STUDY OF FLAVONOID BASED DYES FOR DYE SENSITIZED SOLAR CELLS

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In the 21st century, there is an urgent need of clean sustainable energy to cater to the constantly increasing energy consumption by a growing human population. Conventional energy sources have either been depleted or have pollution concerns and so alternative energy sources must be found. The abundant, freely available solar energy has the potential to be this alternative. A small percentage of the energy from the sun is sufficient to meet all the energy needs of the planet. If effectively harnessed, solar energy is the most attractive way to increase the electricity production to meet the day to day energy needs of today. Researchers continue to search for new ways to harness and use solar energy effectively.

Inorganic compounds formed the building blocks of the first- and second- generation solar cells but the development of the Dye Sensitized Solar Cells (DSSCs) by O'Regan and Gratzel in 1991 ushered in the era of the third-generation energy conversion devices which could replace the conventional Silicon (Si) solar cells. It was indeed a major step in the development, design and fabrication of efficient solar cells which would be low cost, environmentally friendly and cost effective.

The best photovoltaic device for DSSC in terms of both conversion yield and long-term stability till date has been achieved with polypyridyl complexes of Ruthenium (Ru). However, Ru is a chemically costly, environmentally unfriendly, scarce natural resource and the required complexes are difficult to synthesize. Hence, abundantly available, environment friendly and low-cost natural dyes have been considered as alternative photosensitizers with appreciable efficiencies. In an attempt to identify such materials, various parts of the plant have been characterized over the last two decades to identify the most suitable photosensitizers.

Plants which mainly depend on absorbance of light for their existence are rich in pigments like Betalains, Carotenoids, Chlorophyll and Flavonoids. Flavonoids particularly are widely available as they are present in most plant pigments for flower coloration producing yellow, red or blue pigmentation in petals. Some of the sources of flavonoids are citrus fruits, berries, onions (particularly red onion) and green tea. The structural features of a flavonoid pigment including degrees of double bond conjugation, presence of oxygen and the hydroxyl groups make them a natural choice for application in DSSCs. Flavonoids are further classified into Anthocyanidins, Anthoxanthins, Flavanones, Flavanonols and Flavans. A study of the electronic and optical properties of these dye-sensitizers will help in designing more efficient light harvesting molecular systems for DSSCs.

A DSSC must have the five major requirements for good performance in DSSCs:

- Excited state of the dye should be above the conduction band of the semiconductor, so that it can inject electrons easily into the semiconductor. Additionally, the ground state of the dye should be below the redox couple of the electrolyte, so that it can regenerate an electron from the electrolyte solution.
- The dye should have a broad absorption spectrum in the visible region for optimum light harvesting with a high molar extinction coefficient is desirable. For improved light harvesting efficiency, the dye's absorption spectra should match with the solar spectrum as much as possible.
- Fast regeneration of the ground state together with minimal- or zero-charge recombination of the excited state of the dye is necessary to ensure efficient charge transfer to the conduction band of semiconductor.

- The Light Harvesting Efficiency (LHE) of the dye should be high and the Exciton Binding Energy (EBE) should be low to maximize the photocurrent response and hence the efficiency of the solar cell.
- Intramolecular Charge Transfer (ICT) from the donor to acceptor side of the molecular system is one of the most important requirements for metal-free organic DSSC applications.

The advantage of theoretically designing systems of molecules suitable for DSSC applications is to give experimentalists a head-start as to what to expect before actual experimentation. This will cut cost considerably in their choice of chemicals and so avoid wastage and disposal issues.

In this study, the ground state properties such as geometrical parameters, Natural Population Analysis (NPA), Molecular Electrostatic Potential (MEP) and optical properties of dye sensitizers are investigated to understand the physical and chemical properties of the dye. The excited state properties such as UV-Vis absorption spectra, prediction of free energy change of electron injection and dye regeneration of organic dyes, LHE, EBE and ICT are studied to determine the charge transfer characteristics of these sensitizers before and after binding with Titanium dioxide (TiO_2). The dye is then modified to optimize those characteristics that are desired for photon to electron conversion. Again, the ground state and excited state properties of the optimized dye system, after binding with TiO_2 are computed at the molecular level. All these computations were carried out and viewed with the Gaussian software packages. SWizard program, Revision 5.0 is used to generate the theoretical absorption spectra. The workflow of the investigation is shown in the **Fig 1 and 2**.

