Int. J. Electrochem. Sci., 10 **(2015)** 1822 - 1832

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Comparative Study of the Structural, Electronic and Charge Transport Properties of Benzothiazole- and Indole-Based Squaraine Sensitizers

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Received: 20 September 2014 / *Accepted:* 29 November 2014 / *Published:* 30 December 2014

The donor organic sensitizers and acceptor inorganic part (e.g. TiO_2 nanoparticles) gained significant attention in the field of photo-excitation, electrochemistry and hetero-junction solar cells. In the present study structural, electronic and charge transport parameters have been calculated with respected to benzothiazole- and indole-based squaraine dyes as donor while Si/TiO_2 as acceptor then compared with previously studied hetero-junction solar cell materials. We have optimized the ground state geometries of benzothiazole- and indole-based squaraine dyes by density functional theory (DFT). The geometries of neutral, cation and anion species have been optimized by restricted and unrestricted B3LYP/6-31G** level of theories, respectively. The 2-3-(2-ethoxy-2-oxoethyl)benzo[d]thiazol-2(3H)-ylidene)methyl)-4-((3-(2-ethoxy-2-oxoethyl)benzo[d]-thiazol-3-ium-2-yl)methyl-ene)-3-oxocyclobut-1-enolate (BTSQD1) has been synthesized by our group. Moreover, we have designed derivatives of the benzothiazole- (BTSQD2 and BTSQD3 which have –COOH and –OCH_3 at terminal –R positions, respectively) and indole-based squaraine dyes (ISQD1-ISQD3). The structures of the benzothiazole- and indole-based dyes investigated here are same except that in later ones the "sulfur" has been substituted by -$C(CH_3)_2$. We have compared the geometries, electronic properties, ionization potentials, electron affinities, reorganization energies, relationship between the energies of highest occupied molecular orbitals/lowest unoccupied molecular orbitals and open-circuit voltages (V_{oc}), diagonal band gaps and short circuit current densities (J_{sc}), fill factors (FF) and factors affecting on the external quantum efficiency.

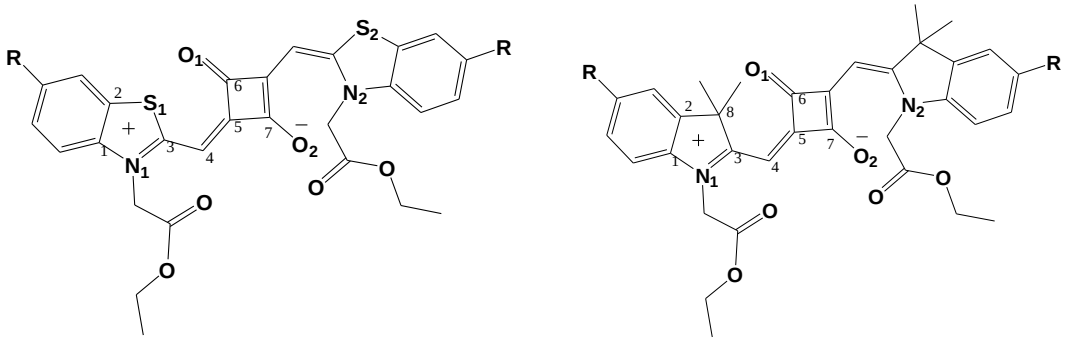
Keywords: Solar cells; squaraine dyes; TiO_2 nanoparticles; Density functional theory; Charge transport properties

1. INTRODUCTION

The metal free organic compounds are gaining significant attention in the field of renewable, sustainable energy [1-4], photoexcitation and photo-electrochemical processes [5] due to cheap, easy chemical modification, and structural flexibility [6-13]. Recently, we showed that metal free organic materials are good candidates for solar cells to enhance the efficiency, stability and intra-molecular charge transfer (ICT)[3, 14, 15]. To enhance the power conversion efficiency of the solar cells, absorption spectrum of the organic compound must be broadened. Recently, a number of studies have been carried out to fabricate the inorganic-organic hetero-junction solar cells (HJSC) to achieve the benefits coupled with both material groups [16] which improved the stability and power conversion efficiencies [17-19]. The efficiency of solar cell reduced due to the charge recombination and aggregation [20-23].

