CH-(10,16%)+ π N-Me2 (8,24%)+ π Ph2 (5,13%)
89	-0,2015	HOMO	π N-Me2 (39,43%)+ π Ph2 (37,99%)+ π -CH=CH-(11,62%)+π Ch (8,47%)+ π Ph1(2,15%)
90	-0,1016	LUMO	π Ch (50,20%)+π Ph1(29,89%)+ π -CH=CH-(11,24%)+ π Ph2 (6,04%)+ π N-Me2 (1,99%)
91	-0,0507	LUMO 1	π -CH=CH-(27,67%)+ π Ph1(27,28%)+π Ph2 (22,72%)+π Ch (17,22%)+π N-Me2 (4,72%)

(b) – Ch-orbitals localized predominantly on chelate ring and (b) – Ph-orbitals localized predominantly on substituents.

Table 4

The parameters of calculated **1** absorption spectrum (S_0- S^*-transitions) for structurally relaxed excited state.

State	E, nm	f	Transition (contribution,%)
1 A	499,7387	0,613	89-90 (99)
2 A	347,4921	0,604	88-90 (70), 89-91 (29
3 A	316,1274	0,087	88-90 (28), 89-91(65)
5 A	299,1199	0,024	85-90 (13), 86-90 (76)
7 A	280,3826	0,082	83-90 (25), 85-96 (53)
9 A	275,8905	0,020	83-90 (67), 84-90 (13), 85-90 (19)
10 A	269,7089	0,087	84-90 (79)
11 A	253,031	0,029	88-91 (87)
12 A	236,6129	0,052	89-94 (84)
14 A	230,5414	0,016	89-95 (96)
15 A	229,0085	0,049	87-91 (84)

Table 5

Energies, types, and compositions of some molecular orbitals of cation **1** for excited Franck-Condon state

N	E, a.e.	Type	Composition
85	-0.4967	B3MO-4	πPh[a]2(98,41%)
86	-0.476	B3MO-3	π Ch[b] (47,66%)+πPh2(31,28%)+π -CH=CH-(13,64%)+πPh1(3,48%)+π F2 (1,84%)+ π 2*Me(1,61%)
87	-0.4432	B3MO-2	πCh(31,58%)+πPh1(28,00%)+π -CH=CH-(19,44%)+πPh2(19,26%)
88	-0.4149	B3MO-1	π Ph1(99,14%)
89	-0.4056	B3MO 0	πPh1(50,61%)+πCh (34,65%)+π -CH=CH-(8,57%)+πPh2(5,69%)
90	-0.0692	HCMO 0	πPh2(44,95%)+πCh (20,69%)+π -CH=CH-(19,49%)+π2*Me(7,44%)+πPh1(6,96%)
91	-0.0277	HCMO +1	σ 2*Me(39,95%)+ σ Ph2 (35,22%)+ σ N-H19 (24,58%)
92	-0.0255	HCMO +2	π Ph2(68,44%)+π -CH=CH- (14,08%)+π 2*Me(11,01%)+π Ch (4,01%) +π N-H19(1,43%)

(a) –Ph-orbitals localized predominantly on substituents and (b) – Ch-orbitals localized predominantly on chelate ring.

Table 6

The parameters of calculated cation **1** absorption spectrum (S_0- S^*-transitions).