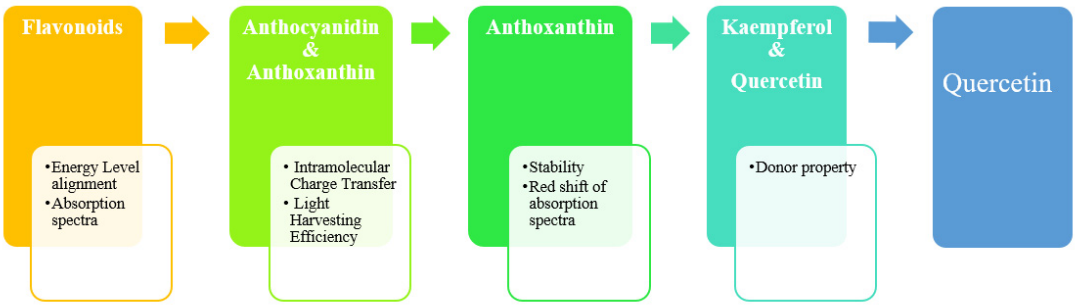

Figure 1 Choosing the optimum dye for DSSC applications

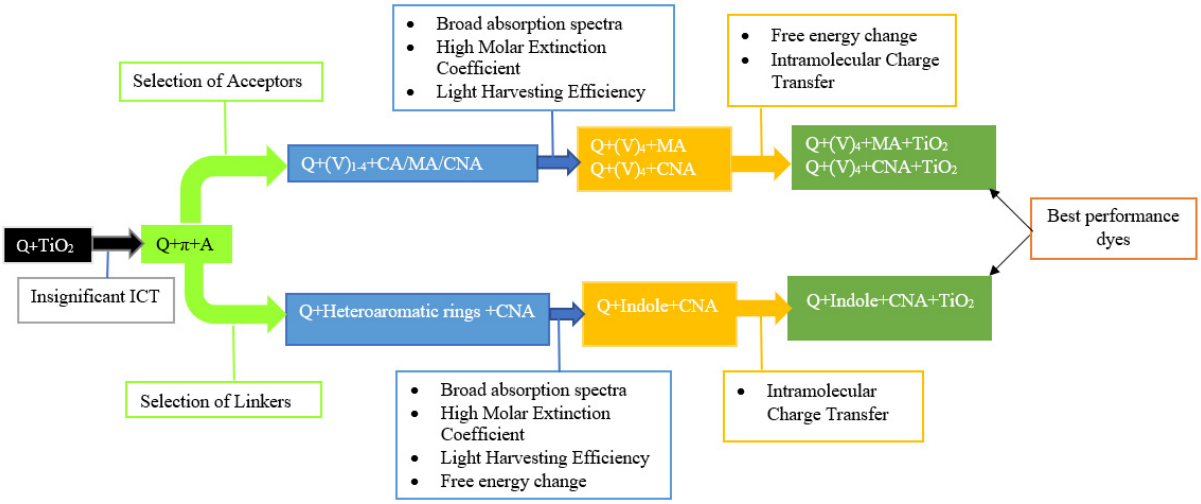

Figure 2 Choosing the best performance dye systems for DSSC applications

The thesis is organized into six main chapters: The first chapter introduces the topic, delves into the literature survey and highlights the motivation for the study. The second chapter on Methodology describes the techniques used in the study. These two chapters are followed by a report of the actual work done spread out into four chapters. There is a final brief section on "Conclusions and Future Directions". Appendices A and B contain the supplementary data and research articles published in the peer reviewed scientific journals respectively. The following is a summary of the contents of each chapter.

Chapter 1 traces the origins of solar energy utilization, describes basic concepts and the evolution of a DSSC. This chapter also describes the structure, working principle and electron transfer processes employed in DSSC. Molecular modeling of the dye molecule based on the requirements to enhance the efficiency of the DSSC are explained. A brief review of the research work in existing literature for the dye systems is also reported. Additionally, the motivation, aim and overview of the research work is stated.

The theoretical background of the various quantum chemical methods is first traced in **Chapter 2** which discusses the importance of functionals and basis sets used in molecular modelling studies. The computational methods used in determining the ground state properties such as geometry optimization parameters, NPA, MEP and optical properties of the dye system are described. Additionally, the requirements that the sensitized molecular dye system must have for DSSC applications such as energy level alignment, absorption spectra, free energy change of electron injection and dye regeneration, LHE, EBE and ICT, used in this investigation are explained in detail.

