

Effects of the polymethine chain length on the spectral response of dye sensitized devices

P.K.D.D.P. Pitigala,^{a, b, c, *} M. M Henary,^d and A.G.U. Perera^c

^a*Department of Physics, University of Sri Jayawardenepura, Gangodavila*

^b*Center for Advanced Material Research, University of Sri Jayawardenepura, Gangodavila*

^c*Department of Physics and Astronomy, Georgia State University, Atlanta GA, USA.*

^d*Department of Chemistry, Georgia State University, Atlanta GA, USA.*

Abstract

In a dye sensitized (DS) devices, the working principle is based on the excitation and injection of electrons in the dye molecules. Due to the narrower spectral response of the dyes used as the sensitizer in the DS devices, the efficiency of the DS solar cells remains low, which is a major drawback in popularizing and commercializing DS solar cells. Therefore, the study of spectral response broadening methods applicable to DS devices is vital. In general, when synthesizing novel dyes, long carbon chains have been used to absorb infrared radiation. In this study, cyanine dye molecules containing carbon chains of different chain lengths were used to observe the variations in the spectral response of the DS structures. Four cyanine dye derivatives, with different carbon ligands were investigated under the configuration, n-D-p structure. TiO₂ was used as the n-type semiconductor, and the CuSCN was used as the p-type semiconductor, representing the n and p in the above configuration respectively. The device sensitized with the dye containing the longest central polymethine chain have shown a red shift in the spectral response threshold, extending up to ~900 nm. Additionally, the other dye molecules with shorter carbon ligands have a lesser extension in the spectral response.

Keywords: *Cyanine, dye-sensitized, polymethine, spectral response*

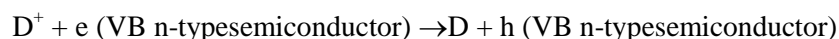
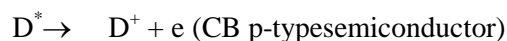
1. INTRODUCTION

The importance of developing novel highly efficient renewable energy conversion devices is obvious due to the ever increasing demand for energy, and safety issues, environmentally unfriendly operation, and the limited availability of widely utilized energy resources. Development of solid/quasi-solid state dye sensitised solar cells (DSSCs) based on nano-crystalline semiconductors is important due to their low

*Corresponding author: Email: dpitigala@sjp.ac.lk

production cost. It is equally important to identify and understand the possible effects of different ligands attached to the dyes on the performance of the device in order to implement modifications to enhance the device performance.

Extensive work has been conducted in the area of dye-sensitization introducing original solar cell and photon detector device concepts. Dye-sensitized (DS) and bulk heterojunction (BHJ) solar cells, organic light emitting diode (OLED) and organic field effect transistors (OFET) are the prototype organic electronic devices that greatly encourage further research in the area of organic optoelectronics [1-3]. The main difference between the dye sensitized solar cell and p-n junction solar cells is in the photon energy absorber. In p-n junction solar cells, photon energy is absorbed directly by the semiconductor at the junction, but in dye sensitized solar cells, the light is absorbed by the dye chromospheres and the electron-hole pair is generated in the dye molecule. In a DS solar cell, the excited dye molecules, anchored to a high-band gap semiconductor surface, inject carriers to an energy band, thereby separating charges and driving a current in an external circuit [4]. The whole electron transfer process of the DSSC heterojunction structure can be summarized by the following three reactions, where the excited dye molecule is denoted as D^* .



Similarly, the operative principle of BHJ solar cell is based on decomposition of photo-generated excitons at an interface between donor (p-type) and acceptor (n-type) phases, and transfer of separated carriers to the electrodes along percolative paths [2-4]. Although many technical hurdles were initially encountered in fabrication of stable cells, the efficiency of DS solar cells still remains well below that of the silicon cell. One reason for lower efficiency results from the narrower spectral response of DS solar cells compared to that of the silicon cell. Different alterations such as the use of multiple dye layers and other modifications to support strong bonding to the semiconductor have been introduced into the dye molecules, in order to extend the spectral response of the DS solar cell [5-8]. Another factor affecting the efficiencies is the rate of injection of the carriers to the bands of the semiconductor and the slow back reaction. Strong electronic coupling of the dye molecule onto the semiconductor surface can cause fast and efficient injection of carriers.

