Computational Design of Small Phenothiazine Dyes for Dye-Sensitized Solar Cells by Functionalizations Affecting the Thiophene Unit

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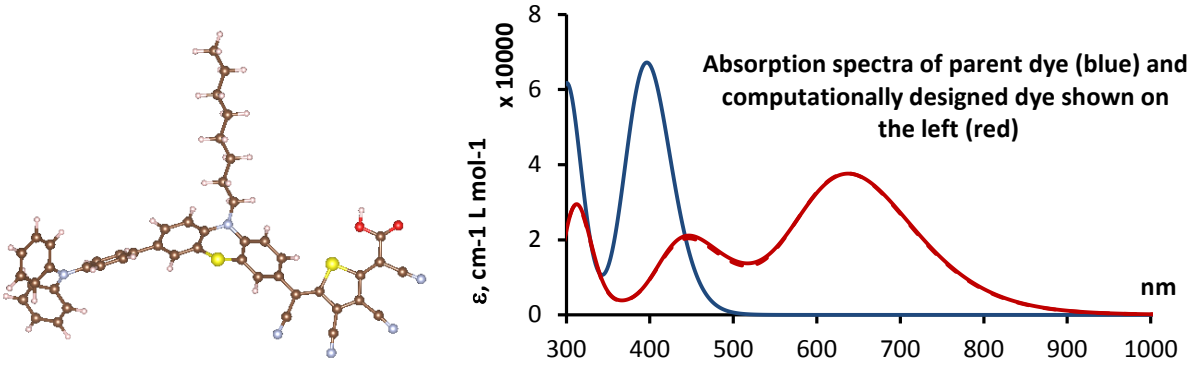
We present a computational density functional theory study of possibilities to improve the solar absorbance of small organic dyes featuring a phenothiazine donor and an acceptor moiety combining a thiophene unit and a cyanoacrylic group. We consider different conjugation orders and functional groups on and around the thiophene unit, including electron donating and electron withdrawing moieties (H, F, CH_3, CF_3, and CN). We predict that by combining change of conjugation order and functionalization with electron withdrawing CN groups, it must be possible ***to decrease the excitation energy by up to 60%*** vs. the parent dye (which would correspond to a redshift of the absorption peak maximum from 450 nm to 726 nm), effectively enabling red light absorption with small dyes. The contraction of the band gap is mostly due to the stabilization of the LUMO (by up to 1.8 eV) so that in spite of the kinetic redundancy of the parent dye with respect to the conduction band minimum of TiO_2, care must be taken to ensure efficient injection when using the dyes in dye-sensitized solar cells. By studying 50 dyes, of which 44 new dyes first studied in this work, we identify what parameters (such as charges, dihedral angles between donor and acceptor groups, bond length alternation) can serve as predictors of the bandgap. We find that bond length alternation or dihedral angles are not good predictors, while the charge on the thiophene unit is.



References:

1. W.-H. Tu, Y.-Y. Tan, S. Manzhos: Achieving improved solar absorbance of small organic dyes featuring quinoidized five-membered heterocycles, MRS Proc., 1667 (2014) DOI: 10.1557/opl.2014.736
2. Y. Y. Tan, W. H. Tu, S. Manzhos: Computational design of small organic dyes with strong visible absorption by controlled quinoidization of the thiophene unit, Chem. Phys. Lett., 593, 14-19 (2014)