Brief Communications

Effect of hydration on the luminescence properties of 2,2-difluoro-4-methylnaphto[2,1-*e*]-1,3,2-dioxaborine. Quantum chemical modeling and experiment.

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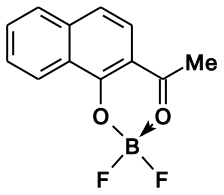
The effect of hydration on the spectral luminescence properties of solutions of 2,2-difluoro-4-methylnaphto[2,1-*e*]-1,3,2-dioxaborine in organic solvents is studied. Quenching of luminescence and color changes of the solutions associated with hydration of luminophore molecules were observed. Quantum chemical modeling of the structure of the hydrate complex is carried out.

Key words: quantum chemical calculations, density functional theory, difluoroboron β-diketonates, luminescence, hydrogen bond.

Fluorescent dyes immobilized in polymeric matrices and capable of "on" and "off" switching their luminescence are promising systems for the design of reversible, reusable luminescence on-off optical fiber sensors.[1—3]

Difluoroboron β-diketonates exhibit bright fluorescence in the crystalline state[4] and in solutions,[5—7] thus being promising compounds for use as luminescent dyes for polymers.[8,9] In the present work, we report for the first time on reversible on-off luminescence switching of solutions of 2,2-difluoro-4-methylnaphtho[2,1-*e*]-[1,3,2]dioxaborine (**1**) in organic solvents upon addition of water.



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There is a number of on-off luminescence switching mechanisms, *e.g.*, (i) inversion of nπ—ππ states due to involvement of n-electrons of heteroatoms in the forma-

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tion of hydrogen bonds[10] and (ii) changes in intermolecular interactions.[3] Difluoroboron β-diketonates can form excimers, which often luminesce much brighter than monomers.[11] In this connection, quenching of luminescence can be due to the formation of a solvation shell and violation of excimer formation. The aim of this work is to establish the mechanism of on-off luminescence switching in the hydration of compound **1**.

Experimental

Compound **1** was synthesized by a known procedure.[12] Anhydrous solvents (acetone, THF, EtOH) were prepared according to conventional procedures.[13]

Luminescence spectra were recorded on a SDL-1 spectrometer at 300 K using a DRSh-250 lamp as the source of excitation and an UFS-6 filter (λ_{ex} = 365 nm). Electronic absorption spectra were recorded on an SF-256 spectrophotometer. The luminescence decay kinetics was measured on a PicoQuant FluoTime 200 picosecond laser spectrofluorimeter.

Quantum chemical calculations. The effect of solvents on the luminescence properties of compound **1** was studied using quantum chemical calculations of hydrates with different mutual arrangement of water molecule and substrate. We performed the search for the most plausible location of water molecules and studied the effect of hydration on the electronic structure and luminescence properties of the difluoroboron complex.

Modeling of systems with weak intermolecular interactions requires consideration of the electron correlation and augmentation of the basis set with polarizaton functions to extend the wave function to the long-range region. The most accurate solution to such a problem can be obtained by optimizing the geometry of the molecular system in a rather wide basis set augmented with polarizaton functions. However, such calculations are too time-consuming; therefore, the solution to the problem was split into two steps.

First, we constructed a total of eleven initial model systems with different location of water molecule in the vicinity of substrate (compound **1**). The geometry was optimized by the *ab initio* method in the Hartree—Fock approximation with the 6-311G basis set (no polarization functions). A number of local energy minima were found, which correspond to structures with different location of water molecules.

Then, the geometries of the lowest-total-energy structures found in the preceding step were additionally optimized by the B3LYP5/6-31G** method.

We also calculated the electronic absorption spectra for 20 states of the substrate molecule and the most plausible hydrated systems in the framework of time-dependent density functional theory (TDDFT).

All calculations were carried out using the GAMESS/Firefly program.[14]

Results and Discussion

The addition of water to solutions of **1** in acetone causes a threefold decrease in fluorescence intensity; in addition, the aquamarine fluorescence turns blue (Fig. 1, *a*). In THF, the luminescence of **1** is almost completely quenched upon addition of water (the luminescence intensity decreases by a factor of 11, see Fig 1,*b*). Subsequent addition of a dehydrating agent (*e.g.*, $CaCl_2$) to the luminophore solution leads to recovery of the luminescence intensity. The on-off luminescence switching is