This paper discusses the effects on the spectral response of four different newly synthesized cyanine dyes, having different carbon chain lengths and different ligands.

2.METHODOLOGY

A schematic of the typical layered structure of a DSSC is shown in Figure 1. Here a thin film of TiO_2 was grown on a fluorine doped tin-oxide (FTO) coated glass. The TiO_2 ($1 \times 1 \text{ cm}^2$) films were deposited on the FTO glass plates ($1 \times 1.5 \text{ cm}^2$) by hydrolysis of titanium isopropoxide (5 ml) in the mixture of 75% propan-2-ol (15 ml) and acetic acid (5 ml) to form a colloidal TiO_2 suspension. The hydrolyzed product is mixed with Degussa P25 TiO_2 powder and the viscous slurry formed was spread over the FTO plate. The plate is heated to $120 \text{ }^\circ\text{C}$ for 10 min and after blowing off the loose crust of TiO_2 particles not

adhered to the FTO surface, film is sintered at 425 °C for 10 min. By repetition of the process, TiO₂ film has been grown to a desired thickness of ~8 μm.

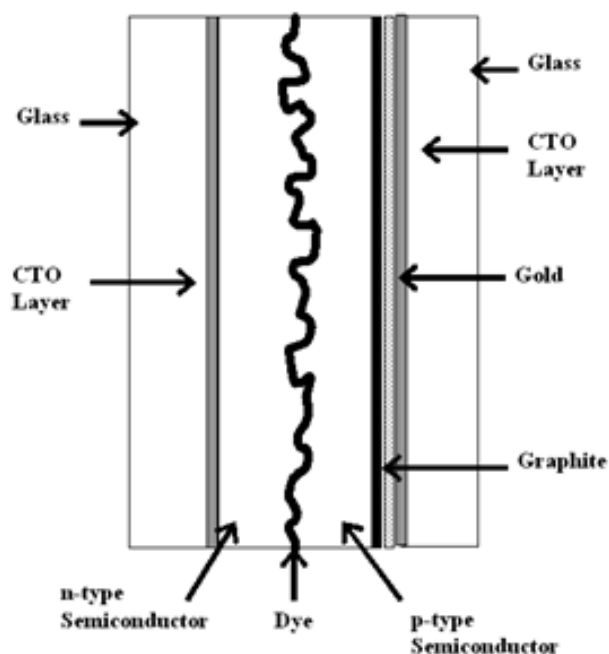


Figure 1: Schematic diagram illustrating the cross section of Dye sensitized photovoltaic cell of heterostructure configuration of n-type semiconductor / Dye / p-type semiconductor.

Newly synthesized cyanine dyes named QBN1, T-23, ES-21 and SP-2-56 were coated on the TiO₂ electrodes. The structure of the dye molecules that were studied are shown in Fig.2. These dyes were separately coated over the TiO₂ films after thoroughly cleaning the TiO₂ films with alkaline 50% propan-2-ol followed by water and 99% propan-2-ol and then drying at 120 °C. Then a dried plate is positioned vertically at the bottom of a glass tube and immersed in the dye solution (in 90% ethanol) at a constant temperature (20°C) for 24 hrs to adsorb and form the dye layer. In general a monolayer of dye will be attached on the TiO₂ film.

The film is then dried in air at ambient temperature and a thin layer of p-CuSCN is deposited over the dye coated surface from a solution in n-propyl sulfide, by keeping the dye coated TiO₂ sample on top of a hot-plate at ~120 °C. A layer of graphite is painted over the CuSCN surface to improve the back contact. And the back electrode is formed by pressing a FTO glass plate to secure the external electrical contacts.

