

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

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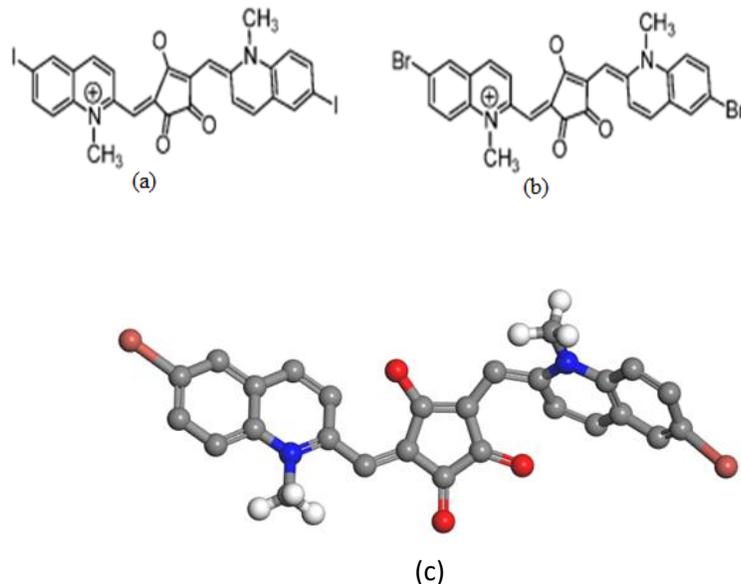
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**Abstract.** Density functional theory (DFT) has been used to study the electronic and optical properties of selected Croconate dye molecules (CR2-I and CR3-Br). The generalized gradient approximation (GGA) was used in the scheme of Perdew-Burke Ernzerhof to describe the exchange-correlation function as implemented in the CASTEP package in material studio of BIOVIA. 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 calculated HOMO-LUMO gap was found to be 2.08 eV and 1.09 eV for CR2-I and CR3-Br respectively, the highest percentage of light harvesting efficiency was found to be 97 % for CR2-I and 98 % for CR3-Br. The results obtained shows that CR2-I and CR3-Br dye molecules can improve the efficiency of DSSCs as they shows absorption shift to the near infrared, which increase the absorption range from the visible on the solar spectrum.

## 1. Introduction

Solar energy is the perfect key to sustainable development for future energy requirements. Solar cells are promising devices to generate clean energy. Dye sensitive solar cells (DSSCs) consist of a photo electrode which combines semiconductor material (TiO<sub>2</sub>) and sensitized dye molecule [1]. The dye molecule is a sensitizer material that absorbs photons from the sun, excites an electron into 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* [4] investigated various single and double deprotonated forms of the dye bound to a TiO<sub>2</sub> cluster, taking advantage of the presence of the carboxyl (-CO<sub>2</sub>H), hydroxyl (-OH), and sulfonic (-SO<sub>3</sub>H) groups as possible anchors. They reported that anchoring modes of the dye onto the TiO<sub>2</sub> surface are of crucial importance to the DSSCs performance through the bonding type and the extent of electronic coupling between the dye excited state and the conduction band edge of the semiconductor [4]. As most of the theoretical studies so far have been focused on the sensitizers with the carboxyl groups as anchors, with advantage of the opportunity offered by the protonated form of the Mordant Yellow 10 dye, which has -OH, -CO<sub>2</sub>H and -SO<sub>3</sub>H groups. These theoretical studies are based on understanding various anchors, binding configurations as well as propensities for electron transfer [4]. On the same work Corneliu *et al* [4] 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<sub>2</sub> cluster. They provide the electronic structure and simulated UV-Vis spectra of the dyes and discussed the properties of the adsorbed dye molecule on the TiO<sub>2</sub> surface, which matches with the solar spectrum. Their results were compared with the experimental data available and discuss the key issues that influence the device performance like absorption spectra, the energy level alignment between the dye, the oxide and the electrolyte, and the adsorption of the dye to the substrate. In the current study we focuses on the understanding of different properties (electronic and optical properties) of selected Croconate dye molecules shown in figure 1 (CR2-I and CR3-Br) using the density functional theory (DFT).



