DFT Study of selected croconate dye molecules for application in dye sensitized solar cells

T S Ranwaha[1], N E Maluta[1,2], R.R Maphanga[2,3]

[1]University of Venda, Department of Physics, P/Bag X 5050, Thohoyandou, 0950.
[2]National Institute for Theoretical Physics (NITheP), Gauteng, South Africa.
[3]Council for Scientific and Industrial Research, P.O.Box 395, Pretoria, 0001.

E-mail: funawahau@gmail.com

Abstract. Dye-sensitized solar cells (DSSCs) have attracted considerable attention in recent years as they offer the possibility of low-cost conversion of photovoltaic energy. DSSCs use the dye molecules adsorbed on the TiO_2 semiconductor in nano architecture with the role of absorbing photon from the sun. The electronic structure and excitation properties of dye sensitizer determine the efficiency of the DSSCs. The dye molecule is a sensitizer that absorbs the photon from the sun and inject an excited electron on the TiO_2 semiconductor. The study focuses on the understanding of different properties (electronic and optical properties) of selected Croconate dye molecules (CR2-I and CR3-Br) employing density functional theory (DFT) calculations. The calculations are based on the determinations of Absorption spectrum, UV-Vis spectrum, Light Harvesting Efficiency and Homo-Lumo gap of the dye molecules. The results obtained shows that Croconate dye molecules can improve the efficiency of DSSCs as they shows absorption shift to the near infrared, which increase the absorption range from visible on the solar spectrum.

1. Introduction

Dye sensitized solar cell (DSSC) is a pillar of modern PV technology particularly in solar cell due to its low cost with high efficiency and its flexible device application. Solar energy is the perfect key to sustainable development for future energy requirements. Especially, solar cells are promising devices to generate clean energy. DSSC is a type of photoelectrochemical cell looking like a sandwich structure, whose working principle is based on photovoltaic effect. DSSC have a photo electrode which combines semiconductor material (TiO_2) and sensitized dye molecule [1].The dye molecule is a sensitizer material that absorbs photon from the sun, become excited and inject the electron to the semiconductor, while the electrolyte regenerate the excited dye to complete the electron transport. [2, 3], It's role requires well matched energy level to facilitate efficient electron injection and dye regeneration, strong physical anchoring to photoanode, sufficient absorption of solar light, and stable operation for a long period [1-3]. Corneliu et al investigated various single and double deprotonated forms of the dye bound to a TiO_2 cluster, taking advantage of the presence of the carboxyl (–CO_2H), hydroxyl (–OH), and sulfonic (–SO_3H) groups as possible anchors, and they reported that anchoring modes of the dye onto the TiO_2 surface are of crucial importance to the DSSC performance through the bonding type and the extent of electronic coupling between the dye excited state and the conduction band edge of the semiconductor. As most of the theoretical studies so far have been focused

on the sensitizers with the carboxyl groups as anchors, they took advantage of the opportunity offered by the protonated form of the Mordant Yellow 10 dye, which has a –OH, –CO_2H and –SO_3H groups, to perform a comparative study of the various anchors, binding configurations as well as propensities for electron transfer [4]. On the same work Corneliu et al reported the results of density functional theory (DFT) and time-dependent DFT (TD-DFT) studies of several coumarin-based dyes, as well as complex systems consisting of the dye bound to a TiO_2 cluster. They also provide the electronic structure and simulated UV-Vis spectra of the dyes alone and adsorbed to the cluster and discussed the matching with the solar spectrum. They displayed the energy level diagrams and the electron density of the key molecular orbitals and analyze the electron transfer from the dye to the oxide. Finally, they compared their theoretical results with the experimental data available and discuss the key issues that influence the device performance [4]. They also examined the absorption spectra, which influence the light harvesting properties of the dyes, the energy level alignment between the dye, the oxide and the electrolyte, which affect the electron injection and the dye regeneration and the adsorption of the dye to the substrate, determining the charge transfer. In the current study we focuses on the understanding of different properties (electronic and optical properties) of selected Croconate dye molecules (CR2-I and CR3-Br) using the density functional theory (DFT) calculations.