The thickness of the dye film was estimated by extracting the dye molecules from sample films and spectrophotometric estimating of the dye content. Briefly, the process first generated a set of calibration data using known concentrations of the dye solutions and measuring the relative absorbance. Then the dye molecules on the TiO₂ film were stripped off the film by dipping the dye coated TiO₂ film in a dilute KOH solution. Then the absorbance of this solution is measured and the concentration estimated by interpolating or extrapolating the calibration data. Using the estimated concentration of the extracted dye molecules, the number of dye molecules are estimated. Using the estimated area of the dye molecule and

the effective surface area of the TiO₂ film (500×projection area) the thicknesses of the dye layers were estimated to be about one monolayer (0.8 - 1.1 monolayers).

—

Figure 2. Structures of the dye formula QBN1, T-23, ES-21 and SP-2-56

The I-V characteristics of the cells were recorded using a KETHLY 2400 source meter under a 1000 W/m² light source and a monochromator set-up coupled with the KETHLY 2400 was used to measure the photocurrent action spectra of each device.

3.RESULTS AND DISCUSSION

The normalized spectral response of the dyes are shown in Fig.3. The QBN-1, with the longest polymethine chain, has a response threshold extending to ~900 nm; the SP2-56 has the next longest threshold at ~850 nm, and the threshold of the other two dyes, the ES-21 and T-23, are around 750 nm and 760 nm respectively. It is interesting to note that, both the ES-21 and T-23 have the same number of carbon atoms in the central polymethine chain, *i.e.*, an equal polymethine chain length. But the T-23 has a CH₃ ligand attached on the pyrrolidinium ring, while the ES-23 has a CH₃CH₂ ligand which is longer. The extra length in this ligand has resulted in the red shift observed in the response spectra, at peak maxima and at the threshold, as can be observed in Fig 3. Again the SP-2-56 has a much longer ligand ((CH₃)₂N(CH₂)₃) compared to the ES-21 and T-23, hence the response spectra is further red shifted in SP-2-56 compared to the other two. In contrast the QBN-1 has the longest center polymethine chain out of the four dyes, and it has the longest red shift in the spectral response. Even though the other ligands attached to the dye molecule can influence the shifts observed in the spectral response, these results imply the dominance of the polymethine chain length in extending the spectral response.

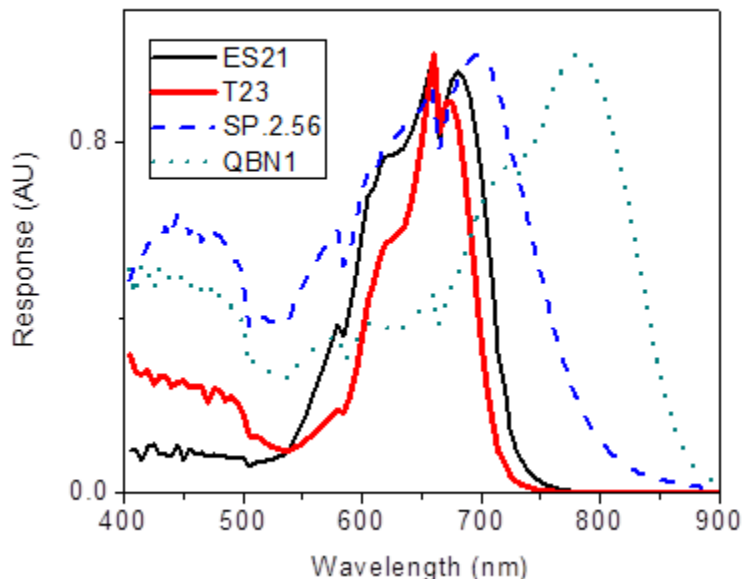


Figure 3 Normalized spectral responses (given in arbitrary Units) of the $\text{TiO}_2/\text{Dye}/\text{CuSCN}$ heterojunction configuration structures coated with the dyes QBN1, T-23, ES-21 and SP-2-56.