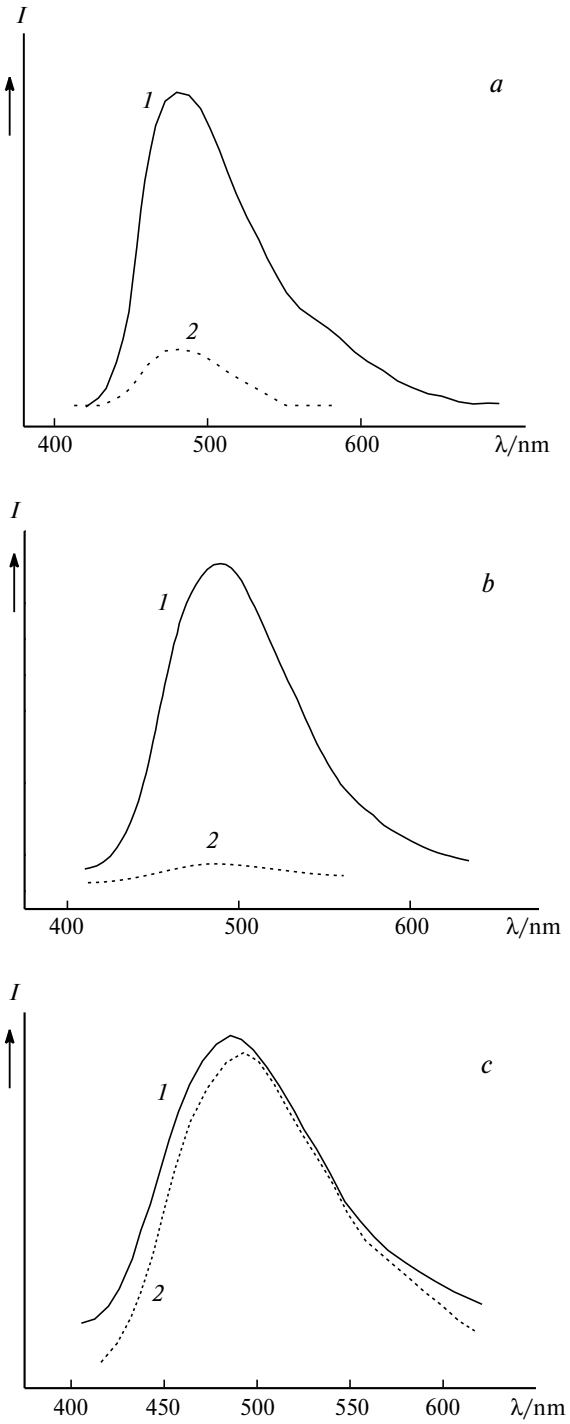

Fig. 1. Luminescence spectra of compound **1** in acetone (*a*), THF (*b*), and EtOH (*c*) recorded in anhydrous solvent (*1*) and in solvent—water (9 : 1) mixture (*2*).

accompanied by changes in the solution color (decoloration of yellow solution) (Fig. 2, *a*). Unlike the solutions of compound **1** in aprotic solvents (acetone and THF), in the protic solvent (EtOH) the luminescence intensity is initially weak and decreases insignificantly upon addition of water (see Fig. 1, *c*). The solution of **1** in EtOH also retains its color (see Fig. 2, *b*). A possible mechanism of luminescence quenching after the addition of water is the formation of hydrogen bonds between the luminophore and water molecules (EtOH).

To establish the mechanism of the observed phenomena, we carried out quantum chemical calculations of hydrated systems with different mutual arrangement of a water molecule and molecule **1**. Three lowest-energy structures (**A—C**) were located (Fig. 3).

According to calculations, the interaction of the water molecule with the fluorine atom is the most probable. Localization of the water molecule in hydrophobic regions of the substrate is energetically less favorable (on average, by 0.3 eV). In the low-energy structures, the water molecule is above the plane of the substrate molecule.

Hydration is accompanied by distortion of the planar structure of compound **1**. In particular, the torsion angle B(1)—O(1)—C(1)—C(2) in structure **1** is 13°. The MO composition for compound **1** and its hydrated structure **A** are listed in Table 1. The calculated electronic absorption spectra of compound **1** and hydrated structure **A** for twenty excited states originated from the allowed singlet-singlet transitions are listed in Tables 2 and 3 and shown in Fig. 4. Hydration of **1** causes a hypsochromic shift of spectral bands (see Fig. 4), which is in excellent agree-

