Fluorescence Quenching of 3,5-Diphenyl-8-CF₃-BODIPY Luminophores Bearing Aminophenyl Substituents by Aromatic Molecules

A. V. Gadomska^{a,*}, A. V. Nevidimov^{a,b}, S. A. Tovstun^{a,b}, O. V. Petrova^c, L. N. Sobenina^c,
B. A. Trofimov^c, and V. F. Razumov^{a,b,d}

^a Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia

^b Moscow Institute of Physics and Technology (State University), Dolgoprudny, Moscow oblast, 141701 Russia

^c Favorsky Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, Irkutsk, 664033 Russia

^d Photochemistry Center of Federal Scientific Research Center “Crystallography and Photonics”, Russian Academy of Sciences, Moscow, 119421 Russia

*e-mail: ann.gadomsky@gmail.com

Received December 28, 2020; revised January 14, 2021; accepted January 15, 2021

Abstract—It has been found that the fluorescence quantum yield of 3,5-diphenyl-8-CF₃-BODIPY luminophores with aminophenyl substituents in aromatic solvents strongly depends on the position of the aniline amino group with respect to the position of attachment to the core of the BODIPY molecule. It has been suggested and substantiated that the reason for quenching of BODIPY *meta*-isomers is the specific interaction of luminophore molecules with aromatic molecules.

Keywords: BODIPY, quenching, conformers, luminescence, Stern–Volmer

DOI: 10.1134/S0018143921030024

INTRODUCTION

It is known that fluorescence of luminophores based on derivatives of 4-boron-3a,4a-diaza-*s*-indacene (BODIPY) can strongly depend on the polarity of the solvent. This is due to the fact that the processes of emission and absorption of light in these molecules are accompanied by intramolecular charge transfer and, in this case, the dipole moment of the molecule can change greatly.

Examples of such compounds are aminophenyl derivatives of BODIPY studied in this work, whose

structures are shown in Scheme 1. In these compounds, two fluorine atoms at position 4 and the CF₃ group at position 8 are strong electron acceptors, whereas the aminophenyl substituents at positions 3 and 5 exhibit significant electron donating properties. The intramolecular charge transfer for the structures shown in Scheme 1 is most pronounced for compounds **P1** and **P2**, in which the amino group is in the *para* position with respect to the substitution sites at positions 3 and 5.

Scheme 1. Derivatives of 8-CF₃-BODIPY studied in this work.

In nonpolar solutions of aliphatic hydrocarbons, compounds **M1**, **M2**, **P1**, and **P2** have a high fluores-

cence quantum yield, but in polar solvents, the luminescence efficiency decreases significantly. Intramo-

molecular spatial charge separation arising upon photo-excitation of BODIPY dyes is stabilized by polar aprotic solvents such as 1,4-dioxane, ethyl acetate, acetonitrile, dimethyl sulfoxide (DMSO), and makes these compounds practically nonluminescent [1].

The sharp decrease in the luminescence quantum yield in polar solvents is associated with the fact that, as a result of a strong interaction with dipole solvent molecules, the electronic level of the excited state sharply decreases, which leads to a significant increase in the constant of nonradiative transition to the ground state [2].

At the same time, the luminescence quantum yield of compounds **M1** and **M2**, in which the amino group is in the *meta* position, decreases in a DMSO solution and in similar polar solvents, but not as significantly as is observed for compounds **P1** and **P2**. This is apparently due to the fact that, due to the weaker interaction of compounds **M1** and **M2** with dipole solvent molecules, the level of the excited electronic state of compounds **M1** and **M2** does not decrease as much as it occurs for **P1** and **P2** molecules.

In this work, it has been found that in aromatic solvents (benzene, toluene, and *o*-xylene), the luminescence characteristics of the luminophores depend very strongly on the position of the aniline amino group with respect to the position of the attachment to the core of the BODIPY molecule. In [3], a special study was carried out on the effects of polarity, polarizability, and pH of solvents on the position of the electronic spectra of molecules with intramolecular charge transfer. To explain the special role of aromatic solvents, a new empirical parameter was introduced, the so-called dipolarity value (SdP), which, along with such values as the polarity and polarizability of the solvent, permits finding an empirical correspondence of the shifts of the absorption and luminescence bands of molecules in which electronic transitions are associated with the internal charge separation. Without going into details, it can be stated that the effect of aromatic solvents is the greater, the more the dipole moment of the luminophore molecule changes as a result of the transition to the excited state. However, in the case of BODIPY molecules, for compounds **M1**, **M2**, **P1**, and **P2** in aromatic solvents (benzene, toluene, and *o*-xylene), the opposite effect is observed: luminescence of *meta*-isomers (compounds **M1** and **M2**) is quenched much stronger than luminescence of *para*-isomers (compounds **P1** and **P2**), although the intramolecular charge transfer in the *meta*-isomers is much less than that in the *para*-isomers.

Hence, this anomalous behavior of the *meta*- and *para*-isomers in aromatic solvents cannot be explained by intramolecular charge transfer. In particular, attempts to use the concept of the dipolarity parameter, according to which benzene and toluene can be conventionally considered as some intermediate case between nonpolar *n*-hexane and polar solvents, will be

fruitless. In that case, quenching of luminescence of the *para*-isomer should be much greater than that for the *meta*-isomer, which is not observed in the experiment, whose details will be discussed below. This contradiction served as a motivation for this work.

EXPERIMENTAL

Reagents and Materials

The following solvents were used in the work: *n*-hexane (99%, HPLC, Scharlau), cyclohexane (99%, Sigma–Aldrich), benzene (99%, Sigma–Aldrich), toluene (99.99%, HPLC, Fisher Scientific), *o*-xylene (99%, Sigma–Aldrich). All reagents and organic solvents used were not subjected to additional purification.

Spectral Measurements

The absorption spectra were recorded on a Shimadzu UV 3101PC spectrophotometer and the luminescence spectra on a Shimadzu RF 6000 spectrofluorimeter. The luminescence decay kinetics were measured on a PicoQuant FluoTime 200 time-resolved spectrofluorometer; a semiconductor laser with a wavelength of 467 nm was used as an excitation source.

The luminescence quantum yields were determined at the absorbance of the samples at an excitation wavelength of no more than 0.1. An ethanol solution of rhodamine 6G was used as a standard for measuring the luminescence quantum yield (the quantum yield in an ethanol solution is 95% [4]). When calculating the luminescence quantum yields, the refractive indices of the corresponding solvents were taken into account [5].