**Figure 1:** Structures of the Croconate Dyes molecules CR2-I and CR3-Br (a) and (b) from Ref [5], and (c) optimised geometry structure built using a Material Studio package and the colours used in this work (red is Oxygen, grey is Carbon, white is Hydrogen, blue is Nitrogen and brown is Iodine for CR 2- I and Bromine for CR 3-Br).

Figure 1 shows the structures of Croconate dye molecules investigated in this study, CR 2-I and CR 3-Br with halide functional group and containing the oxyallyl subgroup in the parent structure. CR 2- I and CR 3-Br exhibit strong absorption in the infrared, and possess donor–acceptor–donor type structure. These dye molecules can be synthesized easily and give rise to DSSCs that are flexible and interact strongly with light

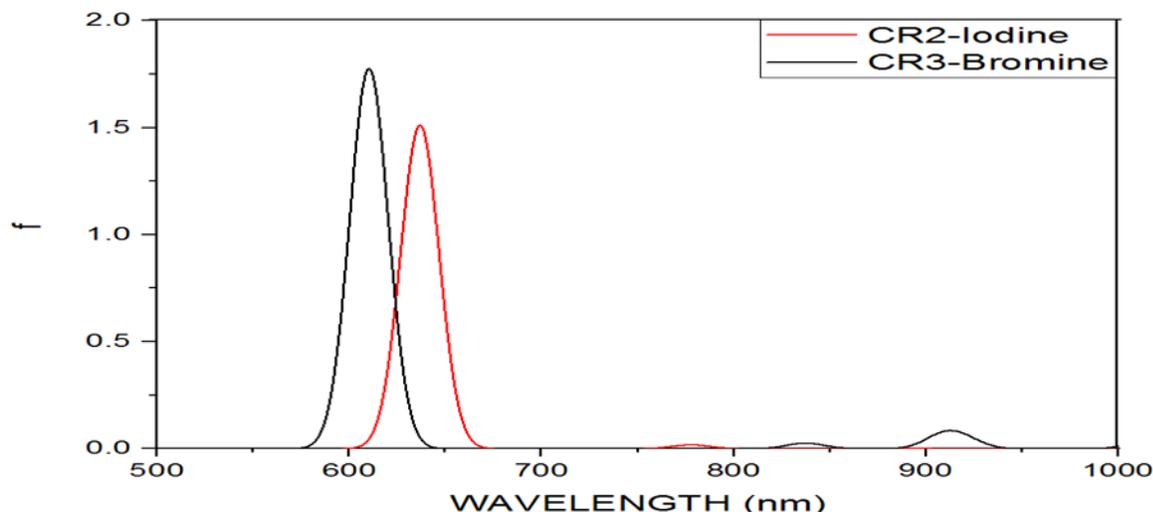
## 2. Computational method

The structures of the selected Croconate dye molecules were built using a Material Studio package. The dye molecules structure was cleaned so that the atoms are reoriented in their lattice positions. Geometrical optimization and calculation of optical absorption of the dye molecules were performed by the CASTEP code in Material Studio package using density functional theory (DFT), which uses a plane-wave pseudopotential method of generalized gradient approximation (GGA) in the scheme of Perdew-Bruke-Ernzerhof (PBE) to describe the exchange-correlation functional using the coarse quality and all band/EDFT as electronic minimizer [6]. The ground state structures obtained through geometrical optimization structures were imported into a new 3D atomistic window and the calculation of electronic properties and UV-Vis of the dye molecule were performed using the VAMP module within the Material Studio package [7].

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



**Figure 2:** Calculated UV-Vis spectrum for CR2-Iodine and CR3-Bromine dye molecules.

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 ( $\lambda$ ).

