

## Comparison and Determine Characteristics Potentials of HOMO/ LUMO and Relationship between $E_a$ and $I_p$ for Squaraine Dyes ( $SQ1$ , $SQ2$ ) by Using Cyclic Voltammetry and DFT/TD-DFT

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### Abstract

The electrochemical properties of the squaraine dyes ( $SQ1$  &  $SQ2$ ) were investigated. The effects of the chemical structures of two  $SQ1$  &  $SQ2$  dyes were selected in relation to the variable property of -COOH substituent for  $SQ1$  compared to  $SQ2$  which is without substituent and determine their potential energy levels in ground and excited states HOMO and LUMO. The HOMO energy levels of the  $SQ1$  &  $SQ2$  dyes are -5.19 eV and -5.16 eV. The LUMO energy levels are calculated to be -3.08 eV and -3.1eV respectively. The ground state geometry has been computed by applying density functional theory (DFT). The excitation energy was calculated by using time-dependent (DFT-TD) at DFT/B3LYP/6-31G\*\* level of theory. The -COOH substituent affect the potential values, but the effect is small. The  $I_p$  range from -4.901 to -6.072 eV for  $SQ1$  and -4.971 to -6.362 eV for  $SQ2$  showed that the -COOH acid substituent exert a small effect on the frontier orbital energy level. The relationship between  $E_a$  and  $I_p$  was evaluated as a good slope 0.99 between HOMO and LUMO for  $SQ1$  &  $SQ2$ , this implies the feasibility and validity of the theoretical estimation and the experimental determination.

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## 1. Introduction

In recent years, in contrast to costly inorganic sensors, non-expensive organic sensors have been explored as highly efficient substitutes for the next generation of dye-sensitized solar cells (DSSC) because of their low cost and flexibility in molecular modification and environmental compatibility [10]. Several organic dyes for example, coumarin[1], indoline[2] triphenylamine [3,4], hemicyanine [5,6], squaraine dyes [7], phthalocyanine [8], and perylene [9,10] have been developed and used in DSSC. In addition, the squaraine dyes are particularly important in research they are eco-friendly, low-cost and are give high-performance, this resulting from photovoltaic and electrochemical stability as well as high molar extinction coefficients in the visible region [11, 12]. Squaraine dyes (SQ) are a category of organic dyes that is conjugated with a strong absorption bands in the visible region to the nearby infrared region where it contains squaric acid which features four-organic aromatic ring structure as the core. In recent years, squaraine dyes have attracted attention of the researchers on a large scale as a result of their behaviour and the optical properties. SQ dyes have been developed over the past years for many different applications [13, 14], including organic electronics [15-17], dye-sensitized solar cells [18], sensors [19, 20], and photo dynamic therapies (PDT)[21, 22].

Cyclic voltammetry is a very suitable way for an extensive range of applications. Furthermore, in squaraine dyes, cyclic voltammetry is one of the usual strategies techniques used for characterization [23]. The cyclic voltammetry is considered one of the most useful ways to characterize squaraine dyes and estimated the band gap [24-26]. Also, HOMO represents the energy required to extract an electron from a molecule, which is an oxidation process, and LUMO is the energy necessary to inject an electron to a molecule, hence implying a reduction process [27]. The HOMO and LUMO energy can be measured by used of cyclic voltammetry method through measuring the redox potentials  $E_{red}$  and  $E_{ox}$ . Ferrocene is used as an acknowledged reference to calculate the energy of the HOMO and LUMO levels, which include the ferrocene value of -4.4 eV. The HOMO and LUMO energy levels have been calculated by the usage of the following empirical equations [28].

$$E_{(HOMO)} = -e [E_{ox}^{onest} + 4.4] \quad (1)$$

$$E_{(LUMO)} = -e [E_{red}^{onest} + 4.4] \quad (2)$$

In organic squaraine dyes the electronic states in energy levels are compatible with the energy carried by visible radiation or ultraviolet radiation. At resonance, molecules can absorb enough energy to transmit electromagnetic radiation moving the electron from a low-energy orbital to a high-energy orbital [29]. These electronic transitions can be measured using the UV-Vis spectrophotometer, where that  $E_{opt}$  corresponds to the long wavelength edge energy of the exciton absorption band [30]. To calculate the optical band gap energy, we have used the longest absorption wavelength  $\lambda_{onset}$  to according of the following equation [31]:

$$E_g = 1242/\lambda_{onset} \quad (3)$$

In this presented work, the effects of the chemical structures of two squaraine dyes (*SQ1* & *SQ2*) were selected in relation to the variable property of -COOH substituent for 4-((5 carboxy-1-(3-methoxy-3-oxopropyl)-3,3-dimethyl-3*H*-indolium-2-yl)methylene)-2-((5-carboxy-1-(3-methoxy-3-oxopropyl)-3,3-dimethyl-lindo-lin-2-ylidene)methyl)-3-oxocyclobut-1-enolate(*SQ1*) compare to 2-((3-(2-ethoxy-2-oxoethyl)benzo[d]thiazol-2(3*H*)-ylidene)methyl)-4-((3-(2-ethoxy-2-oxoethyl)benzo[d]thiazol-3-ium-2-yl)methylene)-3-oxocyclobut-1-enolate (*SQ2*) and determined their potential energy levels in ground and excited states HOMO and LUMO respectevily. All theoretically computational calculations of *SQ1* and *SQ2* for energy potential and the electron distribution of HOMO /LUMO states have been done through optimized geometries of final dye with the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) at B3LYP/6-311G\*\* level of calculations using Gaussian 03 program package

[32, 33]. Thus, this principle is pretty beneficial for the utility of electron chemistry, due to the fact HOMO /LUMO potentials involve the capabilities of proton transfer or unshared pair/empty orbital interaction[34-39].

## 2. EXPERIMENTAL PARTS

### 2.1 Materials and instruments

All chemicals, tetrabutylammonium hexafluorophosphate (NBu<sub>4</sub> PF<sub>6</sub>) and ferrocene (Fc/Fc<sup>+</sup>) were purchased from Alfa easer. Dichloromethane is used a solvent. UV-Visible absorption spectrum was recorded on a Perkin Elmer Lambda 20 spectrophotometer in dichloromethane. Squaraine dyes (SQ1 & SQ2) were synthesized in the laboratory (see figure1) for chemical structure of SQ1 & SQ2.

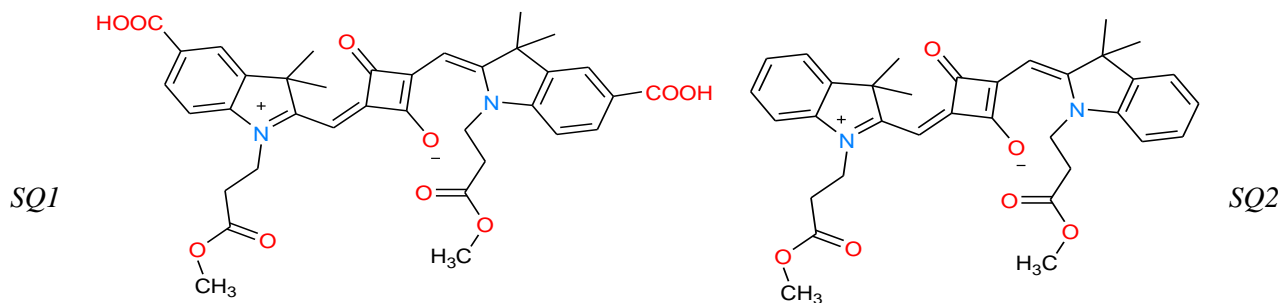
### 2.2 Electrochemical Measurements (cyclic voltammetry)

Cyclic voltammetry (CV) measurement was performed on a Metrohm Autolab PGSTAT128N (Metrohm B.V., Utrecht, Netherlands) with three electrode systems consists of a saturated Ag/AgCl reference electrode, a platinum wire auxiliary electrode and Pt electrode as working electrode. Cyclic voltammetry measurements were performed in DMC solution using 0.1M tetrabutylammonium hexafluorophosphate (NBu<sub>4</sub>PF<sub>6</sub>) as supporting electrode, 0.01M ferrocene (Fc/Fc<sup>+</sup>) as internal standard and 0.001M of SQ1 & SQ2 dyes at room temperature. The potential scan was taken from 0.0 to 0.8 V at various scan rates from 25-300 mV/s.