All spectral and spectral-kinetic measurements were carried out at room temperature in quartz fluorescent cells with an optical path length of 10 mm. The spectral resolution in luminescence measurements was 3, and 5 nm for samples with a low quantum yield.

^1H (400 MHz), ^{13}C (100 MHz), ^{15}N (41 MHz), and ^{19}F (377 MHz) NMR spectra were recorded on a Bruker Avance 400 instrument in CDCl_3 and $\text{DMSO-}d_6$. Chemical shifts are reported in ppm. The assignment of the signals in the ^1H NMR spectra was carried out using COSY and NOESY experiments. The resonance signals of carbon atoms were established on the basis of ^1H – ^{13}C HSQC and ^1H – ^{13}C HMBC experiments, and the δ values of ^{15}N on the basis of $^2\text{D}^1\text{H}$ – ^{15}N HMBC experiment. Chemical shifts (δ) of ^1H are given in relation to the signals of residual protons of deuterated solvents (7.27 ppm for CDCl_3 and 2.50 ppm for $\text{DMSO-}d_6$), chemical shifts in ^{13}C spectra are given in relation to the peaks of deuterated solvents (77.1 ppm for CDCl_3 and 39.5 ppm for $\text{DMSO-}d_6$), those in ^{15}N spectra are given in relation to MeNO_2 (0.0 ppm), and those in ^{19}F spectra in relation to CFCl_3 (0.0 ppm). The spin–spin coupling constants were measured in hertz (Hz) from one-dimensional ^1H spectra. IR spectra were obtained on a

Bruker IFS-25 spectrometer (400–4000 cm⁻¹, KBr). Microanalysis (C, H, N) was performed on a FlashEA 1112 CHNS-O/MAS instrument (CHN Analyzer). The fluorine content was determined on a SPECOL 11 spectrometer (Carl Zeiss, Jena, Germany). Melting points (without correction) were determined using a StuartScientificSMP3 digital meter.

Quantum chemical calculations for optimization of the geometry of the structures in the ground and excited states were performed using the freely distributed ORCA program [6, 7]. For the ground state, the electronic density functional theory (DFT) was used, and for the excited state, TD-DFT with the PBE0 functional and the 6-311G** basis was used. For the geometry found, the matrix of second derivatives was calculated to make sure that the found minimum is true. The search for the geometry of the excited state began with the optimal geometry found for the ground state. For the optimal geometries found, the energies of vertical transitions were calculated: from the optimized S₀ state to S₁ without changing the nuclear configuration and from the unoptimized S₀ state to the optimized S₁ state (also without changing the nuclear configuration).

Molecular dynamics calculations in the NAMD program [8] were used to study the geometric structure

of possible complexes of BODIPY with benzene. For this purpose, a cell with periodic boundary conditions was considered, in the center of which a dye molecule was placed, and the rest of the space was filled with benzene. The atomic charges of the dye molecule were taken from the results of quantum chemical calculations [9]. The integration of the classical equations of motion was performed according to the Verlet scheme with velocities with an integration step of 1 fs; the total length of the molecular dynamics trajectory was 1.1 ns, of which the first 0.1 ns was used to minimize the energy. In every 100 steps, the current coordinates of all atoms were saved into a trajectory file, from the analysis of which the possible structures of BODIPY complexes with benzene were found. The structures found were optimized using the ORCA program as described above.

Synthesis of Luminophores **M1**, **M2**, **P1**, and **P2**

The synthesis of luminophores **M1** and **P1** is described in detail in [1].

Luminophores **M2** and **P2** were obtained for the first time by the method described in [10] from 2-(3- and 4-aminophenyl)pyrroles **5a**, **5b**, which were synthesized from the corresponding acetophenone oximes and acetylene by the Trofimov reaction [11].

3-NH₂ (**a**, **P2**), 4-NH₂ (**b**, **M2**)

Scheme 2. Scheme of the synthesis of luminophores **M2** and **P2**.

Scheme 2 shows the following stages of the synthesis of luminophores **M2** and **P2**: (i) protection of the amino group of 2-(3- and 4-aminophenyl)pyrroles **1a**, **1b** by acetic anhydride; (ii) trifluoroacetylation of 2-(3- and 4-acetamidophenyl)pyrroles **2a**, **2b** by trifluoroacetic anhydride; (iii) reduction of 2-trifluoroacetylpyrroles **3a**, **3b** by NaBH₄; (iv) condensation of trifluoromethyl(pyrrole)ethanols **4a,b** with 2-(3- and 4-acetamidophenyl)pyrroles **2a**, **2b**; (v) removal of acetamide protection in dipyrromethanes **5a**, **5b**; and (vi) oxidation/complexation of dipyrromethanes **6a,b** into luminophores **M2** and **P2**.

The synthesis and spectral properties of pyrroles **1a,b–4a,b** are described in [1].

Synthesis of Dipyrromethanes **5a**, **5b**

A mixture of pyrroles **2a,b** (0.200 g, 1.0 mmol), **4a**, **4b** (0.298 g, 1.0 mmol), and P₂O₅ (0.142 g, 1.0 mmol) in MeCN (30 mL) was stirred at room temperature for 24 h. Then NaHCO₃ (0.101 g, 1.2 mmol) was added and the reaction mixture was stirred for 1.5 h. The precipitate was filtered off and washed with MeCN (3 × 5 mL). The solvent was removed from the filtrate. Dipyrromethane **5a**, **5b** was isolated from the precipitate by column chromatography (SiO₂, eluent MeCN/*n*-hexane/CH₂Cl₂ in a ratio of 20 : 1 : 1).

N,N'-[(2,2,2-trifluoroethane-1,1-diyl)bis(1*H*-pyrrole-5,2-diyl-3,1-phenylene)]diacetamide (5a). Yield 0.226 g (47%), mp 148–150°C.

¹H NMR (400 MHz, DMSO-*d*₆), δ: 11.35 (br s, 2 H, NH), 9.90 (br s, 2 H, NHCO), 7.79 (m, 2 H, H-2 Ph), 7.36 (m, 2 H, H-4 Ph), 7.28 (m, 4 H, H-5,6 Ph), 6.37 (m, 2 H, H-4), 6.22 (m, 2 H, H-3), 5.11 (q, *J* = 9.5 Hz, 1 H, CH), 2.06 (s, 6 H, Me).

¹³C NMR (100 MHz, DMSO-*d*₆), δ: 168.2, 139.5, 133.0, 131.5, 129.5, 125.4, 125.4 (q, *J* = 279.5 Hz, CF₃), 118.6, 117.0, 114.7, 109.3, 105.9, 42.1 (q, *J* = 30.1 Hz, CH), 23.9.