The I-V characteristics of the devices are shown in Fig 4. Here the device sensitized with QBN-1 has the highest short-circuit photocurrent and ES 21, T-23 and SP2-56 have their short-circuit currents decreasing in the given order. Here, no clear relation between the polymethine chain length and the short-circuit photocurrent was found. Clearly the chain length does not show a major influence on the photocurrent, similar to the way it affects the broadening or red shifting of the spectral response or response threshold. The differences in the photocurrent of the devices are due to a combined effect of the additional ligands attached to the dye molecule, but not the sole effect of the polymethine chain length itself on carrier injection rate. It can be concluded that the T-23, with two highly electronegative fluorine atoms attached, has a lower photocurrent compared to the ES-21. The electron affinity of the other ligands attached to the dye molecule can affect the charge injection rate as well as the strength of the chelation between the dye and the semiconductor surface, which has affected the total photocurrent of the device. It was not clear which effect had the most influence in limiting the carrier transitions, affecting the photocurrent of the device.

In contrast, the open-circuit voltage (V_{oc}) shows a dependence on the polymethine chain length, as can be seen in Fig. 4. The polymethine chain length of ES-21 and T-23 are similar, so is the open circuit voltage. QBN-1 has the lengthiest polymethine chain length and also the lowest V_{oc} . But the electron affinity of the other ligands attached to the molecule has also affected the V_{oc} of each device; hence SP2-56 has the lowest V_{oc} in the three dyes with the same polymethine chain length.