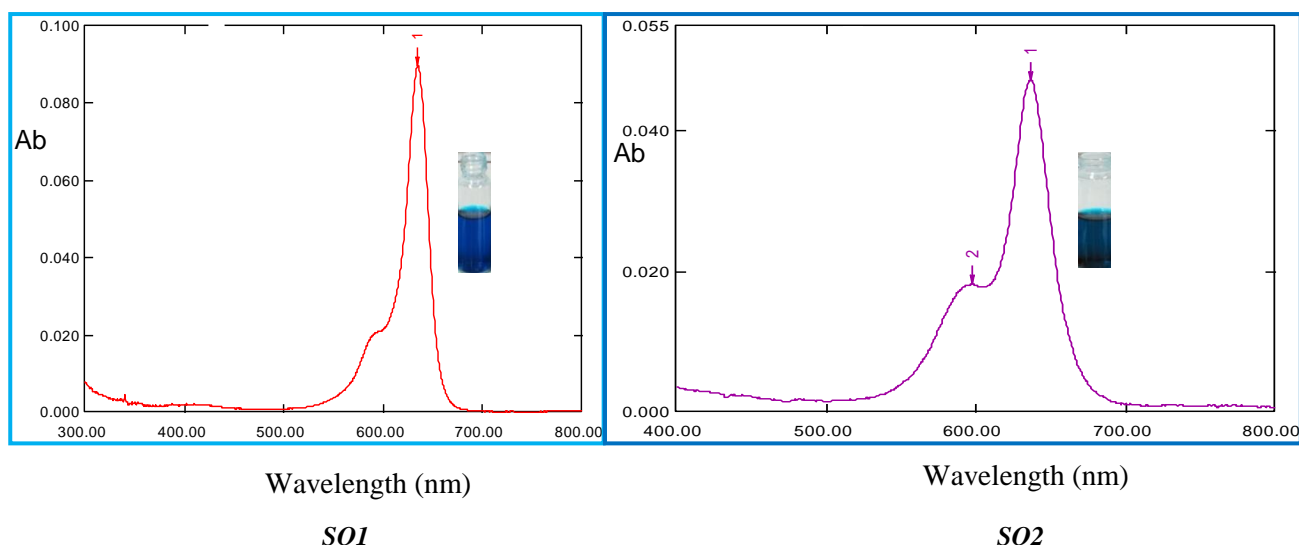
## 3. Results and Discussions

### 3.1. Optical properties

In 0.001M of SQ1 and SQ2 in 25 ml dichloromethane solution showed the normalized UV-vis absorption bands maxima located around 664 and 635 nm with high molar extinction coefficient of  $> 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ . The recorded spectral data showed a strong cut off 600 and 590 nm for SQ1 & SQ2 respectively, where the absorbance values are minimal. The optical band gaps of SQ1 & SQ2 are 2.07eV and 2.11 eV respectively (see table .1).



**Figure1.** Chemical structure of SQ1 and SQ2



**Figure 2.** The UV-vis absorption spectra in dichloromethane (DCM) exhibited  $\lambda_{\max}$  at 664 and 635 nm for *SQ1* & *SQ2* respectively.

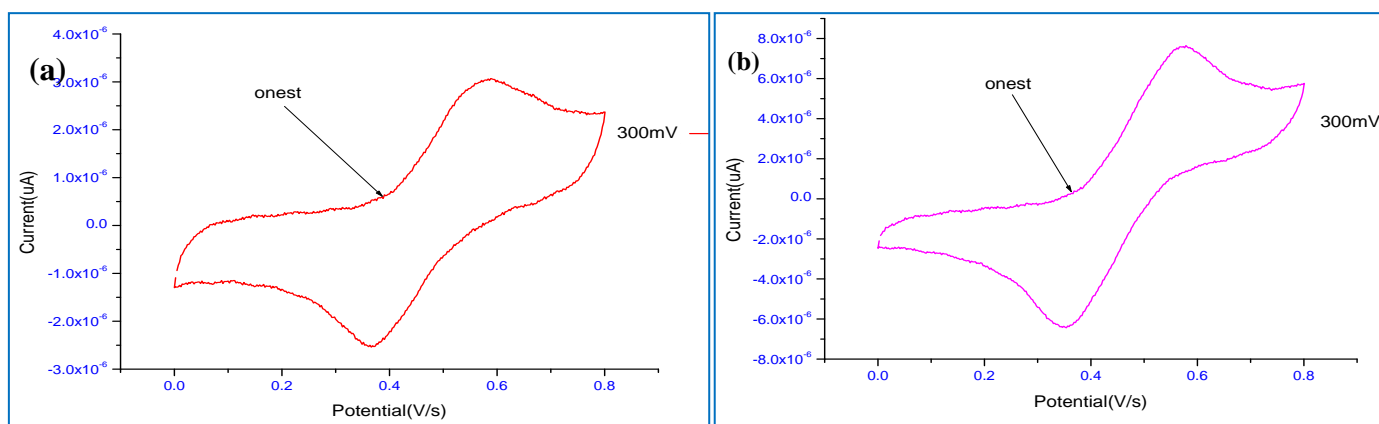
**Table 1.** Optical properties of *SQ1* & *SQ2* dyes

Dye	Absorption $\lambda_{\text{abs max}}$ (nm)	$^a\lambda_{\text{abs}} = \text{Cut off wavelength}$	$E_g^{\text{opt}}$ (eV) <sup>b</sup>
<i>SQ1</i>	644	600	2.07
<i>SQ2</i>	635	590	2.11

Band Gap Energy ( $E$ ) =  $h \cdot C / \lambda$ ,  $h$  = Plank's constant =  $6.626 \times 10^{-34}$  Joules sec.  $C$  = Speed of light =  $3.0 \times 10^8$  meter/sec,  $^a\lambda$  = Cut off wavelength =  $600 \times 10^{-9}$  meters,  $^b$ Where  $1\text{eV} = 1.6 \times 10^{-19}$  Joules (conversion factor)