¹⁹F NMR (377 MHz, CDCl₃), δ: –67.8 d (*J* = 9.6 Hz).

¹⁵N NMR (41 MHz, DMSO-*d*₆), δ: –245.5 (*J* = 90.8 Hz, NHCO), –226.5 (¹*J*_{NH} = 95.5 Hz, NH).

IR (KBr), ν: 3406, 3303, 3110, 2930, 1672, 1614, 1594, 1540, 1500, 1429, 1384, 1372, 1256, 1189, 1158, 1108, 1075, 1046, 882, 866, 775, 713, 690, 538 cm^{–1}.

Calculated for C₂₆H₂₃F₃N₄O₂ (480.49): C, 64.99; H, 4.83; F, 11.86; N, 11.66. Found: C, 64.72; H, 4.95; F, 11.68; N, 11.58.

N,N'-[(2,2,2-trifluoroethane-1,1-diyl)bis(1*H*-pyrrole-5,2-diyl-4,1-phenylene)]diacetamide (5b). Yield 0.207 g (43%), mp 154–156°C.

¹H NMR (400 MHz, DMSO-*d*₆), δ: 11.23 (br s, 2 H, NH), 9.91 (br s, 2 H, NHCO), 7.55 (m, 8 H, H-2,3,5,6 Ph), 6.39 (m, 2 H, H-4), 6.18 (m, 2 H, H-3), 5.03 (q, *J* = 9.7 Hz, 1 H, CH), 2.04 (s, 6 H, Me).

¹³C NMR (100 MHz, DMSO-*d*₆), δ: 168.2, 137.3, 131.5, 127.7, 125.4 (q, *J* = 279.3 Hz, CF₃), 124.9, 123.9, 119.3, 109.3, 105.4, 42.2 (q, *J* = 30.3 Hz, CH), 24.0.

¹⁹F NMR (377 MHz, CDCl₃), δ: –67.9 (d, *J* = 9.7 Hz).

¹⁵N NMR (41 MHz, DMSO-*d*₆), δ: –246.5 (*J* = 90.4 Hz, NHCO), –226.9 (*J* = 95.3 Hz, NH).

IR (KBr), ν: 3402, 3304, 2930, 1673, 1600, 1524, 1426, 1370, 1318, 1254, 1158, 1107, 831, 776 cm^{–1}.

Calculated for C₂₆H₂₃F₃N₄O₂ (480.49): C, 64.99; H, 4.83; F, 11.86; N, 11.66. Found: C, 64.78; H, 5.09; F, 11.63; N, 11.85.

Synthesis of Dipyrromethanes **6a**, **6b**

A solution of dipyrromethane **5a**, **5b** (1.201 g, 2.5 mmol) in MeOH (80 mL) was refluxed in the presence of 15% HCl for 2 h. After cooling, water (40 mL) and NH₄OH solution (to pH ~ 7–8) were added to the mixture. Then the mixture was extracted with CH₂Cl₂ (4 × 30 mL), the precipitates were washed with water (3 × 20 mL) and dried over Na₂SO₄. The solvent was removed and the residue was purified by column chromatography (SiO₂, ether) to give dipyrromethane **6a**, **6b**.

3,3'-[(2,2,2-trifluoroethane-1,1-diyl)bis(1*H*-pyrrole-5,2-diyl)]dianiline (6a). Yield 0.888 g (90%), mp 126–127°C.

¹H NMR (400 MHz, DMSO-*d*₆), δ: 11.19 (br s, 2 H, NH), 7.00 (m, 2 H, H-5 Ph), 6.79 (m, 4 H, H-2,6 Ph), 6.41 (m, 2 H, H-4 Ph), 6.29 (m, 2 H, H-4), 6.16 (m, 2 H, H-3), 5.07 (q, *J* = 9.8 Hz, 1 H, CH), 5.01 (br s, 4 H, NH₂).

¹³C NMR (100 MHz, DMSO-*d*₆), δ: 148.7, 133.2, 132.3, 129.1, 125.5 (q, *J* = 279.8 Hz, CF₃), 124.8, 112.1, 111.9, 109.4, 109.1, 105.3, 42.0 (q, *J* = 30.2 Hz, CH).

IR (KBr), ν: 3426, 3396, 2957, 2925, 2864, 1615, 1506, 1471, 1330, 1253, 1194, 1158, 1106, 864, 778, 691 cm^{–1}.

Calculated for C₂₂H₁₉F₃N₄ (396.42): C, 66.66; H, 4.83; F, 14.38; N, 14.13. Found: C, 66.39; H, 4.99; F, 14.27; N, 14.35.

4,4'-[(2,2,2-trifluoroethane-1,1-diyl)bis(1*H*-pyrrole-5,2-diyl)]dianiline (6b). Yield 0.829 g (84%), mp 182–183°C.

¹H NMR (400 MHz, DMSO-*d*₆), δ: 10.93 (br s, 2 H, NH), 7.29 (m, 4 H, H-3,5 Ph), 6.56 (m, 4 H, H-2,6 Ph), 6.15 (m, 2 H, H-4), 6.09 (m, 2 H, H-3), 5.06 (br s, 4 H, NH₂), 4.98 (q, *J* = 9.9 Hz, 1 H, CH).

¹³C NMR (100 MHz, DMSO-*d*₆), δ: 146.9, 132.6, 125.6 (q, *J* = 280.3 Hz, CF₃), 124.8, 123.7, 121.1, 114.1, 108.8, 103.1, 42.2 (q, *J* = 30.3 Hz, CH).

IR (KBr), ν : 3430, 2925, 2825, 1622, 1600, 1524, 1479, 1333, 1258, 1158, 1105, 832, 778 cm⁻¹.

Calculated for C₂₂H₁₉F₃N₄ (396.42): C, 66.66; H, 4.83; F, 14.38; N, 14.13. Found: C, 66.58; H, 4.94; F, 14.25; N, 14.23.

