



# Combined theoretical and experimental approaches for development of squaraine dyes with small energy barrier for electron injection



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## ABSTRACT

A series of far-red sensitizing squaraine dyes has been systematically designed and synthesized in order to correlate the theoretically calculated values with their corresponding experimental parameters. Efforts have been directed towards determining the minimum thermodynamic energy barrier for the electron injection in the nanoporous TiO<sub>2</sub> by logical molecular design. Theoretical calculations using Gaussian program package were performed for ground and excited states in both of the isolated gaseous state as well as in solution including the solvent effect using a self-consistent reaction field polarizable continuum model (PCM). Implementation of the PCM model or use of LSDA functional under TD-DFT calculations gives much better results for energetics as well as absorption maximum for all of the sensitizers used in this work. Newly designed symmetrical squaraine dye SQ-5 exhibits a minimum energy barrier of 0.16 eV for electron injection and shows photon harvesting behavior in far-red region with external photoconversion efficiency of 2.02% under simulated solar irradiation.

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## 1. Introduction

Dye-sensitized solar cells (DSSCs) have seen tremendous growth and received a good deal of attentions from material science community pertaining to the economical and environment friendly solar energy harvesting as compared to traditional silicon based solar cells [1]. Optimization of DSSC performance in terms of wide band gap mesoporous semiconductor, potential photosensitizers, redox electrolyte and counter electrodes have led to the attainment of photoconversion efficiency over 10% similar to amorphous silicon solar cells [2–5]. Last 10 years of research and development have witnessed the appreciable success in the attainment of nearly quantitative photon harvesting by DSSCs utilizing ruthenium complex based inorganic as well as metal free organic sensitizers [6,7]. A perusal of the photoconversion by potential sensitizers used in DSSCs corroborates that it is possible to achieve the photoconversion efficiency beyond 12% even having photon harvesting mainly in the visible region (400–750 nm) of the solar spectrum [8,9]. This indicates a good hope, potentiality and urgent need for the development of efficient sensitizers having the capability of photon harvesting in NIR-IR wavelength region for the further enhancement in the overall photoconversion efficiency. Utilization of lead chalcogenides (PbS/PbSe) based quantum dots as sensitizers have also been advocated towards the

fabrication of quantum dot sensitized solar cells (QDSSCs) owing to their band gap tunability due to the quantum size effect, high absorption coefficient and multi-electron generation from single photons [10–12]. However, observed photoconversion efficiency is still low in spite of visible to NIR wavelength photon harvesting which is attributed to huge charge recombination caused by the porous nature of working electrode leading to poor observed open circuit voltage [13]. At the same time, a perusal of their photon harvesting behavior reveals that they exhibit broad photon harvesting from visible to NIR/IR wavelength region offering difficulty to utilize them in hybrid or tandem DSSC architecture in order to further enhance the photoconversion efficiency of QDSSCs [14]. In this context, efforts are being directed to design and develop novel sensitizers having efficient photon harvesting mainly in the far-red to NIR wavelength for the DSSC application and efficient photo-sensitization in the far-red region has already been achieved but efficient photosensitization in the NIR region has still to be achieved [15–18].

In spite of having high molar extinction coefficient and suitable anchoring group, a suitable sensitizer for DSSC application must possess the energetic matching with respect to wide band gap semiconductor and redox electrolyte for facile electron injection and dye regeneration, respectively. Since sensitizing dyes play a pivotal role in controlling the photoconversion efficiency, development of suitable dyes working efficiently in the far-red to near infra-red (NIR) region is still challenging owing to their relatively smaller band gap ( $E_g$ ) and needs the attentions of the material science community. Relatively small  $E_g$  of NIR sensitizers needs the

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strict control on the energetics for their optimal functioning and a judicious molecular design is necessary. Taking model far-red sensitive squaraine dyes we have recently demonstrated that it is possible to control of energetics within 0.6 eV only by the alteration of alkyl chain length [19]. At the same time, introduction of fluoro-alkyl substituent leads to drastic decrease in the energy of their highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) [19,20].

To facilitate the development of sensitizers owing to enormous structural possibilities, state-of-art theoretical calculations using Gaussian program package have gained the good deal of attentions in the recent past [21,22]. We have recently shown that amongst several hybrid functional available under density functional theory (DFT), there is a need for the judicious selection of optimum functional for predicting the energetics and electronic absorption spectrum of unsymmetrical squaraine dye [23]. To screen out the optimum molecular structure especially dyes having capability of photon harvesting in the far-red to NIR region, theoretical prediction of energy of dye molecules in the ground and excited states along with the electronic absorption spectra have been found to be extremely useful. Aim of the present investigation is to design and develop followed by selection of suitable molecular structure having minimum driving force for electron injection by the excited dye molecules to the conduction band (CB) of nanoporous TiO<sub>2</sub> which is highly required for the development of NIR sensitizers. For this purpose, we have selected some model far-red sensitizers belonging to the squaraine dye family having the molecular structure shown in Fig. 1. In parallel, these sensitizing molecules were synthesized and characterized also to correlate the theoretical results with the experimental values. Calculated results on energy of molecules in the ground and excited states, band gap, absorption maximum for these molecules were then compared with experimentally observed values to find the optimum molecular structure with smallest driving force for electron injection.