Due to large absorption coefficients in the red and near-infrared, squaraine dyes are good contenders which are being used in solar cells [24-28] and they showed enhanced efficiency [29-31]. Recently, Rao and co-workers pointed out that efficiency of bulk hetero-junction solar cell can be improved by incorporating the squaraine dye [32]. More recently, we synthesized two hydrazone dyes, i.e., 2-{4-[2-(2-hydroxybenzylidene)hydrazino]phenyl}ethylene-1,1,2-tricarbonitrile (HBHT1) and 2-{4-[2-(4-hydroxybenzylidene)hydrazino]phenyl}ethylene-1,1,2-tricarbonitrile (HBHT2). We fabricated the HJSC devices (dye/Si/TiO_2 nanoparticles) and measured their efficiencies then discussed the relationship between diagonal band gap of the heterojunction and open-circuit voltage (V_{oc}), relationship between the highest occupied molecular orbitals (HOMOs) energies/ionization potentials and the V_{oc}, diagonal band gap and short circuit current density (J_{sc}) and fill factor (FF) by density functional theory (DFT) and correlated with experimental data.

In the present article we have calculated the vertical/adiabatic ionization potentials, vertical/adiabatic electron affinities, reorganization energies, diagonal band gaps dyes/Si/TiO_2, HOMOs energies, lowest unoccupied molecular orbitals (LUMOs) energies then discussed the relationship between diagonal band gap and open-circuit voltage (V_{oc}), relationship between the HOMO energies/ionization potentials and the V_{oc}, diagonal band gap and short circuit current density (J_{sc}) and fill factor (FF), relationship between LUMOs energies and V_{oc} and factors affecting on the external quantum efficiency with the aim to shed light on the charge transport behavior in benzothiazole- and indole-based squaraine dyes (see Fig. 1). Previously, it was showed that V_{oc} strongly depends on the E_{LUMO} [33]. Moreover, we have compared the above mentioned charge transport parameters of the benzothiazole- and indole-based squaraine dyes with previously studied hydrazone dyes which showed efficiency 3.6% [34] and anthra[2,3-b]thiophene derivatives (DATP-a-DATP-f) [4]. The technical findings are motivating which would stimulate the experimentalists to use benzothiazole- and indole-based squaraine dyes in the field of HJSCs.



BTSQD1, R = H
BTSQD2, R = COOH
BTSQD3, R = OCH_3

ISQD1, R = H
ISQD2, R = COOH
ISQD3, R = OCH_3

Figure 1. The structures of the benzothiazole- (left) and indole-based squaraine dyes (right) investigated in the presented study along with atom numbers.

2. COMPUTATIONAL DETAILS

In previous studies it has been proved that DFT is reasonable and accurate choice which reproduces the experimental data of small organic compounds [4, 35-41]. Among different DFT functionals, B3LYP is a best functional [4, 36, 39, 40, 42-44]. Guillaumont and Nakamura pointed out that B3LYP functional is good approach which reproduces the absorption wavelengths of hydrazone, azobenzene, anthraquinone, phenylamine and indigo dyes [45]. It has been shown that B3LYP and TD-B3LYP functionals are good one which imitate the experimental structural, electronic, optical and charge transport properties more accurately [46-48] e.g. hydrazones [1, 2], triphenylamines [14], chemosensors [49], phthalocyanines [50], biologically active molecules [51], and oxadiazoles . Huong et al. optimized the geometries of naphtho[2,3-*b*]thiophene at B3LYP/6-31G** and PBE0/6-31G** levels of theories then discussed and compared their electronic and charge transport parameters with available experimental evidences where they concluded that B3LYP/6-31G** level of theory is more accurate and reasonable approach [52].

