

Theoretical Study of Electron Transfer Properties of Squaraine Dyes for Dye Sensitized Solar Cell

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Abstract. The environmental issues and high cost of Ru create many scientists to explore cheaper and safer sensitizer as alternative for dye sensitized solar cells (DSCs). Dyes play an important role in solar energy conversion efficiency. The squaraine (SQ) dyes has good spectral match with the solar spectra, therefore, SQ dyes have great potential for the applications in DSCs. SQ01_CA is an unsymmetrical SQ dye, reported by Grätzel and colleagues in 2007, featuring a D- π -spacer-A framework and has a carboxylic acid anchoring group. The electron donating ability of indolium in SQ01_CA and SQ01_CAA dyes is relatively weak, better performance may be achieved by introducing an additional donor moiety into indolium [1]. In this study, we investigate six unsymmetrical SQ dyes adsorbed on a (TiO₂)₃₈ cluster [2] using density functional theory (DFT) and time-dependent DFT to study electron transfer properties of squaraine dyes on their photophysical. SQ01_CA, WH-SQ01_CA, and WH-SQ02_CA use a carboxylic acid group as its electron acceptor. Furthermore, SQ01_CAA, WH-SQ01_CAA, and WH-SQ02_CAA use a cyanoacrylic acid group as its electron acceptor. WH-SQ01_CA and WH-SQ01_CAA have an alkyl, while WH-SQ02_CA and WH-SQ02_CAA have alkoxy substituted diarylamines to the indolium donor of sensitizer SQ01_CA. Our calculations show with additional diarylamines in donor tail of WH-SQ02_CAA, the SQ dyes have red-shifted absorption and have slightly larger probability of electron density transferred to TiO₂ moiety. Furthermore, an additional -CN group as electron withdrawing group in the acceptor exhibits red-shifted absorption and enhances the electron density transferred to TiO₂ and anchoring moiety after photo-excitation. The tendency of calculated probabilities of electron density being delocalized into TiO₂ and driving force for excited-state electron injection of these studied SQ dyes is compatible with their experimentally observed.

Key word: *Squaraine Dyes, Electron Injection Mechanism, Driving Force, Density Functional Theory, Electron Withdrawing Group*



1. Introduction

Dye sensitized solar cells (DSCs) is renewable energy source. It has promising technology because low production cost, large area, flexible, colorful, transparency and light weight devices [3],[4]. DSCs component consist of photosensitizer, a counter electrode, and a redox couple. Photosensitizer is one of the most important component because responsible for light harvesting and electron injection [5]. Grätzel and coworkers introducing ruthenium (Ru) complex as a photosensitizer in a DSCs such as the N3/N719 [6] dyes and the black dye N749 [7] with conversion efficiency of 10.8% [8]. They are promising sensitizers for DSCs, exhibit high performance and good stability [9]. However, Ru is very expensive, low natural abundance [10], and the difficulty for purification [9]. Recently, using porphyrin sensitizers dye SM315, which features structure of a donor- π bridge-acceptor with the cobalt (II/III) redox resulted Q-band absorption to 668 nm significantly red shifted. It is new result short-circuit current density (J_{sc}) of 18.1 mA cm^{-2} , and a power conversion efficiency (η) of 13% [11]. DSCs organic dyes (metal-free) is potential use as a photosensitizer. Ru-free organic dyes (e.g. triphenylamines, coumarins, and indolines) can absorb like as Ru dyes in 450-600 nm [12]. Replacing ruthenium based sensitizer with organic dyes is big chance for friendly environment and low cost. Organic sensitizer such as porphyrins, phthalocyanines, cyanines, and squaraine are the most interesting because they absorb strongly in the red and NIR regions [3]. Moreover, they are still growing for increased efficiency. The squaraine (SQ) dyes are interesting attention due to their unique photophysical and photochemical properties. These characterized by an aromatic four-membered ring system derived from squaric acid [13]. The SQ dye exhibit higher molar extinction coefficients [14], excellent performance in light harvesting [5], strong absorption because valency π - π^* excitation in the long wavelength region and known their intense absorption in the red/near-IR region [13].

