A REPORT

ON

EXPANDED PORPHYRIN - DITHIENOPYRROLE BASED EFFICIENT DYE SENSITIZED SOLAR CELLS - DESIGN, SYNTHESIS AND FABRICATION

By

Shantanu Kallakuri 2010B2A1595H Chemical Engineering

Prepared in partial fulfilment of the course

Practice School-2, Course BITS C412

At

Indian Institute of Chemical Technology (CSIR-IICT)

Hyderabad

A PRACTICE SCHOOL – II STATION OF

Birla Institute of Technology & Science, Pilani

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BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE

PILANI (RAJASTHAN)

Practice School Division

PS2 Station - Indian Institute of Chemical Technology (CSIR-IICT)
Duration - 6 months
Date of Start - 4th July, 2014 **Date of Submission –** 8th December, 2014

Title Of Project - Expanded Porphyrin - Dithienopyrrole Based Efficient Dye Sensitized Solar Cells **:** Design, Synthesis and Fabrication.

Name of Student	**ID Number**	**Discipline**
Shantanu Kallakuri	2010B2A1595H	Chemical Engineering

Name(S) Of Expert(S)	**Designation**
Dr. Lingamallu Giribabu	Senior Scientist, Nanomaterials Lab
Dr. Gokulnath Sabapathi	DST - Inspire Faculty

Name of Ps Faculty – Dr. V. S. Prasad and Dr. P. R. Deepa

Key Words – Photosensitizer, Porphyrin, Sapphyrin, Dithienopyrrole, Solar Cell.

Project Area(s) – Solar Cells, Nanotechnology, Photoelectrochemistry, Porphyrin, Dithienopyrroles, dye photosensitizers, photocatalysis, sapphyrin

Abstract – Dye Sensitized Solar Cells are **Third Generation Thin Film Solar Technologies** that utilize nanomaterials, photosensitizers, redox couples electrolytes, electrodes, as a system to convert sunlight into electricity in an inexpensive,` unlimited manner. This project has been focused on the design, synthesis and fabrication of a Dye-Sensitized Solar Cell, which is a cheaper alternative to the expensive Traditional Silicon Solar Cell. We have engineered a Porphyrin based Photo-Sensitizer which releases electrons in the presence of Sunlight. Similar work has been done in the past, but we have focused on developing a novel molecule and tuned it chemically to give better a power conversion efficiency. Efficiency measurements are being conducted simultaneously by another group independent of this study. This is then anchored to a Titania nanomaterial electrode which directs the electrons towards the load to be powered. Once the load is powered, the electrons move to a Platinum Photoelectrode that then releases the electrons back to the Dye Sensitizer through an electrolyte medium. This project covers the Design, Synthesis of the Dye sensitizer, and its characterization.

Signature of Student **Signature of PS Faculty**

Signature of Guide **Date -**

BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE

PILANI (RAJASTHAN)

Practice School Division

Response Option Sheet

Station : CSIR – Indian Institute of Chemical Technology **Centre** : HYDERABAD

ID No. & Name : 2010B2A1595H, SHANTANU KALLAKURI

Title Of the Project : EXPANDED PORPHYRIN – DITHIENOPYRROLE BASED EFFICIENT DYE-SENSITIZED SOLAR CELLS - DESIGN, SYNTHESIS AND FABRICATION

Usefulness of the project to the on-campus courses of study in various disciplines. Project should be scrutinized keeping in view the following response options.

Code No.	Response Options	Course No. & Name
1.	A new course can be designed out of this project	BITS C462 : Renewable Energy
2.	The project can help modification of the course content Of some of the existing courses.	BITS C462 : Renewable Energy CE C394 : Green Buildings And Energy Conservation
3.	The project can be used directly in some of the existing Compulsory Discipline courses (CDC) /Disciplines Compulsory Discipline courses (DCOC) / Emerging Area (EA) etc. Courses	Yes. In solar cell technologies in the course renewable energy (bits c462)
4.	The project can be used in preparatory courses like Analysis and Application Oriented Courses (AAOC)/ Engineering Science (ES)/ Technical Art (TA) and Core Courses.	Not the project but some techniques involved in it like nmr, thin layer and column chromatography, spin coating
5.	This project cannot come under any of the above-mentioned options as it relates to the professional work of the host organization.	NO. It does come, as mentioned above.

Signature Of Student Signature Of Faculty

ACKNOWLEDGEMENTS

I am really grateful to Dr. Lakshmi Kantam, Director, IICT for this wonderful opportunity that allows us students to pursue innovative research at a renowned and World class Research Facility.

I extend my warm regards to Dr. Usha Virendra, Head, Chemical Engineering Department for her supportive guidance without which the completion of my work and this report would have been impossible.

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I wholeheartedly thank Dr. Vedanta Prasad and Dr. P. R. Deepa, my PS-II instructors, for their invaluable guidance, support and feedback which helped me in the completion of my work and this report.

A very special mention for two highly experienced people, my Guide, Dr.Lingamallu Giribabu (Senior Scientist, Nanomaterials Lab) and my Mentor, Dr.Gokulnath Sabapathy (DST - Inspire Faculty) , who have been guiding me tirelessly throughout the entire process at every step and because of whom I have been able to complete this work efficiently and in time.

My heartfelt gratitude to all the Scientists and HOD's who have been mentoring and guiding me through the past 6 months.

And finally but the most important, I am thankful for the constant support pillars of my life, my Parents and family without whose concern, encouragement and guidance, none of this would have been possible.

AIM AND OBJECTIVES

The aim of this project is to design, synthesize and fabricate an Expanded Porphyrin – Dithienopyrrole Based Dye Sensitized Solar Cell that gives a high Solar Power Conversion Efficiency (PCE).

Its main objectives are :

- To provide a comprehensive understanding of Dye Solar Sensitized Cells, their working, principles and methods for fabrication.
- To develop an understanding of electron transfer methods in Solar cells analogous to naturally available Chlorophyll and hemoglobin Moieties.
- To explain in brief the synthesis methods involved in this type of Solar Cell.
- To achieve an understanding of how Photosensitizers work and the different types.
- To comprehend the basics of Porphyrins, Sapphyrins, Dithienopyrroles, and other optically active moieties, which are frequently used in Solar Cells, and Organic Semiconductors (as in OLED, AMOLED).
- To understand some crucial scientific parameters of Photovoltaic Theory.
- To understand how a Solar Cell works and the electrode-electrolyte systems used in a DSSC
- To understand the current challenges and issues faced in Solar Cell Fabrication today and aspects of its Commercialization.

CONTENTS

LIST OF ABBREVIATIONS

1. **CSIR** - COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
2. **DSSC** – DYE SENSITIZED SOLAR CELL
3. **I sc** – SHORT CIRCUIT CURRENT
4. **V oc** – OPEN CIRCUIT VOLTAGE
5. **FF** – FILL FACTOR
6. **IPCE** – INCIDENT PHOTON TO CURRENT EFFICIENCY
7. **TLC** – Thin Layer Chromatography
8. **NMR** – Nuclear Magnetic Resonance
9. **DTP -** Dithienopyrrole

ORGANIZATIONAL PROFILE

CSIR - Indian Institute of Chemical Technology is located in the city of Hyderabad (Telangana), India. Its roots start with the establishment of Board of Scientific & Industrial Research (BSIR) in 1940 which later evolved into the Central Laboratories for Scientific and Industrial Research (CLSIR) with a vision by the then Nizam of Hyderabad in 1944.

The First patent was filed in 1949 on “Super-heated cylinder oil”. From then on, the lab underwent many changes with being taken over by Council of Scientific & Industrial Research (CSIR) in 1956 and being renamed as “Regional Research Laboratory” to a laboratory of national and international acclaim forcing its re-christening as “Indian Institute of Chemical Technology” in 1989.

Today, IICT has the highest number of publications, cumulative impact factor and total number of patents filed in the CSIR system which comprises of 37 National Laboratories. Its patents (in force) count to 197. It heads the research race in Basic and applied chemistry, biochemistry, bioinformatics, chemical engineering and provides science and technology inputs to the industrial and economic development of the country. The lab was headed by 7 eminent scientists in the past and is presently directed by Dr. (Ms.) M Lakshmi Kantam. She became the first lady director for the lab in the history of IICT.

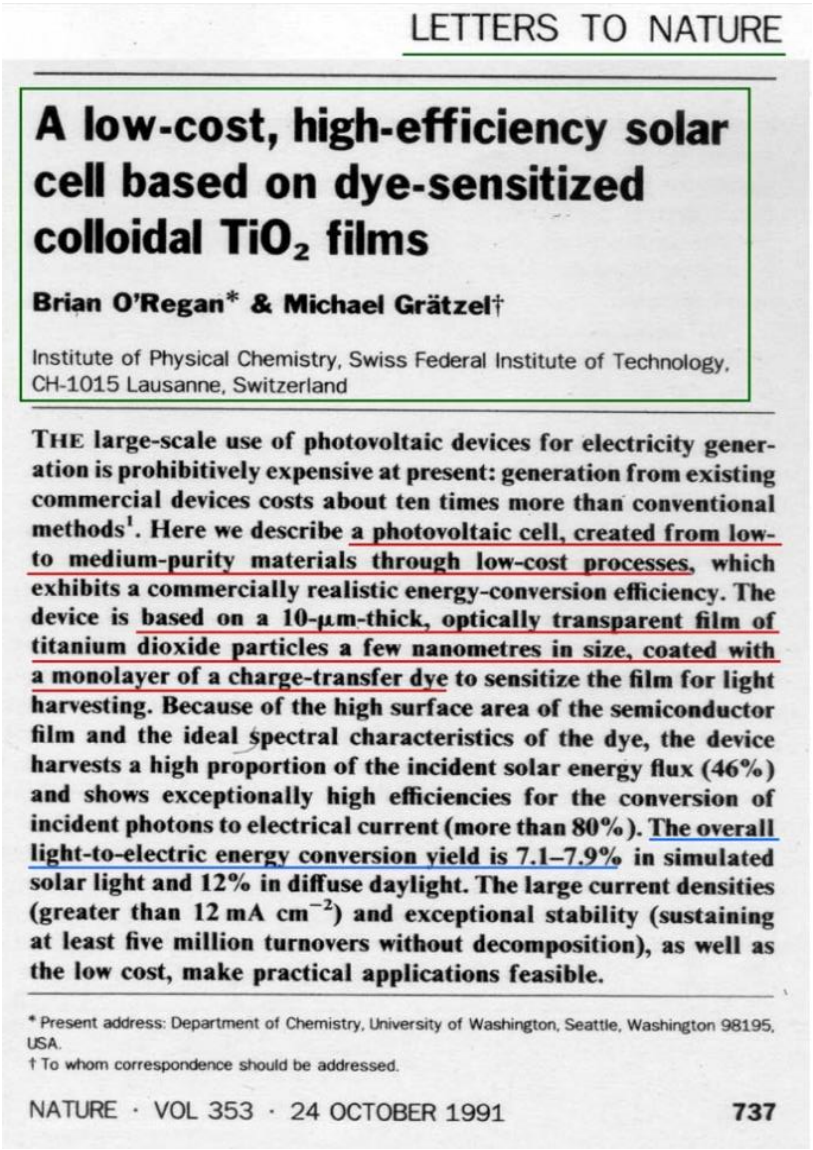
1. Introduction

Over the current decade, Energy demands have shot up drastically. Possible alternative sources for energy generation must be explored as soon as possible since existing fuels will mostly likely run out over the next fifty years or so.

In this respect, Dye-sensitized solar cells (DSSCs) are an attractive alternative because they are made from inexpensive materials that do not need to be highly purified and can be printed at low cost.

The benefits of this are

- it is inexpensive with only initial costs involved, and even these are recovered completely over the payback period since solar energy is free
- The solar energy is available directly at your home or the required destination and thus there are no transportation costs, losses or scale-ups involved.
- Solar energy is free, clean, and unlimited



LETTERS TO NATURE

A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films

Brian O'Regan* & Michael Grätzel†

Institute of Physical Chemistry, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland

THE large-scale use of photovoltaic devices for electricity generation is prohibitively expensive at present: generation from existing commercial devices costs about ten times more than conventional methods[1]. Here we describe a photovoltaic cell, created from low- to medium-purity materials through low-cost processes, which exhibits a commercially realistic energy-conversion efficiency. The device is based on a 10-μm-thick, optically transparent film of titanium dioxide particles a few nanometres in size, coated with a monolayer of a charge-transfer dye to sensitize the film for light harvesting. Because of the high surface area of the semiconductor film and the ideal spectral characteristics of the dye, the device harvests a high proportion of the incident solar energy flux (46%) and shows exceptionally high efficiencies for the conversion of incident photons to electrical current (more than 80%). The overall light-to-electric energy conversion yield is 7.1–7.9% in simulated solar light and 12% in diffuse daylight. The large current densities (greater than 12 mA cm^{-2}) and exceptional stability (sustaining at least five million turnovers without decomposition), as well as the low cost, make practical applications feasible.

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NATURE · VOL 353 · 24 OCTOBER 1991 737

Fig. 1

The original Research Paper by Michael Gratzel announcing the Invention of DSSC's

2. Overview

DSSCs are unique compared with almost all other kinds of solar cells in that electron transport, light absorption and hole transport are each handled by different materials in the cell. In a DSSC, light is absorbed by a sensitizer, which is anchored to the surface of a wide band semiconductor.The charge separation takes place at the **interface** via photo-induced electron injection from the dye into the conduction band of the semiconductor, and this charge is then conducted to power the load and then into the counter electrode.In this way, the electrons released by the dye pass through the photoanode and then into the load that needs to be powered through to the counter electrode which then conducts them through the electrolyte back into the photoanode. The cycle continues in this way.

The sensitizing dye (photosensitive dye that releases electrons in presence of light) in a DSSC is anchored to a wide-bandgap semiconductor such as TiO_2 or ZnO. When the dye absorbs light, the photoexcited electron rapidly transfers to the conduction band of the semiconductor, which carries the electron to one of the electrodes. A redox couple, usually comprised of iodide/triiodide (I^-/I_3^-), then reduces the oxidized dye back to its neutral state and transports the positive charge to the platinized counter-electrode.

In 1991, O'Regan and Grätzel demonstrated that a film of Titania (TiO_2) nanoparticles deposited on a DSC would act as a mesoporous n-type photoanode and thereby increase the available surface area for dye attachment by a factor of more than a thousand. This approach dramatically improved light absorption and brought power-conversion efficiencies into a range that allowed the DSSC to be viewed as a serious competitor to other solar cell technologies.
During the 1990s and the early 2000s, researchers found that organometallic complexes based on ruthenium provided the highest power-conversion efficiencies. Iodide/triiodide was found to be the most effective redox couple. The record power-conversion efficiency rapidly climbed to 10% in the late 1990s and then slowly settled to 11.5%.

The iodide/triiodide system has been particularly successful in DSSCs because of the slow recombination kinetics (reduction of back combination of released electrons into the dye due to time delays in conduction or due to holes left by previous electrons that bind the new ones) between electrons in the titania with the oxidized dye and the triiodide in the electrolyte, which leads to long-lived electron lifetimes (between ms and 1 s). Iodide reduces the oxidized dye to form an intermediate ionic species (such as I) that then disproportionates to triiodide and diffuses to the counter-electrode, providing two electrons per molecule, and relatively fast dye regeneration rates of the I. The slow recombination - redox couple have resulted in near-unity internal quantum efficiencies. The small size of the I–/I Redox components allows for relatively fast diffusion within the mesopores, and the two-electron system allows for a greater current to be passed for a given electrolyte concentration. Unfortunately, the I–/I system is corrosive and dissolves commonly used sealants and metals. This major challenges to DSSC's is what led to the development of alternative electrolytes, and similar technologies such as the Solid state DSSC.

