2-Difluoroboryl-3-(quinolin-2-ylmethylene)isoindolin-1-one: Efficient Synthesis Method, TD-DFT Analysis and Electrical Properties of Thin Films

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The reaction of phthalimide and quinaldine in the presence of zinc oxide results in formation of 3-(quinolin-2-ylmethylene)isoindolin-1-one, the interaction of which with $BF_3 \cdot Et2O$ in the presence of a base gives 2-difluoroboryl-3-(quinolin-2-ylmethylene)isoindolin-1-one. The complex was characterized by general spectroscopic methods such as ^1H and ^{13}C NMR, COSY, HSQC, HMBC, mass, UV-Vis and fluorescence. The complex possesses intense fluorescence with high quantum yield. A TD-DFT analysis of its energy characteristics has been carried out. It has been established that the results closest to the experiment are provided by the SPW91LDA functional. The electrical properties of thin films of the complex have been studied. It is a semiconductor with a specific conductivity of $1.7 \cdot 10^{-10}$ S/cm, and characterized by activation energy of 1.1 eV.

Keywords: BODIPY analogs, synthesis, boron complex, fluorescence, thin films, conductivity.

2-Дифторборил-3-(хинолин-2-илметилен)изоиндолин-1-он: эффективный метод синтеза, TD-DFT анализ и электрические свойства тонких пленок

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Реакцией фталимида с хинальдином в присутствии оксида цинка синтезирован 3-(хинолин-2-илметилен)изоиндолин-1-он, при взаимодействии которого с $BF_3 \cdot Et_2O$ в присутствии основания образуется 2-дифторборил-3-(хинолин-2-илметилен)изоиндолин-1-он. Комплекс охарактеризован основными спектральными методами, такими как ^1H и ^{13}C ЯМР, COSY, HSQC, HMBC, масс-спектрометрия, электронная и флуоресцентная спектроскопия. Комплекс обладает интенсивной флуоресценцией с высоким квантовым выходом. Проведен TD-DFT анализ его энергетических характеристик. Установлено, что наиболее близкие к эксперименту результаты обеспечивает функционал SPW91LDA. Изучены электрические свойства тонких пленок комплекса. Он является полупроводником с удельной проводимостью $1.7 \cdot 10^{-10}$ См/см, характеризуется энергией активации 1.1 эВ.

Ключевые слова: Аналоги BODIPY, синтез, комплекс бора, флуоресценция, тонкие пленки, проводимость.

Introduction

One of the interesting groups of organic dyes currently undergoing intensive research is the complexes of boron with dipyrrometene derivatives, better known as BODIPY. These compounds have unique properties such as strong and easily controlled absorption and fluorescence, usually with a high quantum yield, high photostability, and good

solubility in organic solvents of different polarities.[1-3] Such properties make it possible to use BODIPY as chemosensors, drugs for photodynamic therapy, components of optoelectronic devices.[4-8] Unsymmetrical analogs of BODIPY are also of considerable interest.[9,10] Lowering the symmetry of the fluorophore core leads, among other things, to a decrease in π–π interactions in the solid state. This causes the presence of intense fluorescence of asymmetric boron complexes both in solutions and in powders and films, and also leads to an increase in Stokes shifts.[11-14] These compounds, among others, include 2-difluoroboryl-3-(quinolin-2-ylmethylene)isoindolin-1-one (**1**).[14] Earlier, complex **1** was obtained by the reaction of 3-(quinolin-2-ylmethylene)isoindolin-1-one (**2**)[15-17] with BF₃·Et₂O in dichloromethane in the presence of N-ethyldiisopropylamine as a base. The main synthetic difficulty lies, in our opinion, in the synthesis of the starting compound **2**. There are several ways of its synthesis (Scheme 1).

