Predicting Fluorescence Efficiency of J-aggregate Squaraine Dyes as (Semi)Transparent Solar Concentrator Luminophores

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Reliable prediction of fluorescence quantum yield (QY) from first principles is essential for the rational design of high-performance fluorophores [1], particularly for applications in transparent luminescent solar concentrators (TLSCs). In this study, we employ a combination of density functional theory (DFT) and time-dependent DFT (TD-DFT) methods to investigate the electronic, optical, and photophysical properties of squaraine-based J-aggregates in toluene for application as (semi)transparent luminophores.

Radiative and non-radiative rate constants are calculated using Fermi's Golden Rule within the framework of the vertical harmonic approximation (VH) model for both ground and excited states. To evaluate the accuracy of quantum yield predictions, we systematically analyze the effect of different lineshape broadening functions (Gaussian, Lorentzian, and Voigt) on predicted transition rates.

Applying these methods to a series of covalently bound squaraine oligomers—dimers, trimers, and tetramers—we identify the SQA tetramer (or larger) J-aggregate, composed of monomeric subunits with a central squaric acid ring and two oxygen atoms, as a promising NIR-active luminophore. These systems exhibit selective near-infrared (NIR) absorption and emission, along with high predicted fluorescence QY [2]. Their tunable and size-dependent photophysical properties suggest strong potential for further optimization and integration into transparent solar-harvesting systems.

Our findings highlight the importance of accurate vibrational structure modeling in the prediction of QY and demonstrate how theoretical methods can effectively guide the development of new, efficient fluorophores for luminescent solar technologies.

References:

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