Abstract:

The present thesis entitled '**Design and Synthesis of Near-Infrared Functional Dyes for Optoelectronic Applications'** focuses on the design, synthesis and characterization of novel squaraine (SQ) dyes for solar cell applications. In solar cell devices, sensitizer plays an important role in determining photovoltaic performance of the device. The optical and electrochemical properties were investigated by using absorption, luminescence spectroscopy, cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The thesis consists of five chapters. The first chapter deals with the introduction to Dye Sensitized Solar cells (DSSCs), while consequent chapters deal with the detailed work.

Introduction:

The inadequate quantity of our present energy supplies desires an inexhaustible source, i.e. solar energy, which is a clean and unlimited energy source. The main challenges associated with this energy is converting it into a form that solar energy can be utilized for various applications. In this regard, dye sensitized solar cells (DSSCs) cells, which directly convert solar energy into electricity, have been well established as a promising long-term solution for harvesting solar energy. In particular, DSSCs have attracted a lot of attention because of their lower production cost as well as their flexible and large panels with high photovoltaic performance.[1] In DSSCs metal-free organic light absorbers have advantage as promising class of sensitizers because their molar absorptivities are often higher than those of the metal containing dyes and versatile molecular design. Even though metal containing dyes reached efficiencies >13%, they are limited due to their expense, toxicity in nature and low molar extinction coefficients.[2] Recently, organic dyes have drawn immense interest owing to their high molar extinction coefficient, ease of purification, structural diversity and ease of fabrication.[3] Among all organic sensitizers, near-IR sensitizers exhibit a strong absorption in the visible and near-IR regions and include porphyrins,[4] arylamines,[5] indolines,[6] coumarins,[7] phthalocyanines[8] and squaraines.[9]

Squaraine dyes are an old class of organic dyes and are divided into symmetrical and unsymmetrical dyes. Symmetrical dyes can be prepared via a condensation reaction of squaric acid and electron rich compounds. While unsymmetrical squaraine dyes are prepared via a condensation reaction of an indolium salt and squaric acid followed by treatment with another indolium salt to obtain the squaraine dyes.[10] In point of their synthesis, symmetrical dyes are

easily synthesized when compared to unsymmetrical dyes. Squaraine dyes have drawn immense attention in the field of optoelectronics owing to their sensitizing abilities in the near-IR region of solar flux. Due to its Donor–Acceptor–Donor (D-A-D) type molecular structure, they have wide potential applications in organic solar cells, field-effect transistors, fluorescence probes, bio-sensing applications, photodynamic therapy and non-linear optics. To date, *cis* configured squaraine dyes are the most promising candidates for DSSC and result in high efficiency when compared to symmetrical and asymmetrical squaraine dyes. At present, different types of architectures of organic dyes have been developed, which can be divided into acceptor–donor (A–D) type, donor–acceptor–spacer–donor (D–A–π–D) type, acceptor–donor–acceptor (A–D–A) etc. Metal-free systems were strategically synthesized to increase the intramolecular charge transfer and extend the absorption from visible to NIR region, respectively. However, majority of these dyes were efficient sensitizers in the NIR region, but photocurrent response in the NIR region needed to be improved for better PCE.

Statement of Problem: The power conversion efficiencies currently oscillating around 25% for crystalline Si based cells and of 28% for thin film cells. The silicon based solar cells are very high cost and their tedious production process has forced researcher across the globe to think and develop alternate technologies with easy and cheap production. In this context, excellent progress has been made on DSSCs, organic field effect transistors (OFETs), small molecule organic photovoltaic (OPV) and perovskite solar cells technologies. Further research and development is needed to improve the device efficiency and stability/lifetime in order to compete favorably with inorganic PV cells. Materials with both high and broad absorption are still lacking. In order to harness solar energy cheaply and efficiently, molecular design plays an important role for tuning of the molecular energy levels, red-shift of the charge-transfer absorption band, and distinct improvement of photovoltaic performance and stability.

Methodology(s) used: The designed and synthesized molecules including squaraine sensitizers and small organic molecules were prepared by alkylations, condensation, bromination, Miyaura borylation, Suzuki, and Stille couplings. The prepared intermediates and final compounds were purified by column chromatography, systematically characterized by ^{1}H, ^{13}C NMR, and Mass. Furthermore, the HOMO/LUMO frontier orbital energy levels are determined by cyclic voltammetry, differential pulse voltammetry (DPV) to know the essential

information about the electronic properties and charge transfer processes. This method allows for the selection of the most promising candidates, which can be employed for the fabrication of efficient PV devices.