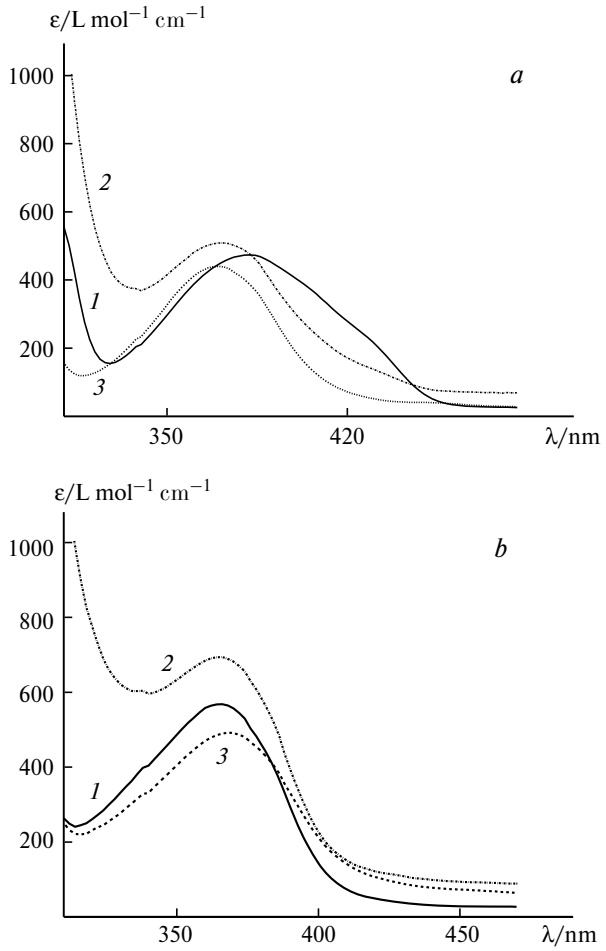

Fig. 2. Absorption spectra of compound **1** in THF (*a*) and EtOH (*b*) recorded at different concentrations of **1**: 0.012 mol L^{-1} (*1*) and 0.0012 mol L^{-1} (*2*); those recorded in solvent—water (9 : 1) mixtures at C_1 = 0.012 mol L^{-1} (*3*).

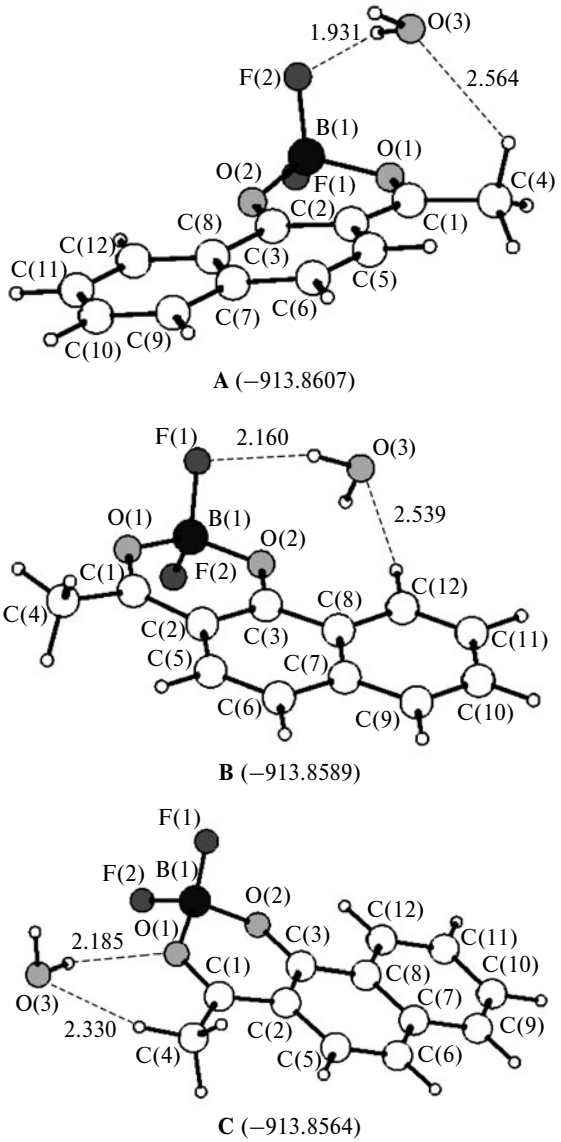

Fig. 3. Minimum-energy hydrated structures **A—C** of compound **1**. Shown are the distances (Å) between particular atoms of the substrate and water molecule. The energies (*E*/a.u.) of the corresponding structures are given in parentheses.

ment with the experimental data. Our model for hydration includes only one water molecule. Real systems contain tens of water molecules; therefore, there are grounds to believe that calculations of complex hydrated systems will predict a more pronounced hypsochromic shift.