In the present study, DFT has been used to optimize the ground state geometries of benzothiazole- and indole-based squaraine dyes by applying the hybrid exchange correlation functional B3LYP [53-55] with 6-31G** basis sets [56-63]. The cation and anion geometries have been optimized by unrestricted (U) B3LYP/6-31G** level of theory. The geometric relaxation energy of a molecule from the neutral to the charged (cation / anion) states and from the charged (cation / anion) to the neutral state is known as reorganization energy (λ). We have computed the reorganization energies for hole (λ_h) and electron (λ_e) by using the following equation:

$$\lambda_{h/e} = \lambda_{cation/anion} + \lambda_{X/Y}. \quad (1)$$

where $\lambda_{cation/anion}$ means the energy of geometry relaxation from neutral to charged states and $\lambda_{X/Y}$ is the relaxation energy of a molecule from charged (cation / anion) states to neutral one [64, 65]. Both of the terms were computed from the adiabatic potential energy surfaces [66-68]. The λ_h is calculated by using the following equation:

$$\lambda_h = \lambda_{cation} + \lambda_X = [\, E^1 (M)^+ - E^0 (M)^+ \,] + [\, E^1 (M) - E^0 (M)] \quad (2)$$

E^0 (M), E^0 $(M)^+$ are the energies of optimized neutral and cation species at ground state, E^1 (M) is the energy of neutral state at the optimized cation species, and E^1 $(M)^+$ is energy of the cations state at the geometry of the optimized neutral species. The λ_e have been evaluated by using the following equation:

$$\lambda_e = \lambda_{anion} + \lambda_Y = [\, E^1 (N)^- - E^0 (N)^- \,] + [\, E^1 (N) - E^0 (N) \,] \quad (3)$$

E^0 (N) and E^0 $(N)^-$ are the energies of neutral and anion species optimized at ground state, E^1 (N) is the energy of neutral molecule at the geometry of the optimized anion species, and E^1 $(N)^-$ is energy of the anion species at the geometry of the optimized neutral species. The adiabatic/vertical ionization potentials (IPa)/(IPv) and electron affinities (EAa)/(EAv) have been calculated at the B3LYP/6-31G** level of theory as follows:

$$IPa = E^0 (M)^+ - E^0 (M) \quad \text{and} \quad IPv = E^1 (M)^+ - E^0 (M) \quad (4)$$

$$EAa = E^0 (N) - E^0 (N)^- \quad \text{and} \quad EAv = E^0 (N) - E^1 (N)^- \quad (5)$$

E^0 (M)/E^0 (N), E^0 $(M)^+$ and E^0 $(N)^-$ are the energies of the neutral molecule at the ground state, the energies of cation and anion states, respectively. The E^1 $(M)^+$ and E^1 $(N)^-$ are the energies of cation and anion states at the geometry of the optimized neutral molecule, respectively.

3. RESULT AND DISCUSSION

3.1. Geometries

In Fig. 2, we have illustrated the selected bond lengths in angstrom (Å) and bond angles in degrees (°) of benzothiazole- and indole-based squaraine dyes. The C_1-C_2 and C_3-N_1 bond lengths shortened while C_1-N_1 bond distance lengthened in ISQD1-ISQD3 compared to BTSQD1-BTSQD3. In ISQD1-ISQD3, the shortening (lengthening) in C_3-N_1 (C_1-N_1) bond lengths have been observed 0.015, 0.007, 0.006 Å (0.015, 0.009, 0.009 Å), respectively compared to their counterparts, i.e., BTSQD1-BTSQD3. The major alteration in the C_1-N_1-C_3 and C_3-C_4-C_5 bond angles has been noticed. In ISQD1-ISQD3, C_1-N_1-C_3 (C_3-C_4-C_5) bond angles decreases (increases) i.e., 3.44, 3.42, 3.41^o (4.94, 4.90, 4.85^o) compared to the BTSQD1-BTSQD3, respectively. We have perceived no significant alternation in bond lengths and bond angles by substituting the electron withdrawing groups (-COOH) or electron donating groups (-OCH_3) at terminal positions (-R). The major changes in the bond lengths and bond angles is due to the replacement of "S" by -$C(CH_3)_2$. The shortening of C_3-N_1 bond length in indole-based squaraine dyes is might be due to the strong electron donating behavior of dimethyl which donates the electrons to C_3 atom which attract the N_1 atom towards itself ultimately shortened the C_3-N_1 bond length resulting C_1-N_1 bond length lengthened. The electron donating behavior altered the bond length is in good agreement with the previously published work [69].