Sample results with interpretation: The results are presented in five individual chapters, first chapter deals with the introduction to DSSCs, organic field effect transistors (OFETs) while 2, 3, 4 and 5 chapter's deals with detailed work. A brief, chapter-wise account of the results is presented below.

In the first chapter of this thesis, we have discussed about the importance of solar energy and conversion of solar radiation into electricity using various generations of devices, like DSSCs and Thin Film Transistors. Literature survey on development of squaraine dyes as photosensitizers and thin film transistors materials are also discussed.

***Chapter 2 is divided in two parts, in chapter 2* A**, two novel panchromatic asymmetrical squaraine sensitizers (**SPSQ1** and **SPSQ2** shown in figure 1) have been synthesized, characterized and effectively used for TiO_2-based dye sensitized solar cells. In a solution, both dyes display a highly intense near-IR absorption (**SPSQ1**; 651 nm and **SPSQ2**; 692 nm), the red shifted absorption of **SPSQ2** was attributed to the incorporation of the auxiliary acceptor dicyanovinyl unit on the squaraine moiety. Interestingly, the dicyanovinyl unit lowered the LUMO level of **SPSQ2**, which decreased the band gap and red shifted the absorption when compared to **SPSQ1**. These dyes possess suitable HOMO and LUMO levels to work as efficient sensitizers in DSSCs. Under standard global AM 1.5 G solar conditions, the DSSC based on **SPSQ2** exhibited a high-power conversion efficiency of 3.1% with a high short circuit current density (J_{SC}) attributed to the broadening of the IPCE spectra in the UV-vis and near-IR regions when compared to **SPSQ1** (2.5%).

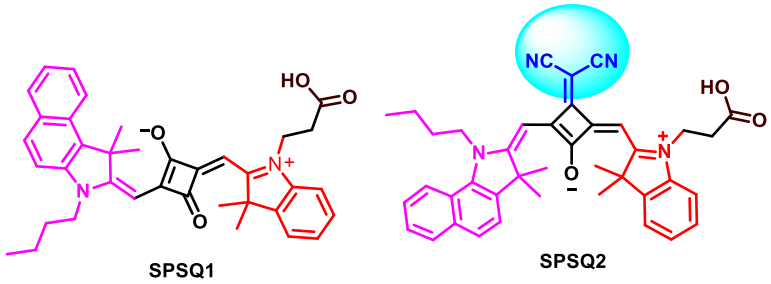

Figure 1. Molecular structures of **SPSQ1** and **SPSQ2** dyes.

In chapter 2 B, A combination of squaraine-based dyes (**SPSQ1** and **SPSQ2**) and a ruthenium-based dye (**N3**) (Figure 2) were chosen as co-sensitizers to construct efficient dye-sensitized solar cells. The co-sensitization of squaraine dyes with **N3** enhanced their light-harvesting properties as a result of the broad spectral coverage in the region 350–800 nm. The co-sensitized solar cells based on **SPSQ2+N3** showed the highest short circuit current density of 17.10 mA cm^{-2}, an open circuit voltage of 0.66 V and a fill factor of 0.73, resulting in the highest power conversion efficiency of 8.2%, which is higher than that of the dye-sensitized solar cells based on the individual **SPSQ1** and **SPSQ2** dyes.

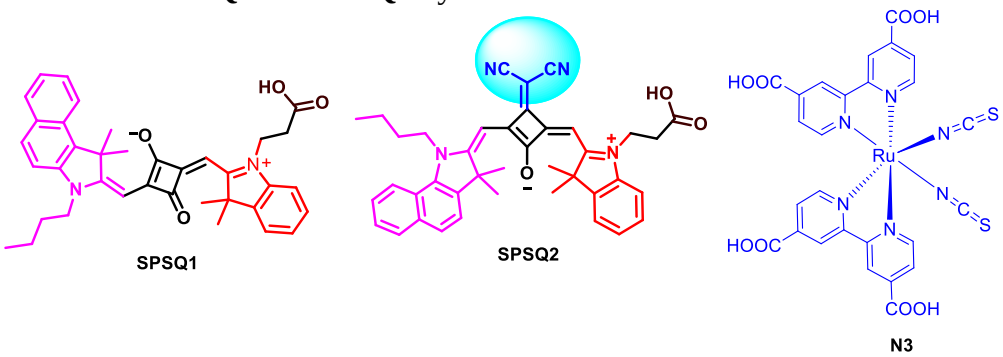

Figure 2. Molecular structures of **SPSQ1**, **SPSQ2** and **N3** dyes.