When studying real solutions, one should take into account a superposition of intermolecular interactions including aggregation and solvation of luminophore molecules, which significantly change the photophysical properties of complexes. In the long-wavelength region, the absorption spectra of the solutions of compound **1** in aprotic solvents (concentration 10^{-3} mol L^{-1}) exhibit a kink at 430 nm, which becomes less pronounced as the concentration of the solution decreases (Fig. 2, *a*, curves

Table 1. The HOMO types, compositions, and energies (E_{HOMO}) of compound **1** and hydrated structure **A** obtained from B3LYP5/6-31G** calculations

1				**A**			
N	Type	Composition[a]	$-E_{HOMO}$/eV	*N*	Type	Composition[a]	$-E_{HOMO}$/eV
60	π	C_r(85) + O(13)	6.10	65	π	C_r(86) + O(11)	6.14
59	π	C_r(94)	7.27	64	π	C_r(93)	7.28
58	π	C_r(81) + O(15)	7.57	63	π	C_r(67) + O(12)	7.60
57	σ	O(55) + C_r(28)	8.40	62	π + H_2O[b]	H_2O(78) + C_r(17)	7.78
56	π	C_r(50) + F(43)	9.00	61	σ	O(54) + C_r(30)	8.47
55	π	F(49) + C_r(46)	9.34	60	π	C_r(71) + F(16) + O(10)	9.12
54	π	F(79) + C_r(10)	9.38	59	π	F(56) + H_2O(20) + C_r(19)	9.46
53	σ	C_r(54) + O(12) + F(11)	9.52	58	π	C_r(53) + F(15)	9.56
52	σ	F(43) + C_r(26) + O(18)	9.68	57	σ	F(57) + C_r(18) + O(12)	9.64
51	σ	F(50) + C_r(30)	9.99	56	σ	F(31) + C_r(24) + H_2O(17) + O(13)	9.83
50	σ	C_r(40) + F(31) + O(15)	10.10	55	σ	H_2O(37) + C_r(22) + F(15) + O(11)	9.93
49	σ	C_r(68) + O(17) + F(13)	10.36	54	σ	F(50) + C_r(26) + O(14)	10.12
48	σ	C_r(46) + O(20) + F(16)	10.51	53	σ	C_r(34) + F(28) + O(20)	10.16

[a] C_r is the sum of the contributions of the orbitals of the aromatic ring atoms C(3)—C(12); O and F are the sums of the contributions of the oxygen and fluorine AO, respectively; H_2O is the sum of the contributions of the water oxygen and hydrogen AO. The AO contributions in per cent are given in parentheses. Contributions smaller that 10% are omitted.
[b] π-MO with a large contribution from the water oxygen and hydrogen AO.

Table 2. Energies (*E*) and oscillator strengths (*f*) of singlet—singlet transitions in the electronic absorption spectrum of compound **1** according to B3LYP5/6-31G** calculations

State	*E*/eV	*E*/cm^{-1}	*E*/nm	*f*	Transition*
1	3.21	25920	385.81	0.10	60—61 (96)
2	4.15	33492	298.57	0.02	59—61 (56) + 60—62 (41)
3	4.53	36543	273.65	0.01	58—61 (94)
4	4.67	37607	265.91	0.00	57—61 (98)
5	4.80	38721	258.26	0.67	60—62 (52) + 59—61 (39)
6	5.13	41354	241.81	0.02	60—63 (55) + 59—62 (42)
7	5.69	45902	217.85	0.02	56—61 (46) + 58—62 (42)
8	5.80	46806	213.65	0.04	56—61 (50) + 58—62 (28) + 60—64 (8)
9	5.98	48206	207.44	0.00	53—61 (70) + 52—61 (17)
10	6.01	48434	206.47	0.32	59—62 (36) + 60—63 (29) + 55—61 (18)
11	6.14	49542	201.85	0.01	55—61 (71) + 60—64 (10)
12	6.21	50051	199.80	0.02	54—61 (81) + 60—64 (13)
13	6.22	50149	199.40	0.00	52—61 (60) + 53—61 (26) + 57—62 (11)
14	6.35	51216	195.25	0.00	57—62 (79) + 52—61 (18)
15	6.43	51844	192.89	0.11	60—64 (44) + 58—62 (17) + 59—63 (12) + 54—61 (8)
16	6.64	53542	186.77	0.00	51—61 (91)
17	6.70	54078	184.92	0.00	50—61 (91)
18	6.77	54632	183.04	0.13	58—63 (62) + 59—64 (27)
19	6.91	55759	179.34	0.13	59—63 (71) + 49—61 (9)
20	7.01	56537	176.88	0.00	48—61 (89)

* The MO numbers are the same as those in Table 1. The contributions of the transitions in per cent are given in parentheses.

