

Computational investigation on photonics of boron and zinc dipyrromethene complexes

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The last decades were characterized by increased interest in the development of various optical devices based on complex molecular compounds. Depending on the structure, they are widely used including active laser media of tunable lasers, laser limiters, fluorescent tags, optical sensors in various fields of science and technology [1]. Currently, dipyrromethenes with p- and d- elements are the most promising compounds to apply as elements of these devices. The most perspective members of this family are boron fluorinated complexes of dipyrromethenes (BODIPY). BODIPYs possess intense fluorescence in the visible range and good photostability. Dipyrromethenes can form stable complexes with ions of d-elements such as Zn(II). In comparison with BODIPY, an advantage of complexes of d-metals with dipyrromethenes is high sensitivity of the photonics characteristics to changes in the chromophore structure and nature of the solvent as well as easier “self-assembly” of these complexes. It makes them very promising for fluorescent probes dipyrromethenates have efficient absorption and emission in the visible spectral region and they are sensitive to structural changes in their molecular environment.

New derivatives are been synthesizing with increasing intensity but at the same time theoretical researches of their physical and chemical properties to develop optical devices is going essentially slower. Experimental investigation complemented with theoretical-computational studies accompaniment lead to deeper understanding of electronic structure, pathways of electronic transitions, and specific spectral-luminescence features to develop more efficient fluorescent probes, optical sensors and triplet photosensitizers. Therefore, the purpose of the present work is theoretical research of photophysical and photochemical processes occurring in dipyrromethenes molecules and depending on their structure, nature of the solvent and the characteristics of the exciting radiation.

In order to optimize the compounds in ground and excited states as well as to investigate their electronic structures, schemes of excited energy dissipation, several TD-DFT functionals accompanied with various basis sets were used. Two CH₃-BODIPY absorption bands in the experiment with $\lambda_{\max} = 504$ nm ($\epsilon = 84000$) and 350 nm ($\epsilon = 4200$) were in agreement with calculated wavelengths of 476 nm ($\epsilon = 24678$) and 397 nm ($\epsilon = 1204$), respectively, where as the experimental [Zn(dpm)₂] bands with $\lambda_{\max} = 485$ nm ($\epsilon = 146200$) and 346 nm ($\epsilon = 9750$) were at 457 nm ($\epsilon = 260000$) and 403 nm ($\epsilon = 32400$) in calculations [2]. The calculated wavelengths are in satisfactory agreement with the experimental ones (the difference is about 30 nm). The molar extinction coefficients differ, but their trends are correctly reproduced.

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References

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2. R.T. Kuznetsova et al., *J. Mol. Liq.* **278** (2019), 5.