The first method was developed in 2005[16] and consisted of the interaction of phthalimide with quinaldine in boiling trichlorobenzene (Route A). Yield of **2** turned out to be insignificant and amounted to 11 %. The second method was proposed in 2007.[15] It consisted in the reduction of phthalimide with tin in an acidic medium followed by condensation of the obtained isoindolin-1-one with quinoline-2-carbaldehyde in toluene in the presence of K₂CO₃ with a yield of 60 % at the last stage (Route C). Finally, the third route, carried out in 2017,[17] is based on the condensation of quinaldine with phthalimide in N,N-dimethylaniline in the presence of anhydrous ZnCl₂ (Route B). Yield of **2** in this case reaches 81 %. All these methods are characterized by either a low product yield, or the use of expensive reagents, or a long synthesis time. The low yield of compound **2** in Routes A and C is apparently due to the absence of a template. The zinc ion is a template in Route B and contributes to an increase in the yield of the product.

In this work, we report on an efficient method for the synthesis of compound **2** and a boron complex **1** based on it, the results of experimental and theoretical (TD-DFT) studies of the spectral properties of the complex, as well as its electrophysical characteristics.
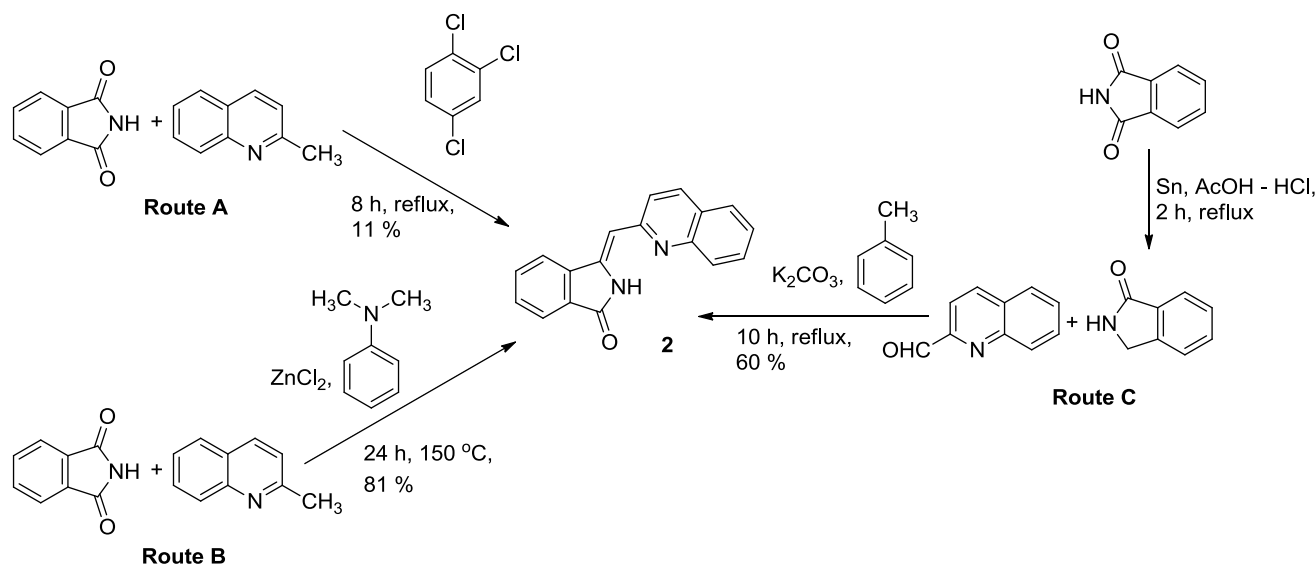
Experimental

Mass spectra (LDI-TOF, no matrix) were recorded on a Shimadzu AXIMA Confidence instrument. ¹H (500 MHz), ¹³C (125 MHz) and ¹¹B (160 MHz) NMR spectra were recorded on a Bruker Avance-500 instrument in DMSO-D₆. The signals of the residual protons of the solvent at 2.51 ppm for ¹H, 39.63 ppm for ¹³C were used as reference, for ¹¹B BF₃·Et₂O is used as an external standard. Electronic absorption spectra were measured on a Helios Zeta spectrophotometer, fluorescence spectra – on a Shimadzu RF-6000 spectrofluorimeter in rectangular quartz cuvettes with an absorbing layer thickness of 10 mm at 25 °C. For spectral measurements, we used chemically pure chloroform.