The SQ01_CA has planar molecule structure, its cause intermolecular close π - π aggregation. The additional of nonplanar triphenylamine groups to SQ01_CA can prevent the aggregation of the dyes and increase the distance between oxidizing hole and TiO_2 surface. The indolium donor has weak ability for injection on TiO_2 , so it better introducing an additional donor into indolium [15]. New unsymmetrical squaraine dyes SQ01_CA, SQ01_CAA, WH-SQ01_CA, WH-SQ01_CAA, WH-SQ02_CA, and WH-SQ02_CAA as potential alternative by intense absorption in the far red region. In most cases of photosensitizer employ electron withdrawing -COOH and CN-COOH as anchoring groups, due to a more favorable electronic stabilization [16]. WH-SQ01_CA and WH-SQ02_CA have modified donor moiety with additional diarylamines varied alkyl or alkoxy chains, such as methyl and methoxy groups [15] while anchor by additional -CN groups for WH-SQ01_CAA and WH-SQ02_CAA. Introducing -CN groups as a strongly electron withdrawing has effect on the squaraine absorption. In this research, we want to investigate the influence of indoline which containing diarylamines as donor and acceptor (anchor) with additional -CN group.

2. Computational Methods

The ground state geometries of all structure dyes have been optimized in deprotonated forms by density functional theory (DFT) theory using B3LYP functional couple with 6-31G(d,p) basis set then excitation energies were calculated by time-dependent-DFT (TD-DFT) in solvent (EtOH). The solvation effect is simulated using the conducting polarizable continuum model (C-PCM). Based on optimized geometries in neutral form, the optical properties were obtained by calculating singlet-singlet excited state in ethanol solution using TD-DFT with the long-range corrected functional CAM-B3LYP and 6-31G(d,p) basis set [17]. All calculation is performed with GAUSSIAN09 program package. The optimized geometry of dye on TiO_2 were performed in the gas phase with DFT calculation by using B3LYP 6-31G (d,p) basis set, while UV-Vis spectra by TD-DFT calculation use CAM-B3LYP 6-31G(d,p) basis set. The electronic density difference map (EDDM) to visualization electron density before and after transition connected using GaussSum. The DSCs performance consider the $(\text{TiO}_2)_{38}$ clusters as acceptor materials. The dyes adsorbed on the anatase (101) surface of the $(\text{TiO}_2)_{38}$ cluster [10].

3. Result and Discussion

3.1. Molecular Geometries

In this study, we investigate six unsymmetrical SQ-derived dyes. These dyes have similar π -conjugated moiety, but have different donor moieties and acceptor groups. The optimized structure parameters of studied SQ dyes computed at the B3LYP/6-31G (d, p) basis set with C-PCM ethanol solvent. Figure 1 shows structural parameter of the dyes, primary bond lengths and dihedral angles of two aromatic rings which give effect in absorption spectra. Moreover, the length of the bonds between the aromatic rings and electron donor groups are in the range 1.38 and 1.39 Å shorter than normal bond length C-C (1.54 Å), showing especially bond character which favors intra molecular charge transfer. Six unsymmetrical SQ-derived dyes have dihedral angles of backbone and anchor close to 0°. These dyes performed coplanar conformations. This coplanar molecule structure can be smoothly injected electron from the donor moiety to anchoring groups (carboxylic acid or cyanoacrylic acid) through the squaraic ring unit.