| State	E, nm	E, eV	E, cm^{-1}	f	Transition (contribution,%)
1 A	389,52	3,183	25672,42	0,672	89-90 (100)
2 A	371,32	3,339	26930,64	0,01	88-90 (98)
3 A	318,56	3,892	31390,85	0,105	87-90 (97)
4 A	310,35	3,995	32221,59	0,036	89-91 (97)
5 A	293,32	4,227	34092,78	0,331	85-90 (29), 86-90 (40), 89-92 (27)
6 A	288,74	4,294	34633,17	0,161	85-90 (48), 89-92 (45)
7 A	281,59	4,403	35512,31	0,014	88-91 (88), 88-92 (9)
8 A	274,49	4,517	36431,77	0,065	88-91 (11), 88-92(75)
9 A	270,59	4,582	36956,03	0,112	85-90 (12), 86-90 (49), 89-92 (27)
10 A	266,81	4,647	37480,28	0	89-93 (98)
11 A	262,07	4,731	38157,79	0,011	84-90 (8), 86-91 (9), 87-91 (77)
12 A	248,57	4,988	40230,61	0,007	84-90 (26), 86-91(47), 87-91 (18)
13 A	247,72	5,005	40367,73	0	88-93 (100)
14 A	245,66	5,047	40706,48	0,037	87-92 (87)
15 A	231,88	5,347	43126,12	0,003	83-90 (88)
16 A	230,93	5,369	43303,56	0	87-93 (95)
17 A	229,14	5,411	43642,31	0,005	85-92 (14), 86-92 (53)
18 A	224,65	5,519	44513,38	0,028	82-90 (11), 86-91 (18), 84-90 (28), 85-92 (16)
19 A	223,88	5,538	44666,63	0,038	81-90 (14), 84-90 (20), 86-91 (11), 86-92 (26)
20 A	221,64	5,594	45118,29	0,001	82-90 (51), 85-91 (14), 85-92 (24)