Synthesis of BODIPY M2 and P2

A mixture of dipyrromethane **6a,b** (0.595 g, 1.50 mmol) and DDQ (2,3-dichloro-5,6-dicyanobenzoquinone, 0.341 g, 1.50 mmol) in CH₂Cl₂ (45 mL) was stirred at room temperature for 1.5 h. Then (*i*-Pr)₂NEt (1.939 g, 15.0 mmol) was added, the resulting solution was stirred for 10 min, and BF₃OEt₂ (3.193 g, 22.5 mmol) was added dropwise to the solution for 30 min. The reaction mixture was stirred at room temperature for 22 h and diluted with saturated NaHCO₃ solution, the organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 20 mL). The combined organic salts were washed with water (3 × 30 mL) and dried over K₂CO₃. After removal of solvent from the residue, BODIPY **M2** and **P2** were isolated by column chromatography (SiO₂, eluent *n*-hexane/ether, gradient from 1 : 1 to 0 : 1 for **2a**; and *n*-hexane/CH₂Cl₂, gradient from 1 : 1 to 0 : 1 for **4b**).

4,4-difluoro-3,5-bis(3-aniline)-8-trifluoromethyl-4-boron-3a,4a-diaza-*s*-indacene (M2). Yield 0.061 g (9%), mp 164–166°C.

¹H NMR (400 MHz, CDCl₃), δ : 7.42 (m, 2 H, H-2 Ph), 7.21 (m, 4 H, H-5,6 Ph), 7.17 (m, 2 H, H-1,7), 6.75 (m, 2 H, H-2,6), 6.70 (m, 2 H, H-4 Ph), 3.75 (br s, 4 H, NH₂).

¹³C NMR (100 MHz, CDCl₃), δ : 162.2, 146.4, 133.4, 132.9, 130.1, 129.3, 126.5 (q, J = 31.5 Hz, C-8), 123.1, 122.8 (q, J = 276.0 Hz, CF₃), 120.2 (t, J = 2.8 Hz), 117.3, 115.9 (t, J = 4.0 Hz).

IR (KBr), ν : 3442, 3371, 2924, 2859, 1620, 1566, 1509, 1474, 1421, 1306, 1269, 1225, 1135, 1085, 978, 902, 783 cm⁻¹.

Calculated for C₂₂H₁₆BF₅N₄ (442.20); C, 59.76; H, 3.65; B, 2.44; F, 21.48; N, 12.67. Found: C, 59.84; H, 3.48; F, 21.68; N, 12.79.

4,4-difluoro-3,5-bis(4-aniline)-8-trifluoromethyl-4-boron-3a,4a-diaza-*s*-indacene (P2). Yield 0.093 g (14%), mp 165–167°C.

¹H NMR (400 MHz, CDCl₃), δ : 7.81 (m, 4 H, H-2,6 Ph), 7.34 (m, 2 H, H-1,7), 6.71 (m, 2 H, H-2,6), 6.68 (m, 4 H, H-3,5 Ph), 4.00 (br s, 4 H, NH₂).

¹³C NMR (100 MHz, CDCl₃), δ : 160.5, 148.9, 133.4, 131.8, 131.7, 128.9, 123.2 (q, J = 276.0 Hz, CF₃), 123.0 (q, J = 32.0 Hz, C-8), 122.0, 114.6.

IR (KBr), ν : 3480, 3390, 3216, 2922, 2854, 1623, 1563, 1470, 1446, 1304, 1276, 1226, 1133, 1080, 907, 730 cm⁻¹.

Calculated for C₂₂H₁₆BF₅N₄ (442.20); C, 59.76; H, 3.65; B, 2.44; F, 21.48; N, 12.67. Found: C, 59.94; H, 3.38; F, 21.25; N, 12.87.

RESULTS AND DISCUSSION

Table 1 summarizes the experimental data on the positions of the absorption and luminescence spectral maxima, Stokes shifts, and luminescence quantum yields and lifetimes. In addition, for comparison, Table 1 shows the same characteristics for 3,5-diphenyl-8-CF₃-BODIPY (**F2**) in different solvents and for **P1**, **M1** in a polar solvent, DMSO, taken from [1].

First, it should be noted that the electron-donating character of aminophenyl substituents is clearly manifested in the bathochromic shift of the absorption and luminescence spectra of the compounds under study, measured in a nonpolar solvent (*n*-hexane or cyclohexane), as compared to compound **F2**. It can be seen that the shift for *meta*-isomers is much smaller ($\Delta\lambda_{\text{lum}}$ = 10 and 16 nm for **M1** and **M2**, respectively) than for *para* isomers ($\Delta\lambda_{\text{lum}}$ = 38 and 70 nm for **P1** and **P2**, respectively), while the presence of two aminophenyl substituents shifts the luminescence spectrum more strongly than one substituent.

The Stokes shift in nonpolar solvents such as *n*-hexane is approximately the same for all these compounds. The same applies to the value of the luminescence quantum yield: in general, it is quite high and is in the range of 80–25%, while a decrease is observed when the luminescence maximum shifts to longer wavelengths. In polar solvents, as already discussed in the introduction, a sharp drop in luminescence (by a factor of 10³–10⁴) is observed for all studied aminophenyl derivatives of BODIPY. It is important to note that luminescence quenching for *para*-isomers is greater than for *meta*-isomers, while the luminescence quantum yield of **F2** remains practically unchanged even in the most polar solvent, DMSO.

Second, attention is drawn to the unusual effect of the aromatic solvents benzene and toluene on the studied aminophenyl derivatives of BODIPY, which was mentioned in the introduction. While for the *para*-isomers **P1** and **P2** in benzene and toluene solutions, the quantum yield and lifetime of photoluminescence change insignificantly, for the *meta*-isomers **M1** and **M2**, the luminescence quenching occurs more than 100 times, but the lifetime does not change. As already mentioned in the introduction, the unusual character of this effect is that the *meta*-isomers **M1** and **M2** are characterized by a lower value of intramolecular charge transfer upon absorption of a quantum of light than the *para*-isomers **P1** and **P2**. This is confirmed by the data in Table 1. Indeed, the Stokes shift and luminescence quenching in a polar solvent, DMSO, are much greater for the *para*-isomers than for the *meta*-isomers, while in aromatic solvents (benzene and toluene), the opposite is true. Therefore, the

Table 1. Spectral characteristics of BODIPY in different solvents: positions of absorption and luminescence peaks (λ_{abs} and λ_{lum} , respectively), Stokes shift ($\Delta\nu$), luminescence quantum yield (ϕ), and excited state lifetime (τ)