### 3.2 Cyclic voltammetry measurements

The electrochemical properties of the sensitizer *SQ1* differ from the electrochemical properties of *SQ2*. Cyclic voltammetry measurements were performed in DMC solution using 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{NBu}_4\text{PF}_6$ ) as supporting electrolyte and 0.01M ferrocene ( $\text{Fc}/\text{Fc}^+$ ) as internal standard. In Figure 3, the cyclic voltammetry measurements for *SQ1* and *SQ2* dyes showed a similar reversible one-electron oxidation wave, determined of  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  through energy oxidation onset and energy reduction onset at scan rate 300 mV/s found 0.39-0.32V and 0.36-0.30V for *SQ1* & *SQ2* respectively, which means that the HOMO energy levels of the two dyes are -5.19 eV and -5.16 eV and are mainly attributed to the similar electron-donating capability of COOH indoline. The LUMO energy levels of *SQ1* & *SQ2* are calculated to be -3.08 eV and -3.1eV respectively, which are deduced from the HOMO levels and the corresponding optical band gaps [40]. According to cyclic voltammetry and Optical absorption measurements showed that both *SQ1* and *SQ2* dyes are wide-band gap semiconductors with high electron affinity ( $E_{\text{LUMO}} \sim -3.08$  to  $-3.1$  eV) and high positive oxidation potential compared to dyenitro dye (see table 2). These properties indicate *SQ1* and *SQ2* dye as good candidates as acceptor materials for dye-sensitized solar cells compared to dyenitro dye [41]. In Figure 4 the cyclic voltammograms of the squaraine *SQ1* & *SQ2* showed broad, reversible oxidation and reduction waves. The cyclic voltammetry experiments carried out between 0.0-0.8 V. 0.001M of both *SQ1* & *SQ2* dyes were used in 25 ml of dichloromethane at various scan rates from 25, 50, 100, 150, 200, 250 and 300 mV/s for *SQ1* & *SQ2*, respectively, with 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{NBu}_4\text{PF}_6$ ) as the supporting electrolyte and 0.01 M ferrocene ( $\text{Fc}/\text{Fc}^+$ ) as the internal electrode assuming that the oxidation potential ( $E_{\text{ox}}$ ) and reduction potential ( $E_{\text{red}}$ ) corresponds to the HOMO and LUMO levels of the dyes.

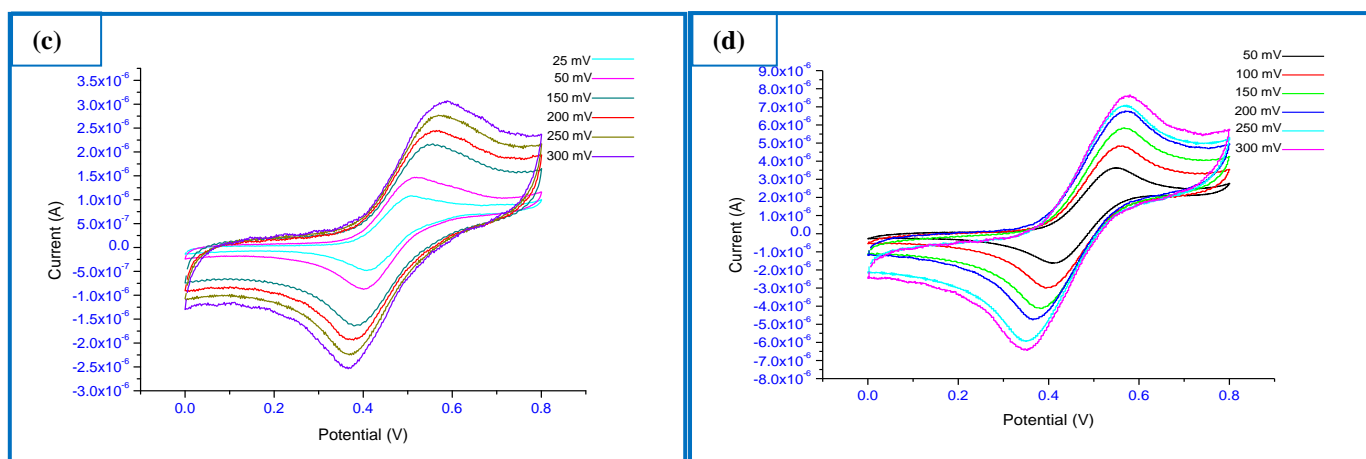


**Figure 3.** (a) Cyclic voltammetry curve for *SQ1* (b) Cyclic voltammetry curve for *SQ2* and determined of HOMO and LUMO through of energy oxidation onest  $E_{ox}^{onest}$ , energy reduction onest  $E_{red}^{onest}$  in 0.1 M tetrabutylammonium hexafluorophosphate (NBu<sub>4</sub>PF<sub>6</sub>) as the supporting electrolyte and 0.01 M ferrocene (Fc/Fc+) as the internal electrode at scan rate 300 mV/s.