(1)
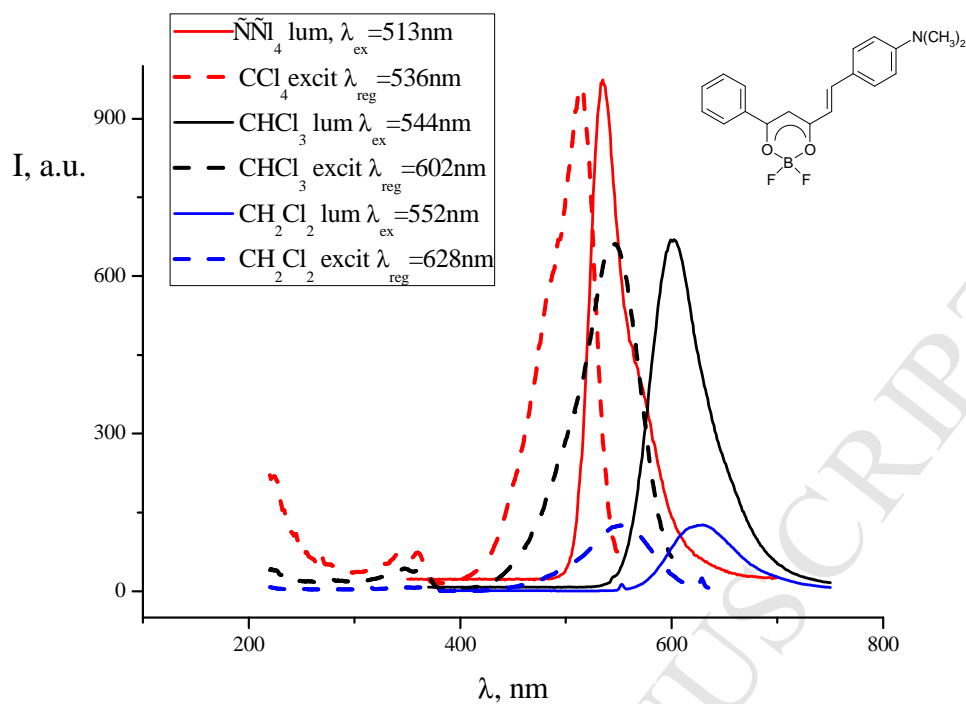
Long-wave luminescence and excitation spectra solution of solution **1** C = 5•10^{-6} mol/l in different solvents. Red-orange region of the spectrum.
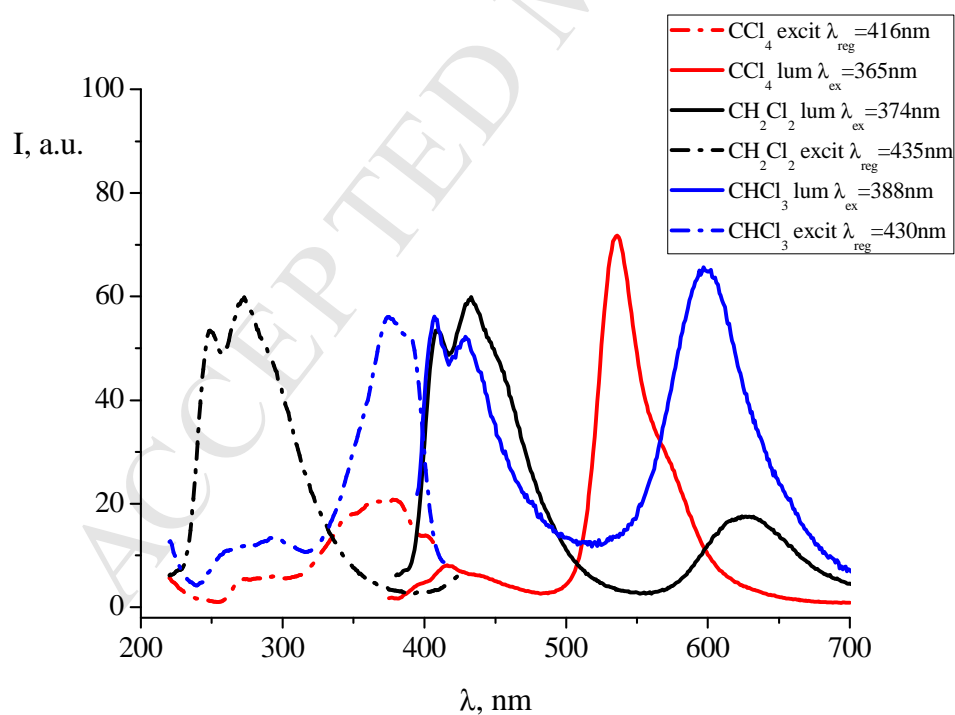
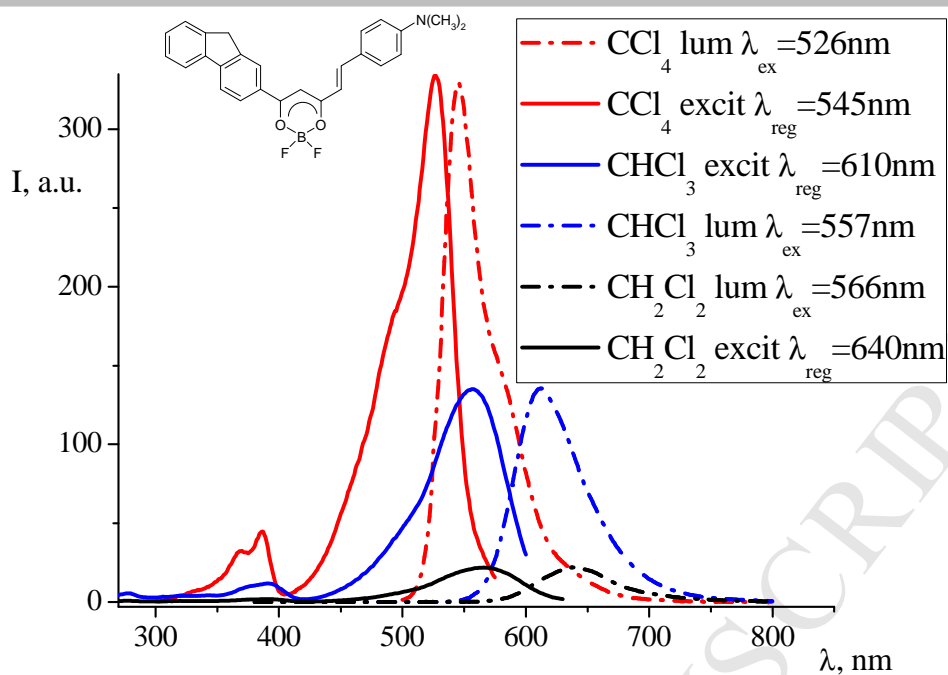