No.	Solvent	λ_{abs} , nm	λ_{lum} , nm	$\Delta\nu$, cm^{-1}	ϕ	τ , ns
M1	<i>n</i> -Hexane	598	632	895	0.53	5.16
	Cyclohexane	601	634	878	0.52	5.16
	Benzene	605	636	810	0.011	5.34
	Toluene	606	636	797	0.017	5.42
	DMSO ^a	600	648	1180	0.0004	<0.1
M2	<i>n</i> -Hexane	605	638	863	0.42	5.41
	Cyclohexane	607	642	920	0.43	5.41
	Benzene	610	646	893	0.003	5.41
	Toluene	612	652	991	0.002	5.35
P1	<i>n</i> -Hexane	632	660	735	0.425	4.3
	Cyclohexane	635	665	729	0.40	4.3
	Benzene	647	692	1044	0.19	2.1
	Toluene	648	693	1056	0.21	2.2
	DMSO ^a	676	754	1530	n.d.	<0.1
P2	<i>n</i> -Hexane	662	692	685	0.26	2.35
	Cyclohexane	665	696	691	0.24	2.35
	Benzene	682	730	977	0.15	2.35
	Toluene	685	730	961	0.19	2.3
F2^a	<i>n</i> -Hexane	592	622	820	0.8	6.29
	1,4-Dioxane	594	630	950	0.83	5.89
	Ethyl acetate	592	626	940	0.82	6.13
	Acetonitrile	586	626	1090	0.84	6.43
	DMSO	599	639	1030	0.71	5.08

^a Data taken from [1].

mechanism for luminescence quenching in aromatic solvents should apparently be sought in some specific interaction controlled by the structural correspondence of the solvent and luminophore molecules. For a more detailed study of the mechanism of this process, we measured the luminescence quantum yields of solutions of **M1**, **M2**, **P1**, and **P2** in *n*-hexane as a function of the concentration of aromatic molecules (benzene, toluene, *o*-xylene) added to the solution.

Figure 1 shows for comparison the change in the relative luminescence quantum yield of the *meta*- (**M1**) and *para*- (**P1**) isomers as a function of the toluene concentration. The addition of only 1 mol % of toluene to the *n*-hexane solution leads to luminescence quenching of compound **M1** by 40%, while **P1** is quenched by only 3.5%. It is possible that a specific interaction of toluene occurs for both compounds **M1** and **P1**. However, for compound **P1**, this interaction is much weaker. The measurement of the same concen-

tration dependences for compounds **M1** and **P1** in the case of the addition of benzene and *o*-xylene, as well as for compounds **M2** and **P2** upon the addition of toluene, benzene, and *o*-xylene, led to qualitatively similar results. In other words, luminescence of *meta*-isomers is quenched upon an increase in the concentration of aromatic additives much more strongly than in the case of *para*-isomers.

Figure 2 presents the results of two series of experiments on luminescence quenching of compounds **M1** and **M2** in *n*-hexane solutions as a function of the mole fraction of toluene in the Stern–Volmer coordinates assuming only the dynamic quenching mechanism (Fig. 2a) and mixed quenching (Fig. 2b), that is, dynamic and static quenching simultaneously.

Dynamic luminescence quenching is described by the following equation:

Fig. 1. Dependence of the luminescence quantum yield of compounds **M1** (circles) and **P1** (triangles) on the concentration of toluene in *n*-hexane. Here, ϕ_0 and ϕ are the luminescence quantum yields in the absence and in the presence of the quencher, respectively.

$$\frac{\phi_0}{\phi} = 1 + k_q \tau_0 [Q] = 1 + K_D [Q],$$

where k_q is the bimolecular rate constant of the dynamic quenching reaction of the excited state of the luminophore molecule, τ_0 is the luminescence decay time in the absence of a quencher, $[Q]$ is the concentration of a quencher, and $K_D = k_q \tau_0$ is the Stern–Volmer dynamic quenching constant. Static quenching occurs when a quencher molecule forms a nonlumi-

nescent complex with a luminophore molecule. In this case, the luminescence quenching is described by the following equation:

$$\frac{\phi_0}{\phi} = 1 + K_S [Q],$$

where K_S is the equilibrium constant of the chemical reaction of the formation of a nonluminescent complex. In both cases, the concentration dependence should be linear in the Stern–Volmer coordinates: $\phi_0/\phi \rightarrow [Q]$. As can be seen from Fig. 2a, in our case the luminescence quenching is not described by either a purely dynamic or a purely static quenching mechanism. If quenching occurs by a mixed mechanism, that is, by two mechanisms simultaneously, then the dependence of ϕ_0/ϕ on the quencher concentration is quadratic [12]:

$$\frac{\phi_0}{\phi} = (1 + K_S [Q])(1 + K_D [Q]). \quad (1)$$

In this case, the concentration dependence should be linear in the following coordinates:

$$\frac{1}{[Q]} \left(\frac{\phi_0}{\phi} - 1 \right) \rightarrow [Q]. \quad (2)$$

It can be seen from Fig. 2b that the experimental data are well linearized in coordinates (2), that is, for the mixed quenching mechanism. These experimental data are described by Eq. (1) with the reliability criteria $R^2 = 0.9994$ and 0.9991 for compounds **M1** and **M2**, respectively, evaluated by the least squares

Fig. 2. Processing of the experimental data for compounds **M1** and **M2** following the Stern–Volmer equation: (a) dynamic quenching, (b) mixed dynamic and static quenching.

Fig. 3. (a, b) Structure of complexes of benzene with **M1** of composition 1 : 1: (a) frontal and (b) top views; (c) structure of a complex of **M2** with benzene of composition 1 : 2.

method. It is easy to see that the slope of the linear plots in Fig. 2b determines the product of the dynamic and static quenching constants, and the ordinate intercept determines the sum of these constants. For **M1**, the solution of the corresponding quadratic equation allows determining the values of the constants up to permutation: $K_D = 5.5$, $K_S = 1.3$ [M^{-1}] ($K_S = 5.5$, $K_D = 1.3$ [M^{-1}]). For **M2**, there are no real solutions for the constants. Hence, the quenching mechanism for luminophore **M2** with two aminophenyl groups is more complex.

As a working hypothesis, we assumed that luminescence quenching of the molecule of luminophore **M2** with two aminophenyl groups could occur as a result of the formation of two complexes of compositions 1 : 1 and 1 : 2; that is, the luminophore molecule can form a complex with both one and two quencher molecules. Figure 3 shows the structure of such complexes. The complexes are formed as a result of the simultaneous interaction of the benzene ring with the amino group and fluorine atoms.