Table 3. Energies (E) and oscillator strengths (f) of singlet-singlet transitions in the electronic absorption spectrum of hydrated structure **A** calculated by the B3LYP5/6-31G** method

State	E/eV	E/cm^{-1}	E/nm	f	Transition*
1	3.23	26083	383.39	0.10	65—66 (96)
2	4.16	33577	297.83	0.03	64—66 (59) + 65—67 (39)
3	4.46	35954	278.13	0.04	63—66 (67) + 62—66 (25)
4	4.63	37320	267.95	0.01	62—66 (60) + 63—66 (26)
5	4.74	38217	261.66	0.01	61—66 (94)
6	4.85	39096	255.78	0.64	65—67 (45) + 64—66 (33) + 62—66 (12)
7	5.14	41486	241.04	0.02	65—68 (54) + 64—67 (42)
8	5.74	46305	215.96	0.05	63—67 (63) + 60—66 (16) + 65—69 (12)
9	5.91	47637	209.92	0.02	60—66 (70)
10	5.98	48234	207.32	0.05	62—67 (69) + 64—67 (10)
11	6.05	48760	205.09	0.13	58—66 (38) + 62—67 (12) + 64—67 (11) + 65—68 (11)
12	6.06	48844	204.73	0.15	58—66 (26) + 64—67 (15) + 65—68 (15) + 65—69 (10)
13	6.20	50043	199.83	0.00	59—66 (87)
14	6.29	50769	196.97	0.01	61—67 (31) + 56—66 (29) + 58—66 (25)
15	6.37	51396	194.57	0.01	57—66 (42) + 65—69 (21) + 61—67 (14)
16	6.44	51944	192.51	0.00	61—67 (44) + 56—66 (29) + 65—69 (10)
17	6.51	52471	190.58	0.07	57—66 (34) + 65—69 (20) + 64—68 (13)
18	6.64	53528	186.82	0.01	55—66 (66) + 56—66 (23)
19	6.72	54190	184.54	0.00	54—66 (56) + 53—66 (33)
20	6.79	54758	182.62	0.08	63—68 (51) + 64—69 (24) + 64—68 (11)

* The MO numbers are the same as those in Table 1. The contributions of the transitions in percent are given in parentheses.

1 and *2*). This behavior of the absorption spectrum is characteristic of the formation of electron donor-acceptor complex (EDAC) in the ground state.[15] As shown earlier,[16] compound **1** can readily form excimers in chloroform owing to the planar structure and high polarity of its molecules.[17] The formation of excimers in THF and acetone at high concentrations of **1** involves the formation of EDAC. The energy profile of excimer formation is shown in Fig. 5.

According to quantum chemical calculations, the best position of water molecule in the hydration complex is above the plane of the luminophore molecule. This precludes parallel arrangement of the molecules of compound **1**, which is necessary for the formation of EDAC and excimers.[17] Decoloration of the yellow solutions in THF and acetone observed upon addition of water is an indication of the decomposition of EDAC (Fig. 2, *a*, curve *3*). No EDAC absorption band is observed in the solution in EtOH and the addition of water causes no spectral changes because of the formation of hydrogen bonds between the alcohol and luminophore molecules (Fig. 1, *c* and Fig. 2, *b*). As water is added to the solutions of **1** in acetone and THF, the excited-state lifetime (τ) of

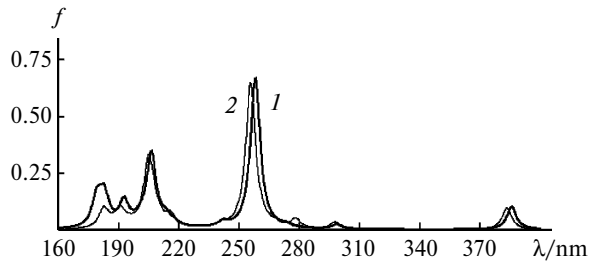

Fig. 4. Electronic absorption spectra of compound **1** (*1*) and hydrated structure **A** (*2*) obtained from B3LYP5/6-31G** calculations.