Short-wave luminescence and excitation spectra of solution **1** C = 5•10^{-6} mol/l in different solvents.
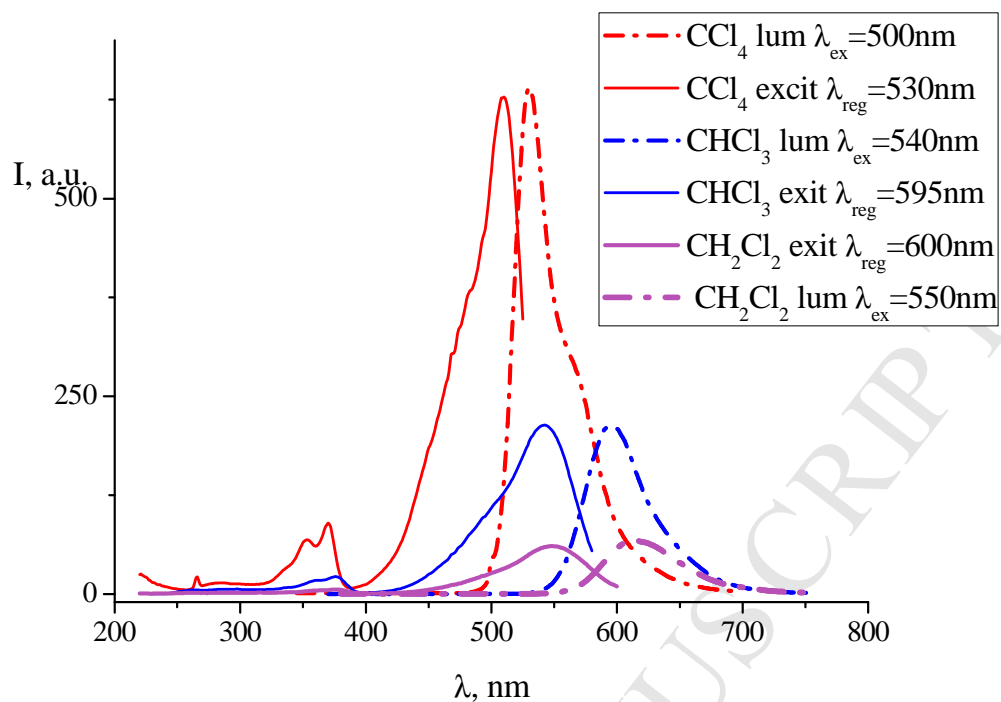
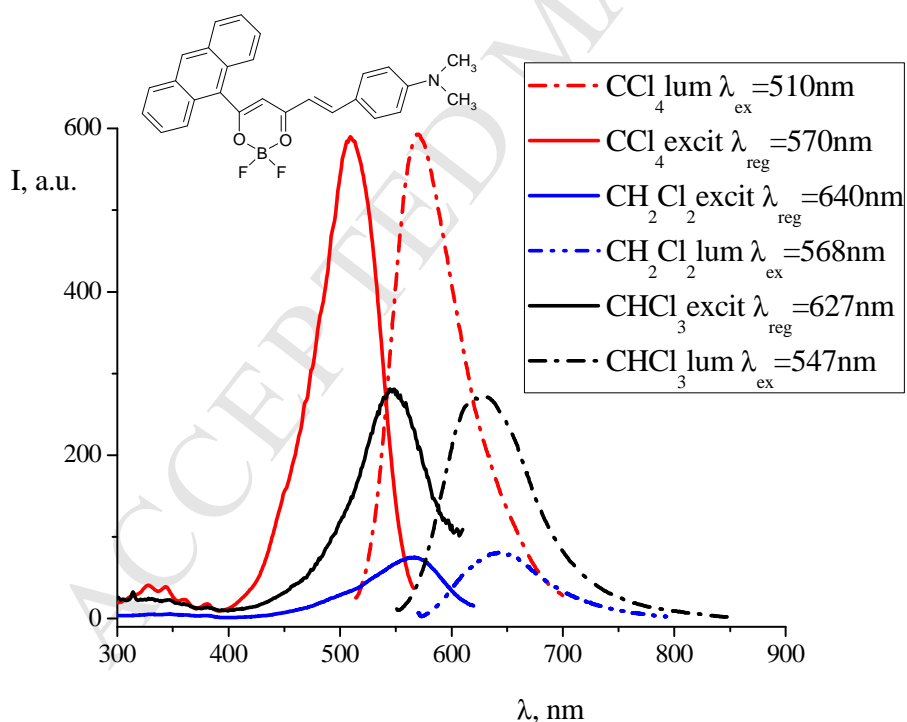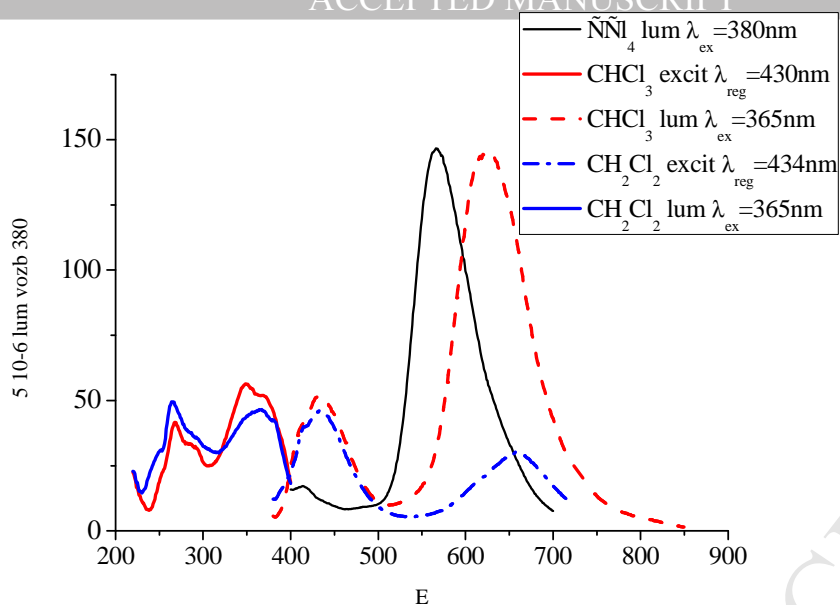Long-wave luminescence and excitation spectra of