**Table 2.** The calculated  $E_{ox}^{onest}$ ,  $E_{red}^{onest}$ ,  $E_{HOMO}$ ,  $E_{LUMO}$ ,  $E_g$  approximated as well as the band gap (from CV). The highest occupied molecular orbital energies ( $E_{HOMO}$ ), lowest occupied molecular orbital energies ( $E_{LUMO}$ ) and energy gaps ( $E_g$ ) of *SQ1* & *SQ2* (in dichloromethane) at B3LYP/6-31G\*\* and TD-B3LYP/6-31G\*\* level of theories.

[a,b and d] calculated from CV and [c,e] calculated by Gaussian 03 at B3LYP/6-31G\*\* and TD-B3LYP/6-31G\*\* level of theories.

Compound	$E_{ox}^{onest}$ (V) <sup>a</sup>	$E_{red}^{onest}$ (V) <sup>a</sup>	$E_{HOMO}$ (eV) <sup>b</sup>	$E_{LUMO}$ (eV) <sup>b</sup>	$E_{HOMO}$ (eV) <sup>c</sup>	$E_{LUMO}$ (eV) <sup>c</sup>	$E_{gap}$ (eV) <sup>d</sup>	$E_{gap}$ (eV) <sup>e</sup>	Ref. No
* <i>Dyenitro</i>	-1.1	0.6	5.0	2.3	-6.43	-3.62	2.7	2.82	[42]
<i>SQ1</i>	0.39	0.32	-5.19	-3.08	-5.71	-3.56	2.11	2.15	[43,44]
<i>SQ2</i>	0.36	0.30	-5.16	-3.1	-5.7	-3.48	2.31	2.22	[43,44]



**Figure 4.** (c) Cyclic voltammetry of *SQ1* (d) Cyclic voltammetry of *SQ2* at different scan rate with 0.1 M tetrabutylammonium hexafluorophosphate (NBu<sub>4</sub>PF<sub>6</sub>) as the supporting electrolyte and 0.01 M ferrocene (Fc/Fc+) as the internal electrode at scan rate from 25, 50, 100, 150, 200, 250 and 300 mV/s.