2. Computational Method

The structure of the dye molecules were built using Material Studio on 3D atomistic window, material studio software was used for the simulation of the absorption bands and optical absorption respectively. Geometrical optimizations of the dye molecules were performed using the first principles calculations based on density functional theory (DFT) which uses a plane-wave pseudopotential method. We used generalized gradient approximation (GGA) in the scheme of Perdew-Bruke-Ernzerhof (PBE) [5] to describe the exchange-correlation functional using the coarse quality and all band/EDFT as electronic minimizer. The calculation were carried out using Cambridge Serial Total Energy Package (CASTEP) code [6, 7] which is a package within the framework of the Materials Studio software to obtain the ground state properties of the dye molecules. The ground state structures obtained through geometrical optimization was imported into a new 3D atomistic window and the optical properties were calculated using Material Studio CASTEP code. Then the calculations of electronic properties of the ground state structures were done Vulnerability Analysis Methodology Program (VAMP).

3. Results and Discussion

3.1. Excitation and absorption spectrum of the Dyes

The UV-Vis spectrum of the two dye molecules used in this study shows that these molecules can absorb more photons at visible spectrum to the near infrared region of solar spectrum with a stronger peak at 610 nm with oscillator strength (Absorbance) of 1.78 for CR3-Bromine and stronger peak at 635nm with oscillator strength (Absorbance) of 1.51 for CR2-Iodine. There are some weak absorption peaks at near infrared region in both CR2-iodine and CR3-Bromine. The following spectrum shows that there is an activity in visible to near infrared region of solar spectrum, therefore this molecules can enhance performance of solar cells.

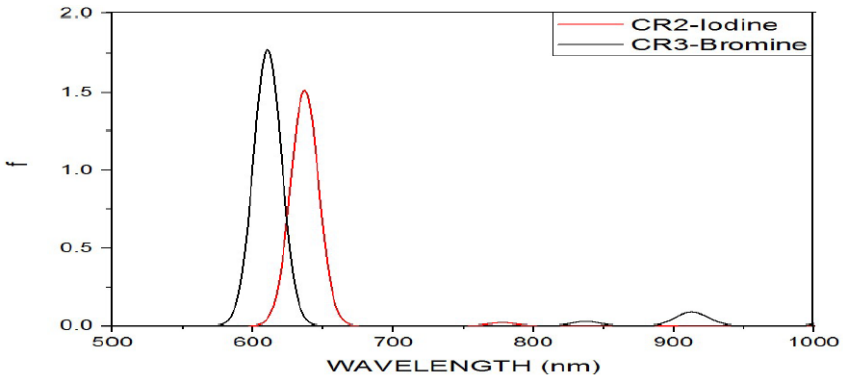

Figure 1. Calculated UV-Vis spectrum for CR2-Iodine and CR3-Bromine dye molecules.

3.2. Light harvesting efficiency of the dyes

Light harvesting efficiency of CR2-Iodine and CR3-Bromine at the absorption peaks was calculated using equation:

$$LHE(\lambda) = 1 - 10^{-f} \tag{1}$$

where f denotes the absorption also called the oscillator strength of sensitizer at a given wavelength (λ).

Table 1. LHE of CR2-Iodine at a particular wavelength.

wavelength (nm)	Absorption	LHE	LHE (%)
635	1.51	0.97	97
777	0.018	0.04	4

Table 2. LHE of CR3-Bromine at a particular wavelength.

wavelength (nm)	Absorption	LHE	LHE (%)
610	1.78	0.98	95
837	0.03	0.05	5
912	0.09	0.18	18

The optical absorption of CR2-Iodine and CR3-Bromine dye molecules are plotted and illustrated in figure 2, the figure shows an absorption activity on the visible to near infrared region. The absorption on the ultraviolet region for CR2-Iodine and CR3-Bromine are common for many synthesizer. Croconate dyes CR2-Iodine and CR3-Bromine are synthesizers that absorb photons in the visible and infrared region can improve the performance of DSSCs as shown by figure 2.

