

First-principles informed screening of dye monomers for excitonic delocalization

German Barcenas¹, Austin Biaggne¹, Maia Ketterdige¹, Lawrence Spear¹, Lan Li^{1,2}

¹Micron School of Materials Science and Engineering, Boise State University. ²Center for Advanced Energy Studies, Idaho Falls.

Dyes, molecules composed of chromophores, are observed to exhibit excitonic delocalization in nature. [1] Excitonic delocalization, a sign of quantum entanglement in dye aggregates, is a phenomenon sensitive to nanoscale orientation and dipole coupling. [2] Therefore, strength of exciton delocalization can be controlled by engineering dye aggregation propensity and dipole characteristics. This abstract focuses on the squaraine (SQ) dye, a similar dye to the commercially available cyanine dye, and its potential as a candidate for dye aggregates created by DNA nanotechnology.

SQ is modified with potential substituents to engender larger static difference (Δd) and transition dipoles (μ), as well as increase solvation energy (ΔG_{solv}) to promote aggregation. To evaluate these quantities, Density Functional Theory (DFT) and Time Dependent (TD)-DFT were used in conjunction with the empirical Hammett constant (σ_p) which quantifies substituents as electron withdrawing (W) or electronic donating (D) groups. In addition, dye symmetry was considered as a further variable in enhancing dipole moments. In our published work [3], we found that substituents did not have a significant impact on μ , but there was a more pronounced impact on Δd . Specifically, Δd was found to increase with W substituents, and W groups with larger σ_p showed higher Δd . In addition, higher absolute values of D and W showed higher ΔG_{solv} , and slight redshifts away from the unmodified SQ dye absorption spectrum. Finally, the asymmetric conformers of SQ were evaluated and more asymmetric SQ (via both symmetry and substituent) were found to promote higher Δd .

In an effort to increase our dye screening capabilities and further identify structural properties of interest, we created machine learning (ML) models trained using public datasets of various molecules. Increasing the sample size will give us insight into how to modify dyes to increase μ . Our work can inform the design of dye aggregates to promote excitonic delocalization.

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