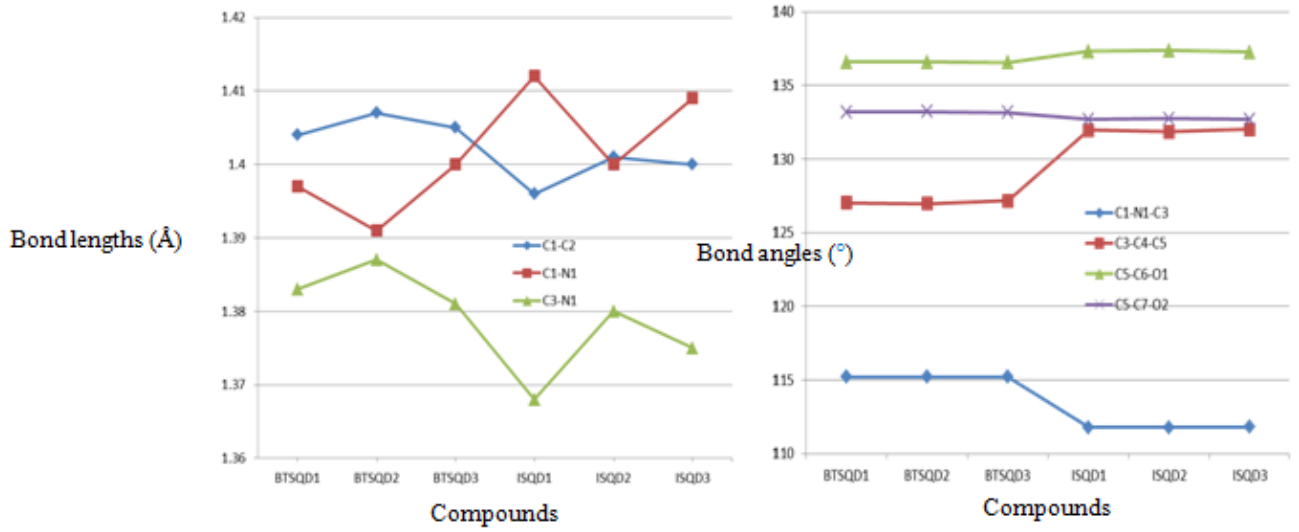


Figure 2. The bond lengths (left) in Å and bond angles (right) in degree (°) of benzothiazole- and indole-based squaraine dyes optimized at B3LYP/6-31G** level of theory.