2.1 -Aspects of a DSSC

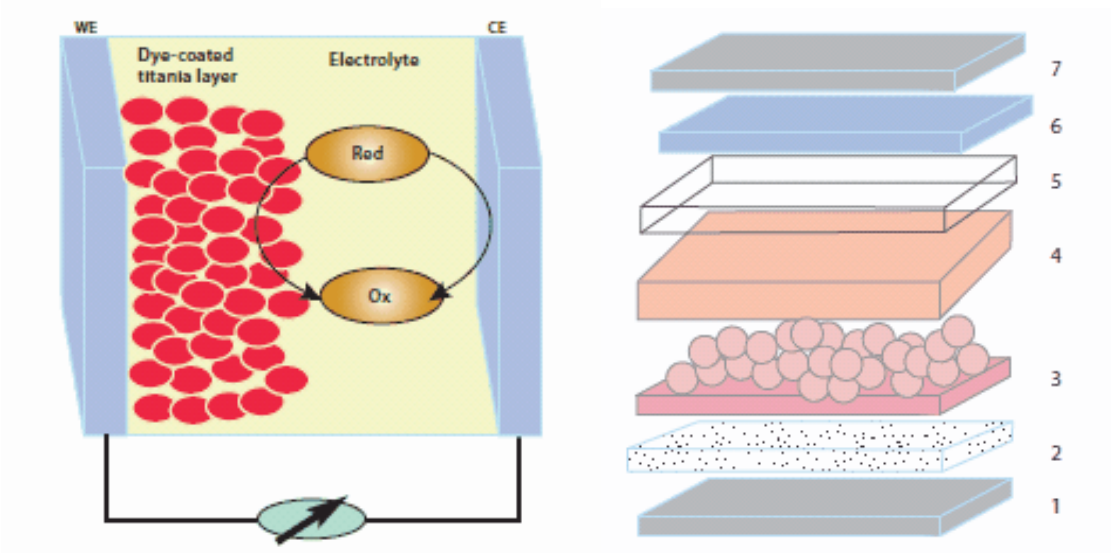


Fig. 2 – Exploded view of a dye-sensitized solar cell.
GRATZEL, M. and KALYANASUNSARAM, K., *Material Matters,* **2009,** 4.4, 88

Figure 2 gives an exploded view of a dye-sensitized solar cell showing key components:

1. Transparent conducting oxide, TCO (working electrode, WE);
2. Under layer (mesoporous oxide);
3. Photoactive mesoporous oxide with coated dye molecules;
4. Electrolyte containing redox mediators;
5. Sealing gasket/separator;
6. Finely divided Pt catalyst layer and
7. Transparent conducting oxide, TCO (counter-electrode, CE).

- **Nanostructured Photoelectrode**

  - In the **old generations** of photo-electrochemical solar cells (PSC) photo-electrodes were made from bulky semiconductor materials such as **Si, GaAs or CdS.**
  - However, these kinds of photo-electrodes when exposed to light they undergo **photo-corrosion** that results in poor stability of the photo-electrochemical cell.
  - The use of sensitized wide band-gap semiconductors such as **TiO_2, or ZnO** resulted in high chemical stability of the cell due to their resistance to photo-corrosion.
  - The problem with bulky single or poly-crystalline wide band gap is the low **light to current conversion efficiency** mainly due to inadequate adsorption of sensitizer because of limited surface area of the electrode.
  - One approach to enhance **light-harvesting efficiency (LHE)** and hence the light to current conversion efficiency is to increase surface area (the roughness factor) of the sensitized photo-electrode.

- **Nanoporous TiO_2 layer as a photo-electrode**

  - One of the important factors that affect the cell's efficiency is the **thickness** of the nanostructured TiO_2 layer which must be less than 20 nm to ensure that the diffusion length of the photoelectrons is greater than that of the nano-crystalline TiO_2 layer.
  - **TiO_2 is the most common**ly used nano-crystalline semiconductor oxide electrode in the DSSC as an electron acceptor to support a molecular or quantum dot QD sensitizer is TiO_2 (Grätzel, 2003).
  - Other wide band gap semiconductor oxides is becoming common is the **zinc oxide ZnO**. ZnO possesses a band gap of 3.37 eV and a large excitation binding energy of 60 meV.

- **Advantages of the Mesoporous Nano-Oxide Layers**

Photosensitization of semiconductors had been examined earlier with single crystal electrodes and the process was found to be relatively inefficient. Observed photocurrents were very low (few μA/cm), leading to an overall light conversion efficiency of <<1%. Several unique features of the DSC allow pronounced enhancement of the light energy efficiency.

1. Using mesoporous structures, it is possible to control the dye distribution on the surface to achieve locally high concentrations without any side effects.

2. The available surface area for dye distribution is considerably high in a mesoporous structure (surface roughness factor >1,000) and as such it is possible to achieve monolayer coverage without concentration quenching (electron depletion) as observed on flat surfaces.

3. It is also possible to have absorbance of >3 permitting near total absorption of visible light. However, increasing the surface area can lead to lower efficiencies due to the promotion of charge recombination before charges arrive at the collector electrode.

4. Excited state charge injection of an anchored dye to the conduction band of the oxide semiconductor permits a design where the forward electron transfer can occur much faster compared to the backward electron movement, i.e., relaxation of the dye to its ground state. A five to six orders of magnitude difference is feasible permitting near quantitative scavenging of all injected electrons.
5. In homogeneous solvents, back electron transfer tends to occur very rapidly, often within the primary cage itself. In addition to the above differences due to the morphology of the dye-coated oxide substrate, there are other important effects that are responsible for the high overall efficiency of this type of solar cell.

6. In contrast to the flat surfaces of macro-electrodes, a high concentration (typically 0.5 M) of iodide ions in the electrolyte effectively screens out any macroscopic electric fields.

7. Charge separation is primarily driven by the inherent energetics (redox potentials) of the different species at the TiO_2/dye/electrolyte interface rather than by the presence of macroscopic, electrostatic, potential energy gradients.

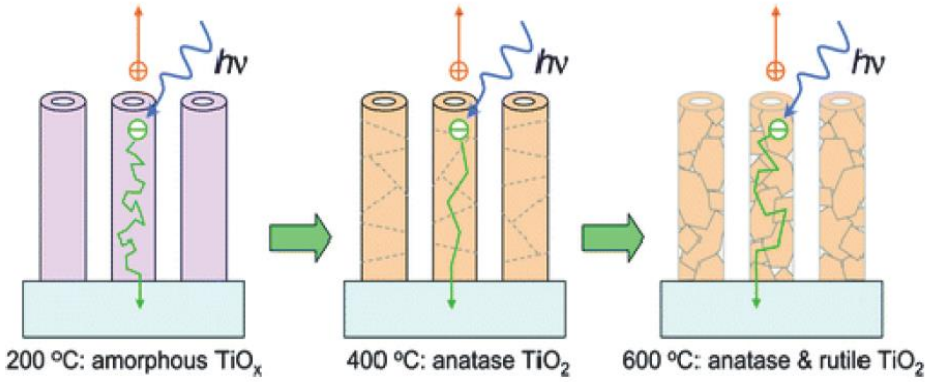


Fig.3 - Schematic illustration of the effects of annealing temperature on the charge-collection and light-harvesting properties of TiO2 nanotube-based dye-sensitized solar cells (Zhu et al., 2010).

- **Dye-Sensitizers**

  - Upon absorption of photon, a dye molecule adsorbed to the surface of TiO_2 gets oxidized and the excited electron is injected into the nanostructured TiO_2.
  - Among the first kind of promising sensitizers were **Polypyridyl compounds of Ru(II)** that have been investigated extensively.
  - E.g. $Ru(dcb)(bpy)_2$, $Os(dcbH_2)(bpy)_2$-$(PF6)_2$.
  - **Natural dye-** shiso leaf pigments, Black rice, Rosella, Natural anthocyanins, Henna etc.
  - The dye that we have been working on is an **Expanded-Porphyrin** (Chlorophyll and Haemoglobin component) based one. We are synthesizing the novel dye which is an expanded Porphyrin moiety.
  - The photosensitizer is the most important part of the DSSC since the electrons are released from this. The energy efficiency of the cell and current produced are ultimately dependent on the properties, purity, structure, functionality of the Sensitizer.

- **Some Sensitizer Moieties**

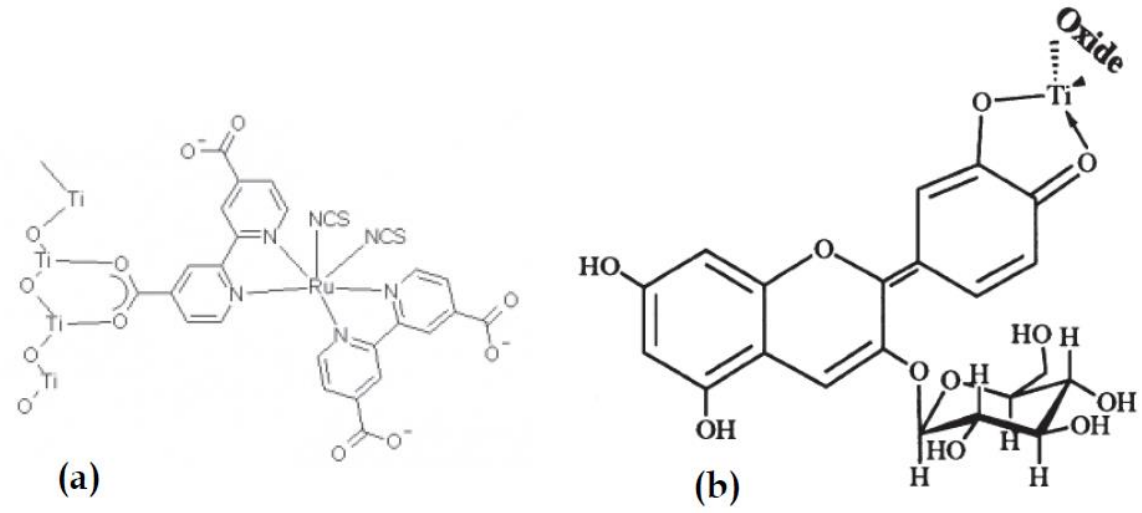


Fig 4.

(a) Ruthenium based red or "N3" dye adsorbed onto a titanium dioxide surface (Martinson et al., 2008), and

(b) Proposed structure of the cyanin dye adsorbed to one of the titanium metal centers on the titanium dioxide surface (Smestad et al., 1988).

- The above **N3 dye** it has been an outstanding solar light absorber and charge-transfer sensitizer.
- The red dye or N3 dye is capable of absorbing photons of wavelength ranging from 400 nm to 900 nm dueto**metal to ligand charge transfer transition**.

- **Light harvesting efficiency (LHE)**

$$LHE(\lambda) = \left(1 - 10^{-A(\lambda)}\right) \times 100$$

- A (λ) is the absorbance of the sample at specific wavelength.
- LHE increases with concentration of dye extract

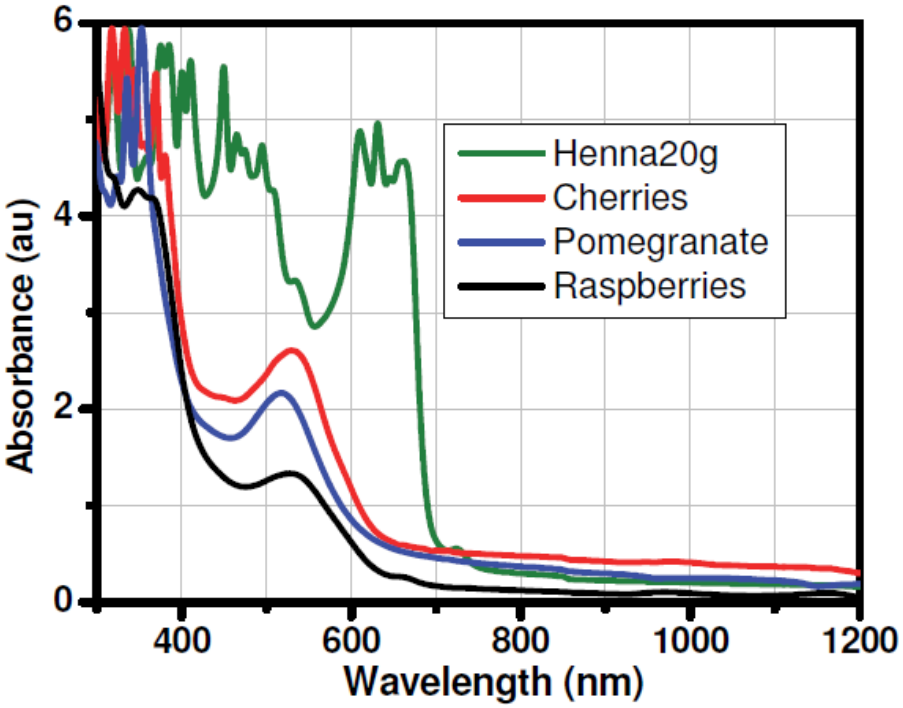


Fig 5. - The Absorbance Spectra of some common dyes, many of which contain Porphyrin moieties. (Zhu et al., 2010)

- **Redox electrolyte**

  - Electrolyte containing **I^-/I^{3-} redox** ions is used in DSSC to regenerate the oxidized dye molecules and hence completing the electric circuit by mediating electrons between the nanostructured electrode and counter electrode.
  - **NaI, LiI and R_4NI** (tetraalkylammonium iodide) are well known examples of mixture of iodide usually dissolved in **aprotic solvents** such as acetonitrile, propylene carbonate and propionitrile to make electrolyte.
  - **Cell performance** is greatly affected by ion conductivity in the electrolyte which is directly affected by the viscosity of the solvent.
  - Innovative classes of electrolytes such as polymeric conductor, PEDOT or PEDOT: TMA, Poly (vinylidene fluoride-co-hexafluoropropylene) to the KI/I2.
  - Zhang et al., investigated organic indoline dye D131 as the sensitizer and poly (3- hexylthiophene) (P3HT) as the hole transporter.

2.2 – Principle and Working of a DSSC

A dye-sensitized solar cell (DSSC), in essence, is a sandwich structure made of two conducting oxide electrodes with an organic redox electrolyte filling the interlayer separation.

The heart of the solar cell is the mesoporous wide band-gap oxide layer deposited onto aconducting oxide substrate. This oxide layer is composed of nano-sized particles that have been sintered together toallow electronic conduction to take place. It has a spongy-like structure that upon immersion in a dye solution picks up the dye molecules giving an intense coloration. Exposure of the solar cell to visible light leads to electronic excitation of the dye, D, to an excited state form (D*), which can inject electrons to the conduction band of the oxide semiconductor.

The original state of the dye D (D+) is subsequently restored by the reduction of the oxidized form of the dye by theredox electrolyte. In the most widely studied version of DSC, the electrolyte is an iodide/triiodide mix dissolved in an organic medium. Electrons injected in the oxide layer hop through the network of the nano-sized particles to reach the back collectorelectrode. Under closed circuit conditions, the electrons flow over the external circuit to arrive at the counter electrodeand reduce the oxidized form of the redox mediator.
This sequence of reactions constitute a light-induced oxidation-reduction cycle or photosensitization of the semiconductor electrode.