**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       |

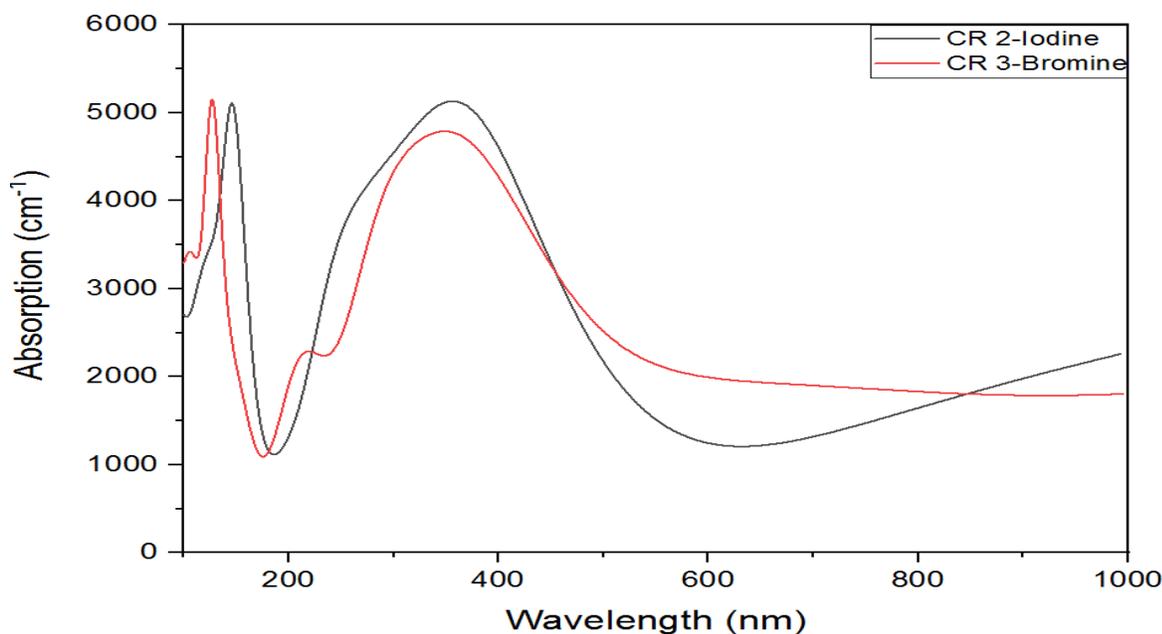
**Table 2:** LHE of CR3-Bromine at a particular wavelength

| Wavelength (nm) | Absorption | LHE  | LHE (%) |
|-----------------|------------|------|---------|
| 610             | 1.78       | 0.98 | 98      |
| 837             | 0.03       | 0.05 | 5       |
| 912             | 0.09       | 0.18 | 18      |

The light harvesting efficiency (LHE) of the sensitizer affects the short-circuit current density ( $J_{SC}$ ), and hence, the overall power conversion efficiency ( $\eta$ ). The calculated LHE values of CR2-I and CR3-Br found are shown in Table 1 and Table 2 respectively. The maximum values of LHE found to be 0.97 (97 %) at  $\lambda_{max} = 635$  nm and 0.98 (98 %) at  $\lambda_{max} = 610$  nm.

### 3.2. Optical absorption property of the dye molecules

Figure 3 illustrate the optical absorption property of CR2-I and CR3-Br dye molecules. The figure shows an absorption activity in the visible to near infrared region. The absorption in the ultraviolet region for CR2-I and CR3-Br are common for many synthesizer. The results illustrate that Croconate dyes CR2-I and CR3-Br as synthesizers in DSSCs can shift the absorption of photons from the ultraviolet region to the visible to near infrared region, hence improve the practical performance of DSSCs.