solution 2 C = 5•10⁻⁶ mol/l in different solvents.
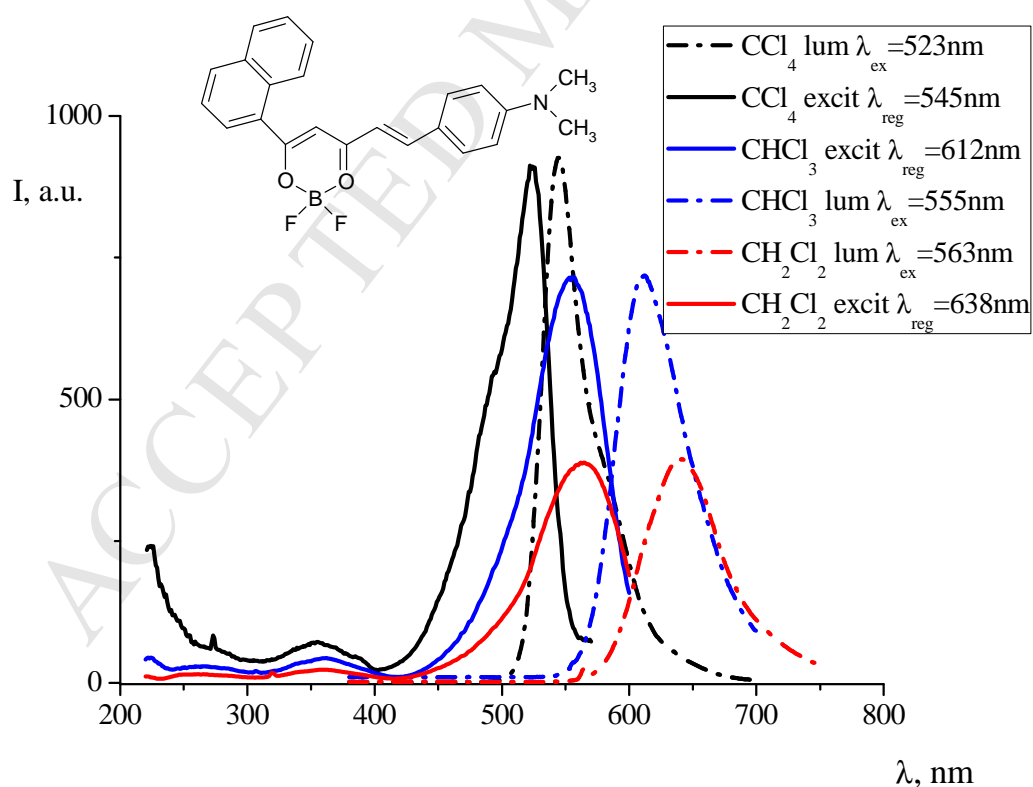
Long-wave luminescence and excitation spectra solution of solution **3** C = 5•10⁻⁶ mol/l in different solvents.
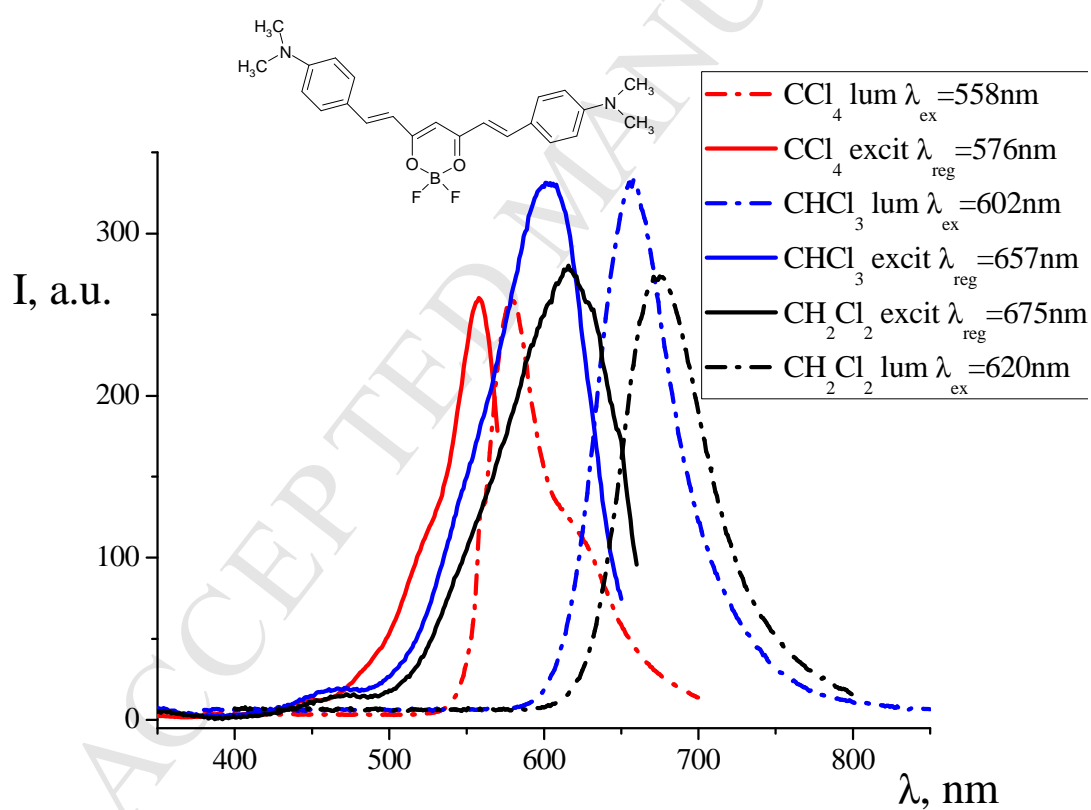