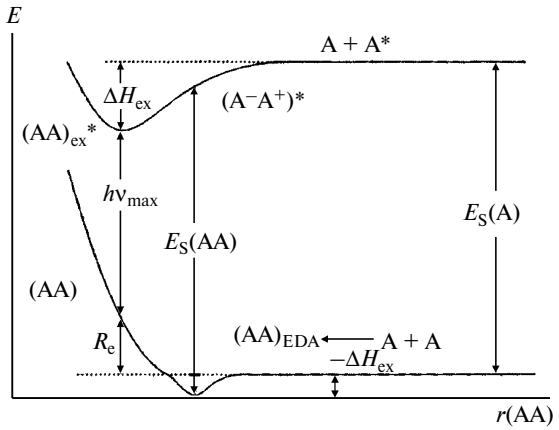

Fig. 5. Energy profile of the formation of excimers of compound **1** involving EDAC. A and A* are the ground-state and excited-state molecules of compound **1**, respectively; (AA) and $(AA)_{EDA}$ are the ground-state dimer and EDAC of molecule **1**, respectively; $(AA)_{ex}$* is the excimer; (A^-A^+) is the radical ion pair; r(AA) is the intermolecular distance; R_c is the repulsive energy; $h\nu_{max}$ is the excimer luminescence; ΔH_{ex} is the enthalpy of formation of the excimer; and E_S(A) and E_S(AA) are the solvation energies of molecule **1** and EDAC, respectively.

molecule **1** also changes (τ_{anh} = 0.99 ns and τ_{aq} = 0.41 ns in THF *vs.* τ_{anh}= 14.49 ns and τ_{aq} = 0.4 ns in acetone). In EtOH, the luminescence decay kinetics remains unchanged ($\tau_{anh} = \tau_{aq}$ = 0.26 ns).

Complete changes in the spectral characteristics of the solutions of compound **1** in aprotic solvents take a rather long time (about 15 min) needed for significant rearrangement of the solvation shell of molecule **1**. Taking a solution of 1-naphthol in isopropyl alcohol as an example, it was shown that upon the addition of water (5%) the content of water in the solvation shell exceeds 50%.[18] Apparently, similar relationships also hold when water is added to the solutions of compound **1**; this provides an explanation for the quenching of luminescence.

The hydration dynamics of compound **1** was monitored from the changes in the lifetime (τ) (Fig. 6). Initially, the fluorescence decay kinetics of **1** in acetone is biexponential, *viz.*, the fluorescence decay times of single molecules (τ_1) and excimers (τ_2) in the solutions with a concentration of 10^{-5} mol L^{-1} are 0.25 and 18.85 ns, respectively. As shown in Fig. 6, the relative intensity of the fluorescence exponent of single molecules increases with time, while the corresponding parameter for excimers decreases.

Thus, our experimental studies and quantum chemical calculations showed that hydration of compound **1** in aprotic solvents leads to reorganization of the solvation shell of the luminophore, formation of hydrogen bonds with water molecules, and breakdown of the EDAC, which causes abrupt changes in the spectral characteristics of **1**.

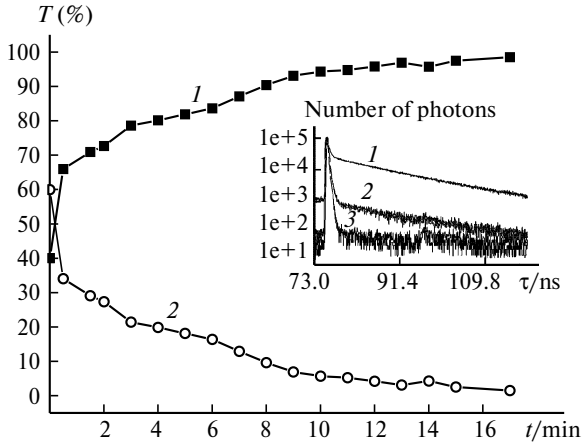

Fig. 6. Hydration kinetics of compound **1** in acetone ($C_{\mathbf{1}} = 10^{-4}$ mol L^{-1}): the contribution of the exponent with τ_1 = 0.25 ns (*1*) and that of the exponent with τ_2 = 18.88 ns (*2*) at a concentration of water in acetone of 0.9 mol L^{-1}. The inset shows the luminescence decay kinetics of compound **1** in anhydrous acetone (*1*) and 1 (*2*) and 17 min (*3*) after the addition of water.

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