If we accept this hypothesis about the presence of two complexes, then the dependence of the luminescence quantum yield on the quencher concentration will have the following form:

$$\frac{\varphi_0}{\varphi} = (1 + K_D[Q])(1 + K_S[Q] + K_S K_{S2}[Q]^2), \quad (3)$$

where K_{S2} is the equilibrium constant in the reaction between the 1 : 1 complex and the second quencher molecule. The experimental data for **M2** were described by Eq. (3) with the reliability criterion $R^2 = 0.9994$. The solution of the corresponding cubic equation gives a unique and unambiguous set of values of the equilibrium constants: $K_D = 3.6$, $K_S = 1.9$, and $K_{S2} = 0.74$ [M^{-1}]. The found values of the quenching constants are in good agreement with the values of $K_D = 5.5$ and $K_S = 1.3$ [M^{-1}] for compound **M1**.

Thus, it seems that the hypothesis of the possibility of the formation of two complexes makes it possible to interpret the obtained experimental data; however, this raises another problem. The thing is that, regardless of the mechanism of static quenching of luminescence, the experimental data on the decrease in the lifetime of the excited state with growing the quencher concentration should be linear in the Stern–Volmer coordinates, but, as will be shown below, this is not observed. Therefore, we turned to a more detailed study of the luminescence decay kinetics as a function of the toluene concentration and the observation wavelength.

As a result of the studies carried out, it was found that for *para*-isomers **P1** and **P2**, the luminescence decay kinetics has a single-exponential character, and with a decrease in the luminescence quantum yield on passing from *n*-hexane to an aromatic solvent, a regular decrease in the luminescence lifetime is observed (see Table 1), whereas for *meta*-isomers **M1** and **M2**, a complex two-exponential kinetics of luminescence decay is observed. Let us consider the data obtained for these compounds in more detail.

Figure 4 shows the effect of addition of benzene, toluene, and *o*-xylene on the form of the curves of the luminescence decay kinetics of compounds **M1** and **M2** in *n*-hexane. It can be seen that in pure *n*-hexane, the curves for both compounds are almost single-exponential, while additives of toluene significantly complicate their form. This form of the curves obtained in the presence of toluene may be due to the fact that each of the studied compounds **M1** and **M2** is a mixture of two luminophores, and aromatic molecules (benzene, toluene, and *o*-xylene) exhibit quenching properties only in relation to one of them. In the case of **M1** and **M2**, the manifestation of this kind of “two-component character” can be associated, for example, with the fact that both compounds are present in solution in the form of at least two different conformers.

Fig. 4. Experimental data on the luminescence decay kinetics for compound **M1** as a function of the addition of (a) benzene, (b) toluene, (c) *o*-xylene, and (d) for **M2** as a function of the addition of toluene. The upper (red) curve in each figure refers to the luminescence decay kinetics in bulk *n*-hexane. The excitation wavelength is 470 nm; the kinetics were measured at the luminescence maximum at a wavelength of 632 nm. Solid black curves result from processing of the experimental data following Eq. (4).

Another alternative, which is associated with the possible presence of an uncontrolled impurity of luminescent molecules of a similar structure, will be considered separately at the end of this work.

To simplify further processing of the experimental data, we assume that each of the compounds **M1** and **M2** is present only as two conformers, one of which interacts with the quencher, and the other does not. In this case, the following equation can be used to process the kinetic curves of luminescence decay:

$$PL(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}, \quad (4)$$

where PL is the luminescence intensity; t is the time after pulsed excitation; τ_1 and τ_2 are the luminescence lifetimes for the 1st and 2nd luminescent conformers, respectively; and A_1 and A_2 are the preexponential factors that determine the relative contributions for the 1st and 2nd conformers, respectively.

The numerical values of the lifetimes and preexponential factors obtained by processing of the kinetic curves of the luminescence decay using Eq. (4) are presented in Table 2. It can be seen that the concentration dependences for compounds **M1** and **M2** are well described by Eq. (4). However, for compound **M1** with one amino group, we obtain with good reliability two lifetimes τ_1 and τ_2 even at the first additive of tol-

uene, while for compound **M2**, this is observed starting from a toluene concentration of 0.45 mol/L. This is apparently due to the fact that in compound **M2**, the second component, which is not quenched by toluene, is much less with respect to the first component (which is quenched) than in the case of compound **M1**.

In order to obtain additional information about these forms of the luminophore, we measured time-resolved emission spectra (TRES) at a toluene concentration in *n*-hexane equal to 0.86 mol/L.

The TRES data are obtained by measuring a set of luminescence decay kinetics recorded at different observation wavelengths, which are a function of two variables $PL(\lambda, t)$, where λ is the wavelength of luminescence detection. In the case of a mixture of two different luminophores, the function $PL(\lambda, t)$ is represented as

$$PL(\lambda, t) = \xi_1 g_1(\lambda) e^{-t/\tau_1} + \xi_2 g_2(\lambda) e^{-t/\tau_2}, \quad (5)$$

where $g_1(\lambda)$ and $g_2(\lambda)$ are the normalized luminescence spectra of the two assumed forms of the luminophore, and ξ_1 and ξ_2 are their relative molar fractions.

Figure 5 shows the results of decomposition of the experimental data using Eq. (5). It can be seen that for compounds **M1** and **M2** at a concentration of toluene

Table 2. Numerical values of lifetimes and preexponential factors obtained as a result of processing of the luminescence decay kinetics of compounds **M1** and **M2** using Eq. (4)

