分子軌道計算によって様々なアンカー期を用いた色素増感太陽電池用の近赤外色素の設計

Computational Molecular Design of NIR Dyes with Varying Anchoring Groups for Dye-Sensitized Solar Cells

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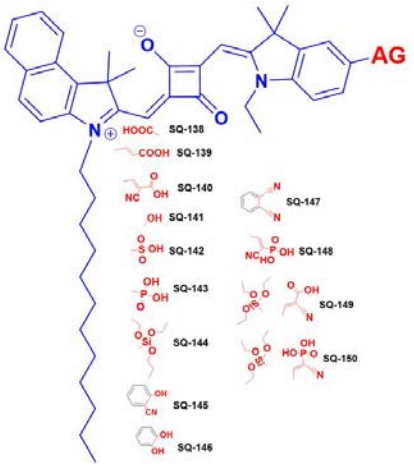
Introduction: Sensitizing dyes are one of the most important components of dye-sensitized solar cells (DSSCs) being photon harvester. Quantitative photon harvesting by potential sensitizers of state-of-art DSSCs developed so far in visible wavelength region and photoconversion efficiency (PCE) >12 % offers a logical hope for the development of novel NIR dyes aiming towards further improvement in the efficiency. An optimal sensitizer must fulfil certain criteria like, presence of a suitable anchoring group, energy band matching as well as good electronic coupling between photoexcited dye molecules and wide gap semiconductor. Nature of the anchoring group not controls the electron injection but also responsible for providing stability to DSSCs, In order to accelerate the development novel sensitizers and save the precious time synthetic chemists, quantum chemical (QC) calculations have emerged as one of the potential tools in the recent past. In this work, efforts have been directed towards the design of novel NIR dyes bearing different anchoring groups and predict their suitability as sensitizers in terms of their energetics and spectral behavior.



Experimental:

As a representative of NIR dyes, a series squaraine dyes (**SQ**) having same π-conjugated framework but varying anchoring group (AG) as shown in the Fig. 1 were designed and subjected to QC calculations in both of the ground and excited states using 6-311G basis set, TD-DFT theory and B3PW91 hybrid functional as implemented in the Gaussian G09 program. Calculated results in terms energetics and absorption spectrum were compared with experimental values of some of the synthesized dyes in order validate the calculated results. Optical band gap (E_{opt}) was estimated from energy corresponding to wavelength at FWHM of calculated absorption spectrum.

Results: First of all, one of the representative dye **SQ-138** bearing **–COOH** as anchoring group was subjected structural optimization at 6-311G/DFT/B3PW91 level of theory using polarization continuum model (PCM) and ethanol solvent followed by TD-DFT absorption spectral calculations. Calculated value HOMO energy, lmax and E_{opt} was found to be 5.15 eV, 595 nm and 706 nm, which are very similar to experimental values of this dye 5.08 eV, 654 nm and 720 nm, respectively exhibiting very well match between theoretically calculated and experimentally observed values. Electron density distribution in HOMO exhibits its main presence in at the central squaric acid core while in LUMO it is more diverted towards outer indole unit bearing the anchoring group. Such an electron density distribution in the HOMO and LUMO represents the intramolecular charge transfer (ICT) and presence and good electron density at anchoring group in LUMO suggests the possibility of good electronic coupling between the photoexcited dye molecules and wide band semiconductor like TiO_2 upon the adsorption of dye molecules. Excited by good correlation between theoretical and experimental values observed for SQ-138, other proposed dye molecular structures (**SQ-139 to SQ-150**) having chemical structures shown in the Fig. 1 were also subjected to similar theoretical calculations for the structure-property correlations. Results on electron density distribution in HOMO and LUMO of these dyes exhibited that ICT was not sufficient for squaraine dyes SQ-141, SQ-144 and SQ-146 bearing hydroxyl, silyl ester and catechol, respectively, as anchoring groups. On the other hand, very good ICT and very high electron density at anchoring groups for sensitizers like SQ-140, SQ-148, SQ-149 and SQ-150 have emerged as potential sensitizers of DSSCs using TiO_2 as wide band semiconductor and I^-/I_3^- as redox electrolyte.

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