Chapter 3 reports the study of naturally occurring flavonoid dyes with the aim of selecting the best performing dyes for DSSC applications. The molecular geometry of flavonoid

dyes namely Anthocyanidin, Anthoxanthins, Flavanone, Flavanonol, Flavans are optimized at the ground state. The excited state properties of the dyes are studied in both the gas and Dimethyl sulfoxide (DMSO) solvent phase with Conductor like Polarizable Continuum Model (C-PCM) solvation. The energy level alignment of Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energies of dyes with redox couple of an electrolyte and the conduction band of TiO_2 are examined. The absorption spectra, LHE and ICT are studied for DSSC requirements. The flavonoid dyes, Anthocyanidin and Anthoxanthins are selected as best suited sensitizers with respect to energy level alignment and absorption spectra. Further investigations however indicated a lower absorption wavelength and insignificant ICT for the anthocyanidin dye molecule. These are not desirable properties and so anthoxanthins dyes were selected for further investigations.

Next, the optimized geometries of the Anthoxanthin (Flavone and Flavonol) dyes are studied at the ground state to investigate the geometrical parameters, NPA and MEP. The excited state properties of these dyes in the gas and DMSO phase are used to study the energy level alignment, free energy change of electron injection and dye regeneration. The molecular orbital diagrams of the dyes are examined for ICT required for DSSC operation. The vertical excitation energies, maximum absorption wavelength and oscillator strengths of the dyes are predicted and their corresponding absorption spectra simulated. The results show that, among anthoxanthin dye, Kaempferol (K) and Quercetin (Q) dye have the optimum properties required for use as sensitizers in the DSSC.

Chapter 4 reports the fabrication of solar cells with natural extracts rich in K and Q as sensitizers and their efficiencies calculated from observations. The UV-Vis absorption spectra of the extracts from Yellow Rose and Moringa are compared with the simulated

absorption spectra of K, Q and a 1:1 ratio of the two molecular system in ethanol solvent. The computational study of the dyes is used to analyse the electron transfer characteristics of the dye systems. The results of charge transfer shows that Q dye acts as a potential electron donor compared to K dye.

The low ICT of the dye is improved by adding effective π conjugative linkers and electron withdrawing anchoring groups at the reactive sites of the Q dye to increase the electron transfer characteristics and further potentially enhance the efficiency of the solar cells. A study of this forms the subject of the following two chapters.

Chapter 5 investigates the ground and excited state geometries of D–π–A system in which Q dye acts as a donor(D), Conjugated vinyl units, n = 1 to 4 acts as π linkers and three electron withdrawing acid moieties – namely Carboxylic (CA), Malonic (MA) and Cyanoacrylic (CNA) – are considered as acceptors (A). The results of minimum energies, charge analysis and optical properties of the dyes confirm that as the conjugation length increases, good electron withdrawing acid moieties will have better charge transfer from donor (Q dye) to acceptor side (acid moieties) of the newly functionalized dye. The energy level diagram, absorption spectra, LHE, EBE, molecular orbital diagram, free energy change of electron injection and dye regeneration reveal that the Q dye systems modified with four vinyl units and acidic moieties MA/CNA, namely MA4 and CNA4, are potentially best suited for DSSC with MA4 indicating slightly better performance than CNA4. After binding of these best suited dyes with TiO_2, the dye shows optimum results in molar extinction coefficient and absorption wavelength.

Chapter 6 examines the Q-π-CNA dye systems in which five-membered ring compounds namely Cyclopentadiene, Furan, Pyrrole, Thiophene, Oxazole, Imidazole and Thiazole and benzene fused five-membered ring compounds namely Isoindene, Benzofuran, Indole,

Benzothiophene, Benzoxazole, Benzimidazole and Benzothiazole are used as linkers. The energy level alignment, absorption spectra, LHE, EBE, free energy change of electron injection and dye regeneration are used to understand the charge transfer properties in the dye systems. The results indicate that the functionalized Q dye, Q-Indole-CNA (FF3), was an effective D-π-A sensitizer for DSSC. After binding with TiO_2, the FF3 dye shows a higher molar extinction coefficient and higher absorption wavelength with better ICT.