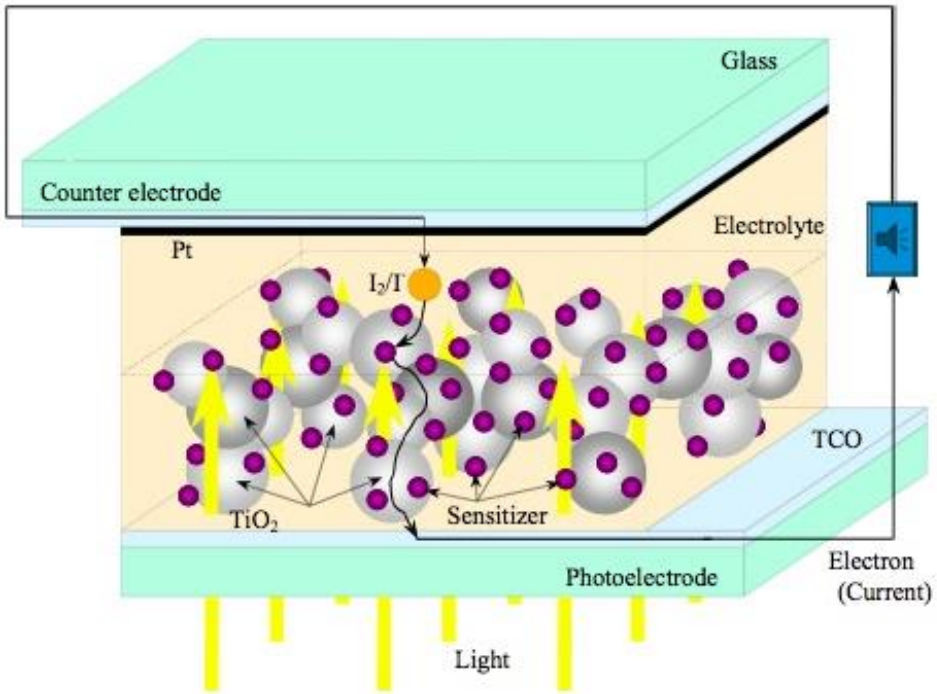


Fig. 6 – DSSC Schematic (Martinson, 2008)

2.3 – Device Schematic and Operation Characteristics of a DSSC

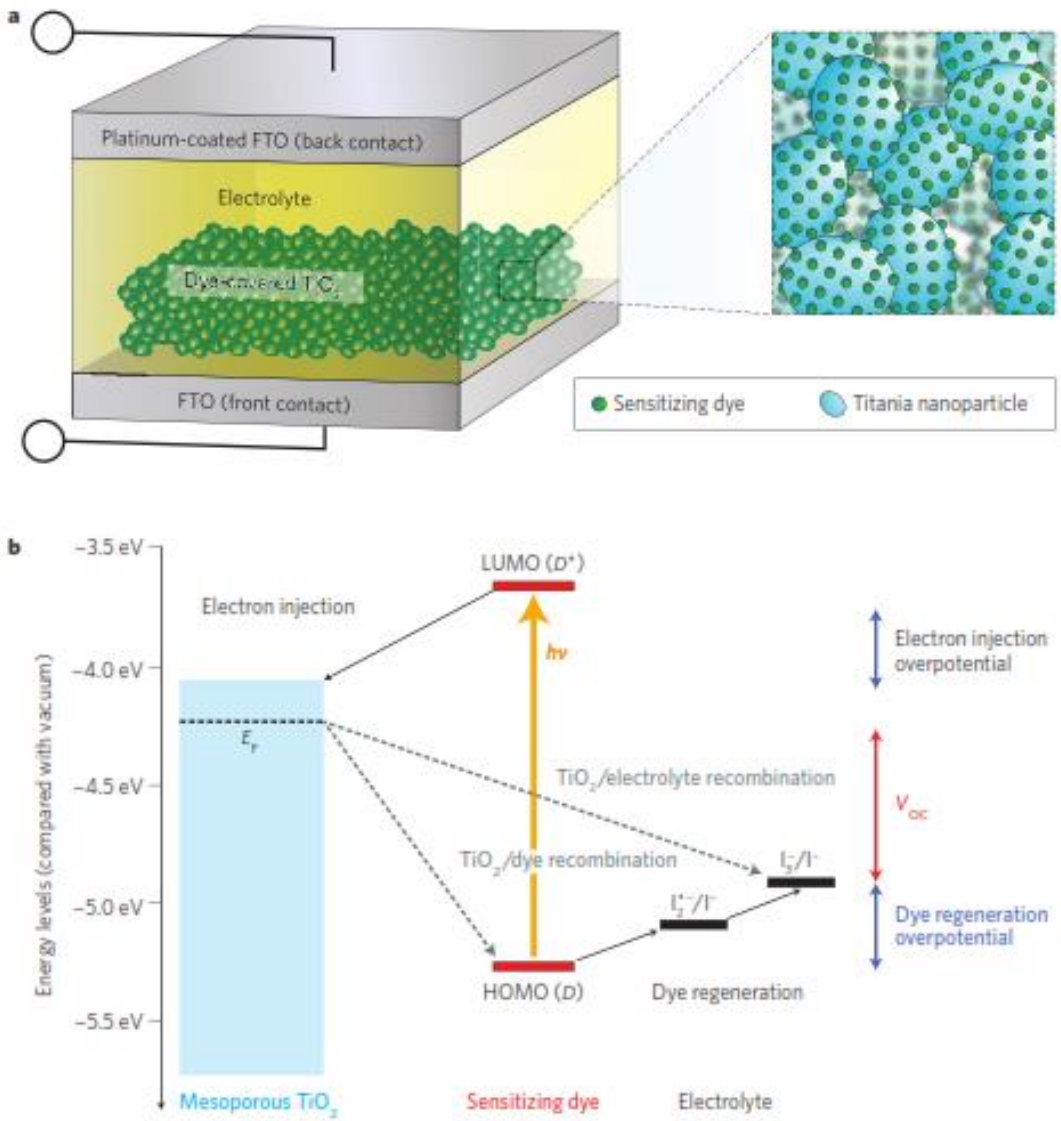


Fig. 7. (Grätzel M., Material Matters, 2009)

a - Dye-sensitized solar cell device schematic and operation
b - HOMO-LUMO Levels and Fermi Energy Levels of the Titania

a. Liquid-based DSSCs are comprised of a transparent conducting oxide (such as fluorine-doped tin oxide, FTO) on glass, a nanoparticle photoanode (such as titania) covered in a monolayer of sensitizing dye, a hole-conducting electrolyte and a platinum-coated, FTO-coated glass back-contact.

b. Energy level and device operation of DSCs; the sensitizing dye absorbs a photon (energy *h*v), the electron is injected into the conduction band of the metal oxide (Titania) and travels to the front electrode (not shown). The oxidized dye is reduced by the electrolyte, which is regenerated at the counter-electrode (not shown) to complete the circuit. *V* is determined by the Fermi level (*E*) of Titania and the redox potential (I^-/I_3^-) of the electrolyte

2.4 – Electron Transfer Process Sequence and Schematic

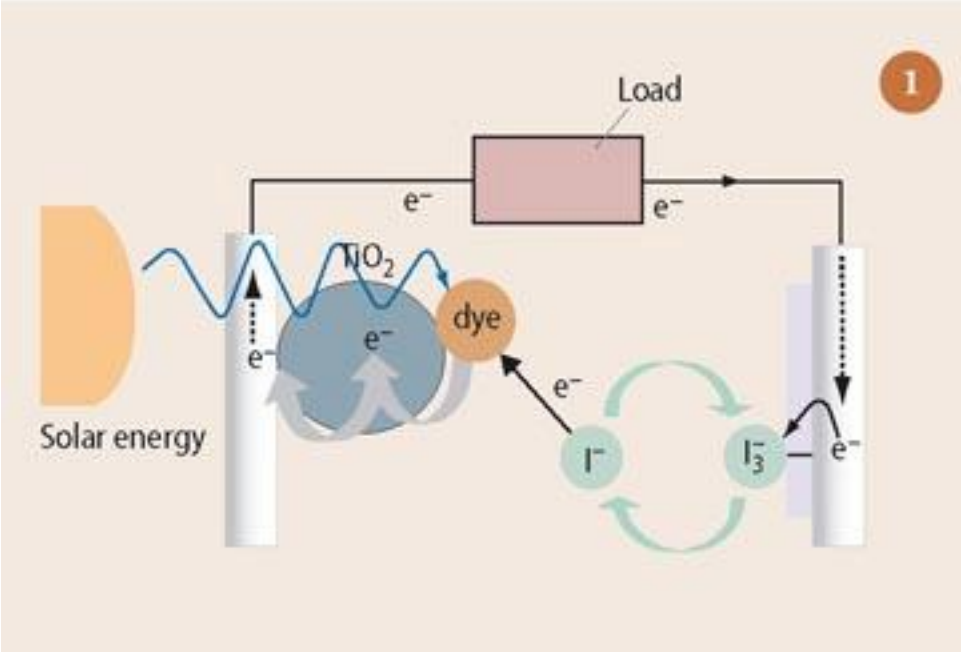


Fig 8. – Electron Transfer Sequence (Zhu et al., 2008)

$$S + photon \rightarrow S^* \qquad \text{(2) Excitation process}$$

$$S^* + TiO_2 \rightarrow e^-_{(TiO_2)} + S^+ \qquad \text{(3) Injection process}$$

$$e^-_{(TiO_2)} + C.E. \rightarrow TiO_2 + e^-_{(C.E)} + \text{electrical energy} \qquad \text{(4) Energy generation}$$

$$S^+ + \frac{3}{2}I^- \rightarrow S + \frac{1}{2}I_3^- \qquad \text{(5) Regeneration of dye}$$

$$\frac{1}{2}I_3^- + e^-_{(C.E.)} \rightarrow \frac{3}{2}I^- + C.E. \qquad \text{(6) e- Recapture reaction}$$

S = Sensitizer
TiO_2= Photoanode Titania Nanomaterial
C.E = Counter Electrode (Platinum)
I, I_3^- = Iodide Couple
e- = Electron

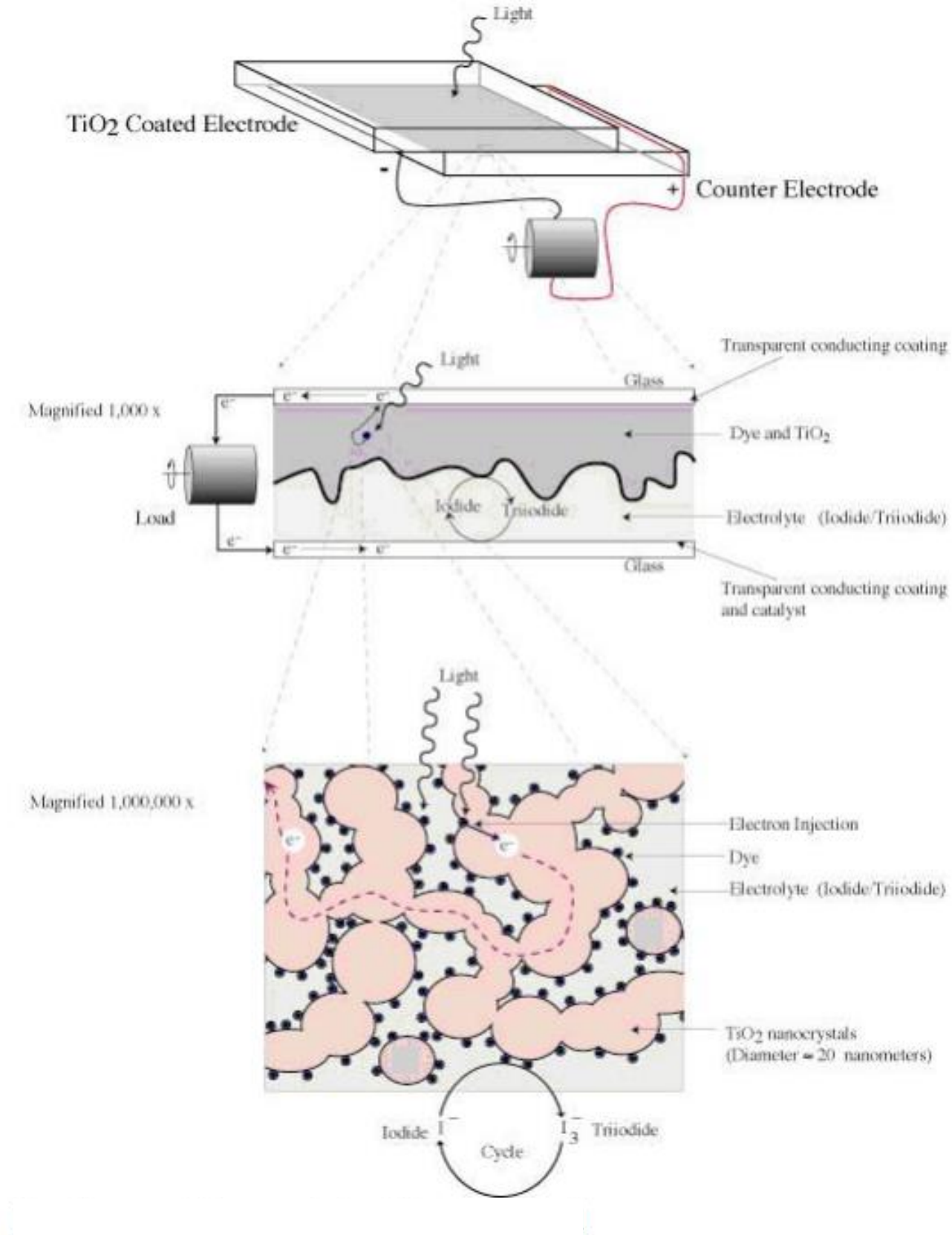


Fig 9. – DSSC Magnified (Kalyanasundaram et al., Nature, 2013)

2.5 – Main Issues and Challenges in DSSC Fabrication

- **Required -** Injection of electrons is fast and efficient.
- **Problems -**
  - Due to evaporation, liquid electrolyte inhibits fabrication of multi-cell modules.
  - Leakage of the electrolyte.
  - Corrosive nature of Iodide Electrolyte.

2.6 – Key Parameter Requirements

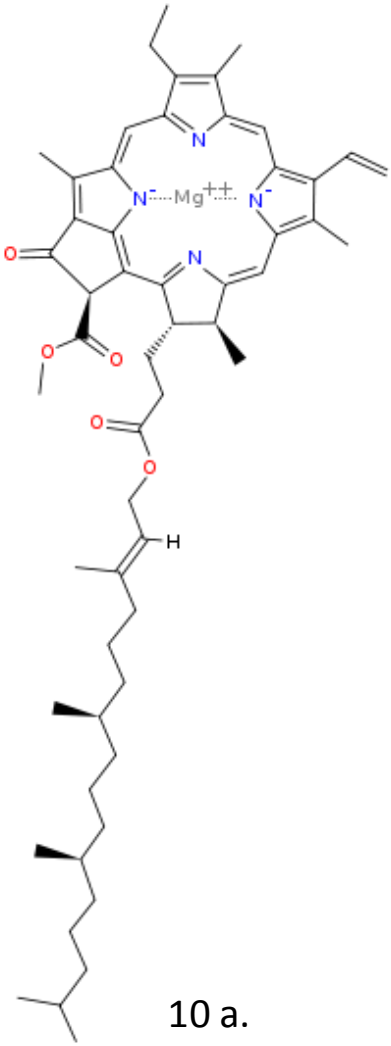
- In conclusion, **Fast recovery** of the Sensitizer is important for attaining long term stability.
- Also, **long-lasting charge separation** is a very important key factor to the performance of solar cells.
- **Backward Charge Recombination** must be prevented or reduced to a maximum.