Long-wave luminescence and excitation spectra solution of solution **4** C = 5•10^{-6} mol/l in different solvents.
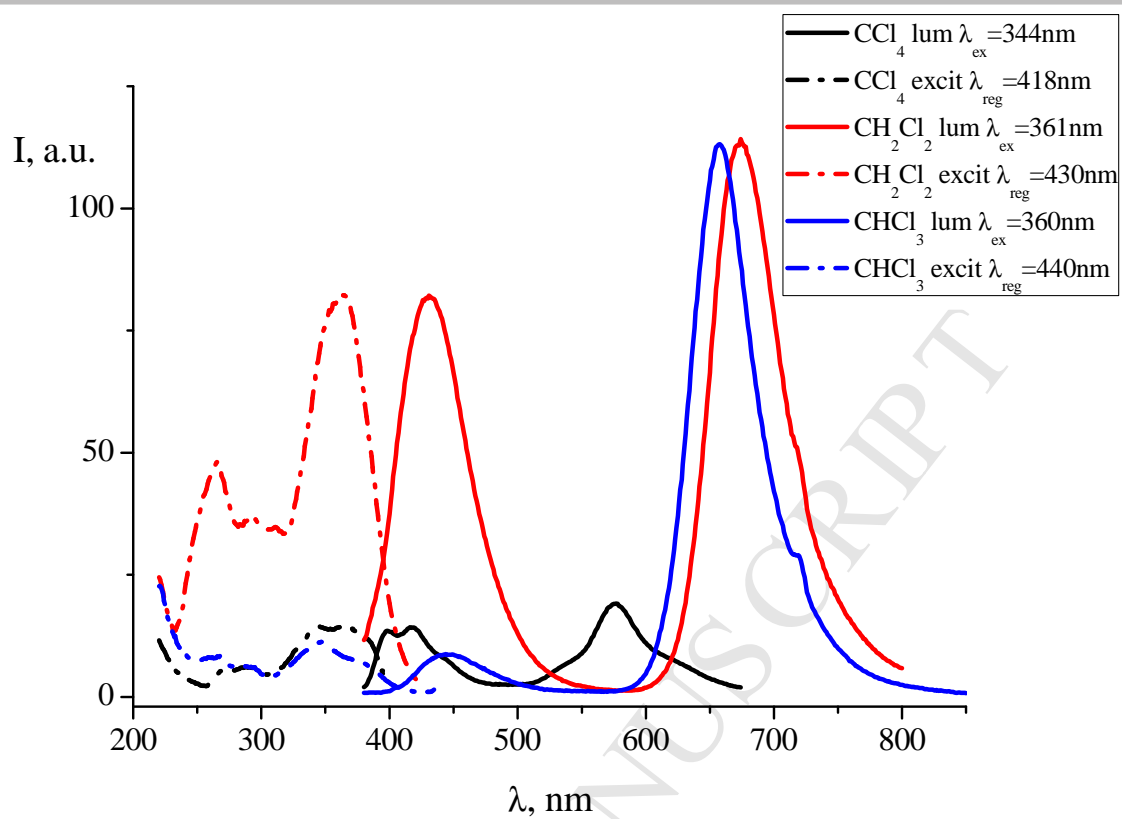

Long-wave luminescence and excitation spectra solution of solution **5** C = 5•10^{-6} mol/l in different solvents

Short-wave luminescence and excitation spectra of solution **5** C = 5•10^{-6} mol/l in different solvents.

Long-wave luminescence and excitation spectra solution of solution **6** C = 5•10^{-6} mol/l in different solvents

Short-wave luminescence and excitation spectra of solution **6** C = 5•10^{-6} mol/l in different solvents.