Thin films of the compound under study were deposited in a VUP-5M thermal vacuum evaporator at a residual pressure of < 10⁻⁵ Torr. The evaporation temperature was controlled with a thermocouple; the average deposition rate was 0.1 – 0.2 nm/s. The thickness of the films was 60 – 80 nm (measured with a TalySurf CCI 2000 non-contact profilometer). The in-plane electrical conductivity of the films was measured in a two-terminal scheme using ceramic substrates with symmetric integdigital nickel electrodes spaced 30 μm apart. Before use, the substrates were washed in an ultrasonic bath in succession with toluene, acetone, and isopropanol, and then dried in an argon flow. Electrical measurements were carried out in air using a Keithley 4200-SCS station in the dark and under illumination with a tungsten halogen lamp providing an illumination of 1.5· 10⁴ lx at room temperature.

The experiments were carried out with the use of the equipment of the Center for Shared Use of Scientific Equipment of the ISUCT, also the equipment of Institute for Physics of Microstructures RAS.

3-(Quinolin-2-ylmethylene)isoindolin-1-one (2). A mixture of 5.0 g (0.03 mol) phthalimide, 10 mL (10.6 g, 0.07 mol) quinaldine, and 2.0 g (0.025 mol) zinc oxide was stirred for 4 h at reflux. At the end of the process, the reaction mass was cooled, transferred into 150 mL of 15% hydrochloric acid, stirred for 30 min, 50 mL of chloroform was added, the organic layer was separated, washed with water, the solvent was distilled off. The residue was dissolved in chloroform and subjected to column chromatography on silica, eluting with a mixture of chloroform and ethanol, 50:1, collecting the main yellow zone. Yield: 6.5 g (70%), yellow substance, soluble in chloroform, acetone, DMSO, DMF. *m/z* (LDI-TOF, negative mode): 272.65 [M]⁻ (calculated for C₁₈H₁₂N₂O: 272.09). UV-Vis (chloroform) λ_max nm (lgε): 382 (4.22).

Scheme 1. Routes of synthesis of compound **2**.

2-Difluoroboryl-3-(quinolin-2-ylmethylene)isoindolin-1-one (1). To a solution of 1.0 g (3.6 mmol) of compound **2** in 50 mL of chloroform, 1.0 mL (1.12 g, 8.0 mmol) of BF₃·Et₂O and 3.0 mL of triethylamine (30.0 mmol) were added, and the mixture was stirred for 6 h at reflux temperature. Then the reaction mass was diluted with 100 mL of water, the organic layer was separated, washed with water many times, the solvent was distilled off. The residue was dissolved in chloroform and chromatographed on silica, eluting first with a mixture of chloroform and ethanol 50:1. In this case, a light yellow zone containing compound **2** was separated. Then eluted with a mixture of chloroform and ethanol, 10:1, collecting a dark yellow, strongly fluorescent zone containing complex **1**. Yield: 0.50 g (43%), yellow-brown substance, soluble in chloroform, acetone, DMSO, DMF. m/z (LDI-TOF, negative mode): 320.47 [M]⁻ (calculated for $C_{18}H_{11}BF_2N_2O$: 320.09). ¹H NMR δ_H ppm: 8.38-8.37 d (1H, J = 8 Hz), 8.26-8.24 d (1H, J = 9 Hz), 8.11-8.09 d (1H, J = 8 Hz), 7.95-7.93 m (1H), 7.86-7.84 d (1H, J = 8 Hz), 7.78-7.76 m (2H), 7.66-7.64 t (2H, J = 9 Hz), 7.58 t (1H, J = 8 Hz), 6.96 s (1H). ¹³C NMR δ_C ppm: 168.35, 156.24, 147.79, 139.03, 138.30, 137.44, 129.06, 126.58, 123.74, 102.93, 79.63. ¹¹B NMR δ_B ppm: 2.85–2.47 t (J = 28 Hz). UV-Vis (chloroform) λ_{max} nm (lgε): 456 (4.58), 429 (4.51).

