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Effect of polar protic solvents on the photophysical properties of bis (BODIPY) dyes

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ABSTRACT

In this paper, detailed comparative analysis of the spectral properties of bis(BODIPY) dyes in various organic solvents: saturated aromatic hydrocarbons, homologous series of alcohols (C_nOH, n = 2–4, 8, 10) and mixture of ethanol-glycerol with different viscosity was carried out. In bis(BODIPY) dimeric molecules, the BODIPY chromophore domains are linked by a methylene spacer at the 2,2-, 2,3-, or 3,3-positions (**1**, **2**, and **3** respectively). The absorption spectra of the bis(BODIPY)s exhibit exciton splitting of band maxima. We showed that bis(BODIPY)s are sensitive to the polarity and acidity of media due to its structural features. The mechanism of fluorescence quenching of **1**–**3** in the series of alcohols are explained in detail. It has been established that the fluorescence quenching efficiency of dimeric dyes in alcohols is determined by both universal and specific interactions. The fluorescence quantum yield of bis(BODIPY)s is minimal in ethanol and increases in the alcohols homologous series due to a reduction in medium polarity and the stability of the bis(BODIPY)$(Solv)_2$ supramolecular structures. In viscous ethanol-glycerol mixtures, fluorescence of **1**–**3** increases because of the limitation of the dye molecules conformational mobility. The results of the study allow us to predict the possibility of practical application of **1**–**3** as alcohols fluorescent sensors in various media.

1. Introduction

It is known that zinc(II) bis(dipyrromethenate)s have a high sensitivity of fluorescence characteristics to the presence of electron donor and aromatic analytes in various media [1]. The authors Ref. [1–3] have demonstrated the potential of using zinc(II) bis (dipyrromethenate)s for the fluorescence detection of different chemical nature analytes. In contrast, the fluorescence characteristics of alkyl-substituted boron(III) dipyrromethenates (BODIPY) are insensitive to the chemical nature of the environment [4–7]. The functionalization of BODIPY molecules allows obtaining sensors for various types of analytes. [5,8–11].

Bis(BODIPY) dimers are of particular interest. It was shown earlier [12–26], that their spectral properties strongly depend on the features of the covalent binding of BODIPY domains to each other. Previous studies by our group [27] showed that bis(BODIPY)s **1**–**3** with a methylene ($-CH_2-$) spacer between two dipyrromethene domains (Scheme 1) showed a high sensitivity of fluorescence characteristics to the medium nature. The results of the analysis of the molecular structure showed that bis(BODIPY)s **1**–**3** have two energetically favorable conformers. These conformers are characterized by different angles of rotation of the BODIPY domain planes relative to each other. A detailed description of the structural and energy parameters of conformers **1–3** was presented in our previous work [27] and is given in SI (Fig. S1, S2, Table S1).

The fluorescence quantum yield of **1**–**3** is significantly higher in non-polar saturated hydrocarbons and decreases by one or two orders of magnitude in proton-donor and electron-donor organic solvents. It was assumed that interactions with solvent molecules in the near solvation shell and the intensity of intramolecular rotation of **1**–**3** can affect the energy loss of molecules in an excited state. This work is a continuation of the study [27].

We explain in detail the fluorescence sensitivity of **1**–**3** to the polarity and acidity of the medium, using the homologous series of alcohols (C_nOH, n = 2–4, 8, 10) and ethanol-glycerol mixtures with different viscosities; the influence of the effects of universal solvation (polarity of the medium) and specific interactions (formation of hydrogen bonds).

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