Spectroscopic properties of bis(BODIPY) complexes

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Abstract. The spectral-luminescence characteristics of binuclear bis(BODIPY) complexes in cyclohexane and ethanol, which exhibit different photophysical and photochemical properties in these solvents, have been investigated. It has been shown that the difference in spectroscopic properties is due to intermolecular interaction of the excited molecules with solvation shell. The possibilities of practical use are discussed.

1. Introduction

Purposeful use of complex organic molecules and their derivatives for creating of various kinds of optical devices (temperature probes, optical sensors, nonlinear switches and limiters of high-power pulsed radiation) requires studying the relationship of spectroscopic characteristics with the structure of molecules, solvation shells and features of the media, in which are embedded these molecules. In recent years, interest in solutions and solid-state polymer media colored with organic dyes, which can be used as active media for tunable lasers, thin-film emitting layers for electroluminescent devices, and organic solar cells, has increased significantly [1, 2].

Boron fluoride dipyrromethene (BODIPY) coordination complexes can successfully solve the problems of practical application. Mononuclear BODIPY compounds have efficient absorption and emission in visible spectrum and depending on the quality and number of substituents in the ligand, their derivatives can change the efficiency of intercombination conversion. It makes possible successfully using such compounds in various fields of science and technology due to their unique spectral characteristics [3]. It is also known that binuclear bis(BODIPY) complexes exhibit impressive spectral properties, for example, the temperature dependence of fluorescence intensity, which can be used in the development of optical sensors to determine the temperature in the range of 300-80K. The creation of optical sensors for temperature in this range is important, for example, in instrument making when developing cryostats.

Targeted synthesis of appropriate structures for a particular application requires that the interrelation of the molecular structure to the properties of compounds of this class should be studied, as well as the influence on this interrelation of the medium in which this compound is placed. In this regard, this research is aimed to studying spectroscopic characteristics of a number of binuclear dipyrromethene complexes bis(BODIPY) in order to identify more efficient compounds to create modern materials for solving specific practical problem, namely the creation of effective optical devices.
2. Objects and methods of research
The objects of research were the series of binuclear coordination complexes of bis(BODIPY) containing a methylene (–CH$_2$–) spacer in different positions of proximal pyrroles. These compounds were compared with a complex 3,3-CHCF$_3$-bis(BODIPY) that has already been studied previously [4]. The structural formulas of investigated compounds are given in figure 1.

![Structure formulas of investigated bis(BODIPY) compounds](image)

**Figure 1.** Structure formulas and denotation of investigated bis(BODIPY)s.

The compounds were synthesized according to the procedures described in [4, 5]. Their purity and identity were controlled by means of elemental analysis, mass spectrometry, and $^1$H NMR spectroscopy. As solvents were used ethanol and cyclohexane of chemically pure grade.

The absorption spectra were measured by a SM2203 (SOLAR) spectrophotometer. The luminescence spectra at room temperatures were recorded on a Varian Cary Eclipse (Varian) spectrometer. The fluorescence quantum yield was measured at concentrations of $10^{-2}$–$10^{-3}$ mM (the absorption at the excitation wavelength was <0.1 cm$^{-1}$) by the relative method with respect to Rhodamine 6G with an error of 10%. All experiments were carried out in standard quartz cuvettes with an optical path length of 1 cm at a temperature of 298 K.

3. Results and discussion
In bis(BODIPY) molecules two BODIPY radicals are connected by –CHCF$_3$– and –CH$_2$– spacers and rotated relative to each other at a considerable angle, while retaining their most functional conformations. Such structural features manifest themselves in spectral-luminescent properties: there are three maxima in the electronic absorption spectra (figure 2). This is due to the actual existence of two chromophores in one compound.
Figure 2. Normalized absorption spectra of 3,3-CHCF$_3$-bis(BODIPY) (a) and 2,2-, 2,3-, 3,3-CH$_2$-bis(BODIPY) (b) complexes in ethanol.

