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Radiative lifetime of a BODIPY dye as calculated by TDDFT and EOM-CCSD methods: Solvent and vibronic effects

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The study and synthesis of BODIPY dyes have become widespread owing to their favorable properties such as large molar absorption coefficients, high fluorescence quantum yields, excellent thermal and photochemical stability, good solubility as well as versatile functionalization¹. A growing number of theoretical studies (see e.g.^{2,3,4}) has also been performed. In this study (R.C. Sia, R.A. Arellano-Reyes, T. Keyes and J. Guthmuller, *Phys. Chem. Chem. Phys.*, (2021), DOI: 10.1039/d1cp03775g), the radiative emission lifetime and associated S1 excited state properties of a BODIPY dye are investigated with TDDFT and EOM-CCSD calculations. The effects of a solvent are described with the polarizable continuum model using the linear response (LR) approach as well as state-specific methods. The Franck-Condon (FC), Herzberg-Teller (HT) and Duschinsky vibronic effects are evaluated for the absorption and emission spectra, and for the radiative lifetime. The transition energies, spectra shapes and radiative lifetime are assessed with respect to experimental results. It is found that the TDDFT transition energies are overestimated by about 0.4-0.5 eV, whereas EOMCCSD improves the vertical emission energy by about 0.1 eV in comparison to TDDFT. The solvatochromic and Stokes shifts are better reproduced by the state-specific solvation methods, which shows that these methods are more suited than the LR model to describe the solvent effects on the BODIPY dye. The vibronic effects lead to an increase of the radiative lifetime of about 0.4 to 1.0 ns depending on the theoretical approach, which highlights the importance of such effects. Moreover, the HT effects are negligible on both the spectra and lifetime, which demonstrates that the FC approximation is accurate for the BODIPY dye. Finally, the comparison with experimental data shows that the radiative lifetimes predicted by EOM-CCSD and TDDFT have comparable accuracy.

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