In chapter 3, we have designed, synthesized and characterized a novel metal free near infrared panchromatic asymmetrical squaraine sensitizers **(SQ-SPS)** (Figure 3) with thienothiophene as π-spacer, dicyanovinyl and cyanoacrylic acid unit as acceptor and successfully used for DSSC application. In contrast, Squaraine dyes generally display a strong narrow half-bandwidth spike like absorption peak in NIR region, beside this they also consist the weak absorption in the visible region, which help in matching the band gap and the energy levels for DSSC. Under AM 1.5 G solar conditions, the isolated SQ-SPS shows the power conversion efficiency of 5.86 %, Voc 0.564 mV, Jsc 15.00 mA cm^{-2} after co-sensitization with **N3** dye there is a tremendous increase in PCE to 8.84%, Voc 0.650 mV, Jsc 15.00 mA cm^{-2}. The increase in efficiency is mainly due to entire spectral coverage of IPCE spectra after co-sensitization.

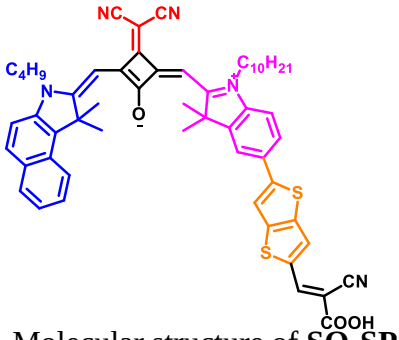

Figure 3. Molecular structure of **SQ-SPS** dye.

In chapter 4, we report synthesis and characterizations of two novel small molecules namely **SQ-BEN-THI** and **SQ-BEN-FUR** (Figure 4) with D-A-D molecular structure consists of squaraine as central unit, benzothiophene and benzo furan as end groups for organic field effect transistor (OFET) devices. The photophysical, electrochemical and density functional theory (DFT) results were combined to elucidate the structural and electronic properties of two squaraine derivatives. Organic field-effect charge transport properties were carried out using bottom gate top contact devices, showed field-effect mobility of 4.0×10^{-5} and 5.4×10^{-5} (cm^2/VS) for **SQ-BEN-THI** and **SQ-BEN-FUR**, respectively. After thermal annealing at 130°C the field-effect mobility would slightly increase up to 7.4×10^{-5} (cm^2/VS) for **SQ-BEN-FUR** and 5.0×10^{-5} for **SQ-BEN-THI**.

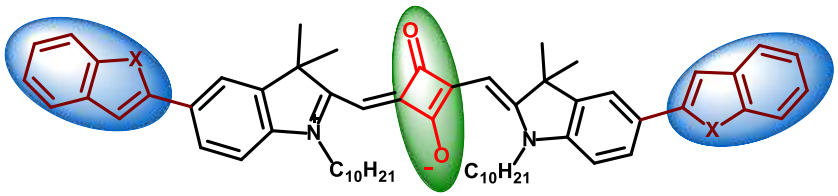

Figure 4. Molecular structures of **SQ-BEN-FUR**, **SQ-BEN-THI** dyes.

In chapter 5, we have synthesized three new small molecules squaraine based functional π-conjugated molecules considering core and wings concept. The molecule SQDICN, SQDIEt-RH, SQDICN-RH were ended caped with three different wings such as malononitrile, 2-(3-hexyl-4-oxothiazolidin-2-ylidene) malononitrile and 3-Ethyl rhodamine. Among all the three dyes

SQDICN-RH shows the high molar extinction coefficient other than two dyes. The photoluminescence of all the SQ dyes contrary to the absorption maximum trend. Further, we carried out solvatochromism to observe the effect of solvent with our dyes. The optical and the electrochemical results of all the SQ dyes are in good agreement with the theoretical studies.

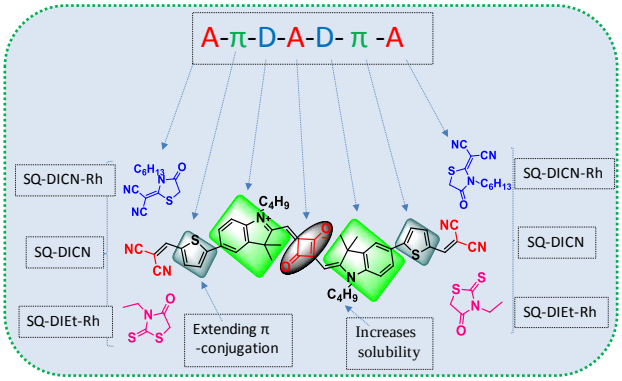

Figure 5. Molecular structures of **SQ-DICN**, **SQ-DICN-Rh** and **SQ-DIEt-Rh** dyes.