3 – Scope of Our Work

Steps involved in the Design and Fabrication of the DSSC are:

1. Design of the Dye Photosensitizer.
2. Molecular engineering of the Dye Photosensitizer.
3. HOMO-LUMO Studies and Molecular Modelling of the Dye Sensitizer.
4. Synthesis of the Dye Sensitizer and Spectral Confirmations.
5. Design and Synthesis of the Photoanode and subsequent infusion of the Dye Sensitizer onto it.
6. Electrode Fabrication and Spin Coating of the Dye Sensitizer onto the Titania Photoanode.
7. Impregnation of Electrolyte or Redox Couple and Sealing.
8. Cyclic Voltammetry Studies and IPCE (Incident Photon Power Conversion Efficiency) efficiency measurements.

4 – Porphyrin Macrocycles

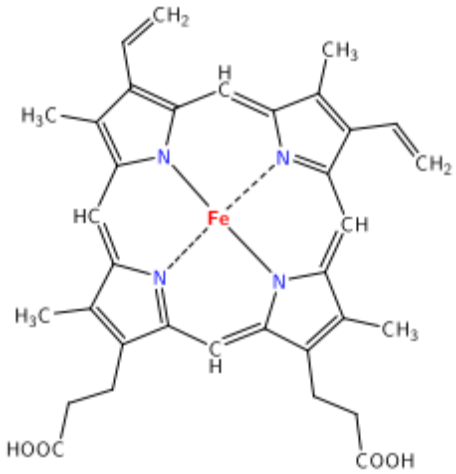


10 a.

Fig. 10 – (Google Images)

a. Structure of Chlorophyll A
b. Heme Protein in hemoglobin

We observe both contain a 4-membered ring macro-cycle which is nothing but a Porphyrin as the one used in our sensitizer.



10 b.

Incident light excites electrons in Porphyrin ring. Chlorophyll injects electrons from excitedlevels into the conduction band giving an anodic photocurrent. Charge separation is irreversible. The electrolyte is oxidized at the chlorophyll molecule and is reduced at the cathode to complete the circuit. They then used this process to measure the absorption spectrum of various chlorophylls and other natural organic dyes.

In the absence of an energy gap the charged chlorophyll molecule is quenched since both holes and electrons can be conducted in metals. They used ZnO semiconductor anode, and Platinum cathode in KCl electrolyte solution.

Both chlorophyll and Haemoglobin have Porphyrin macrocycles. The purpose is a bit different. In chlorophyll it is used for energy capture as in the form of solar energy and conversion while in haemoglobin it is used for electron transfer processes. In chlorophyll a magnesium atom is complexed while in Haemoglobin, an Iron atom is complexed in the Heme moiety.

5 –Photo-Sensitizers

5.1 – Some Common Sensitizers and Efficiencies

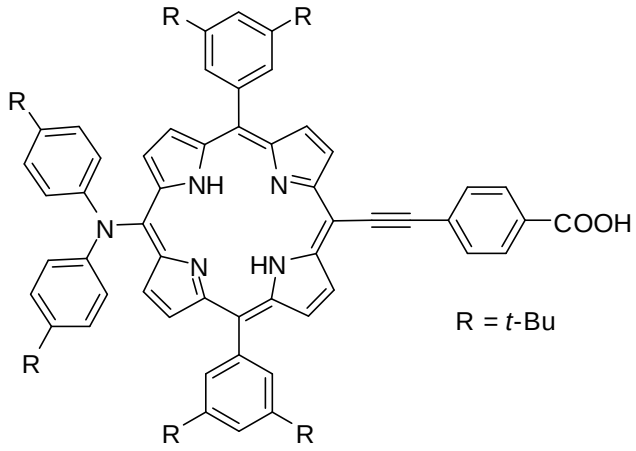


Fig. 11 –

Reported Dye efficiency of 6% in 2009 by Chen-Yu Yeh et al. (Porphyrin)

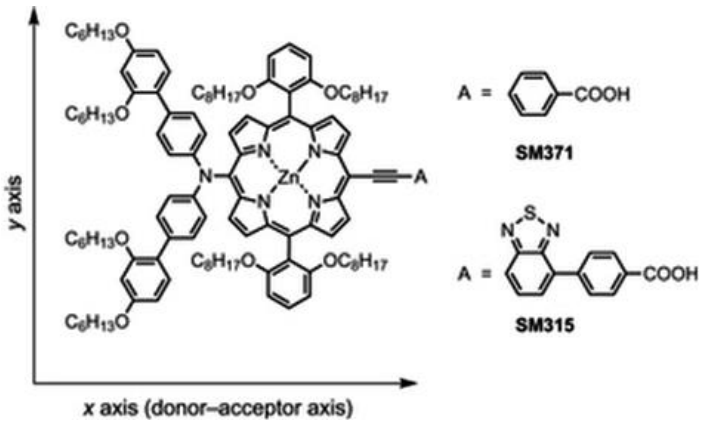


Fig. 12 -

Reported Dye Efficiency of 12-13% in 2014 by Grätzel et al. (Porphyrin)

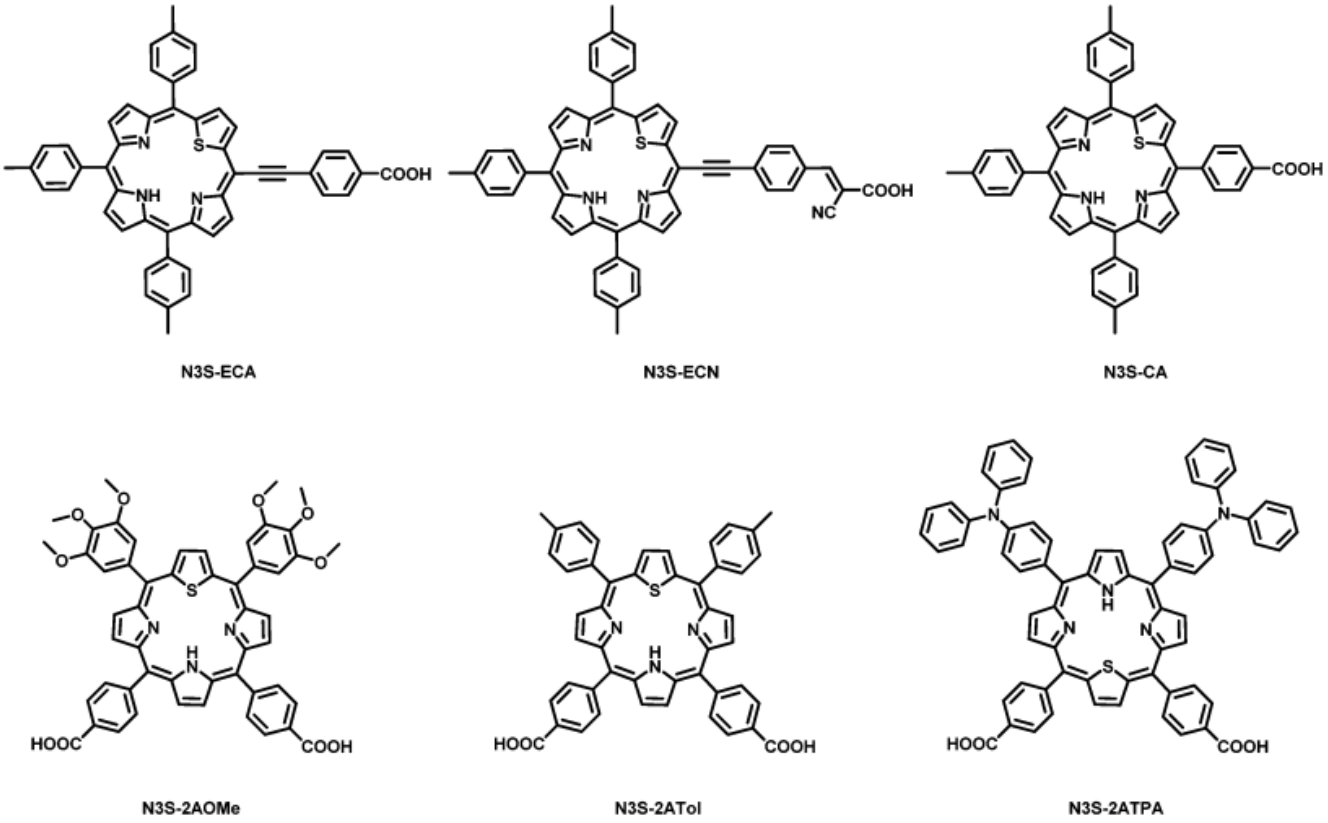


Table 2 Photovoltaic parameters of thiaporphyrin dyes

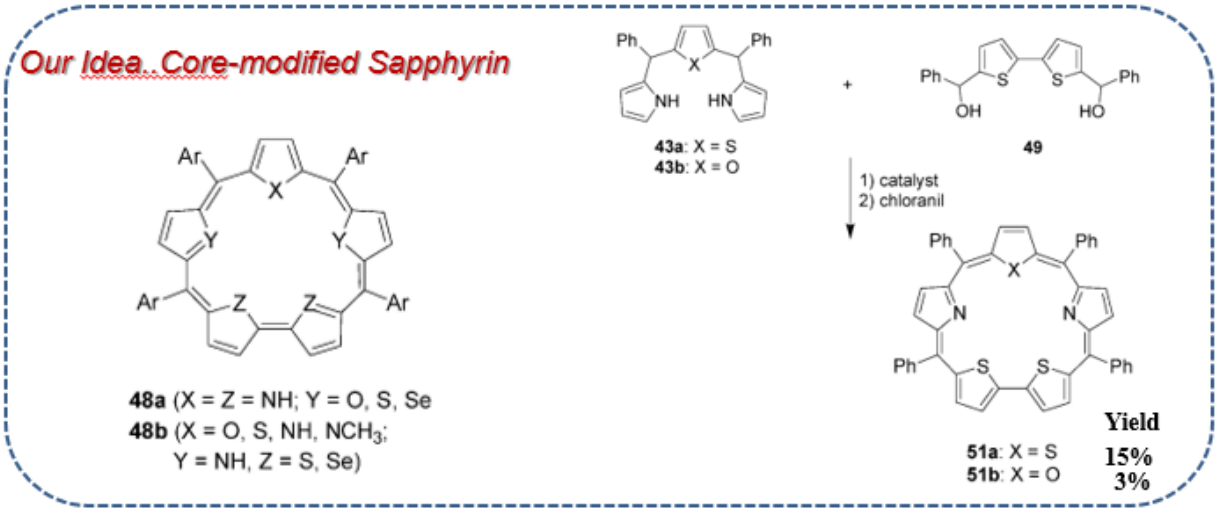
Dye	J_{sc} (mA cm^{-2})	V_{oc} (V)	ff (%)	η (%)
N3S-ECA	0.89	0.41	0.55	0.20
N3S-ECN	5.12	0.49	0.67	1.69
N3S-CA	1.29	0.48	0.64	0.40
N3S-2AOMe	0.67	0.45	0.57	0.17
N3S-2ATol	1.52	0.47	0.65	0.46
N3S-2ATPA	2.84	0.48	0.63	0.86

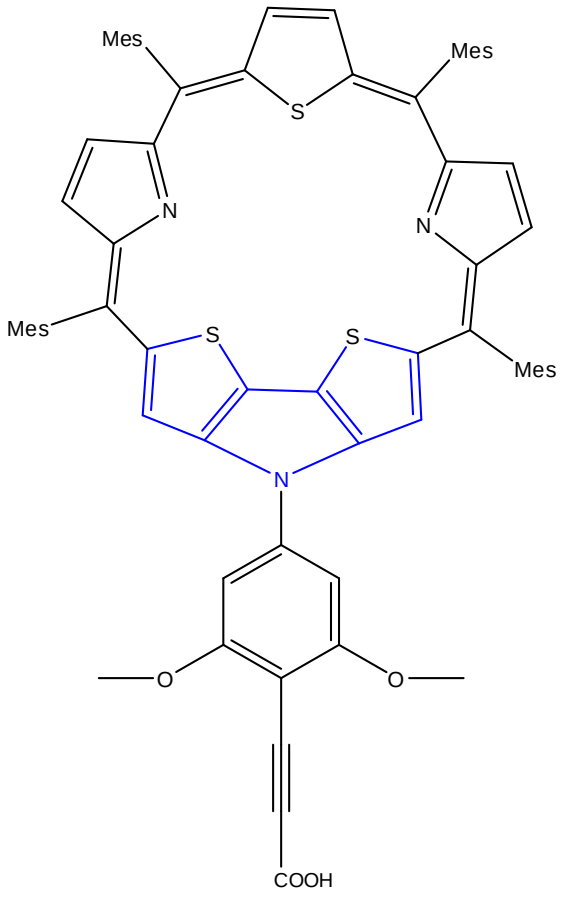
Fig. 13 – Standard Dyes and their Efficiencies.

(Review Paper, Balasingam, 2013)

6- Methodology

6.1 –Scheme





The exact Core-Modified Sapphyrin fused with Dithienopyrrole moiety that our work was on

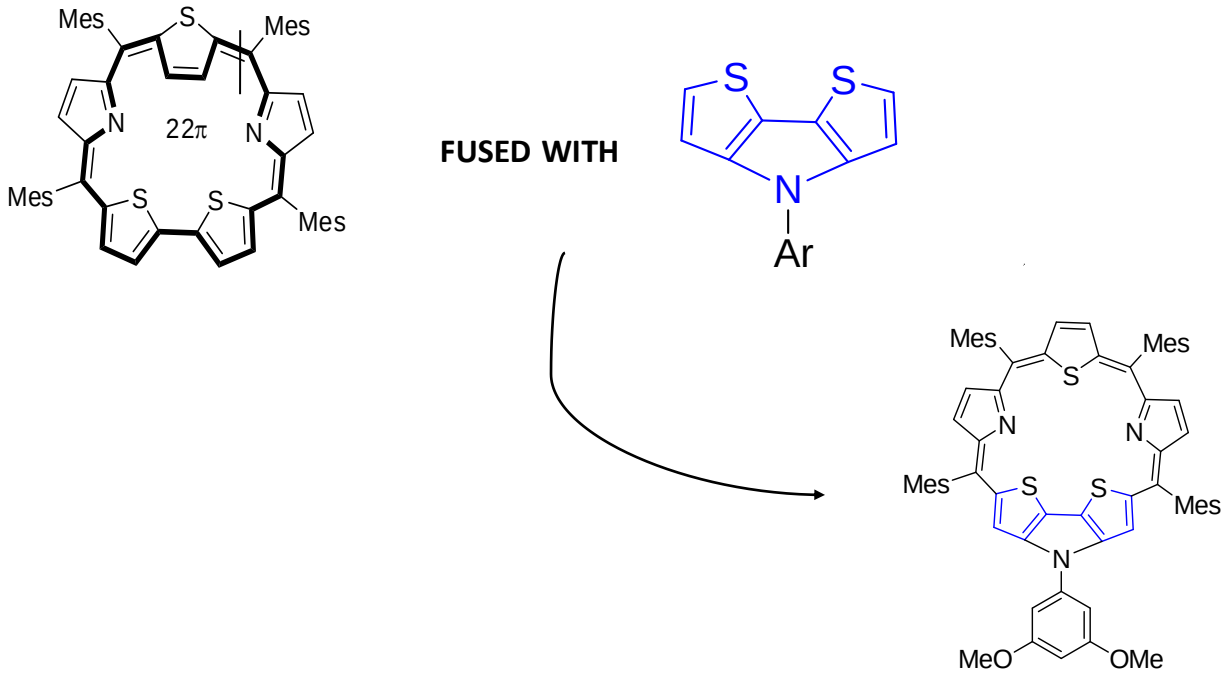
This sensitizer molecule above is what we are synthesizing. It is called a core modified Sapphyrin (Another name for 5-membered Expanded Porphyrin) that is made using a "3"+"2" approach because we synthesize the 3-membered top part of the molecule in one step and the 2-membered bottom part in the next step and then combine the both to get a 5-membered Sapphyrin (Expanded Porphyrin) molecule of the sensitizer.