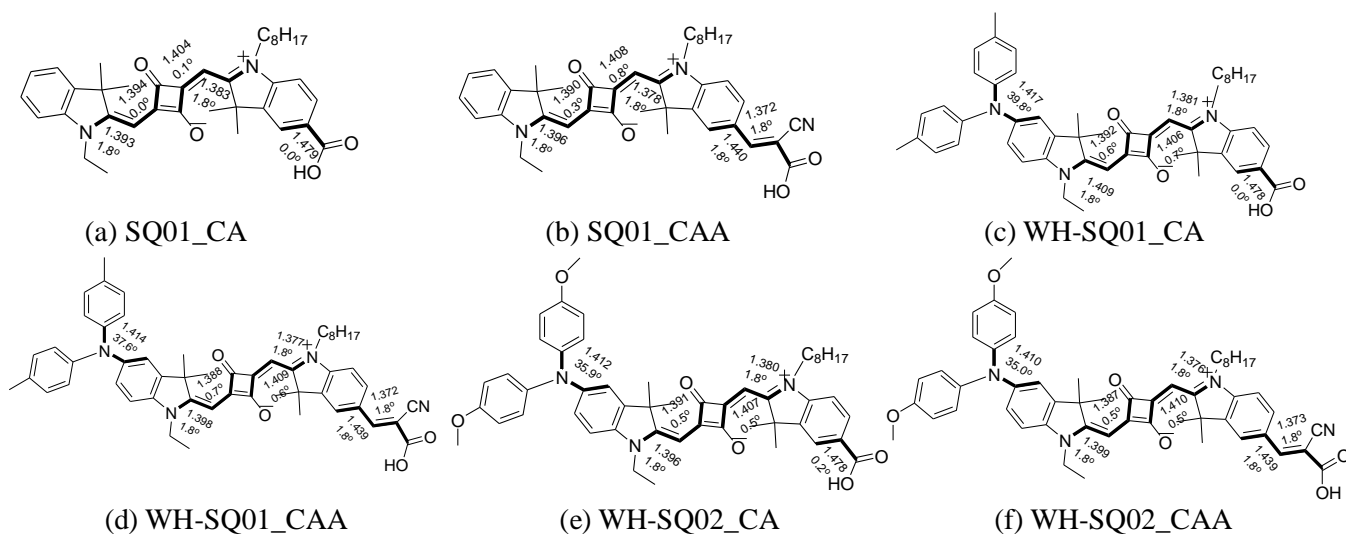


Figure 1. Selected molecular geometry of SQ-derived dyes sensitizer. (a) SQ01_CA, (b) SQ01_CAA, (c) WH-SQ01_CA, (d) WH-SQ01_CAA, (e) WH-SQ02_CA, (f) WH-SQ02_CAA. The bond lengths are labeled Å. The dihedral angle is corresponding central bonds from four consecutive bonds.

3.2. Absorption Spectra of SQ Dyes

The most important of dyes for DSCs is an absorption spectrum matching the solar irradiation spectrum [18]. Moreover, we calculated by TD-DFT the UV-Vis absorption spectra in ethanol solvent for free molecule dyes, while water solvent for TiO₂. The optical data of the squaraine dyes SQ01_CA, SQ01_CAA, WH-SQ01_CA, WH-SQ01_CAA, WH-SQ02_CA and WH-SQ02_CAA in ethanol solution and adsorbed on TiO₂ are provided in Table 1. The computations electronic structure of dyes is performed using TD-DFT calculation CAM-B3LYP functional with 6-31G (d, p) basis set. Both experiment and calculation shows absorption spectra of addition an alkyl and alkoxy substituted diarylamines to the indolium donor, for WH-SQ01_CA, WH-SQ01_CAA, WH-SQ02_CA and WH-SQ02_CAA.

The calculation result of studies free molecule dyes are an agreement with the Han and coworkers experimental report. The calculation with protonated state is more blue shift than experimental. The maximum absorption is 580 nm for WH-SQ02_CA with highest deviation from experimental -78. While, smallest one is -57 for SQ01_CA with λ_{\max} 563 nm. Moreover, WH-SQ02_CAA has high absorption spectra in 599 nm which more red shift than WH-SQ02_CA. The dyes adsorbed on TiO₂ cluster calculated in water. These trends of UV-Vis spectra has similar trend with experimental spectra. The highest absorption spectra dye on TiO₂ in 583 nm for WH-SQ02_CA, and 604 nm for WH-SQ02_CAA. The additional strong electron withdrawing -CN group in anchor has effect to absorption band in the visible region which longer wavelength to the red shifted band. The six dyes have features a single strong absorption band in experiment and computational absorption spectra.

Table 1 Experimental and computational methods of studied SQ dyes in EtOH at their protonated state and adsorbed on TiO₂.

Dyes	In EtOH					Adsorbed on TiO ₂		
	EXP.		Calculation			EXP.	Calculation	
			(Protonated State)					
	ϵ_{max} (M ⁻¹ cm ⁻¹)	λ_{max} (nm)	f^a	λ_{max} (nm)	Deviation from EXP.	λ_{max} (nm)	λ_{max} (nm)	Deviation from EXP.
SQ01_CA	158,500 ^a	620 ^a	1.81	563	-57	622	564	-58
SQ01_CAA	—	—	2.13	582	—	—	585	—
WH-SQ01_CA	86,000	652	2.03	578	-74	626	581	-45
WH-SQ01_CAA	—	—	2.37	598	—	—	602	—
WH-SQ02_CA	122,000	658	2.05	580	-78	630	583	-47
WH-SQ02_CAA	—	—	2.39	599	—	—	604	—

^aOscillator strength

The value of energy HOMO and energy LUMO to indicate driving force for efficient electron injection into TiO₂ conduction band for photo excitation [5][19]. The driving force of SQ dye is adsorbed on TiO₂ are SQ01_CA (0.23), WH-SQ01_CA (0.31), and WH-SQ02_CA (0.36) (see Table 2). These driving force increase with additional diarylamines varied alkyl or alkoxy chains in donor tail. The additional -CN group in acceptor will exhibit a relative low driving force in charge injection.

