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Determination of excited singlet-state dipole moment of biopolymeric photoinitiator based on thioxanthone/chitosan using solvatochromic method

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The aim of this work was to study the absorption and fluorescence characteristics of new biopolymeric photoinitiator derivative of thioxanthone and chitosan in different solvents. The absorption and fluorescence spectra of 10-oxo-10H-dibenzene thiopiran-1-2-dicarboximide/chitosan (TXICh) in various solvents were obtained. Dipole moments in excited states were calculated using solvatochromic data. The ground state dipole moment (μ_G) was calculated by Density functional theory (DFT) method. Singlet excited dipole moment (μ_E) was estimated from three different methods proposed by Lipert-Mataga; Bakhshiev/Kawiski-Chamma-Viallet and Reichardt. The TXICh showed an intense absorption band in the range of 330-410 nm in all the solvents. This band can be attributed the n-π^* e π-π^* transitions. In aprotic solvents, stabilization of π-π^* state and a blue shift of n-π^*state occur. In the case of polar solvents (especially water), it was observed a large Stokes shift in the fluorescence emission spectra of TXICh. For hydroxylic solvents, these results suggest that in the S_0 and S_1 state, the compound act as proton acceptor and proton donor, respectively. Varying the solvent polarity, the shift emission peaks were more affected than absorption peaks, this behavior indicate that $\mu_E > \mu_G$. The μ_G value obtained by DFT was 2.3 Debye. The μ_E values estimated by Lipert-Mataga; Bakhshiev/Kawiski-Chamma-Viallet and Reichardt equations were 9.8, 9.5, and 8.3 Debye, respectively. The singlet excited dipole moment values obtained to biopolymer initiator TXICh were higher than the ground state, which is a indicative that the photoinitiator can be more polar in the excited state that in ground state.

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