6.2 – Why Dithienopyrrole ?

Dithienopyrrole based oligomers (Polymers) are extensively used in OLED (Organic LED's and Organic Semiconductors, Diodes etc.) . They have very good optical properties and have given dye sensitizers whose efficiencies are comparable to that of Porphyrin and Ruthenium dyes.

On the other hand, Porphyrin is nature's favourite pigment present in Haemoglobin and chlorophyll and has proven to be extremely efficient as a dye. What we have made is an expanded Porphyrin (Sapphyrin) based dye sensitizer which has more resonance (Conjugation) than Porphyrin itself thus causing the UV absorption spectra to red shift (To longer wavelength) and thus absorb a larger region of the Solar Spectra. This directly raises the efficiency of electron release of the DSSC and in turn the Power Generation efficiency of the DSSC itself.

What we have done is to synthesize a molecule that incorporates both these excellent optical property possessing moieties and create a fused ring system in order to compare the change in optical properties and electronic properties since we expect a great improvement in the cell efficiency.



6.3 – A Dithienopyrrole Sensitizer

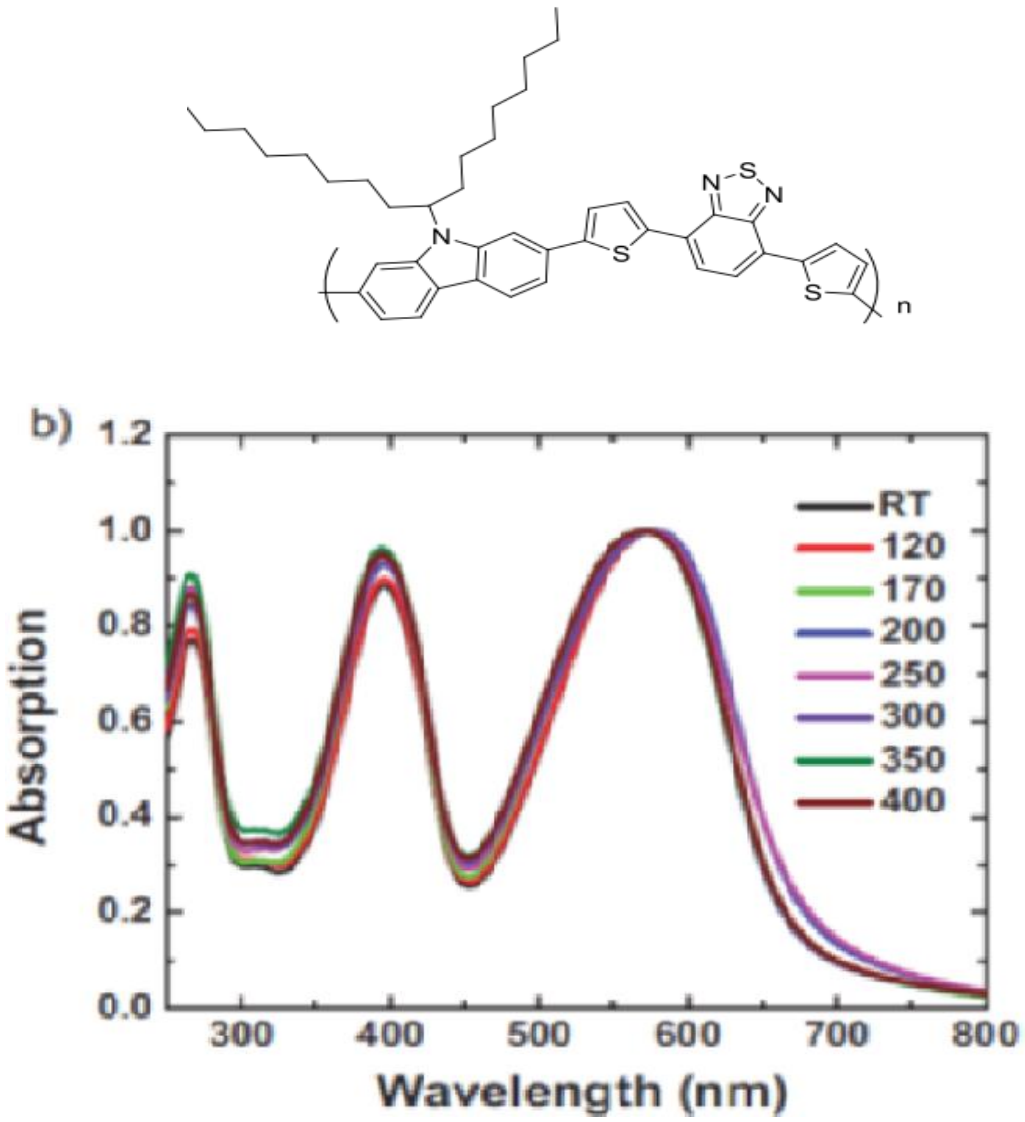
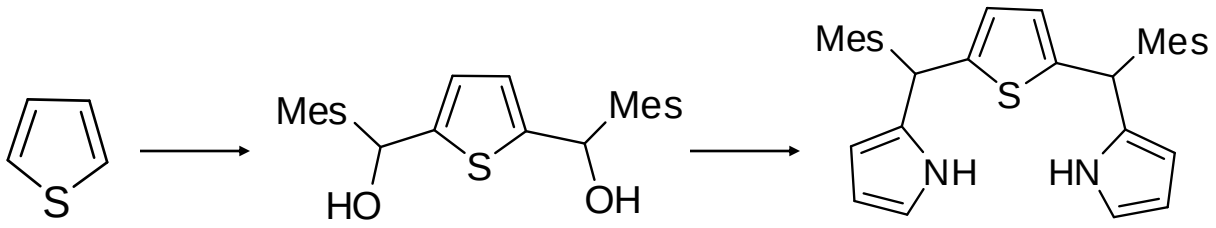


Fig. 14 – UV Absorption Spectra of the Dithienopyrrole moiety (Zoom Solarmer Catalog, 2014)

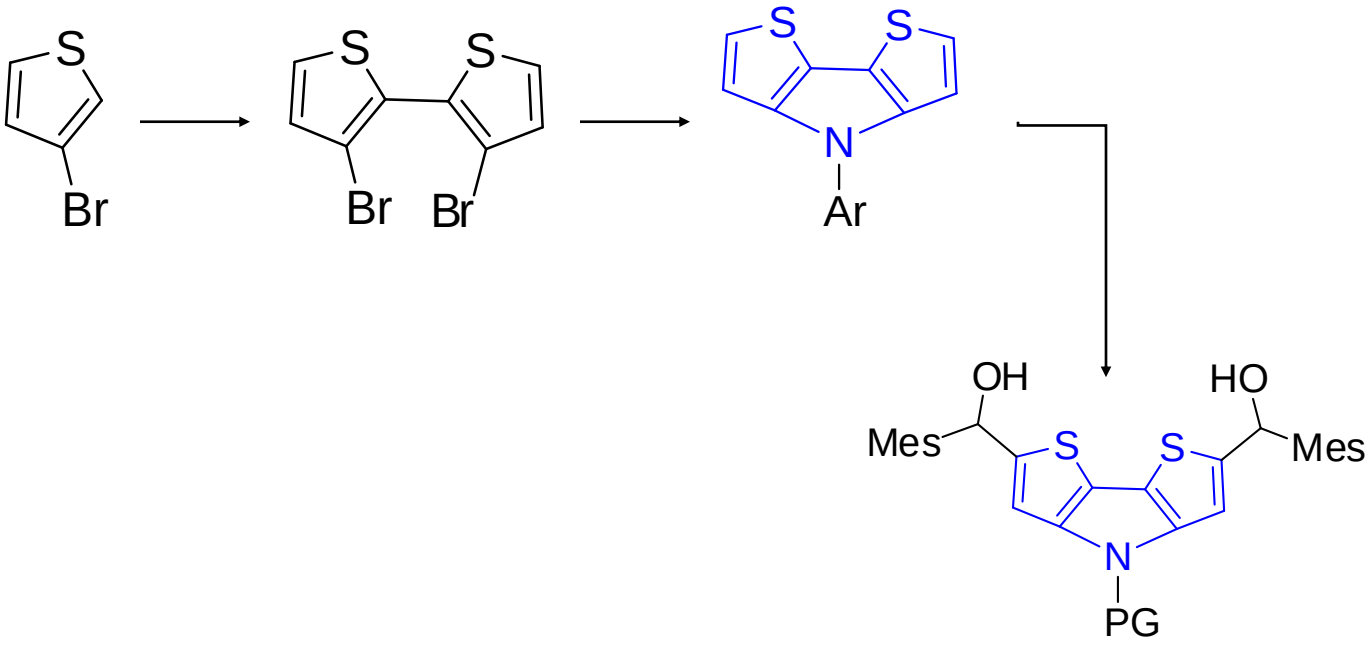
We observe the Dithienopyrrole moiety's UV Absorption spectra spreading over the entire Spectrum. This is what is indicative of high efficiencies since the more are is covered in the spectra, the more fraction of the Solar Spectrum is harnessed by the sensitizer since it is absorbed and consequently the more number of electrons are released and a higher Power Generation efficiency of the cell is observed.

6.4 - Synthetic Scheme

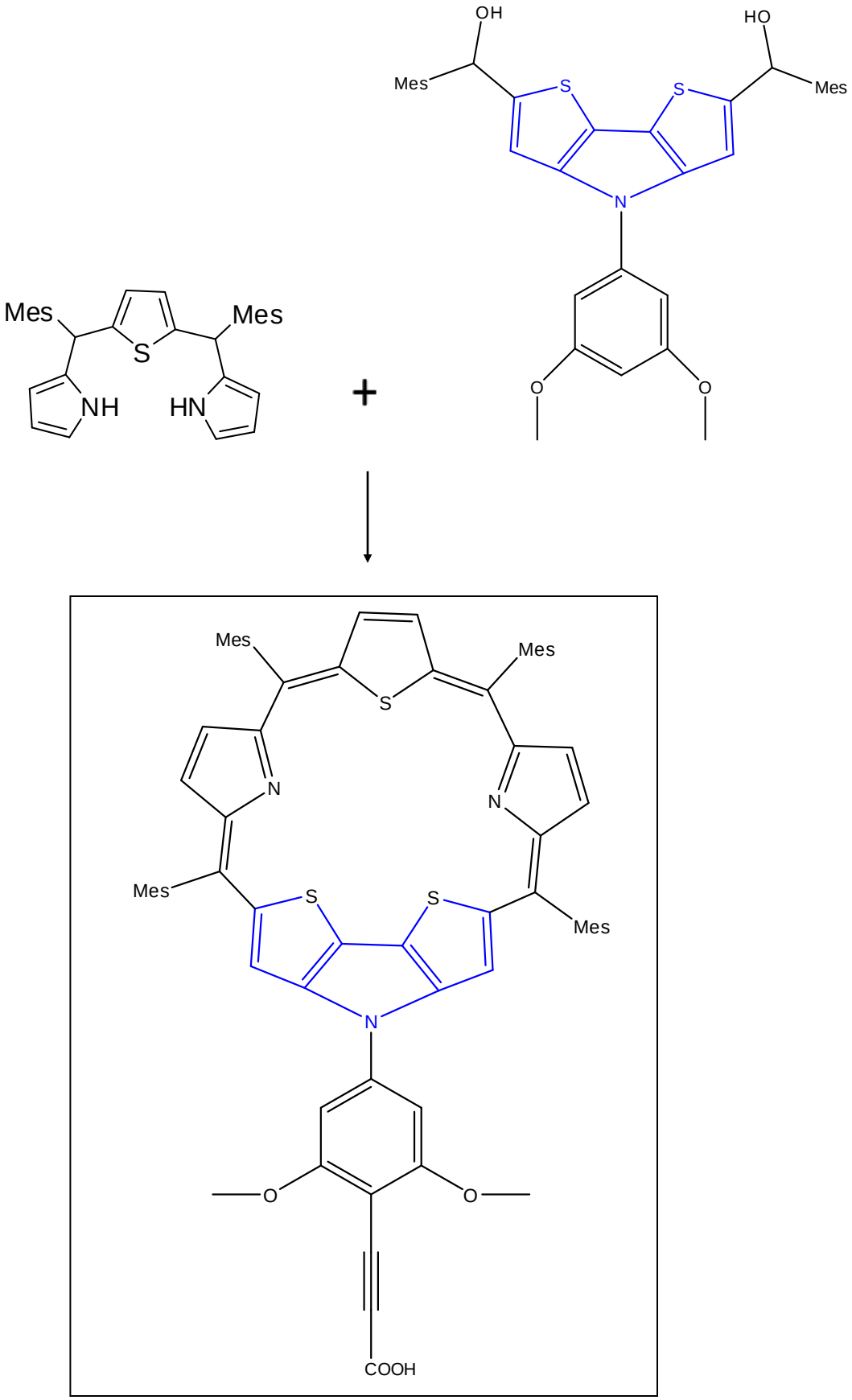
Part A – Synthesis of the 3 Segment Top Portion of the Sapphyrin



Part B – Synthesis of the 2 Segment Bottom Portion of the Sapphyrin



Part C – Coupling Reaction of the 3 and2 Segment Portions of the Sapphyrin



6.5 - Synthetic Procedure

The synthetic procedure involves 6 steps:

Part A – Synthesis of the 3 Segment Top Portion of the Sapphyrin

1. Synthesis of 2,5 Bis (mesitylhydroxymethyl) Thiophene from Thiophene

   (Ref – RAVIKANTH, M. Synthesis of functionalize d core-modified sapphyrins and covalently linked Porphyrin - Sapphyrin dyads, *Tetrahedron, 2012, 68, 1306-1314*)

2. Synthesis of 5,10-dimesityl-16-thiatripyrrane from 2,5 Bis (mesitylhydroxymethyl) Thiophene

   (Ref – RAVIKANTH, M. Synthesis of functionalize d core-modified sapphyrins and covalently linked Porphyrin - Sapphyrin dyads, *Tetrahedron, 2012, 68, 1306-1314*)

Part B – Synthesis of the 2 Segment Bottom Portion of the Sapphyrin

1. Synthesis of 3,3' -Dibromo 2,2'-Bithiophene from 3 – Bromo Thiophene

   (Ref – PATIL, SATISH. Polymer solar cells: design of materials by donor–acceptor approach. *Current Science, 2013, 105, 8.)*

2. Synthesis of N-(Dimethoxy Phenyl) Dithienopyrrole from 3,3' – Dibromo 2,2'-Bithiophene

   (Ref – ADRONOV, ALEX. Supramolecular Functionalization of Single-Walled Carbon Nanotubes (SWNTs) with Dithieno [3,2- b:2 0,3 0-d] pyrrole (DTP) Containing Conjugated Polymers. *Macromolecules, 2011, 44, 9138-9145.)*

3. Synthesis of 2,5Bis(mesitylhydroxymethyl) N-Aryl Dithienopyrrole from N-Aryl Dithienopyrrole

   (Ref – RAVIKANTH, M. Synthesis of functionalize d core-modified sapphyrins and covalently linked Porphyrin - Sapphyrin dyads, *Tetrahedron, 2012, 68, 1306-1314*)

Part C – Synthesis of the 2 Segment Bottom Portion of the Sapphyrin

1. Coupling Reaction of the 3 Segment and 2 Segment portions of the Sapphyrin following a "3+2" Approach.

   (Ref – RAVIKANTH, M. Synthesis of functionalize d core-modified sapphyrins and covalently linked Porphyrin - Sapphyrin dyads, *Tetrahedron, 2012, 68, 1306-1314*)

7 – Results and Discussions

7.1 - Thin Layer Chromatography (TLC) Studies

Thin layer Chromatography is a method of analysis used for checking the progress of reactions, purity of products obtained, extent of reactions, and gives an idea of the progress of a particular step. It can be used qualitatively as well as quantitatively. Here, we have used it qualitatively, in order to compare and verify if our required product has been formed in the reaction and if the reaction has been completed or not.

