Impact of the Keto-Enol Tautomeric Equilibrium on the BODIPY chromophore

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ABSTRACT: An intramolecular tautomeric fluorescent BODIPY sensor has been designed and synthesized. The obtained BODIPY dye is a combination of the 4-bora-3a,4a-diaza -s-indacene core and a diketone fragment. The study of conformational equilibria in the ground and excited states has been completed for a broad range of solvent polarity by steady state and NMR methods as well as by DFT and TD-DFT calculations. The interpretation of the unique emission observed in hydrogen bond accepting solvents under the excitation of the fluorescent dye in the S_0 - S_2 transition has been accomplished. The Jablonski diagram has been analyzed for the observed processes in the BODIPY dye studied on the basis of DFT and TD-DFT calculations.

TOC GRAPHICS

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TEXT. In this study we aim to report on the influence of a tautomeric sensor on the spectral characteristics of the difluoroborondipyrromethene (BODIPY) core in the ground and excited

states based on the experimental results as well as quantum-mechanical calculations. The synthesis and spectroscopic characterization of fluorescent BODIPY dyes have been investigated extensively.¹⁻³ These compounds are used for a large number of applications such as chromogenic probes and ions,⁴ fluorescent switchers,⁵ laser dyes,⁶ pH indicators,⁷ and solar cells.⁸ They are also employed in biochemical and biological applications.^{9,10} Several of these applications are based on the possibility to use fluorescence spectroscopy to measure intracellular concentrations of biologically important ions and molecules. Currently, the design, synthesis, and spectroscopic characterization of novel fluorescent probes continue to be important topics in this dynamic research area.¹¹

In spite of extensive research on these dyes, only limited information is available on the impact of the tautomeric equilibrium and of hydrogen bonding on the charge transfer and spectral characteristics.¹²⁻¹⁵ Recently Akkaya *et al.*^{16,17} have shown the influence of protonation and deprotonation processes on the spectral characteristics of BODIPY dyes. Literature reports^{13,15} investigated the influence of tautomeric equilibrium in *ortho*-hydroxy aryl Schiff bases substituted at the *meso*- or 7-position of the BODIPY core on the position of the absorption and emission bands as well as its influence on the fluorescent quantum yield. The later report¹⁵ shows that the replacement of the salicylideneaniline substituent with a naphthylideneaniline in the *meso*-position of the BODIPY dye brings about a visible decrease of the fluorescent quantum yield of the BODIPY-*meso*-Schiff dye (in methanol from 0.38 to 0.05 and in acetonitrile from 0.48 to 0.05). The authors¹⁵ explained this phenomenon by the presence of a tautomeric equilibrium in the naphthalene derivative of the BODIPY-*meso*-Schiff dye, which results in a charge transfer (PET) from the Schiff fragment (in the ketoimine form) to the BODIPY core. The presence of a tautomeric equilibrium in the ground state is substantiated by changes of the

absorption bands within the 300 – 450 nm region.¹⁵ It is necessary to note that the $S_0 - S_1$ band stays similar upon transfer from a non-polar solute to a polar one (hexane to methanol). A different situation for the BODIPY-Schiff dye was observed as a result of substitution of the *ortho*-hydroxyaryl Schiff fragment at position 7 of the core.¹³ The change from a non-polar solute to apolar one triggers a hypsochromic shift of the main $S_0 - S_1$ absorption band.

A recent paper by Lakshmi and Ravikanth¹⁸ analyzed the effect of phenylhydrazone and 2,4-dinitro-phenylhydrazone substituents on the spectral characteristics of BODIPY dyes. The paper revealed that the formation of an intramolecular hydrogen bond between the -NH-N=CH-C₆H₅ substituent and a hydrogen bonding accepting solvent (DMSO or DMF) causes a bathochromic shift of the absorption band (50 nm) and a significant shift of the ¹H NMR signal (about 3 ppm) towards low field. A stronger bathochromic shift of the absorption band (172 nm) was observed for the 2,4-dinitro-phenylhydrazone derivative of BODIPY as a result of the intramolecular $\rightleftharpoons$ intermolecular hydrogen bond equilibrium, but, with a much smaller ¹H signal shift (~ 1 ppm). These phenomena were explained by the authors by an increase of the electron density on the nitrogen atom and a more stable delocalized structure.

To summarize, the influence of the intramolecular tautomeric equilibrium on the spectral characteristics of the BODIPY chromophore is an interesting topic for further investigations. Thus, the goal of this study is to have a deep understanding of the influence of the tautomeric equilibrium on the spectral characteristics of BODIPY dyes in the ground and excited states. The combination of the BODIPY core and a diketone substituent makes it possible to model the effect of the coupling between the *quasi*-aromatic O=C-C=C-O moiety and the chromophore core on the spectroscopic characteristics by changing the intramolecular hydrogen bonding (Scheme 1).

Scheme 1. Chemical structure of studied BODIPY dye and scheme of the tautomeric equilibria.