## 2. Experimental

### 2.1. Materials and methods

All the chemicals for synthesis or solvents are of analytical/spectroscopic grade and used as received without further purification. Synthesized squaraine (SQ)-dyes and dye intermediates were analyzed by high performance liquid chromatography (HPLC) for purity, matrix assisted laser desorption and ionization (MALDI)-time-of-flight (TOF)-mass and fast ion bombardment

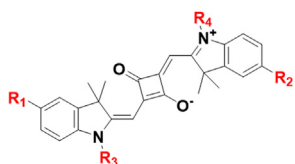
(FAB)-mass spectrometry in the positive ion monitoring mode and nuclear magnetic resonance (NMR) spectroscopy (JEOL, 500 MHz) using Tetramethylsilane (TMS) as internal standard for structural elucidation. Electronic absorption spectroscopic investigations were conducted using a UV-visible spectrophotometer (JASCO model V550). To construct the energy band diagram for the dyes, HOMO energy level was estimated from the photoelectron spectroscopy in air (PESA, model AC3, Riken Keiki, Japan) while the LUMO energy level was estimated using the relation  $LUMO = HOMO + E_g$ , where,  $E_g$  is the optical band gap.  $E_g$  was estimated from the onset of the optical absorption. Theoretical quantum chemical calculations for the structural optimization as well as electronic absorption spectra for the far-red sensitizing squaraine dyes used in this work were conducted on Dell workstation using Gaussian G09 program package [24]. Calculation was done in both of the isolated molecules in gaseous state as well as in solution in the framework of the self-consistent reaction field polarizable continuum model (PCM) [25]. Ethanol was used as a solvent not only for the electronic structure calculation but also for the experimental measurement of solution state electronic absorption spectra and preparation of dye-bath solution for the DSSC fabrication also.

DSSCs were fabricated using Ti-Nanoxide D paste (Solaronix SA) which was coated on a Low E glass (Nippon Sheet Glass Co., Ltd.) by a doctor blade. The substrate was then baked at 450 °C to fabricate TiO<sub>2</sub> layers of about 10 μm thickness. The substrate was dipped in the Ethanolic solution of the respective dyes in the presence of chenodeoxycholic acid (CDCA) for 4 h. The dye concentration was fixed to be 0.25 mM while CDCA concentration was 25 mM. A Pt sputtered SnO<sub>2</sub>/F glass substrate was employed as the counter electrode. Electrolyte containing LiI (500 mM), iodine (50 mM), t-butylpyridine (580 mM), MeEtIm-DCA (ethylmethylimidazolium dicyanoimide) (4:6, wt/wt) (600 mM) in acetonitrile was used to fabricate the DSSC. A Himilan film (Mitsui-DuPont Polychemical Co., Ltd.) of 25 μm thickness was used as a spacer. The cell area was 0.25 cm<sup>2</sup> which was precisely defined using a black metal mask.

The photovoltaic performances of the cells were measured using a solar simulator (CEP-2000 Bunko Keiki Co. Ltd., Japan) equipped with a xenon lamp (Bunko Keiki BSO-X150LC) used as a source of simulated solar irradiation at 100 mW/cm<sup>2</sup>, AM 1.5 G. The power of the light exposure from the solar simulator was also adjusted with an amorphous Si photodetector (Bunko Keiki BS-520S/N 353) to avoid the optical mismatch between the calibration diode and the DSSCs. The photocurrent action spectra as a function of wavelength from 300 to 800 nm were also measured with a constant photon flux of  $1 \times 10^{16}$  photon/cm<sup>2</sup> at each wavelength in DC mode using the action spectrum measurement system connected to the solar simulator (CEP-2000, Bunko Keiki, Japan).

### 2.2. Synthesis of sensitizing dyes

Direct ring carboxy functionalized indole derivative 2,3,3-trimethyl-3 H-indole-5-carboxylic acid used as common anchoring group for the all of the squaraine dyes was synthesized following the method reported by Pham et al. [26]. Details of the synthesis and characterization of this intermediate has published by us previously also [27]. Symmetrical squaraine dyes **SQ-1** and **SQ-2** were synthesized as per our earlier publication [19]. Unsymmetrical squaraine dyes **SQ-6** and **SQ-7** have been synthesized following the methodology adopted by Oswald et al. [28] and our earlier publication [29]. Symmetrical squaraine dyes bearing varying fluoroalkyl substituents (**SQ-3**, **SQ-4** and **SQ-5**) have been synthesized as per the synthetic scheme shown in Fig. 2.



	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
SQ-1	CO <sub>2</sub> H	CO <sub>2</sub> H		
SQ-2	CO <sub>2</sub> H	CO <sub>2</sub> H		
SQ-3	CO <sub>2</sub> H	CO <sub>2</sub> H		
SQ-4	CO <sub>2</sub> H	CO <sub>2</sub> H		
SQ-5	CO <sub>2</sub> H	CO <sub>2</sub> H		
SQ-6	CO <sub>2</sub> H	H		
SQ-7	CO <sub>2</sub> H	H		

Fig. 1. Structure of far-red sensitive squaraine dyes used in the present work.

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