In this method, there is a thin TLC Plate that is usually coated with Silica Gel Nanoparticles or Alumina Nanoparticles. Alumina plates are used when our substrate might decompose in low pH (acidic conditions) or binds to silica gel strongly.

The substrate to be checked or the reaction mixture is dissolved in a low boiling solvent usually and is spotted on the plate using a capillary tube. Another spot containing the starting materials or the starting reaction mixture (crude) is spotted for reference. Now, both the spots are done. Then the plate is placed in a small vial called the TLC chamber, which contains little of the eluting solvent but not too much that the spots dissolve.

After elution, each substrate elutes to a certain height depending on its **Retention factor**, which is dependent on a number of things like Polarity of eluting solvent, polarities of substrates, binding affinity to silica gel, solubility in the eluting solvent, and these lengths are usually characteristic to that substrate in those polarity and solvent conditions. Though sometimes, more than one substrate can have similar Retention factors.

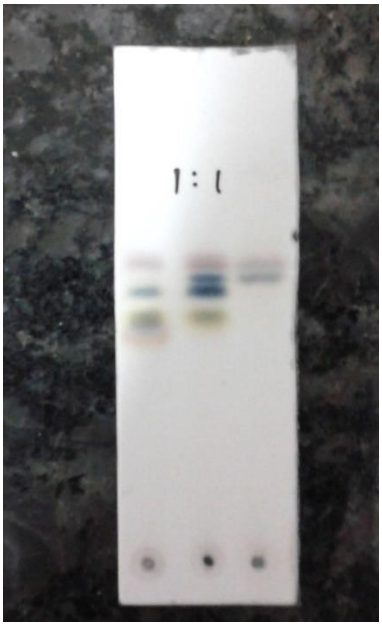


Fig. 15 – Sample TLC Spectrum

The TLC Studies were done at every step of the synthesis to confirm the formation of products, consumption of materials, and reaction extents. Exact structures were confirmed using NMR and Mass Spectrometry.

7.2 - Nuclear Magnetic Resonance (NMR) Spectral Analyses

Nuclear Magnetic Resonance Spectral analyses were done. NMR analyses are based on the magnetic spin of atoms present in a compound when present in an external magnetic field. The spinning electrons once de-excited in the atoms give a spectra that is characteristic to the compound. It informs us about the positions and number of atoms of that type (in this case Hydrogen-NMR) and their coupling constants and structural information of the compound.

NMR - Reference Sapphyrin Synthesis

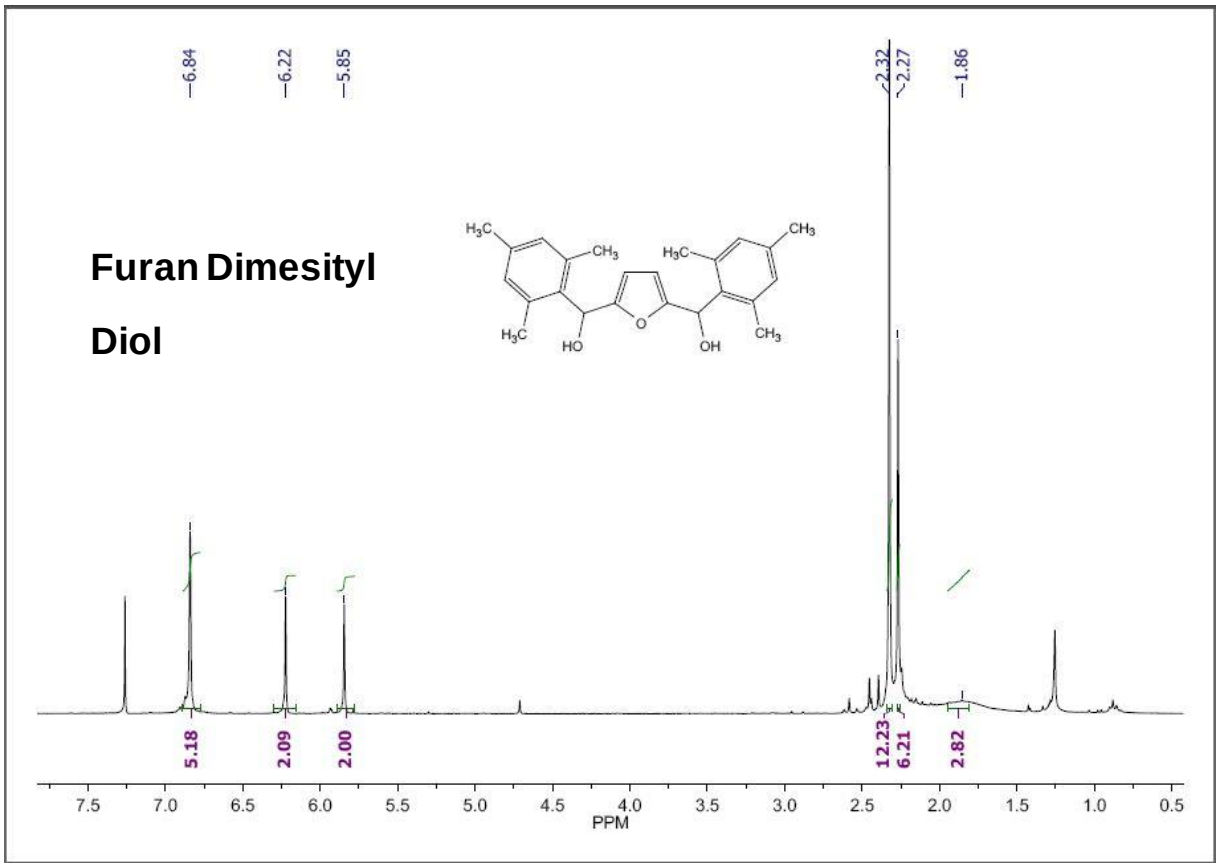


Fig. 16 – NMR Spectral Confirmation of a base material in the synthetic scheme of the reference Sapphyrin

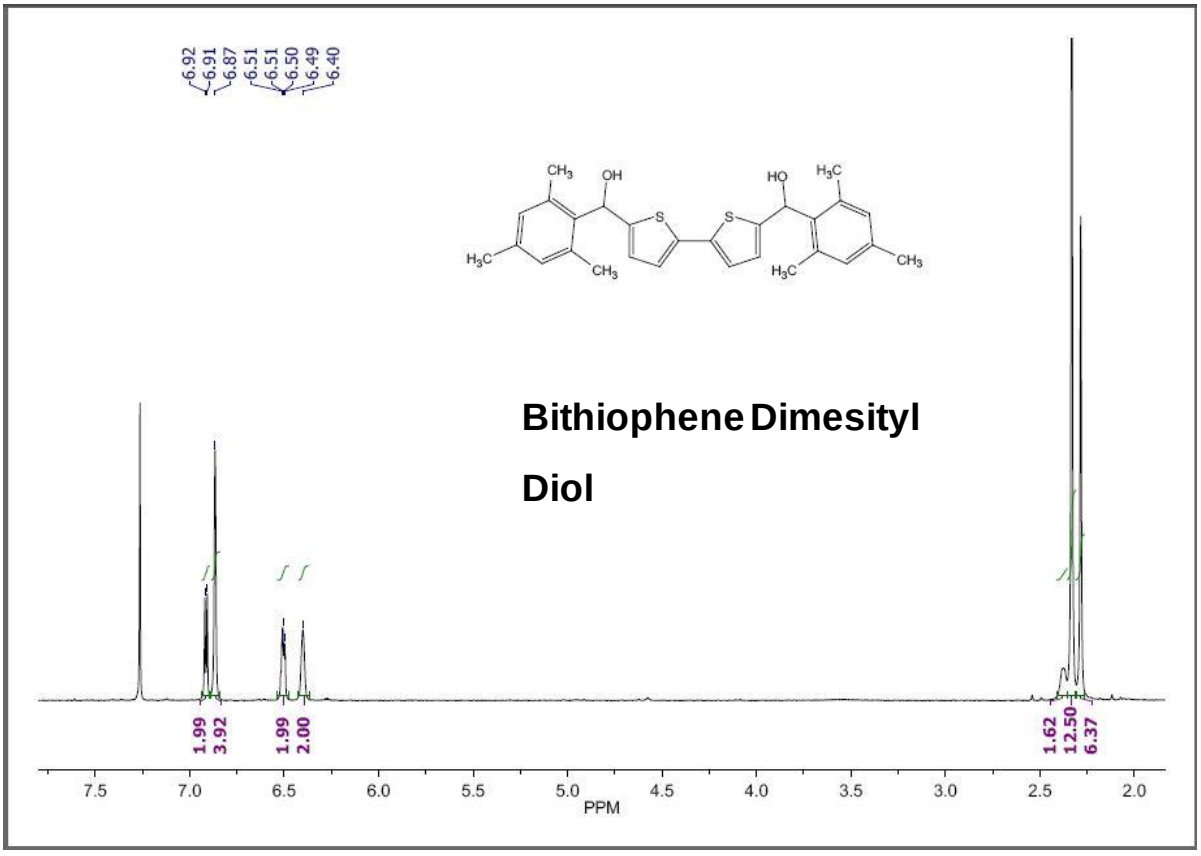


Fig. 17 – NMR Spectral Confirmation of a base material in the synthetic scheme of the reference Sapphyrin

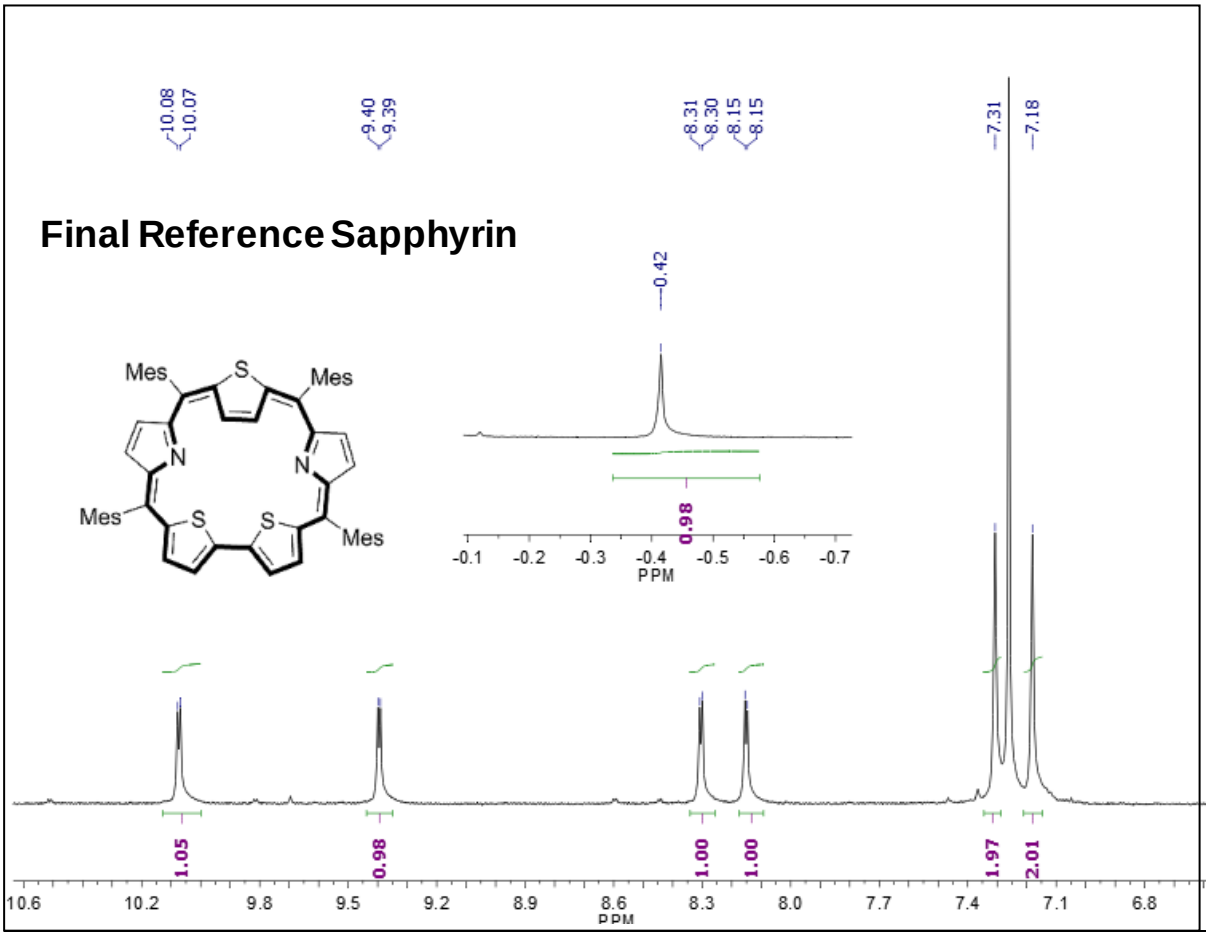


Fig. 18 – NMR Spectral Confirmation of the final Reference Sapphyrin Molecule

NMR - Final Sapphyrin Synthesis

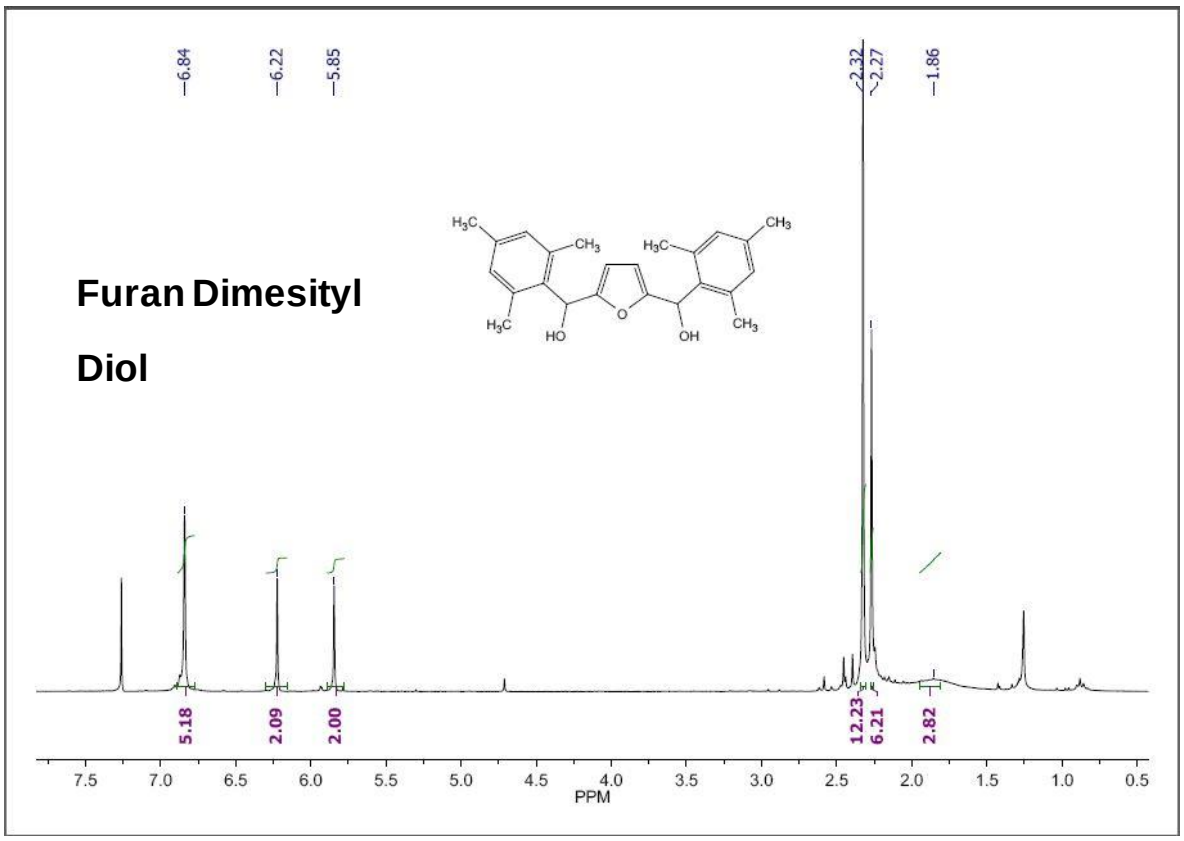


Fig. 19 – NMR Spectral Confirmation of a base material in the synthetic scheme of the final Sapphyrin