Results and Discussion

Synthesis and Characterization of Compounds *1* and *2*

We have synthesized ligand **2** by the most efficient method - by heating phthalimide in a quinaldine solution in the presence of zinc oxide for 4 h, followed by acid treatment. The yield of compound **2** after isolation and purification was 70 %. This method makes it possible to obtain compound **2** in one stage, to reduce significantly the time of its synthesis while maintaining a high yield without use of expensive reagents. According to the usual procedure, complex **1** was synthesized by the interaction of ligand **2** with BF₃·Et₂O in the presence of Et₃N in a chloroform solution (Scheme 2).
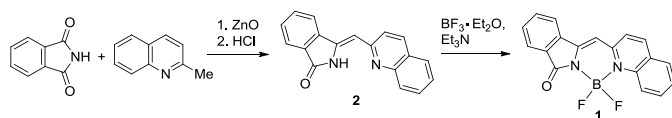
Scheme 2. Synthesis of ligand **2** and boron-based complex **1**.

Compounds **1** and **2** were purified by column chromatography and characterized by LDI-TOF mass spectrometry, one- and two-dimensional NMR spectroscopy (¹H, ¹³C, ¹¹B, COSY, HSQC, HMBC) (Figure S1-S8, Supplementary Information). The ¹H-¹H COSY spectrum shows proton cross peaks at positions 8.37↔7.64 ppm (pyridine ring protons of a quinoline fragment), 8.25↔7.78 ppm and 7.93↔7.58 ppm (protons of the benzene ring of the quinoline fragment). It is important to note that in the ¹³C NMR spectrum (Figure S8) in the strongest field at 79.63 ppm there is a signal of the carbon atom in the *p*-position to the nitrogen of the quinoline fragment. The signal of the *meso*-carbon atom was found in a lower field at 103 ppm, which is confirmed by the spectra of HSQC (Figure S6) and HMBC (Figure S7). The results obtained are in good agreement with the known ones.[15-17]
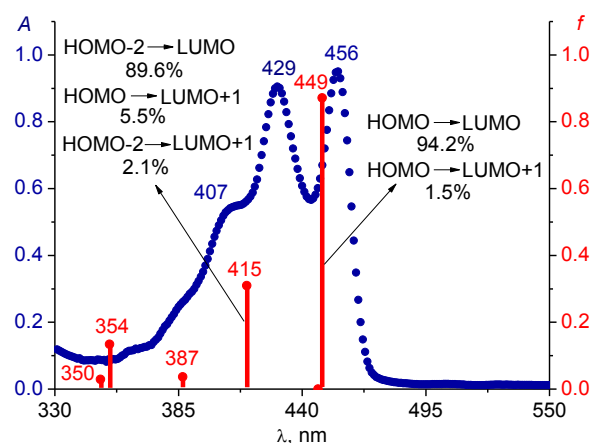
Figure 1. Theoretical absorption spectrum of complex **1** in comparison with experimental.
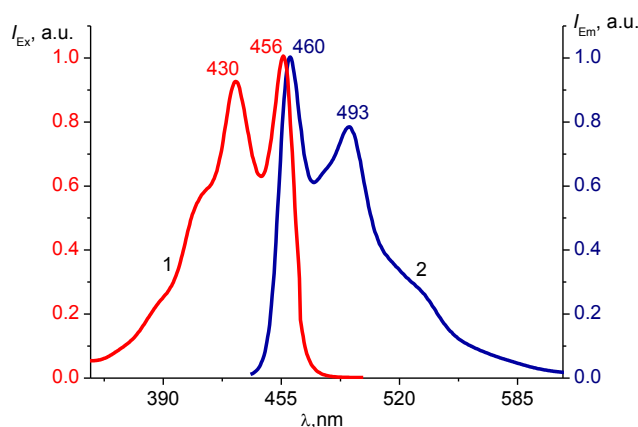
Figure 2. Excitation (1) and fluorescence (2) spectra of complex **1** in chloroform.