3.2. Ionization potentials, electron affinities and reorganization energies

The IPa, IPv, EAa and EAv are the vital properties to compute the charge transport barriers, which were estimated at the B3LYP/6-31G** level of theory. In semiconductors lower IP and higher EA are key parameters to improve the charge transport ability for electron and hole, respectively. The calculated IPa, IPv, EAa and EAv data of all the derivatives has been tabulated in Table 1. Zhang and co-workers pointed out that organic materials which have high EAv and small IPv might be better for n-type and p-type charge injection, respectively [70]. From Table 1, it can be found that EAv of BTSQD1, BTSQD2, BTSQD3, ISQD1, ISQD2 and ISQD3 are 1.15, 1.57, 1.05, 1.25, 1.67 and 1.13 eV, respectively. Usually, the EAv and EAa of the derivatives containing –COOH group are greater than other counterparts. The EAv follow the similar tendency to that of the LUMO energies which is in good agreement with the previous studies that the compounds with greater LUMO energies would have the higher EAv [71]. It can be perceived from Fig. 3 that ISQD2 has the highest LUMO energy followed by BTSQD2 among the studied compounds hence have the highest EAv, i.e., 1.67 and 1.57 eV, respectively. The IPv of BTSQD1-BTSQD3 (5.62, 5.87, 5.43 eV) is smaller than the ISQD1-ISQD3 (5.78, 6.06, 5.53 eV), respectively. The trend of IPv is in good agreement with the HOMO energies. The compounds having larger HOMO energies have the greater IPv values.

To investigate the charge transport behavior and the ability to carry out the charge in semiconductors the reorganization energy is an important quantity [72, 73]. The hole/electron reorganization energies (λ(h) / λ(e)) of BTSQD1, BTSQD2, BTSQD3, ISQD1, ISQD2 and ISQD3 at B3LYP/6-31G** level of theory have been given in Table 1. The calculated λ(h)/λ(e) of BTSQD1-BTSQD3 (0.282/0.276, 0.311/0.269 and 0.291/0.295) are smaller than the ISQD1-ISQD3 (0.420/0.322, 0.461/0.328, and 0.366/0.350), respectively. The smaller λ(h)/λ(e) of BTSQD1-BTSQD3 than ISQD1-ISQD3are esteeming that the charge transport ability of prior compounds would be superior. The λ(e) values of all the studied compounds except ISQD3 are smaller than the diphenyl-

naphtho-dithiophene 0.34 eV [74] and oligofuran 0.40 eV [75] revealing that studied compounds might be proficient electron transporters as compared to the former ones. The λ(h) values of BTSQD1-BTSQD3 are smaller than 2-{4-[2-(2-hydroxybenzylidene)hydrazino]phenyl}ethylene-1,1,2-tricarbonitrile, 2-{4-[2-(4-hydroxybenzylidene)hydrazino]phenyl}ethylene-1,1,2-tricarbonitrile [34], benzo[2,3-b]thiophene derivatives [38]

Table 1. The vertical/adiabatic ionization potentials and electron affinities and hole/electron reorganization energies λ(h)/λ(e) at the B3LYP/6-31G** level of theory. All values in eV.

	BTSQD1	BTSQD2	BTSQD3	ISQD1	ISQD2	ISQD3
IPv	5.62	5.87	5.43	5.78	6.06	5.53
IPa	5.48	5.72	5.29	5.58	5.83	5.36
EAv	1.15	1.57	1.05	1.25	1.67	1.13
EAa	1.29	1.71	1.20	1.42	1.83	1.30
λ(h)	0.282	0.311	0.291	0.420	0.461	0.366
λ(e)	0.276	0.269	0.295	0.322	0.328	0.350

3.3. Electronic properties

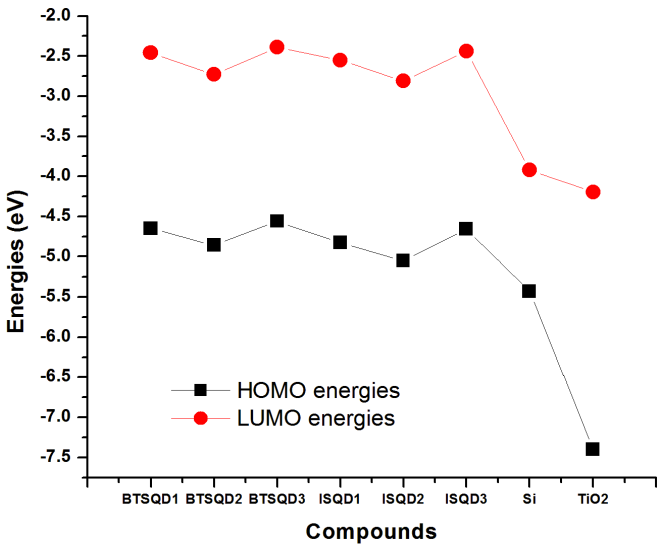


Figure 3. The HOMOs and LUMOs energies of donors and acceptors.