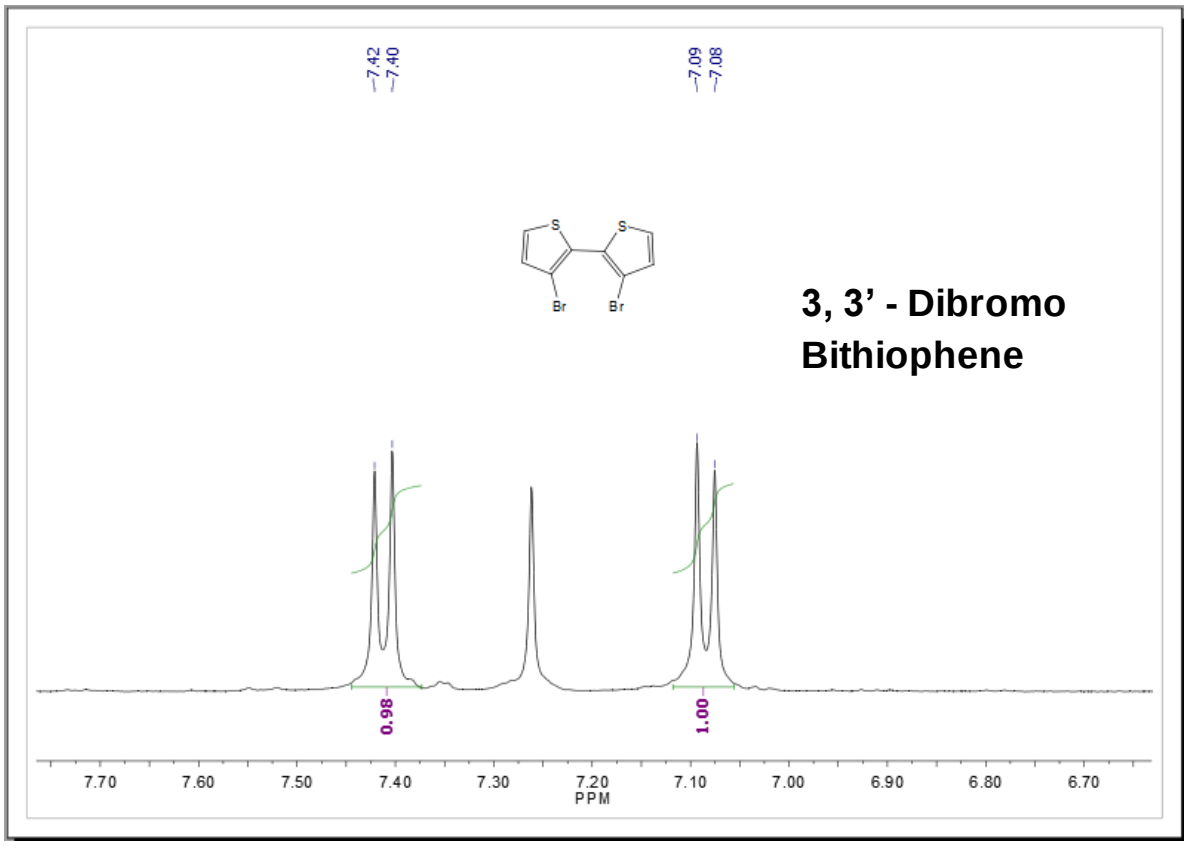


Fig. 20 – NMR Spectral Confirmation of a base material in the synthetic scheme of the final Sapphyrin

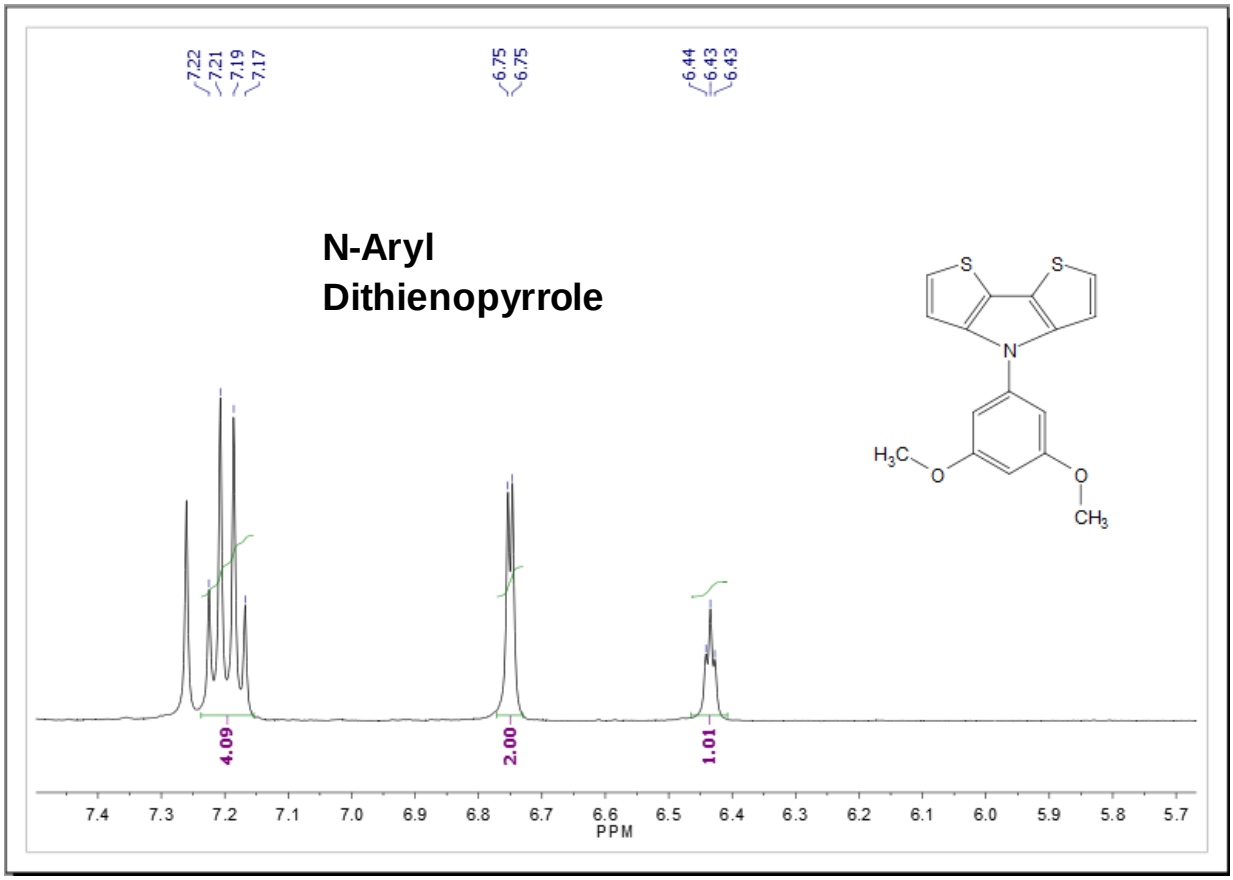


Fig. 21 – NMR Spectral Confirmation of the Dithienopyrrole moiety attached to our base material of the final Sapphyrin indicating success of the reaction scheme.

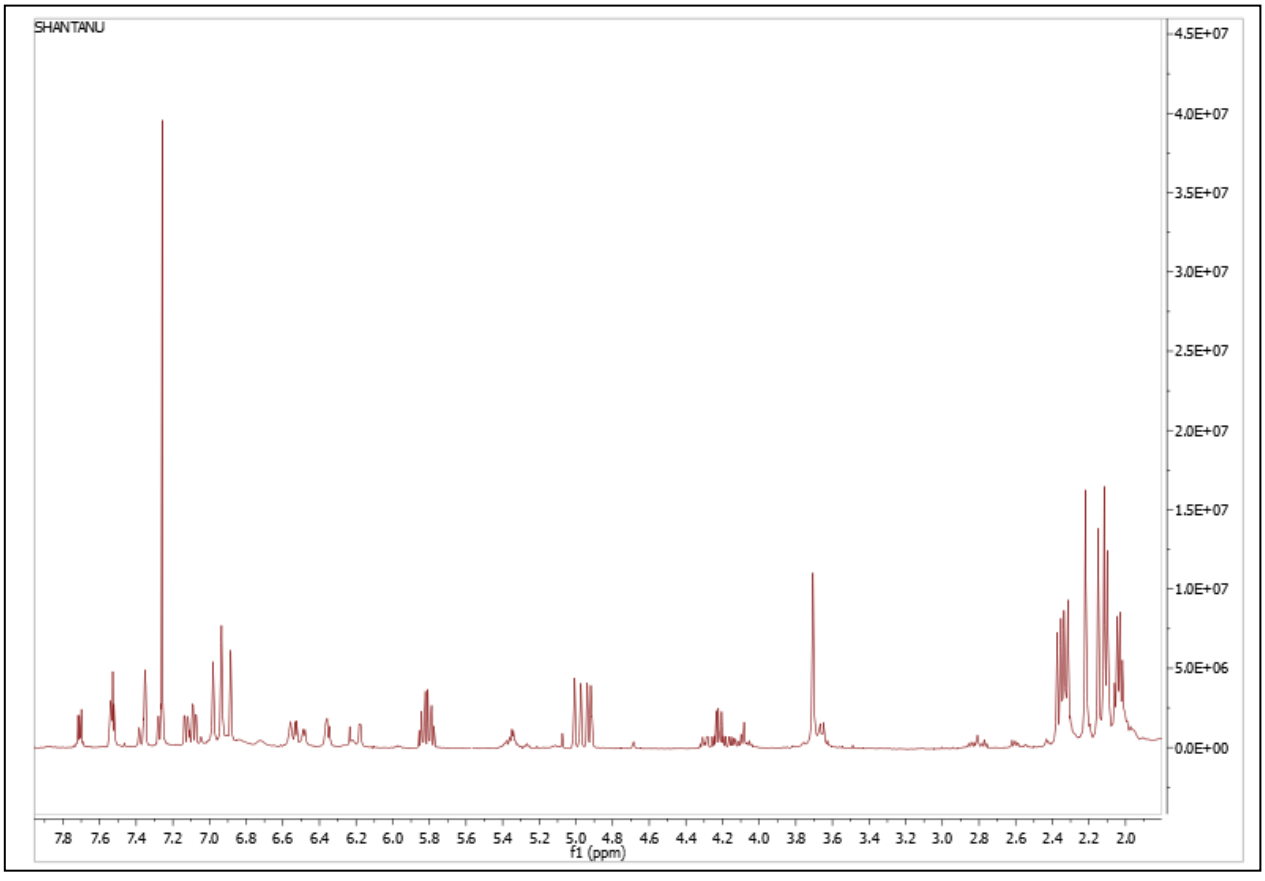


Fig. 22 – NMR Spectral Confirmation of final Sapphyrin – Fused Dithienopyrrole Molecule

7.3 – UV Absorption Spectral Analyses

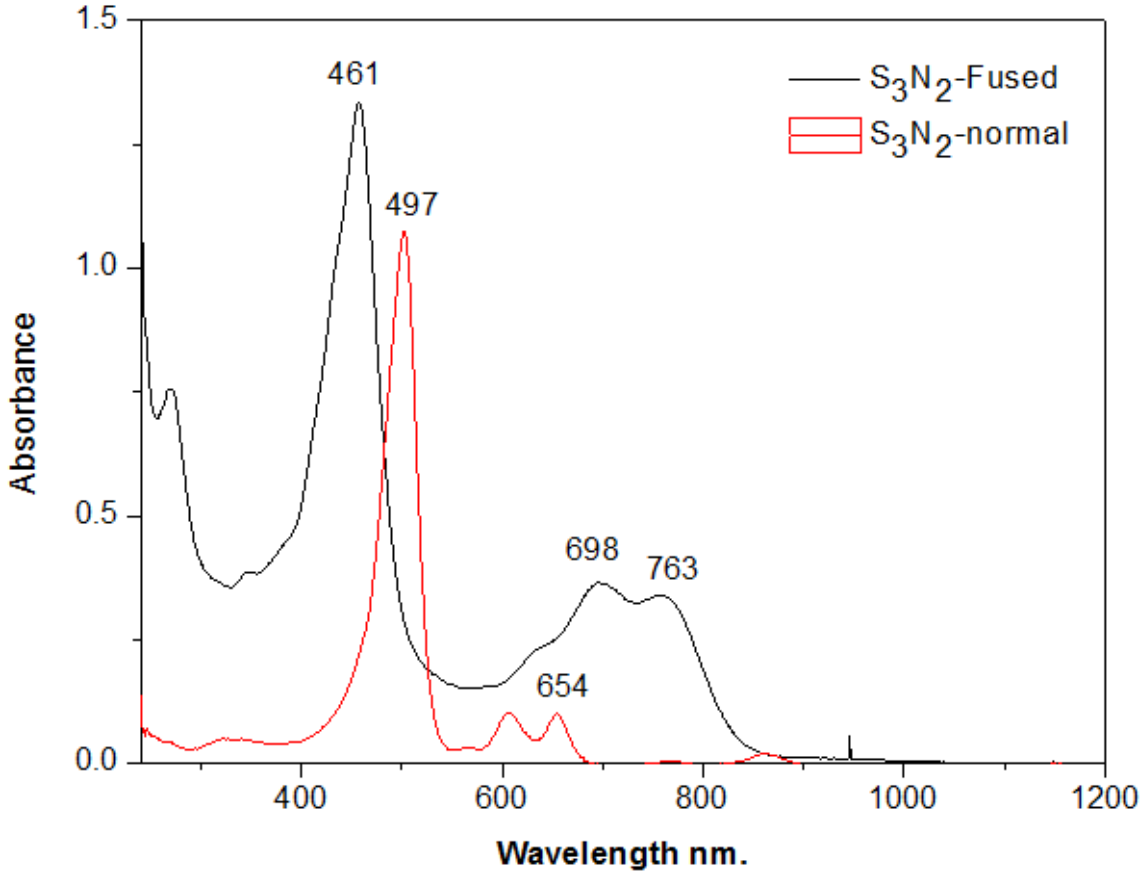


Fig. 23 – UV Spectral analysis of our Final Sapphyrin molecule showing the same characteristic peak as the reference Sapphyrin indicating that the product obtained is indeed a Sapphyrin molecule.