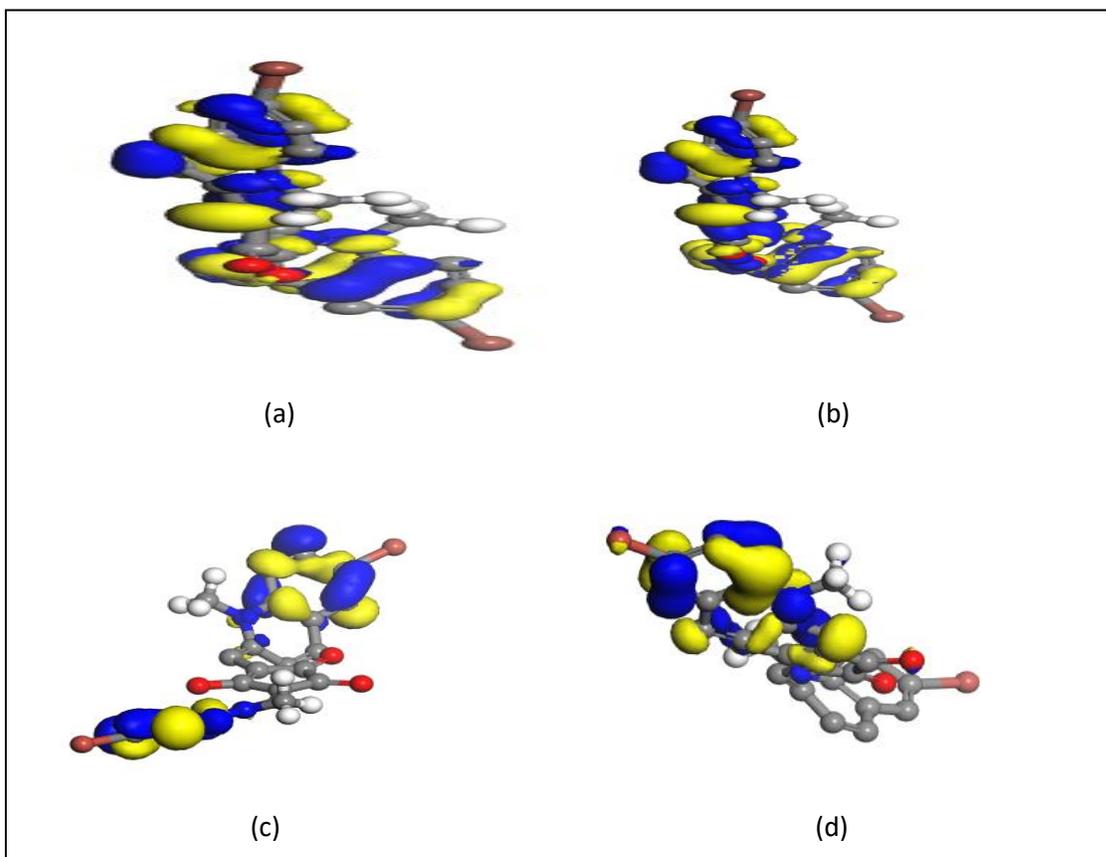
**Figure 3:** Calculated optical absorption for CR2-I and CR3-Br dye molecules.

3.3. Energy levels and isodensity surfaces of the dyes

**Table 3:** The HOMO, LUMO and HOMO-LUMO energy gap of CR 2-I and CR 3-Br dye molecules.

| DYE MOLECULE | HOMO (eV) | LUMO (eV) | HOMO-LUMO GAP (eV) |
|--------------|-----------|-----------|--------------------|
| CR2-I        | -6.53     | -4.45     | 2.08               |
| CR3-Br       | -6.88     | -5.79     | 1.09               |

Table 3 shows the molecular orbitals of CR2-I and CR3-Br. The HOMO energies of CR2-I and CR3-Br are  $-6.53$  eV and  $-6.88$  eV respectively, the LUMO energies of CR2-I and CR3-Br are  $-4.45$  eV and  $-5.79$  eV respectively. The HOMO-LUMO energy gap (HLG) values of CR2-I and CR3-Br were 2.08 eV and 1.09 eV respectively. The smaller HOMO-LUMO gap favors the absorption of photons in the long-wavelength region. Figure 4 shows the molecular orbitals involved in the dominant electron transitions of CR2-I and CR3-Br.



**Figure 4:** Isodensity surfaces of the molecular orbitals of (a) highest occupied molecular orbital of CR2-I (b) lowest unoccupied molecular orbital of CR2-I (c) highest occupied molecular orbital of CR3-Br (d) lowest unoccupied molecular orbital of CR3-Br

#### 4. Conclusion

First principle DFT studies were used to investigate the electronic and optical properties of selected Croconate dye molecules (CR2-I and CR3-Br) with halide functional group. The HOMO-LUMO gap values of two molecules are less than the band gap values of  $\text{TiO}_2$  semiconductors, and this means that electron injection from excited dye molecules to the conduction band of  $\text{TiO}_2$  semiconductor will be efficient. The UV-Vis spectrum and optical absorption 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.

#### 5. Acknowledgement

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