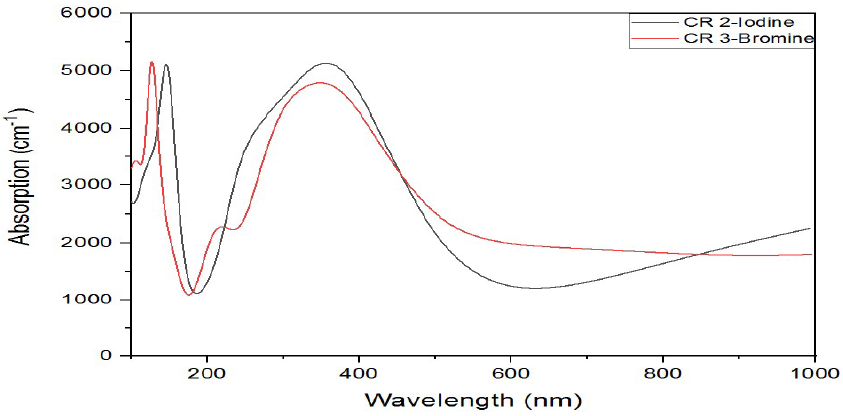

Figure 2. Calculated optical absorption for two dye molecules.

3.3. Energy levels and isodensity surfaces of the dyes

Table 3. The HOMO, LUMO and HOMO-LUMO energy gap of CR1 and CR2 dye molecules.

DYE MOLECULE	HOMO (eV)	LUMO (eV)	HOMO-LUMO GAP (eV)
CR2-Iodine	-6.53	-4.45	2.08
CR3-Bromine	-6.88	-5.79	1.09

The HOMO energies of CR2-Iodine and CR3-Bromine are 6.53 and 6.88 eV respectively, the LUMO energies of CR2-Iodine and CR3-Bromine are 4.45 and 6.88 eV respectively. The HOMO–LUMO energy gap (HLG) values of CR2-Iodine and CR3-Bromine were 2.08 and 1.09 eV respectively. The lower the HOMO-LUMO energy gap of the sensitizer enhance absorption at higher wavelength and the photocurrent response of DSSCs.

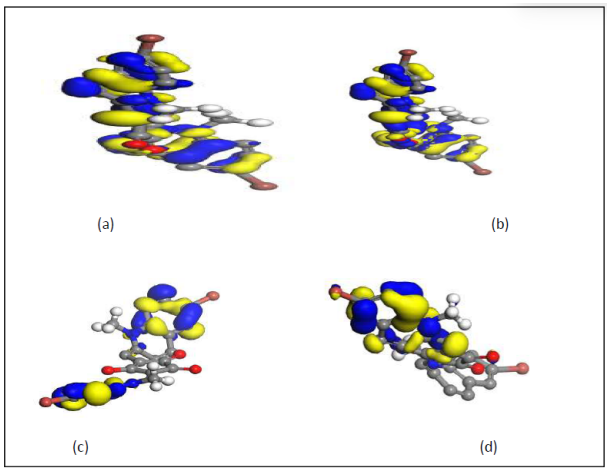

Figure 3. Isodensity surfaces of the molecular orbitals of (a) highest occupied molecular orbital of CR2-Iodine (b) lowest unoccupied molecular orbital of CR2-Iodine (c) highest occupied molecular orbital of CR3-Bromine (d) lowest unoccupied molecular orbital of CR3-Bromine.

4. Conclusion

We performed DFT calculations to investigate the electronic and optical properties of croconate dye molecules with halide functional group. The Homo-Lumo gap values of two molecules are less than the band gap values of TiO_2 semiconductors this means that electron injection from excited dye molecules to the conduction band of TiO_2 semiconductor will be efficient, The UV-Vis spectrum and optical absortion spectrum of the two molecules shows the photon absorption activity in the visible to near infrared region, hence the use of these dye molecules can improve the practical performance of DSSCs.

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6. References

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