The research work concludes that from quantum computational studies, the newly functionalized dyes have potentially maximum absorption wavelength, optimum oscillator strength and good inter- and intramolecular charge transfer characteristics. These results will be helpful to experimentalists in enhancing the efficiency of the DSSCs. Future possible extension of the work is also suggested.

Papers published/Communicated during period of Research

Related to Research work

- Megala. M, & Rajkumar. B. J. M (2020). **Theoretical investigation of enhanced optical absorption of anthoxanthin dye for dye sensitized solar cells**. *Optik* (Communicated).
- Megala. M, Mayandi. J, & Rajkumar. B. J. M (2020). **Optical absorption study of anthoxanthin based natural dyes for dye sensitized solar cells: Experimental and Theoretical investigation.** *Materials Letters (Accepted for publication),* https://doi.org/10.1016/j.matlet.2020.128089 (Impact factor: 3.019).
- Megala. M, & Rajkumar. B. J. M (2019). **Heteroaromatic rings as linkers for Quercetin-based dye-sensitized solar cell applications: a TDDFT investigation.** *Journal of Computational Electronics*, *18*(4), 1128-1138 (Impact factor: 1.637).

- Megala. M, & Rajkumar. B. J. M (2018). **Molecular design of vinyl-functionalized Quercetin dyes with different acceptors for dye-sensitized solar cells: theoretical investigation.** *Journal of Computational Electronics*, *17*(3), 1153-1166 (Impact factor: 1.637).
- Megala. M, & Rajkumar. B. J. M (2016). **Theoretical study of anthoxanthin dyes for dye sensitized solar cells (DSSCs).** *Journal of Computational Electronics*, *15*(2), 557-568 (Impact factor: 1.637).

Unrelated to Research work

- Megala. M, & Rajkumar. B. J. M (2015). **DFT study of electronic transfer properties of carboxyl and nitro substituted benzene.** *AIP Conference Proceedings*, 1665(1)**,** 110045, https://doi.org/10.1063/1.4918101.

Paper Presentation in International/National Conferences

- **"Fused five membered ring compounds as linkers for Quercetin based Dye Sensitized Solar Cell: TDDFT investigations"** – International Conference on Spectroscopy of Biomolecules and Advanced Materials, Christian College, Chengannur, Kerala, during October 4-7, 2017.
- **"Functionalized Quercetin dye for DSSC application: TDDFT study"**- National Conference on Smart Materials, PG and Research Department of Physics and Chemistry held at Lady Doak College, Madurai during February 23-24, 2016.
- **"Role of Thiophene conjugate bridge for Quercetin dye in Dye Sensitized Solar Cells: a TDDFT investigation"** – International Conference on Recent Advances in Materials and Chemical Sciences, Department of Chemistry, Gandhigram Rural Institute, Dindigul district, during December 14-15, 2015.
- **"Theoretical designing of Quercetin dye for Dye Sensitized Solar Cell application: TDDFT investigation"** – International Conference on Nanomaterials for Energy, Environment, Catalysis and Sensors, Department of Physical Chemistry, School of Chemistry, Madurai Kamaraj University, during December 11-12, 2015.

- **"Computational study of four Anthoxanthin dyes for Dye Sensitized Solar Cells (DSSCs)"-** International Conference on Sustainable Energy Technologies held at PSG College of Technology, Coimbatore, during December 11-13, 2014.

Conferences/Seminars/Workshops attended

- International conference on **"Advanced Functional Materials for Energy, Environment and Biomedical Applications"** conducted by School of Physics, Chemistry and Biological Sciences, Madurai Kamaraj University, during December 11-12, 2017.
- International conference and workshop on "**Advances In Biomolecular Sciences and Analytical NMR"** organized by Dr.Vasudevan Ramesh, Professor, School of Chemistry, University of Manchester, UK and Department of Biochemistry, Chemistry and Physics, Srimad Andavan Arts and Science College from August 25-27, 2014.
- Regional interactive seminar on "**Physics of Nanomaterials & its Relevant Ethical Issues**" conducted by PG and Research Department of Physics, Lady Doak College, Madurai on February 24, 2014.
- International seminar on "**Nanostructure – based solar photovoltaics**" organized by the School of Mechanical and Building Sciences (SMBS), VIT Chennai on October, 2013.