The HOMO energies (E_{HOMO}) and LUMO energies (E_{LUMO}) of Si (TiO_2) are –5.43 and -3.92 eV (–7.40 and -4.20 eV), respectively [76, 77]. The HOMO and LUMO energies of the indole-based squaraine dyes are lower than the benzothiazole-based ones. The replacement of "S" by -$C(CH_3)_2$ have significant effect to lower the E_{HOMO} rather than E_{LUMO}, i.e., E_{HOMO} of ISQD1-ISQD3 are 0.18, 0.19 and 0.10 eV lower than BTSQD1-BTSQD3. The E_{HOMO} and E_{LUMO} of the acceptors (Si/TiO_2) are lower than the benzothiazole- and indole-based squaraine dyes. The average E_{HOMO} and E_{LUMO} values of the Si/TiO_2 are -6.41 and -4.06, respectively revealing staggered band alignment hetero-junction which

would be a favorable operation to transfer electrons to the cathode while holes to the anode. Previously, we showed that Si as an acceptor would behave as Nested band alignment hetero-junction while Si/TiO_2 would change the alignment to staggered band alignment hetero-junction. In the present case, we found that Si or Si/TiO_2 as an acceptor both would behave as staggered band alignment hetero-junction, see Fig. 3. For the comparison of present result with previous studies [78] , here we will focus on the Si/TiO_2 as an acceptor.

The excitons formed in the donor side are dissociated at the donor–acceptor interface in hybrid solar cells. The force requisite to overwhelmed the exciton binding energy (EBE) is delivered by the energy level offset (ELO) of the E_{LUMO} of the donor and the conduction band (CB) edge of the acceptor material [79]. The ELO of BTSQD1, BTSQD2, BTSQD3, ISQD1, ISQD2 and ISQD3 have been observed 1.60, 1.33, 1.67, 1.51, 1.25 and 1.62 eV, respectively to overcome the EBE showing that BTSQD2 and ISQD2 would be efficient materials which have smaller ELO. The ELO of the E_{HOMO} of the donor and the valence band (VB) edge of the acceptor material delivered dissociation of excitons (DE) formed in the acceptor material. The ELO of BTSQD1, BTSQD2, BTSQD3, ISQD1, ISQD2 and ISQD3 have been observed 1.76, 1.55, 1.85, 1.58, 1.36 and 1.75 eV, respectively which showed that for BTSQD2 and ISQD2 less energy would be prerequisite to DE. Previously, it was pointed out that V_{oc} is directly proportional to the diagonal band gap (DBG) of the hetero-junction [80]. We have observed that the DBGs 0.59, 0.80, 0.50, 0.77, 0.99 and 0.60 eV for BTSQD1, BTSQD2, BTSQD3, ISQD1, ISQD2 and ISQD3, respectively revealing BTSQD2 and ISQD2 would have superior V_{oc}. Previously, the ELO required to overcome EBE were calculated 1.30, 0.69, 1.34, 0.72, 1.33 and 0.71 eV while to overcome DE 1.36, 1.25, 1.52, 1.42, 1.48 and 1.37 eV for DATP-a-DATP-f, respectively. The smaller/equal ELO of ISQD2 than/to most of the anthra[2,3-b]thiophene derivatives revealing that former squaraine dye might be proficient HJSC material. The DBGs of six anthra[2,3-b]thiophene derivatives, i.e., DATP-a-DATP-f have been calculated 0.99, 1.10, 0.83, 0.93, 0.87 and 0.98 eV, respectively [4]. The superior/equal DBG value of ISQD2 to the DATP-a-DATP-f revealing that former would be efficient HJSC material. The smaller ELO of ISQD1-ISQD3 for EBE and DE as well as superior DBGs than their counterparts BTSQD1-BTSQD3, respectively illuminating that former would be efficient HJSC materials than later ones. Moreover, we observed that –COOH containing compounds (BTSQD2 and ISQD2) would be more efficient than other compounds. By comparing the ELO and DBGs of these dyes with HBHT1 and HBHT2 which have ELO 0.67 and 0.77 for EBE, 0.25 and 0.57 eV for DE while DBGs 2.1 and 1.78 eV, respectively revealed that benzothiazole- and indole-based squaraine dyes would also be good contenders for HJSCs.