This investigation is expected to provide fundamental data for the effective modelling of the physicochemical properties of the chromophores. It is necessary to underline that the influence of hydrogen bonding on the fluorescent quantum yield is not unequivocal; on the one hand, hydrogen bonding diminishes the fluorescence quantum yield, but on the other hand, hydrogen bonding influences the charge transfer between the tautomeric sensor and the fluorophore, which can result in an increase of the fluorescence quantum yield. The elucidation of the role of the π -electronic conjugation between the chromophore and the quasi-aromatic substituent is a significant step forward and this phenomenon is studied here by the determination of the influence of solvent polarity on the photophysical properties of the diketone BODIPY dye.

The absorption spectra of the studied compound were characterized and showed a narrow absorption band with a maximum between 515 nm (trifluoroethanol) and 524 nm (toluene), with the exception of the hydrogen accepting solvents - acetone, acetonitrile, dimethylformamide and dimethylsulfoxide (Figure 1A). The absorption band has a shoulder at around 490 nm (Figure 1A), which can be attributed to vibrational progression.³ In the same series of solvents the emission maxima consist of a relatively narrow band without a fine structure and a maximum

ranging from 533 nm (trifluoroethanol) to 545 nm (toluene). For the same range of solvents the Stokes shift amounts to $700 \pm 50 \text{ cm}^{-1}$ and is nearly independent from solvent polarity. The spectral data as well as the fluorescence quantum yields (Table S1) suggest that in the solvents without hydrogen bonding character only a single absorbing and emitting species is present (prevailing enol tautomeric form, see discussion below, Scheme 1). However, in outspoken intermolecular hydrogen bond accepting solvents, acetone, acetonitrile, dimethylformamide and dimethylsulfoxide, the absorption spectrum consists of a broad unstructured band with maxima at respectively 539 and 542 nm. Hence these maxima are red shifted compared to the nonhydrogen bond accepting solvents. This result shows that these hydrogen bond accepting solvents are characterized by two conformational forms of the molecule in the ground state. Excitation at the maximum of the S_0 - S_1 band (500 – 520 nm) results in an intensive emission band within 540 – 550 nm (Figure 1). In acetone, acetonitrile, dimethylformamide and dimethylsulfoxide the features and maximum of the emission spectra still resemble those of the emitting species in nonhydrogen bond accepting solvents.

Figure 1. The normalized fluorescence (A) excitation spectra and (B) emission spectra of the studied BODIPY dye as function of solvent polarity: THF (black), methanol (red), CH₃CN

(green), toluene (blue), acetone (cyan), ethyl acetate (magenta), 2-propanol (yellow), DMSO (dark yellow), DMF (navy), 1-butanol (purple), TFE (dark cyan), acetic acid (royal).

These changes in absorption and emission accurately mirror the dependences $\lambda_{\text{abs}}/\lambda_{\text{em}} = f(\Delta f)$ and $\Delta\bar{\nu} = f(\Delta f)$ presented in Figure 2 ($\lambda_{\text{abs}}/\lambda_{\text{em}} = f(\Delta E_N^T(30))$ and $\Delta\bar{\nu} = f(\Delta E_N^T(30))$, Figure S2, supplementary). The linear dependencies presented in Figure 2 reveal that the increase of the solvent polarity (except for the solutions with hydrogen bond accepting solvents) evokes a quite insignificant hypsochromic shift of the absorption and emission bands. The results presented above prove that the studied compound does not undergo significant structural changes in these solvents (protic in that number). The hydrogen bond accepting solvents are the exception due to the increase of the shift of λ_{abs} observed for these solvents.

Figure 2. A) Black circles (λ_{abs}) are in respect to the $S_0 \rightarrow S_1$ transition (trend line - $\lambda_{\text{abs}} = -14.299 \Delta f + 524.3$); empty squares (λ_{abs}) are in respect to $S_0 \rightarrow S_2$ transition; empty circles (λ_{em}) are in respect to $S_1^* \rightarrow S_0$ (trend line $\lambda_{\text{em}} = -23.258 \Delta f + 546$); empty squares (λ_{em}) are in respect to $S_x^* \rightarrow S_0$. B) Black circles are in respect to the Stokes shift after excitation at 520 nm (trend

line $\Delta\bar{\nu} = -462.01 \Delta f + 806.67$) and black squares are in respect to the Stokes shift after excitation at 420 nm.

Therefore, the question arises: which tautomeric forms of the studied dye are observed in non-hydrogen bond accepting and in which in hydrogen bond accepting solvents in both the ground and the excited states? To answer this question ^1H NMR spectra have been measured in order to further identify these species in the ground state (Figure 3). All the NMR spectra recorded in toluene, chloroform and dichloromethane show an intense signal at 16.76 ppm (chloroform), 16.69 ppm (dichloromethane) and 17.44 ppm (toluene). This signal is characteristic for an intramolecular hydrogen bond in the enol form of a β -diketone.^{19,20} This suggests that in non-hydrogen bond accepting solvents the dye is present only as the enol tautomeric form (intra-HB). Moreover, the absence of a band within the range of 4 – 5 ppm, diagnostic for the keto form of diketones,^{19,20} proves the lack of the keto form of the studied dye in non-hydrogen bond accepting solvents. However, hydrogen bond accepting solvents feature both the band within the range of 4 – 5 ppm (THF - 4.62 ppm, acetonitrile – 5.40 ppm and acetone – 5.49 ppm) and a significant decrease of the intensity of the band at 16 – 17 ppm. Notably, the ^1H NMR spectra of all the solutions do not reveal an additional wide band, which could point out the presence of an intermolecular hydrogen bond between the hydroxyl group of the dye and solvent molecules. The above-mentioned data make it clear that non-hydrogen bond solvents in the ground state exhibit only keto-enol equilibrium in the absence of a stable intermolecular hydrogen bond between BODIPY and the solvent molecules.