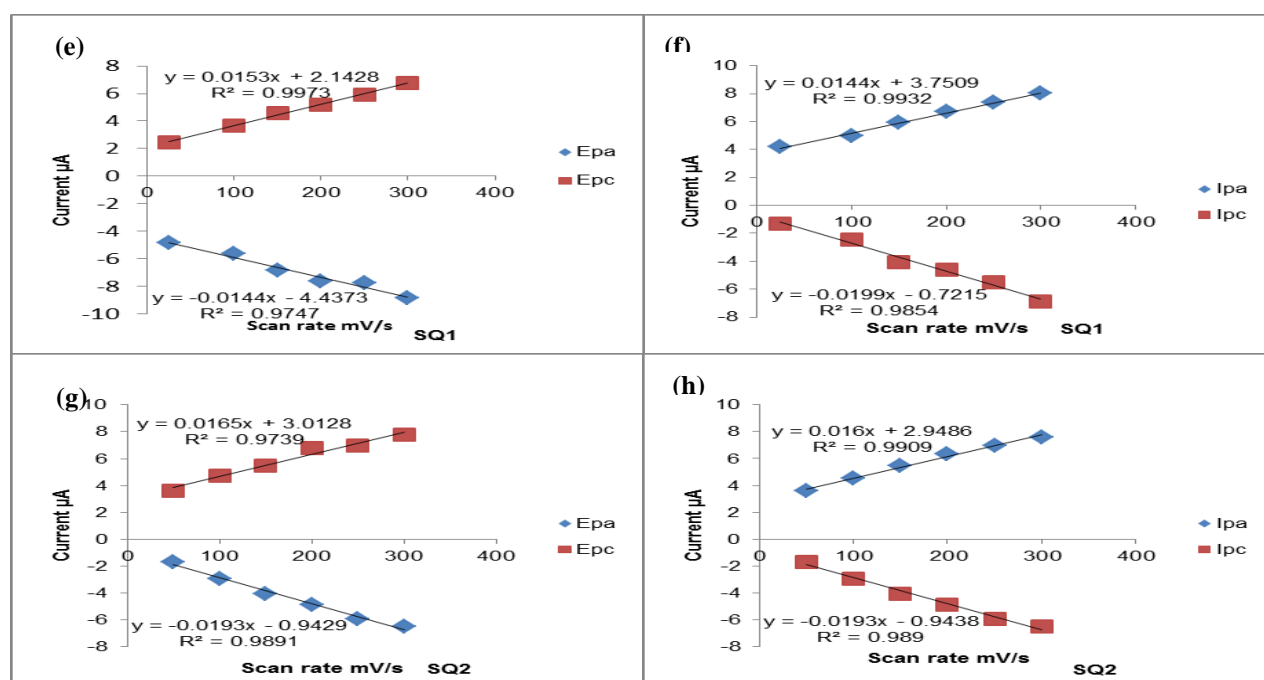
The  $E_{ox}$ ,  $E_{red}$ ,  $I_p$ ,  $E_a$  values were calculated. The oxidation and reduction potentials of *SQ1* & *SQ2* were determined under the same experimental conditions to estimate the ionization potential ( $I_p$ : energy of Highest Occupied Molecular Orbital) and electron affinity ( $E_a$ : energy of Lowest Unoccupied Molecular Orbital). The Peak-to-peak separation, between the corresponding anodic and cathodic peaks increase with increasing scan rate, which points to quasi-reversible behaviour. The values range from 0.501~1.672V, -1.263 ~ -2.531V for the redox potential ( $E_{ox}$ ,  $E_{red}$ ) *SQ1*, and 0.571 ~1.962V, -1.419 ~ -2.715V for the *SQ2* ( $E_{ox}$ ,  $E_{red}$ ) at different scan rate from 25-300mV/s. The -COOH substituent affected on the potential values, but the effect is small. The  $I_p$  range from -4.901 to -6.072 eV for *SQ1* and -4.971 to -6.362 eV for *SQ2* showed that the -COOH acid substituent super exert a small effect on the frontier orbital energy level. This is stratifying with determined results for the oxidation potential. Because the  $I_p$  means the energy required by losing an electron from the molecule, the substituent effect on  $I_p$  should be related to the oxidation potential. So a relationship between  $E_a$  and  $I_p$  was evaluated and the result is shown in Figure 6 (k, l) as a good slope 0.99 between *HOMO* and *LUMO* for *SQ1* & *SQ2*, this implies the feasibility and validity of the theoretical estimation and the experimental determination. This relationship between the  $E_a$  and the  $E_{HOMO}$ , or the  $I_p$ , can be obtained as in equations (4-5) [45].

$$I_p = -(E_{ox} + 4.4)eV \quad (4)$$

$$E_a = -(E_{red} + 4.4)eV \quad (5)$$

where  $E_{ox}$  and  $E_{red}$  are the onset potentials of oxidation and reduction, respectively, while  $E_g$  is the band gap of the material. Comparing  $I_p$  and  $E_a$  of the *SQ1* & *SQ2*, it can be seen that *SQ1* has negatively higher values of  $E_a$  than *SQ2*, which means that for *SQ1* the electron injection process is easier than that for *SQ2*. However,  $I_p$  values of *SQ2* are more negative than *SQ1* suggesting that holes are difficult to be injected from ITO into the squaraine dyes.

From **Figure 5. e, f, g, h** it can be observed that the anodic peak potential (Epa), cathodic peak potential (Epc) and the anodic and cathodic peak current (Ipa & Ipc) increases with increasing scan rate.

