

EuCompChem2025 - Edoardo Buttarazzi - Oral

Combining Theory and Experiments for Modeling the Conformational and Environmental Effects on the Spectroscopical Features of Red-Adsorbing Dyes

The development of efficient and economically viable dye-sensitized solar cells (DSSCs) hinges on a molecular-level understanding of the photophysical behavior of dye sensitizers.[1,2,3] Squaraine dyes, with their strong red-light absorption, are promising candidates; however, their performance is intricately modulated by conformational dynamics and environmental factors such as solvent polarity, pH, and temperature.[4,5,6]

In this study,[7] we present a comprehensive investigation into the electronic structure and vibrational properties of squaraine dyes, employing a synergistic approach that combines Density Functional Theory (DFT), Time-Dependent DFT (TD-DFT), and complementary spectroscopic experiments. The electronic and vibrational properties were characterized using range-separated hybrid functionals within TD-DFT, combined with the conductor-like polarizable continuum model (C-PCM) to simulate solvent effects, enabling accurate reproduction of spectral features across different environmental conditions. We demonstrate that: (i) the principal visible absorption feature is sensitive to conformational flexibility and protonation equilibria; (ii) solvent polarity exerts a significant influence on the position of the UV-vis absorption maximum; and (iii) vibrational spectroscopies (IR and Raman) serve as diagnostic tools for probing structural and protonation-state heterogeneity. While previous theoretical efforts have focused predominantly on vibronic couplings to interpret spectral line shapes, our findings highlight an additional layer of complexity arising from dynamic conformational and acid-base equilibria. This work illustrates the importance of integrating high-level theoretical modeling with experimental spectroscopy to capture the nuanced interplay between structure, environment, and optical response. The insights gained from three prototypical squaraines inform the rational design of next-generation dyes for DSSC applications.

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