Figure 3. NMR spectra of 3-(2,4-dioxopent-3-yl)-8-(2,6-dichlorophen-1-yl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene in acetonitrile (A), dichloromethane (B), tetrahydrofuran (C), chloroform (D) and toluene (E).

For the verification of the observed equilibria quantum-mechanical calculations have been accomplished for the dye in the ground and excited states. The computational analysis was carried out by DFT²¹ and TD-DFT²² methods for the ground and excited states, correspondingly. To make sure that the results are highly reliable, the calculations have been performed by four M06-2X,²³ PBE0,²⁴ CAMB3LYP²⁵ and B3LYP²⁶ functionals. All the calculations showed an analogous trend of the changes after the transition from the enol form to the keto form, except for the calculations by B3LYP functional for the gas phase which are not further discussed. The calculations provide 8 conformers for the ground and excited states (Figure 4). Besides, the calculations show that the conformer with an intramolecular hydrogen bond (conformer C1,

Figure 4) is the least stable. The second most stable conformer is conformer C2 (the molecule in the keto form). The difference of energy between conformers C1 and C2 equals about 4 kcal/mol in the ground and excited states, respectively. The rest of the conformers, C3 – C8, possess very similar energy in the ground and excited states (10 – 15 kcal/mol). As to the calculated spectral characteristics, the transition from the enol form (conformer C1) to the keto form (conformer C2) brings about a bathochromic shift of the absorption band and a hypsochromic shift of the emission band (Tables S3 – S5, supplementary). The results of the calculations are in good agreement with the observed experimental data. The calculations state that the difference of energy between conformer forms rapidly reduces with increasing solvent polarity (gas $\rightarrow$ dichloromethane $\rightarrow$ methanol $\rightarrow$ DMSO) especially for the excited state.

Figure 4. The energy and structure of conformers of obtained with (A) B3LYP/6-31+G(d,p) and (B) TD-B3LYP/6-31+G(d,p) for full optimisation parameters of molecule at ground and excited states, respectively. Gas (blue), dichloromethane (red), methanol (yellow) and DMSO (green).

The most interesting phenomenon for the studied compound seems to be the appearance of an absorption band within 400 – 450 nm in the hydrogen bond accepting solvents. According to literature data,³ this band is assigned to a S_0 - S_2 transition. It is noteworthy that the emission from S^*_2 state has been observed before for BODIPY dyes.²⁷⁻²⁹ It is a surprising fact that the excitation at the $\lambda_{\text{max}}(S_0$ - $S_2)$ band of the studied dye causes a significant emission within the range of 469 – 486 nm with a large Stokes shift ($2500 - 3500 \text{ cm}^{-1}$, Table S1). The intensity of this emission band even exceeds the intensity of the band of S^*_1 - S_0 transition ($\sim 540 \text{ nm}$, Figure 5). However, the obtained results differ from those reported earlier²⁷⁻²⁹ thanks to a significant intensity of the emission and a large (in terms of BODIPY dyes) Stokes shift. The explanation of this phenomenon is presented in Scheme 3 and analysed below.

Figure 5. The fluorescence emission spectra; $\lambda_{\text{ext.}} = 420 \text{ nm}$, $\lambda_{\text{ext.}} = 480 \text{ nm}$ (inset normalized scale).

This significant Stokes shift suggests important structural changes which are caused by the change of tautomeric form^{30, 31} as a result of the transition from a S_2 (keto form) state to an “unknown” $S^*_1(X?)$ one. The “unknown” state $S^*_1(X?)$ cannot be the $S^*_1(\text{keto})$ state or the $S^*_1(\text{enol})$ state, otherwise one would observe the emission at $\lambda_{\text{em}} = 540$ nm, like in non-hydrogen bond accepting solvents. Therefore, the “unknown” $S^*_1(X?)$ state appears to be the excited state of the dye in the tautomeric “open” form, $S^*_1(\text{“open”})$. It is important to mention that this tautomeric state of the dye is stabilized by the intermolecular hydrogen bonding between the hydroxyl group of the BODIPY dye and molecules of the hydrogen bond accepting solvent. Furthermore, the molecule undergoes a transformation from the $S^*_1(\text{open})$ state to the ground state of the dye molecule with the open form ($S_0(\text{open})$) with a consequent non-radioactive transition into the $S_0(\text{keto})$ state.

Scheme 3. Jablonski diagram of studied BODIPY dye.

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Notes

The authors declare no competing financial interests.

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