Spectral Properties of *1*

The electronic absorption spectrum of compound **1**, measured in chloroform, is shown in Figure 1. To determine the electronic structure of complex **1** and the energies of vertical transitions in its molecule, quantum-chemical calculations were carried out. They are executed in the Firefly 8.2.0 software package.[18] To construct the initial geometries, as well as to process and present the results, the Chemcraft software package was used.[19] The molecule was optimized at the DFT/SPW91LDA/def2-TZVPPD level, the vertical transition energies and oscillator strengths were determined at the level of the TD-DFT theory. Preliminary calculations showed that the hybrid functionals B3LYP and PBE0 in combination with different basis sets (6-311G (d, p), cc-PVTZ, def2-TZVPPD) give a significant overestimation of the energies of electronic transitions. For example, in the absorption spectra of **1**, calculated using the B3LYP5 and PBE0 functionals and the def2-TZVPPD basis set,[20] the first absorption band is located at 406 nm and 397 nm, respectively. Therefore, the Slater exchange functional with the 1991 Perdew-Wang local correlation

SPW91LDA[21,22] was chosen for the calculations, which gives results that are closer to the experiment. The effect of the solvent (CHCl₃) was taken into account within the polarized continuum model (PCM). The theoretical absorption spectrum of complex **1** is shown in comparison with the experimental one in Figure 1.

As follows from the data obtained, the main contribution to the formation of the first absorption band is made by the HOMO→LUMO electronic transition. Contributions from other transitions are negligible. The main contribution to the formation of the second absorption band is made by the HOMO-2→LUMO transition with an insignificant participation of the HOMO→LUMO+1 and HOMO-2→LUMO+1 transitions. The excitation spectrum of complex **1** (Figure 2(1)) is very close in character and position of the band maxima to its absorption spectrum, and a rather significant (37 nm) Stokes shift is observed in the fluorescence spectrum (Figure 2(2)). It was previously reported[14] that the quantum yield of fluorescence of compound **1** in dichloromethane solution reaches 0.49; however, the authors, unfortunately, did not report whether this value was absolute or relative and under what conditions the measurements were carried out. Our studies have shown that the relative quantum yield of fluorescence **1** in chloroform solution, calculated by the known method[23] using anthracene as a standard ($\Phi_F = 0.27$ in ethanol),[24] is 0.35. The fluorescence lifetime of the complex in chloroform solution is 3.388 ± 0.006 ns (Figure 3).

The obtained data show that the fluorescence quantum yield and the lifetime of the excited singlet state are close to those for other asymmetric boron complexes.[7,25,26]

An approximately twofold decrease in the fluorescence intensity in the toluene solution was also noted. This negative dependence of the fluorescence intensity on the solvent polarity, characteristic of BODIPY,[27] is probably due to the formation of associates in low-polarity solvents.

The electrochemical behavior of complex **1** was studied earlier by the method of cyclic voltammetry in an acetonitrile solution.[15] It was found that its electron affinity (LUMO level) is –3.45 eV. Our calculations of complex **1** at the DFT/SPW91LDA/def2-TZVPPD level showed a LUMO energy of –3.51 eV (Figure 4). This value is somewhat closer to experiment than that obtained earlier in calculations at the DFT/B3LYP/6-31G level (–2.83 eV).[15]
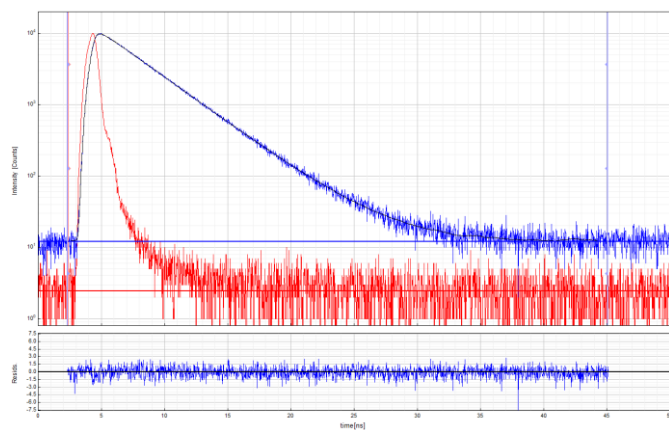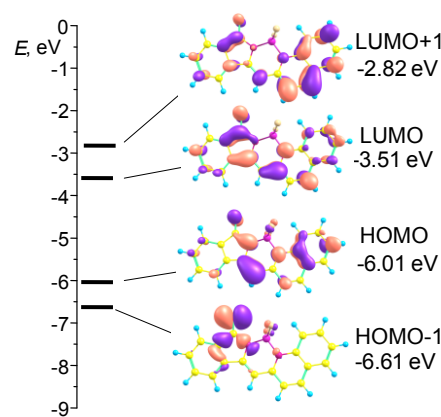

Figure 4. Type and energies of the frontier molecular orbitals of complex **1** (DFT/SPW91LDA/def2-TZVPPD).

