Fluorescence of PRODAN in Water: a Computational QM/MM MD Study

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PRODAN (6-propionyl-2-dimethylaminonaphthalene) and its derivatives are fluorescent probes which are known for a strong dependence of their emission spectra on the solvation state. They are commonly used in many time dependent solvent relaxation studies, in particular in those focused on hydrated bio-membranes. Despite the extensive use, the fluorescence spectra of PRODAN were not yet theoretically resolved. We studied fluorescent properties of PRODAN in water by means of excited state molecular dynamics simulations employing a combined quantum mechanical and molecular mechanical (QM/MM) approach with the time-dependent density functional theory. State of the art coupled cluster method (CREOM-CCSD(T)) was used to benchmark the density functional theory calculations. The issue of the molecular geometry of the excited state PRODAN molecule in water was addressed. The planar conformer is predominantly responsible for the fluorescence; the twisted conformer is strongly stabilized in water, but it does not suffice to explain the experimental spectra due to its low oscillator strength. The influence of the water environment on PRODAN emission was investigated within several computational schemes with varying description of the solvent. The experimental emission spectra are successfully reproduced only after including the polarization effects by employing a polarizable force field into our QM/MM approach.