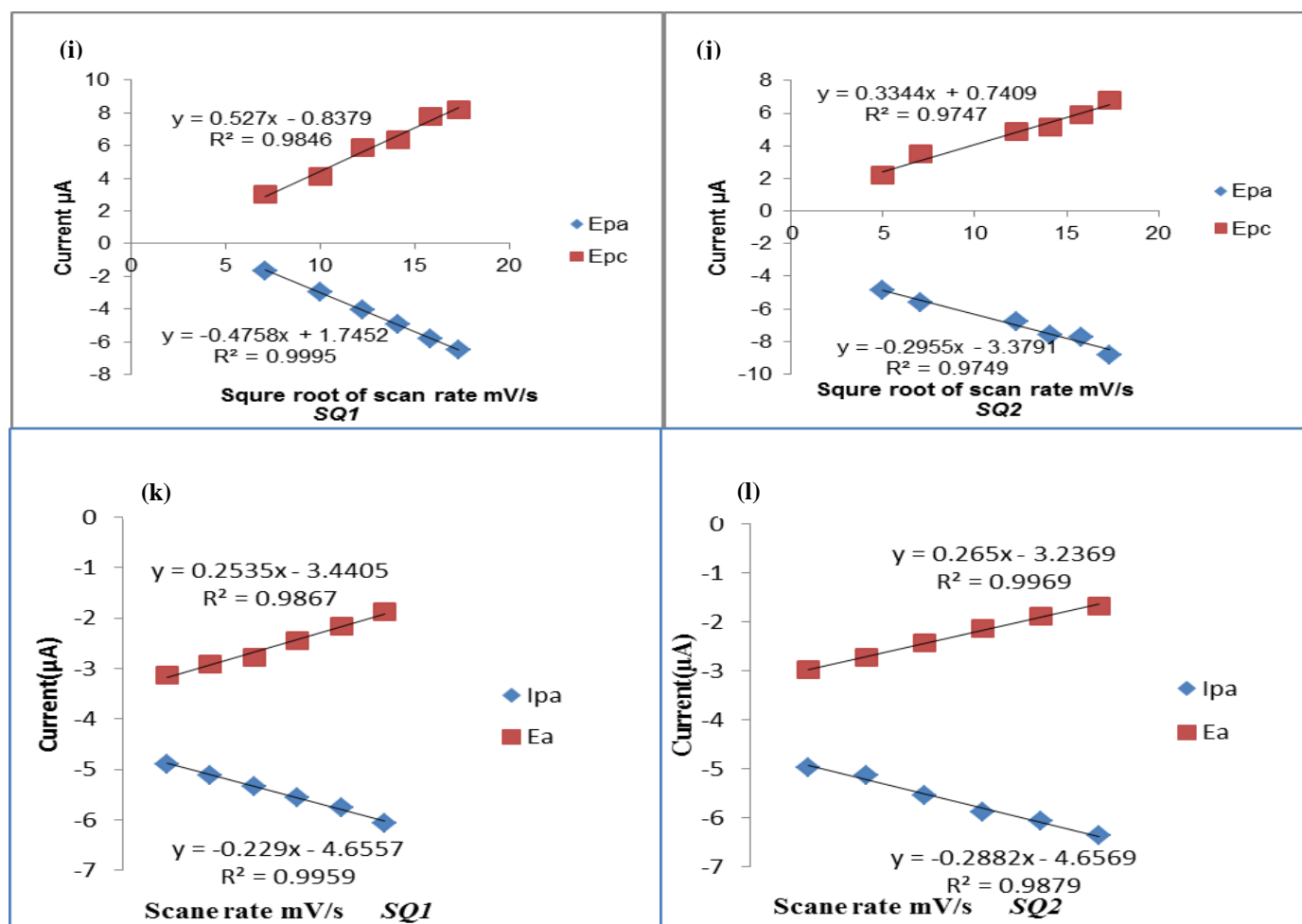


**Figure 5. (e, f).** The plots of peaks current versus scan rate of  $E_{ox}$ ,  $E_{red}$  and  $I_p$ (*HOMO*),  $E_a$ (*LUMO*) of *SQ1* (g, h) The plots of peaks of  $E_{ox}$ ,  $E_{red}$  and  $I_p$ (*HOMO*),  $E_a$ (*LUMO*) for *SQ2* at different scan rate 25,50,100,150,200, 250 and 300 mV/s.



The peak current for *SQ1* & *SQ2* were found linear to scan rate with a regression equation of  $E_{pa}$  ( $\mu A$ ) =  $0.0153x + 2.1428$ ,  $0.165x + 3.0128$  &  $E_{pc}$  ( $\mu A$ ) =  $-0.014x - 4.4373$ ,  $-0.0193x - 0.9429$  with correlation coefficient  $R^2 = 0.997$ ,  $0.974$  &  $R^2 = 0.974$ ,  $0.989$  respectively. Also, the  $I_{pa}$  ( $\mu A$ ) =  $0.044 + 3.7509$ ,  $0.016x + 2.9486$  &  $I_{pc}$  ( $\mu A$ ) =  $-0.0199x - 0.7215$ ,  $-0.0193x - 0.9438$  with correlation coefficient  $R^2 = 0.993$ ,  $0.985$  &  $0.991$ ,  $0.989$  for *SQ1* & *SQ2* respectively.

In figure 6(e, f) the oxidation and reduction peak currents linearly increase with the square root at different scan rate for *SQ1* & *SQ2*. This further confirmed that *SQ1* & *SQ2* dyes show reversible behavior in known reversible redox systems. The relationship between  $E_a$  (HOMO) and  $I_p$  (LUMO) was evaluated and the results are shown in Figure 6(k, l) as a good slope 0.99 between HOMO and LUMO for *SQ1* & *SQ2*, this implies the feasibility and validity of the theoretical estimation and the experimental determination.