Thus, the HOMO – LUMO energy gap in complex **1**, which we calculated by the DFT method, is 2.50 eV, which is close to the results obtained by the authors of [15] by the method of cyclic voltammetry (2.60 eV). To calculate the energy characteristics of the molecule of complex **1** by the DFT method, the SPW91LDA exchange functional was proposed, which gives the results that are closest to the experiment. This functionality can be recommended for DFT and TD-DFT calculations other structural analogs of BODIPY.

*Electrical Properties of Thin Films of **1***

Complex **1** is capable of sublimation in a vacuum without decomposition. This is confirmed by the similarity of the mass spectra of the initial complex and that washed off by the solvent from the substrate. Therefore, the method of thermal vacuum deposition was used to deposit thin solid films on the substrates. For sandwich-type cells, an 80 nm thick aluminum layer was vacuum-deposited over the films of **1** to obtain the second (top) mirror electrode. The dependence of the current density on the voltage for the film of complex **1** with planar electrodes is shown in Figure 5.
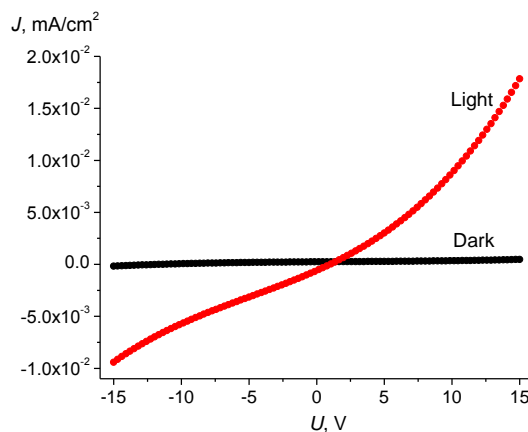

Figure 3. Fluorescence lifetime decay of complex **1** in chloroform.

Figure 5. Current density versus voltage of films of complex **1** with planar electrodes in the dark and under illumination.
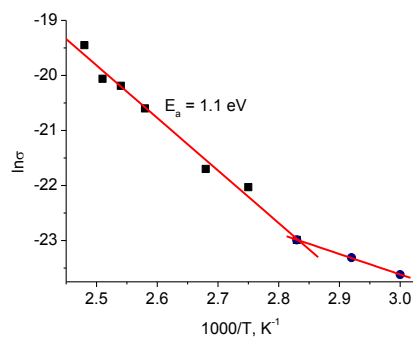
Figure 6. Dependence of the logarithm of electrical conductivity on the reciprocal temperature for the film of complex **1**.

Specific conductivity σ of the film of complex **1** measured on the linear sections of the $J - V$ characteristics in the dark, corresponds to an approximate value of $1.7 \cdot 10^{-10}$ S·cm^{-1}, which is close to the conductivity of subphthalocyanines.[28] Illumination of the sample causes an increase in conductivity by about an order of magnitude ($I_{light}/I_{dark} \approx 12$ at a voltage of 5 V). To determine the activation energy, the dependence of the logarithm of the conductivity on the reciprocal temperature in the dark was measured (Figure 6).

From the data obtained, it follows that the conductivity of the film is impurity (adsorbed oxygen, water) at temperatures up to 80 °C, and becomes intrinsic at temperatures above 80 °C. The activation energy in this case is 1.1 eV. The closeness of the dependence to linear indicates the absence of phase transitions in the temperature range from 80 to 130 °C, would have a significant effect on the morphology of the layer and, as a consequence, its electrophysical parameters.

Conclusions

Thus, in this work, we propose an efficient method for the synthesis of complex **1**, an asymmetric analogue of BODIPY, select a functional for DFT and TD-DFT calculations, which gives the results closest to the experiment, and investigate the electrical properties of its thin films.

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