The J_{sc} is directly proportional to the external quantum efficiency (EQE) which can be assessed by using the following equation:

$$EQE = \eta_{abs} \times \eta_{diff} \times \eta_{diss} \times \eta_{tr} \times \eta_{cc} \quad (7)$$

where η_{abs}, η_{diff}, η_{diss}, η_{tr} and η_{cc} are the absorption yield, ability of an exciton to diffuse to a D–A interface, exciton dissociation yield, efficiency of charge carrier transport throughout the device and efficiency of charge collection at the electrodes, respectively. All the squaraine dyes are good candidates to absorb in red region, on other hand the inorganic acceptors (Si/TiO_2) would enhance the η_{abs}. The η_{diff} is inversely proportional to the rate of recombination. The traps and recombination sites

would hamper the η_{tr} and the attainment of transport depends on the mobility of the accompanying semiconductors [81]. It is expected that long side chains would inhibit the recombination resulting improve the η_{diss} and η_{tr}. Additionally, the higher EA of BTSQD2 and ISQD2 would increase the electron transport toward cathode. The thriving injection of holes into the anode is conceivable if the HOMO level of the donor would be larger than anode ultimately improve the η_{cc}. We observed that HOMO energy levels of benzothiazole- and indole-based squaraine dyes are greater than anode revealing these materials would have superior η_{cc} [43]. The smallest E_{LUMO} have been observed for BTSQD2 and ISQD2 illustrating that these dyes would be effective donor materials.

4. CONCLUSIONS

From the first principles calculations, the following conclusions have been drawn:

a) The major variation in the geometrical parameters has been observed in ISQD1-ISQD3 compared to their complements. The substitution of –COOH or –OCH_3 groups have no significant affect to alter the geometry as compared to the replacement of "S" by -$C(CH_3)_2$ which is lengthening/shortening the bond lengths.

b) The smaller vertical ionization potentials of BTSQD1-BTSQD3 would lead to the reduce injection barrier which are revealing that these materials would be better hole charge transporters.

c) The smaller hole reorganization energies of benzothiazole-based sensitizers showed that these would be efficient hole transport materials.

d) The larger vertical electron affinities and smaller electron reorganization energies of ISQD1-ISQD3 would lead to better electron transport materials.

e) The HOMO and LUMO energies of dyes and Si or average values of the E_{HOMO} and E_{LUMO} of the Si/TiO_2 are close-fitting staggered band alignment hetero-junction solar cells.

f) The smallest energy level offset, dissociation of excitons and larger diagonal band gap (resulting superior V_{oc}) values of BTSQD2 and ISQD2 showed these materials would be efficient.

ACKNOWLEDGEMENT
This Project was funded by the King Abdulaziz City for Science and Technology (KACST) through National Science, Technology and Innovation Plan (NSTIP) under grant number 8-ENE198-3. The authors, therefore, acknowledge with thanks KACST for support for Scientific Research. Also, the authors are thankful to the Deanship of Scientific Research (DSR), King Abdulaziz University for their technical support.

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