	Benzene conc.	τ_1 , ns	τ_2 , ns	A_1	A_2	$A_1\tau_1/(A_1\tau_1 + A_2\tau_2)$	$A_2\tau_2/(A_1\tau_1 + A_2\tau_2)$
M1	0	5.14 ± 0.1	—	20126	—	1	—
	0.04	4.3 ± 0.8	—	19905	—	1	—
	0.22	2.4 ± 0.03	6.1 ± 1.5	17274	446	0.97	0.03
	0.45	1.5 ± 0.04	5.5 ± 0.7	15074	559	0.96	0.04
	0.67	1.0 ± 0.01	5.8 ± 0.5	13257	462	0.97	0.03
	0.90	0.7 ± 0.02	6.0 ± 0.3	11911	426	0.97	0.03
	1.12	0.5 ± 0.01	5.9 ± 0.2	10975	426	0.96	0.04
M1	Toluene conc.	τ_1 , ns	τ_2 , ns	A_1	A_2	$A_1\tau_1/(A_1\tau_1 + A_2\tau_2)$	$A_2\tau_2/(A_1\tau_1 + A_2\tau_2)$
	0	5.30 ± 0.2	—	35647	0	1	0
	0.09	3.4 ± 0.2	7.0 ± 5.1	33292	460	0.99	0.01
	0.18	2.4 ± 0.1	6.8 ± 2.4	30901	613	0.98	0.02
	0.27	1.8 ± 0.1	6.3 ± 1.4	28821	750	0.97	0.03
	0.36	1.4 ± 0.04	6.3 ± 1.1	26955	747	0.97	0.03
	0.45	1.2 ± 0.1	6.2 ± 1.1	25173	754	0.97	0.03
	0.59	0.9 ± 0.04	6.2 ± 0.8	23164	732	0.97	0.03
	0.86	0.6 ± 0.1	6.2 ± 0.9	18812	729	0.96	0.04
M1	<i>o</i> -Xylene conc.	τ_1 , ns	τ_2 , ns	A_1	A_2	$A_1\tau_1/(A_1\tau_1 + A_2\tau_2)$	$A_2\tau_2/(A_1\tau_1 + A_2\tau_2)$
	0	5.05 ± 0.2	—	27726	—	1	—
	0.03	4.1 ± 0.1	—	25570	—	1	—
	0.17	2.1 ± 0.03	6.6 ± 1.4	23160	415	0.98	0.02
	0.33	1.6 ± 0.01	6.0 ± 0.4	20839	541	0.97	0.03
	0.50	0.7 ± 0.01	6.1 ± 0.2	19060	565	0.97	0.03
	0.66	0.5 ± 0.01	6.0 ± 0.3	17442	552	0.97	0.03
	0.83	0.4 ± 0.01	6.0 ± 0.2	16236	562	0.97	0.03
M2	Toluene conc.	τ_1 , ns	τ_2 , ns	A_1	A_2	$A_1\tau_1/(A_1\tau_1 + A_2\tau_2)$	$A_2\tau_2/(A_1\tau_1 + A_2\tau_2)$
	0	4.58 ± 0.2	—	14486	0	1	0
	0.09	3.3 ± 1.6	3.3 ± 3.7	14031	335	0.98	0.02
	0.18	2.4 ± 1.3	3.4 ± 7.5	13052	112	0.99	0.008
	0.27	1.8 ± 0.04	3.9 ± 4.6	12565	213	0.98	0.02
	0.36	1.3 ± 0.03	2.9 ± 7.7	11944	52	0.996	0.004
	0.45	1.1 ± 0.02	4.4 ± 5.9	11535	40	0.996	0.003
	0.59	0.8 ± 0.01	5.2 ± 3.1	10691	37	0.996	0.003
	0.86	0.5 ± 0.02	5.2 ± 2.5	9438	22	0.998	0.002

in *n*-hexane of 0.85 mol/L, there are two luminescent forms of the luminophore, whose spectra differ insignificantly, but the lifetimes of the excited states of these forms differ by an order of magnitude.

We may assume that the two forms of the luminophore are two conformers of the luminophore mole-

cule shown in Fig. 5. The conformers differ from one another by the mutual arrangement of the amino group and the BF₂ group of the BODIPY core. The transition from one conformer to another occurs as a result of rotation of the aminophenyl group around the single bond with which it is attached to the BODIPY

Fig. 5. Luminescence spectra of two forms for compounds **M1** (left) and **M2** (right) obtained from the decomposition of the TRES matrix into two components following Eq. (5).

Fig. 6. Two conformers of **M1** molecule: conformer A (left) and conformer B (right), with different orientation of the amino group.

core at positions 3 or 5. It can be seen from Fig. 6 that a complex of the BODIPY molecule with the aromatic molecule can be formed only for the *meta*-isomers of conformer A.

If we assume that conformer B is not quenched by an aromatic molecule (that is, does not form a corresponding complex) and conformer A is quenched both statically and dynamically, then the dependence of the luminescence quantum yield on the quencher concentration will be determined by the following equation:

$$\frac{\phi_0}{\phi} = 1 + \frac{(K_D + K_S)[Q] + K_D K_S [Q]^2}{1 + K_B (1 + K_D [Q])}, \quad (6)$$

where K_B is the equilibrium constant between the conformers. It is not possible to determine the constant K_B from the spectral data with acceptable accuracy, since even at $K_B = 0$ a good fit of the experimental data to Eq. (6) is obtained. Instead, we may use the data on the quenching kinetics presented in Fig. 4 and Table 2. From Table 2, the equilibrium constant $K_B \approx 0.03$ was obtained, a low value of which means that the constants K_D and K_S almost do not change when the second conformer is introduced into the model.

When adding the second conformer to the model for compound **M2** and performing a similar procedure for approximation of the kinetic curves (see Fig. 4 and

Table 3. Characteristics of complexes with benzene of **M1** and **M2** molecules in the ground and excited (*) states

	M1 +1benzene		M2 +1benzene		M2 +2benzenes	
$\angle \text{Ph-core}$	33	46	33	42	35	45
$\angle \text{Ph-core}^*$	71	42	69	37	68	40
$\angle \text{NH}_2$	22		23	25	24	22
$\angle \text{NH}_2^*$	6		7	30	6	29
$\mu_{\text{opt}} \rightarrow \mu^*, \text{D}$	1.9 $\rightarrow$ 26.1		3.0 $\rightarrow$ 27.2		2.7 $\rightarrow$ 26.5	
$\mu_{\text{opt}}^* \rightarrow \mu, \text{D}$	26.3 $\rightarrow$ 3.3		26.9 $\rightarrow$ 3.5		26.8 $\rightarrow$ 3.2	
$S_{0,\text{opt}} \rightarrow S_1, \text{eV}$	1.95		2.01		2.00	
$S_0 \rightarrow S_{1,\text{opt}}, \text{eV}$	0.89		0.95		0.88	
$q(\text{N})_{\text{opt}}, e^-$	-0.49		-0.49	-0.49	-0.49	-0.49
$q(\text{N})^*, e^-$	-0.17		-0.18	-0.49	-0.18	-0.49
$q(\text{N})_{\text{opt}}^*, e^-$	-0.23		-0.22	-0.48	-0.23	-0.49
$q(\text{N}), e^-$	-0.51		-0.51	-0.48	-0.51	-0.49

Table 2), we obtain the value of the constant $K_B \approx 0.003$. In this case, the introduction of the second conformer into the model also does not lead to a change in the quenching constants K_D , K_S , and K_{S2} .

Quantum chemical calculations of the electronic structure of the studied compounds and computer simulation of BODIPY molecules and their complexes with benzene were carried out.