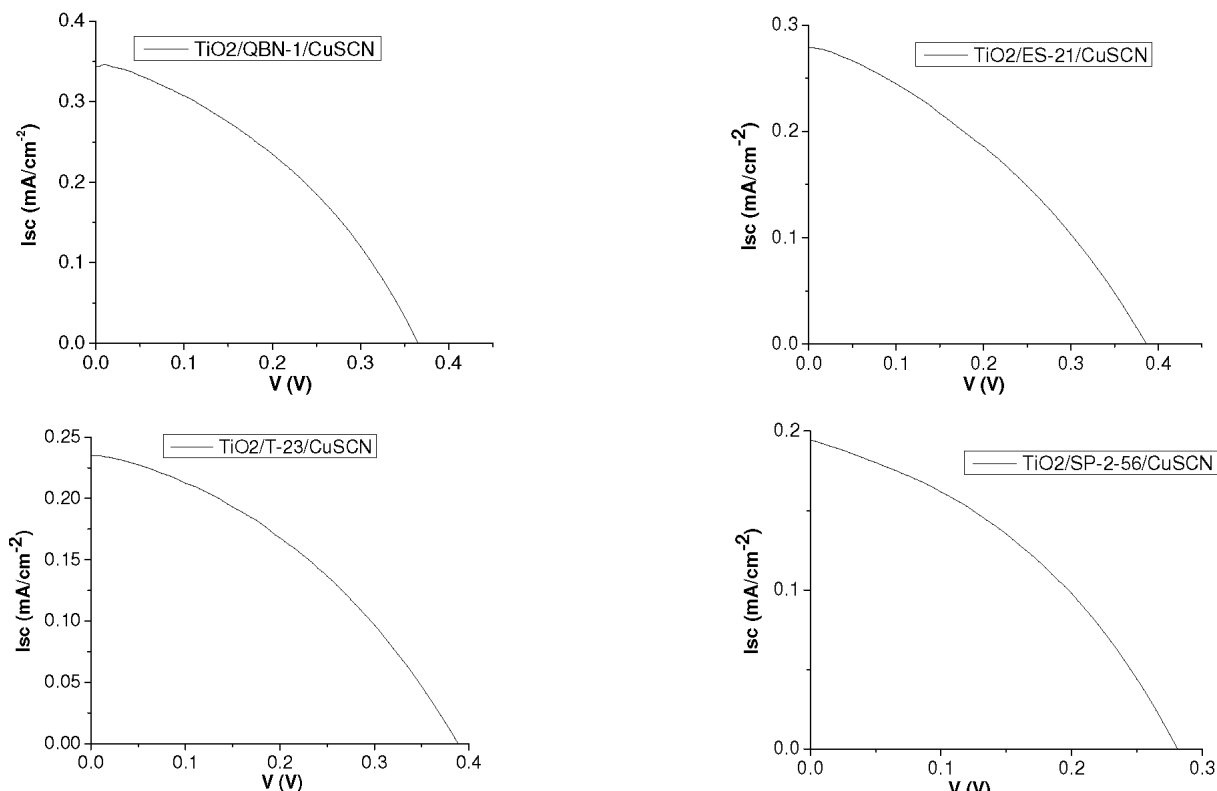


Figure 4. I-V characteristics of the TiO₂/Dye/CuSCN heterojunction configuration structures coated with the dyes QBN1, T-23, ES-21 and SP-2-56.

The effects of electron affinity of the other ligands are not within the scope of this paper, and additional exclusive theoretical and experimental work are needed to combine the effects of the other ligands and justify the effect of these ligands, in the molecules, on the photocurrent and the voltage of the dye sensitized devices. Current results on response broadening and shifting can also be further refined by excluding the additional effects.

4. CONCLUSION

The result shows the effects of the carbon chain lengths in cyanine dye molecules on the spectral response when the dye is used as the sensitizer in the DS device. In the cyanine dyes, the length of the central polymethine chain is more critical in the process of extending the spectral response into the infrared region. Furthermore, the length of the other carbonic ligands attached to the cyclic structures, is also contributing to the broadening of the spectral response of the DS devices and longer ligands have shown a greater red-shift in spectral response. The direct effects of the chain length on the photocurrent and the voltage were inconclusive due to the combined effects of the other legends in the system.

ACKNOWLEDGEMENTS

This work is partially supported by the US National Science Foundation grant NSF ECCS 1232184 and the Research grant # ASP/01/RE/SCI/2018/26 awarded by the research council of the University of Sri Jayewardenepura.

REFERENCES

1. Aswal, D.K., Yakami, V., Eds. (2010). *Molecular and Organic Electronics*, Nova Publishers, New York.
2. Franky, S., (2010). *Organic Electronics: Materials, processing, devices and applications*, CRC Press, New York.
3. Brabec, C.J., Dyakonov, V., Paris, J., Saricifti, N.S., (2003). *Organic Photovoltaics: Concepts and Realization*, Springer, Heidelberg.
4. Regan, B.O., Gratzel, M., (1991) A low cost and high-efficiency solar cell based on colloidal TiO₂ films. *Nature* **353** 737-740.
5. Senevirathne, M. K. I., Pitigala, P. K. D. D. P., Sivakumar, V., Jayaweera, P. V. V., Perera, A. G. U., and Tennakone, K. (2008) Sensitization of TiO₂ and ZnO nanocrystalline films with acriflavine. *J. Photochem. Photobiol. A-Chem.*, **Vol. 195**, 364.
6. Seneviratne, M., Pitigala, P., and Tennakone, K. (2005) Chromophore linked conducting polymers attached to semiconductor surfaces: A strategy for development dye sensitized solar cells. *J. Phys. Chem. B*, **109** 16033.
7. Jayaweera, P. V. V., Perera, A. G. U., and Tennakone, K. (2008) Why gratzel cell works so well. *Inorg. Chim. Acta*, **361**, 707.
8. Perera, V. P. S., Pitigala, P. K. D. D. P., Jayaweera, P. V. V., Bandaranayake, K. M. P., and Tennakone, K. (2003) Dye-sensitized solid-state photovoltaic cells based on dye multilayer-semiconductor nanostructures. *The Journal of Physical Chemistry B*, **107**, 13758.