The peaks at the left are called Soret Bands and the ones on the right of the spectra are called Q Bands. We observe that the Q bands are red-shifted. This is because we have extended conjugation exocyclic to the Thiophene ring in the dithienopyrrole moiety.

The UV Absorption Soret Peaks of Core modified Sapphyrin is around 495 nm. We obtained about 470 nm which is close and has blue-shifted a bit probably due to the lone pair on nitrogen causing it to adopt a slight tetrahedral bend instead of trigonal planar. But the bend is outside the 5 membered Sapphyrin ring and is not in the path of conjugation but is only in the path of the electron transfer through the anchoring groups to the photoanode. So this will not affect the efficiency of electron release of the Dye Sensitizer much since the conjugation pathway isn't affected.

7.4 - Mass Spectral Analyses

The Mass spectral analyses were done for the Final Sapphyrin molecule.
Its actual molecular weight is 1048.42 and we obtained a peak in the mass spectra of 1049. This match in the value of the Mass spectra indicates the confirmation of the Final Sapphyrin molecule having been formed. NMR analysis of the pure final Sapphyrin is the last result which we have submitted and are awaiting. That will decisively confirm the molecule's formation after which Xray Diffraction Analyses (XRD) will directly show us the visible structure and atoms of the molecule.

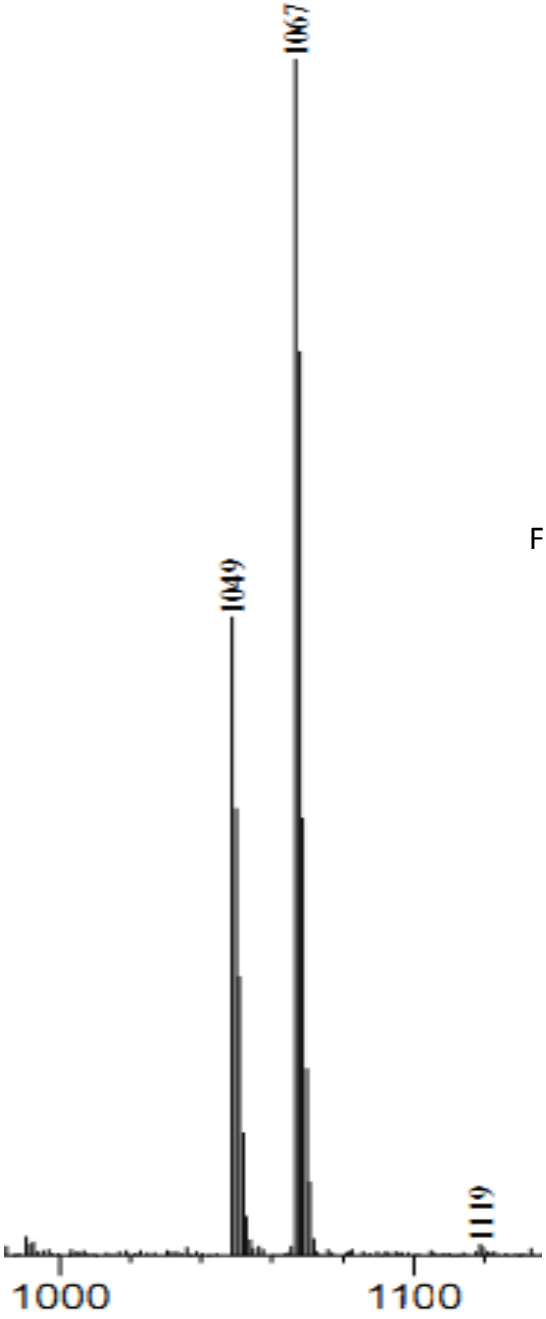


Fig. 24 – Mass Spectral Confirmation of the Final Sapphyrin – Fused Dithienopyrrole Molecule which shows a peak at 1049 while our molecule's molecular weight is 1047.426 which indicates a match with an M+2 Spectra

8 – Summary of DSSC Characteristics and Parameters

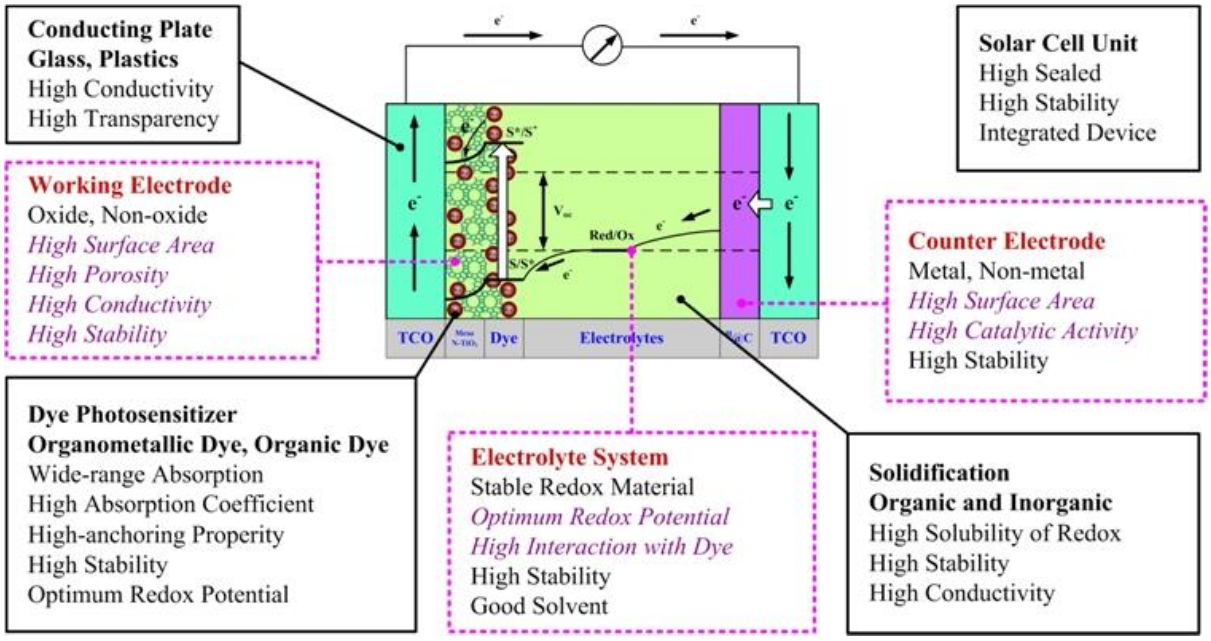
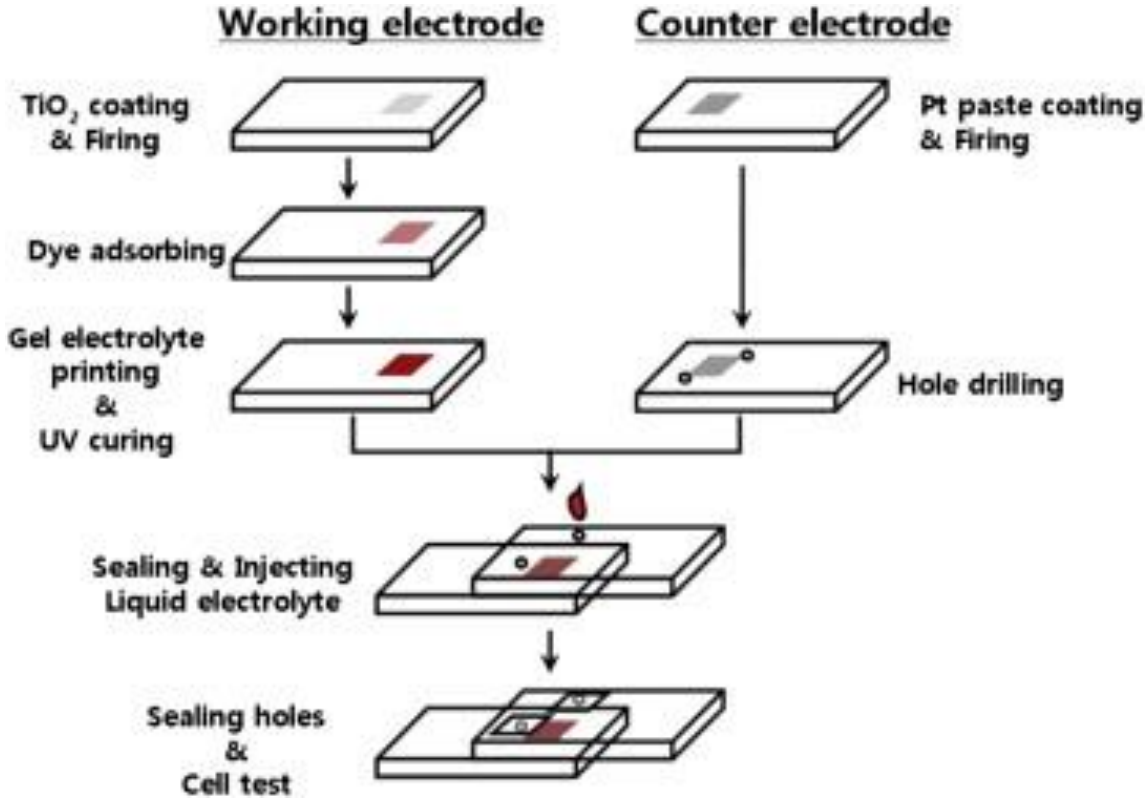


Fig. 25 – Summary of DSSC Parameters (Zhu et al., 2009)

9 – DSSC Fabrication Sequence Schematic



10 – Photovoltaic Performance Assessment

For photovoltaic performance assessment, some critical parameters are to be understood. These are given below :

Under full solar spectrum irradiation with photon flux I_0 = 100 mW / cm^2 (Air Mass 1.5), the photon energy to electricity conversion efficiency is defined as (Gratzel, 2003):

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{I_0}$$

Where Jsc is the short circuit current, Voc the open circuit voltage, and FF is the fill factor of the solar cell which is calculated by multiplying both the photocurrent and voltage resulting in maximum electric power delivered by the cell.

10.1 - Incident Photon-to-CurrentConversion Efficiency (IPCE):

$$IPCE(\lambda) = \frac{1240(eV.nm) \times J_{sc}(\mu A / cm^2)}{\lambda(nm) \times I(\mu W / cm^{-2})}$$

10.2 - Dark Current :

As explained prior, dark current in DSSC is mainly due to the loss of the injected electron from nanostructured wide band gap semiconductor (say TiO_2) to I^{3-} (the hole carrier in solution electrolyte) by either charge recombination or Back Transfer.

$$V_{OC} = \frac{k_B T}{q} \ln\left(\frac{I_{inj}}{I_{dark}} + 1\right)$$

Kb = Boltzmann Constant

T = temperature

Q = charge

I = Incident Power

11 – Some Applications of DSSC's

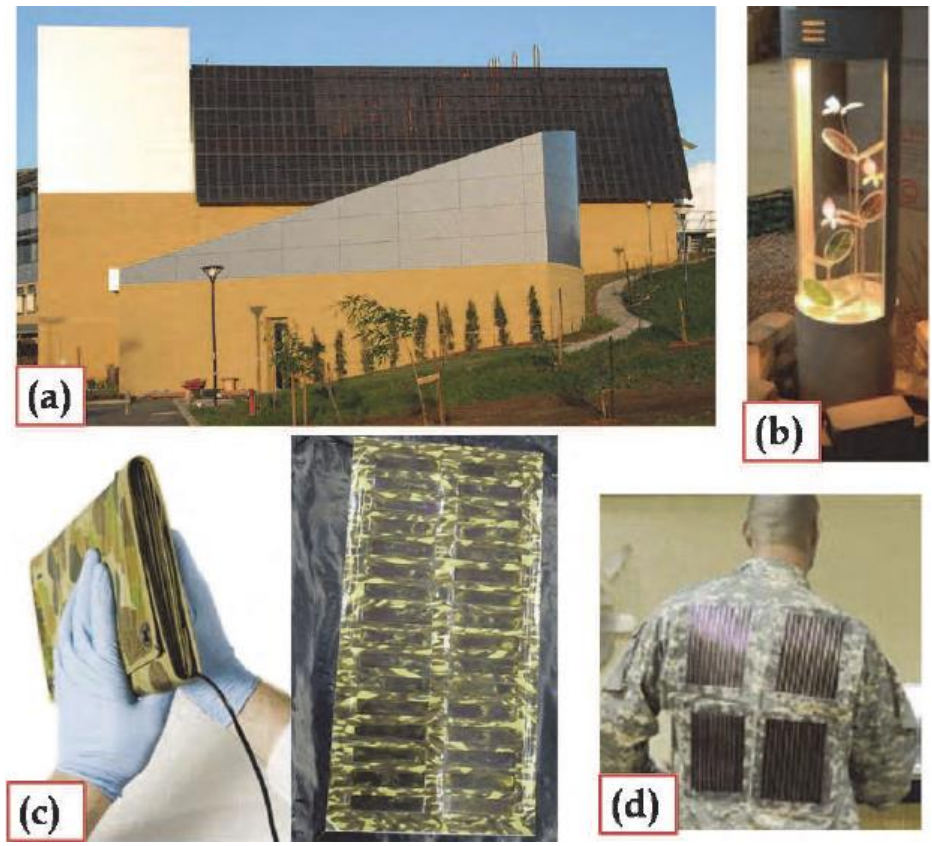


Fig. 26

(a) 200 m^2 of DSSC panels, Newcastle, Australia – the first commercial DSSC module (Ref : http://www.sta.com.au/index.htm)

(b) Indoor ornament of dye sensitized solar cells leaves. (Ref : Aisin Seiki Co., Ltd)

(c) Flexible DSSC-based solar module developed by Dyesol. (Ref : http://www.dyesol.com)

(d) Jacket commercialized by G24i. (Ref : http://www.g24i.com)

CONCLUSIONS AND RECOMMENDATIONS

This contains a highlight of all the major points covered in this report.

- A comprehensive understanding of Dye Solar Sensitized Cells, their working, principles and methods for fabrication.
- Reduction-Oxidation based electron transfer methods in Solar cells analogous to naturally available Chlorophyll and Hemoglobin Moieties.
- Synthesis methods involved in this type of Solar Cell.
- Basics of Sapphyrin, Porphyrin, Dithienopyrrole theory, and Synthetic schemes
- Understanding how Photosensitizers work and the different types of sensitizers currently used with their efficiency parameters.
- Photovoltaic Theory with respect to DSSC's.

Furthermore, some advantages of DSSC's over Si based solar cells dye sensitized solar cells are :-

- Their low cost and ease of production,
- Their performance increases with temperature,
- They possess bifacial configuration - advantage for diffuse light, have transparency for power windows, colour can be varied by selection of the dye, invisible PV-cells based on near-IR sensitizers are feasible, and they outperform amorphous Si.

Some improvements that have been made and could be made to solar cells are :

1. Using Expanded Porphyrin dyes gives more tenability to the electron release.
2. Using electron donating groups like tertiary amines facilitates electron release.
3. Use of Dithienopyrrole type moieties that inherently have good optical properties, with Porphyrins in synergy further enhances the electron release
4. Using electron withdrawing groups like acetylene, acids, gives directionality to electron transfer from the photoanode and prevents charge recombination.
5. Using long alkyl chains in the anchoring group outside the main conjugation pathway so that the molecule's solubility is increased and also so that back transfer or charge recombination of electrons is prevented or reduced.

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