The 3,3-CHCF$_3$-bis(BODIPY) complex was studied in detail in [4] and has close spectral characteristics of absorption: 378, 494, 542 nm - in cyclohexane and 380, 490, 537 nm - in ethanol, respectively. In a series of newly studied compounds with (–CH$_2$–) spacer, complex 2,2-CH$_2$-bis(BODIPY) has the longest wavelength absorption and emission, followed by 2,3-CH$_2$-bis(BODIPY). The shortest wavelength absorption and fluorescence belongs to the 3,3-CH$_2$-bis(BODIPY) complex (table 1).

Table 1. Spectral luminescent properties of bis(BODIPY) complexes.

| Compound, solvent               | $\lambda_{\text{abs}}$ (nm) | $\lambda_{\alpha}$ (nm) ($\lambda_{\text{ex}}$ (nm)) | $\gamma\pm10\%$ |
|--------------------------------|------------------------------|-------------------------------------------------|------------------|
| 2,2-CH$_2$-bis(BODIPY), cyclohexane | 382                          | 538+580 (370,530)                               | 0.99             |
|                                | 500                          | 558                                             |                  |
| 2,2-CH$_2$-bis(BODIPY), ethanol | 380                          | 536+570 (370,530)                               | 0.1              |
|                                | 496                          | 558                                             |                  |
| 2,3-CH$_2$-bis(BODIPY), cyclohexane | 380                          | 564 (370, 535)                                  | 0.99             |
|                                | 500                          | 551                                             |                  |
| 2,3-CH$_2$-bis(BODIPY), ethanol | 384                          | 556 (370, 535)                                  | 0.06             |
|                                | 497                          | 548                                             |                  |
| 3,3-CH$_2$-bis(BODIPY), cyclohexane | 375                          | 551 (370, 530)                                  | 0.99             |
|                                | 500                          | 548                                             |                  |
| 3,3-CH$_2$-bis(BODIPY), ethanol | 372                          | 550 (370, 530)                                  | 0.1              |
|                                | 498                          | 544                                             |                  |
The fluorescence spectra of 2,3-CH$_2$-bis(BODIPY) and 3,3-CH$_2$-bis(BODIPY) have a single band, which is a mirror image of the absorption bands. In the fluorescence spectra of the complex 2,2-CH$_2$-bis(BODIPY), two peaks are observed, the intensity of which depends on the excitation wavelength. Preliminary research results explain this fact by the display of two stable conformations of this compound in the equilibrium excited state. At this stage, work continues and aims to detailed explanation of the reasons for such features.

The main feature of the bis(BODIPY) complexes is a significant change in efficiency of fluorescence depending on polarity of the solvent. The fluorescence quantum yield in ethanol is significantly lower than in cyclohexane (table 1). The reason for this feature is associated with the presence of specific interactions in supramolecular systems formed by solvated molecules of the complexes, their change upon excitation and restructuring of complex solvate shells in the excited state. The restructuring of the solvate environment of binuclear complexes (movement in the solvation shell) in the excited state due to a change in the electron density distribution leads to nonradiative conversion and quenching of fluorescence in polar solvents (ethanol). Moreover, for 3,3-CHCF$_3$-bis(BODIPY) complex in frozen ethanol (77K), the fluorescence intensity increases by two orders of magnitude and approximate with intensity in cyclohexane.

4. Conclusions

The spectroscopic characteristics of binuclear boron fluoride complexes of dipyrromethenes were studied in various solvents depending on the wavelength of the exciting radiation. These complexes demonstrate a significant change in fluorescence efficiency, depending on the polarity of the solvent. This property can be used for creating sensors of the medium (solvent) polarity. In addition, weakly emitting ethanol solutions well limit the powerful radiation due to absorption of excited molecules, which is promising for creating laser limiters.

Acknowledgments

This study was supported by the Russian Foundation for Basic Research (projects nos. 18-33-00284), the State Task of Russian Ministry of Education and Science (project no. 4.6027.2017/8.9) and The Tomsk State University competitiveness improvement programme.

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