

The photophysical properties of the 4,4-difluoro-1,3,5,7-tetraphenyl-2,6-dibromo-4-bora-3a,4a-diaza-s-indacene

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In the recent years lot of research activity has been directed to the studies of the spectroscopic-luminescent properties of pyromethene dyes (BODIPY) with the purpose to create new efficiently working laser-active media. BODIPY dyes are photo, chemically and thermally stable molecules, which absorb light and make fluorescence in the wavelength region of 500-700 nm. That is why BODIPY complexes are very suitable substances for applications in optoelectronics as solid laser-active media, fluorescent sensors for detection of metal ions or biological analytes. Due to the tremendous amount of the work done in the last years on the synthesis of different BODIPY complexes, lot of questions appeared lately in the area of the quantum BODIPY photophysics that need to be solved in order to provide a fundamental knowledge about "structure-properties" relationship, which is very important to develop practical applications of the BODIPY molecules.

We studied on the theoretical level the electronic structure, spectral-luminescent and photophysical properties of the 4,4-difluoro-1,3,5,7-tetraphenyl-2,6-dibromo-4-bora-3a,4a-diaza-s-indacene ($\text{Br}_2\text{Ph}_4\text{-aza-BODIPY}$) with the use of the quantum-chemical software developed on the base of the INDO method utilized special spectroscopic parametrization. $\text{Br}_2\text{Ph}_4\text{-aza-BODIPY}$ as well as its Cl and I-substituted analogues are remarkable molecules as despite that the quantum yield of their fluorescence is very small, being excited with the light these $\text{Ph}_4\text{-aza-BODIPYs}$ do not phosphorescence. This phenomenon can be caused by a short lifetime of the triplet states tended to nonradiative $T\text{-}T$ -deactivation or as a result of high singlet-triplet conversion rate and fast quenching with oxygen. If the life time of the phosphorescent T_1 -state is shorter than 100 ms (minimal delay of the measured phosphorescent radiation), the registration of such phosphorescence with the Cary Eclipse spectrophotometer ("VARIAN") is technically impossible, e.g. phosphorescence is not seen not because it is absent but due to the technical limits of the registration device.

We calculated dipole moments and energy levels of the ground and singlet and triplet electron-excited states, energy and nature of the molecular orbitals, oscillation forces and polarization of electron transitions. On the base of our quantum computations, the light absorption spectra were interpreted, rate constants of the radiative and nonradiative intramolecular photophysical processes between states of equal or different multiplicity were calculated, the values of the quantum yields of phosphorescence and fluorescence were estimated, as well as the quantum yields of $T_i\text{-}S_1$ -intersystem crossing. As the final result of the work, the complete energetic scheme of electron-excited states and occurring photoprocesses in the molecule of $\text{Br}_2\text{Ph}_4\text{-aza-BODIPY}$ was created and the possible ways of the decays of the energy of the electron-excited transition state were analyzed. It was realized that the absence of phosphorescence is caused by many factors not only by the too short radiation time of phosphorescence ($\tau_{\text{rad}}=46 \mu\text{s}$) and also by concurrence with the nonradiative decay of the T_1 -state in the situation when $k_{\text{ic}}(T_1 \rightarrow S_0) \gg k_{\text{ph}}(T_1 \rightarrow S_0)$.