To understand what complexes there can be formed, we first used the molecular dynamics method, in which a dye molecule was surrounded by $\approx 10^3$ benzene molecules. The system was observed for 1000 ns, and the most stable motifs of the interaction of the dye with benzene were noted. Then, for the found applicants for the complexes, the geometry was optimized in the quantum chemical program. As a result, several stable structures were obtained for complexes of **M1** with benzene, characterized by the location of a benzene molecule in a kind of cavity formed by the BF_2 group with the aminophenyl and phenyl rings. The interaction occurs with one or two hydrogen atoms of the phenyl rings with fluorine atoms, as well as all six carbon atoms with the hydrogen atom of the NH_2 group. The largest energy gain is 5 kcal/mol for the structure shown in Fig. 6. Complexes with one or two benzene molecules for dye **M2** have a similar structure. In this case, the largest energy gain is about 11 kcal/mol, which is quite consistent with the low numerical values of K_S and K_{S2} .

For other positions of benzene near **M1** and **M2** molecules, as well as for **P1** and **P2** molecules, the formation of stable BODIPY–benzene structures could not be found. Therefore, if complexes of **M1** and **M2**

with benzene are formed, then their structure should be described by the structures shown in Fig. 6, and is due to the specific interaction of the quencher with the dye.

It can be seen from Table 3 that, as a result of the specific interaction of the benzene molecule with *meta*-isomers, the energy of vertical $S_0 \rightarrow S_1$ transitions decreases. In this case, the benzene molecule stabilizes the state with a large dipole moment. Below are the diagrams of the energy levels for the individual dyes and their complexes with benzene for **M1** (Fig. 7) and **M2** (Fig. 8).

In conclusion, we will return to the discussion of the abovementioned alternative for explanation of the observed experimental data, associated with the possible presence of an uncontrolled impurity of luminescent molecules of a similar structure. Indeed, during the synthesis of compound **M1**, it is possible that we did not completely remove compound 3-(3-acetamidophenyl)-5-phenyl-8- CF_3 -BODIPY, whose spectral and luminescent properties were previously described in the article [1]. However, for compound **M2**, we have no direct evidence of the presence of an uncontrolled luminescent impurity. Nevertheless, it is impossible to vigorously reject this alternative. Therefore, we consider the proposed interpretation of the observed experimental data as a possible hypothesis, since we also do not have direct experimental evidence of the presence of conformers of compounds **M1** and **M2**.

Fig. 7. Energetic transitions $S_0 \rightarrow S_1$ and HOMO and LUMO molecular orbitals in **M1** (left) and **M1**-benzene complex (right).

Fig. 8. Energetic transitions $S_0 \rightarrow S_1$ and HOMO and LUMO molecular orbitals in **M2** (left) and **M2**-benzene complexes (1 : 1 in the center and 1 : 2 on the right).

CONCLUSIONS

As a result of the studies performed, we have shown that luminescence of the derivatives of dye BODIPY with the amino group in the *meta* position, which we considered in this work, is sensitive to the presence of nonpolar aromatic compounds in a mixture with other nonpolar compounds. Noticeable changes in the spectral properties of the dye occur when the mole fraction of benzene or toluene in their mixture with *n*-hexane is below 1%. The reason for such a sharp

change in the spectral properties may be the complexes that are formed between the *meta*-isomers and the aromatic molecule. The formation energy of such complexes is close to the energy of a conventional hydrogen bond (3 kcal/mol), which makes them quite stable at room temperature.

FUNDING

This work was carried out under the state assignment no. AAAA-A19-119070790003-7 and supported by the Russian

Government (agreement no. 074-02-2018-286) and the Russian Science Foundation (project no. 19-73-10063).

OPEN ACCESS

This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

REFERENCES

1. Petrushenko, K.B., Petrushenko, I.K., Petrova, O.V., Sobenina, L.N., Ushakov, I.A., and Trofimov, B.A., *Asian J. Org. Chem.*, 2017, vol. 6, p. 852.
2. Grabowski, Z.R. and Rotkiewicz, K., *Chem. Rev.*, 2003, vol. 103, p. 3899.
3. Catalan, J., *J. Phys. Chem. B*, 2009, vol. 113, p. 5951.
4. Magde, D., Wong, R., and Seybold, P.G., *Photochem. Photobiol.*, 2002, vol. 75, p. 327.
5. Parker, C.A., *Photoluminescence of Solutions with Applications to Photochemistry and Analytical Chemistry*, Amsterdam: Elsevier, 1968.
6. Neese, F., *Comput. Mol. Sci.*, 2012, vol. 2, p. 73.
7. Neese, F., *Comput. Mol. Sci.*, 2017, vol. 8.
8. Phillips, J.C., Braun, R., Wang, W., Gumbart, J., Tajkhorshid, E., Villa, E., Chipot, C., Skeel, R.D., Kale, L., and Schulten, K., *J. Comput. Chem.*, 2005, vol. 26, p. 1781.
9. Nevidimov, A.V., *Russ. J. Phys. Chem. A*, 2020, vol. 5, p. 951.
10. Sobenina, L.N., Vasil'tsov, A.M., Petrova, O.V., Petrushenko, K.B., Ushakov, I.A., Clavier, G., Meallet-Renault, R., Mikhaleva, A.I., and Trofimov, B.A., *Org. Lett.*, 2011, vol. 13, p. 2524.
11. Trofimov, B.A., Mikhaleva, A.I., Schmidt, E.Yu., and Sobenina, L.N., *Chemistry of Pyrroles*, Boca Raton, FL: CRC, 2014.
12. Lakowicz, J.R., *Principles of Fluorescence Spectroscopy*, 3rd ed., Boston: Springer, 2006.
13. Treibs, A. and Kreuzer, F.-H., *Liebigs Ann. Chem.*, 1968, vol. 718, p. 208.
14. Monsma, F.J., Barton, A.C., Kang, H.C., Brassard, D.L., Haughland, R.P., and Sibley, D.R., *J. Neurochem.*, 1989, vol. 52, p. 1641.
15. Golovkova, T.A., Kozlov, D.V., and Neckers, D.C., *Org. Chem.*, 2005, vol. 70, p. 5545.
16. McCusker, C., Carroll, J.B., and Rotello, V.M., *Chem. Commun.*, 2005, vol. 8, p. 996.
17. Hattori, S., Ohkubo, K., Urano, Y., Sunahara, H., Nagano, T., Wada, Y., Tkchanko, N.V., Lemmetyinen, H., and Fukuzumi, S., *J. Phys. Chem. B*, 2005, vol. 109, p. 15368.
18. Boens, N., Verbelen, B., and Dehaen, W., *Eur. J. Org. Chem.*, 2015, p. 6577.

Translated by A. Tatikolov