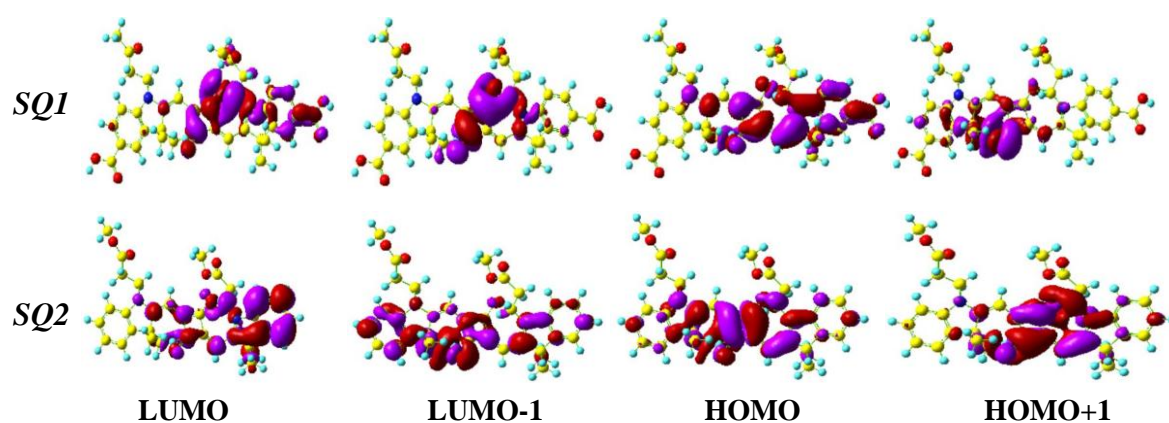


**Figure 6.**(i, j) the square root of scan rate for *SQ1* & *SQ2*, (k, l) relationship between  $I_{pa}$  (HOMO) and  $E_a$  (LUMO) for *SQ1* & *SQ2* at different scan rate 25, 50, 100, 150, 200, 250 and 300 mV/s.

### 3.3 Computational details

In the charge density distribution patterns of the ground state highest occupied molecular orbitals (HOMOs and HOMOs-1), lowest unoccupied molecular orbitals (LUMOs and LUMOs+1) of two *SQ1* and *SQ2* dyes are illustrated in Figure 7. The HOMOs-1 is distributed on squaraine moiety and only on right indole moiety in *SQ1* while distributed on the squaraine moiety and both of the indole units in *SQ2*. The charge densities of LUMO and HOMO are localized on squaraine moiety. In *SQ1*, the electron-withdrawing group is  $-COOH$  and the carbonyl groups of 2-3-(2-

methoxy-2-oxomethyl) units also take part in the formation of LUMOs and LUMOs+1 in *SQ1* and *SQ2*. The LUMOs+1 are localized on both of the left indole units and squaraine moieties. The charge density on carbonyl LUMO and LUMO+1 on 2-3-(2-methoxy-2-oxomethyl) are less than *SQ2*-counterpart. The computed energies of HOMO ( $E_{HOMOs}$ ), LUMO ( $E_{LUMOs}$ ) and LUMOs+1 ( $E_{LUMOs+1}$ ) and energy gaps ( $E_g$ ) of two *SQ1* and *SQ2* dyes at B3LYP/6-31G\*\* level of theory are illustrated in Table 2. The  $E_{HOMOs}$  and  $E_{LUMOs}$  increases in *SQ2* while *SQ1* decreases substituting the electron withdrawing group –COOH. We have observed the smallest  $E_g$  values for *SQ1* which has –COOH group at the –R position. The calculated energies gaps ( $E_g$ ) of all the two squaraine *SQ1* & *SQ2* sensitizers are smaller than that of the dyenitro (2.8 eV) [42] revealing that the absorption spectra of formers would be red shifted and that DSSC efficiency might be improved in the sensitizers *SQ1* and *SQ2*. The smaller  $E_{LUMO}$  of *SQ1* reveals that the injected electrons would be more stable, and the charge transport cannot be quenched in prior ones.



**Figure 7.** The charge density distribution of the frontier molecular orbitals (0.02 contour value) of *SQ1* & *SQ2* dyes at B3LYP/6-31G\*\* level of theory

## 4. Conclusion

The cyclic voltammetry and time dependent density functional theory calculations are accomplished. The electrochemical properties of the *SQ1*, *SQ2* dyes were investigated. The HOMO energy levels of the *SQ1* & *SQ2* dyes were -5.19 eV and -5.16 eV. The LUMO energy levels of *SQ1* & *SQ2* are calculated to be -3.08 eV, -3.1 eV and estimated the band gaps are 2.15 eV, 2.22 eV respectively. The ground state geometry has been computed by applying density functional theory (DFT). The excitation energy was calculated by using time-dependent (DFT-TD) at DFT/B3LYP/6-31G\*\* level of theory. The *SQ1* dye showed better electrochemical properties than *SQ2*. The *Ip* range showed that the -COOH acid substituent super exert a small effect on the frontier orbital energy level. The relationship between *Ea* and *Ip* was evaluated as a good slope 0.99 between HOMO and LUMO for *SQ1* & *SQ2*.

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