Table 2. Calculated driving force of SQ-dyes Adsorbed on (TiO₂)₃₈ Cluster in water solution

Dyes	HOMO	E.abs	Aligned	Driving force
SQ01_CA	-5.91	2.2	-3.71	0.23
SQ01_CAA	-5.94	2.12	-3.82	0.12
WH-SQ01_CA	-5.76	2.13	-3.63	0.31
WH-SQ01_CAA	-5.79	2.06	-3.73	0.21
WH-SQ02_CA	-5.71	2.13	-3.58	0.36
WH-SQ02_CAA	-5.74	2.05	-3.69	0.25

3.3. Electron Transfer of Dyes upon Photo-Excitation

To analyze the propensity for electron transfer of the six dyes adsorbed on TiO₂ for open

photo-excitation, we determined the contribution to electron density of each dye molecule. We use $(\text{TiO}_2)_{38}$ cluster with anatase 101 surface to calculate UV-Vis spectra. Table 3 shows the contribution of EDDM before and after photo-excitation on TiO_2 . The SQ01_CA, WH-SQ01_CA, and WH-SQ02_CA in the excited state have the electron density higher than in the ground state. The absorption SQ01_CA is 564 nm with electronic transition located on TiO_2 9%. Moreover, SQ01_CAA is 13% with λ_{max} 585 nm. WH-SQ02_CAA as acceptor has higher absorption 583 nm and 17% electron density, while 604 nm and 15% electron density for WH-SQ02_CA after photo excitation, it show more red shift transition than others. These mainly transition of the dyes located in HOMO and anchor and some located on TiO_2 . The presence of the donor tail chains (i. e methyl and methoxyl) and the CN groups encourages the electron transfer. The alignment energy levels of all dyes and electron density difference ground state and excited state are reported in Table 2 and Figure 2 (a-f) of SQ01_CA, SQ01_CAA, WH-SQ01_CA, WH-SQ01_CAA, WH-SQ02_CA, and WH-SQ02_CAA. Whereas, the excited state energy level is -3.71, -3.82, -3.63, -3.73, -3.58, and -3.69 eV, respectively. Furthermore, the energy level of experimental in conduction band TiO_2 semiconductor is -3.94 eV.

Table 3. Characters of Electron Density of SQ-dyes Absorbed on $(\text{TiO}_2)_{38}$ Cluster

Dyes	$\lambda_{\text{abs}}/$ f^a	Transitions ^b	Change	Percent Contribution (%)				
				Donor ^c	SQ	Indoline	Anchor	TiO_2
SQ01_CA	564 nm $f=2.08$	$\text{H} \rightarrow \text{L}$ (94%)	before	33	29	37	1	0
			after	28	35	24	3	9
			net	-5	6	-13	2	9
SQ01_CAA	585 nm $f=2.37$	$\text{H} \rightarrow \text{L}$ (88%)	before	31	28	38	3	0
			after	20	24	24	19	13
			net	-11	-4	-14	16	13
WH-SQ01_CA	581 nm $f=2.34$	$\text{H} \rightarrow \text{L}$ (86%) $\text{H-1} \rightarrow \text{L}$ (5%)	before	51	20	27	1	0
			after	29	33	23	3	12
			net	-22	13	-4	2	12
WH-SQ01_CAA	602 nm $f=2.64$	$\text{H} \rightarrow \text{L}$ (80%) $\text{H-1} \rightarrow \text{L}$ (6%)	before	50	21	27	3	0
			after	20	23	23	20	15
			net	-30	3	-4	17	15
WH-SQ02_CA	583 nm $f=2.35$	$\text{H} \rightarrow \text{L}$ (81%) $\text{H-1} \rightarrow \text{L}$ (8%)	before	57	18	24	1	0
			after	27	32	21	3	17
			net	-30	14	-3	2	17
WH-SQ02_CAA	604 nm	$\text{H} \rightarrow \text{L}$ (76%)	before	56	18	24	2	0

$f=2.67$	H-1 \rightarrow L (9%)	after	20	22	23	20	15
		net	-36	4	-1	18	15

(a) Oscillator strength. (b) The transitions with contribution larger than 5% are shown. (c) Indolium for SQ01_CA and SQ01_CAA; methyl substituted diarylamines to indoline donor for WH-SQ01_CA and WH-SQ01_CAA; methoxyl substituted diarylamines to indoline donor for WH-SQ02_CA and WH-SQ02_CAA.

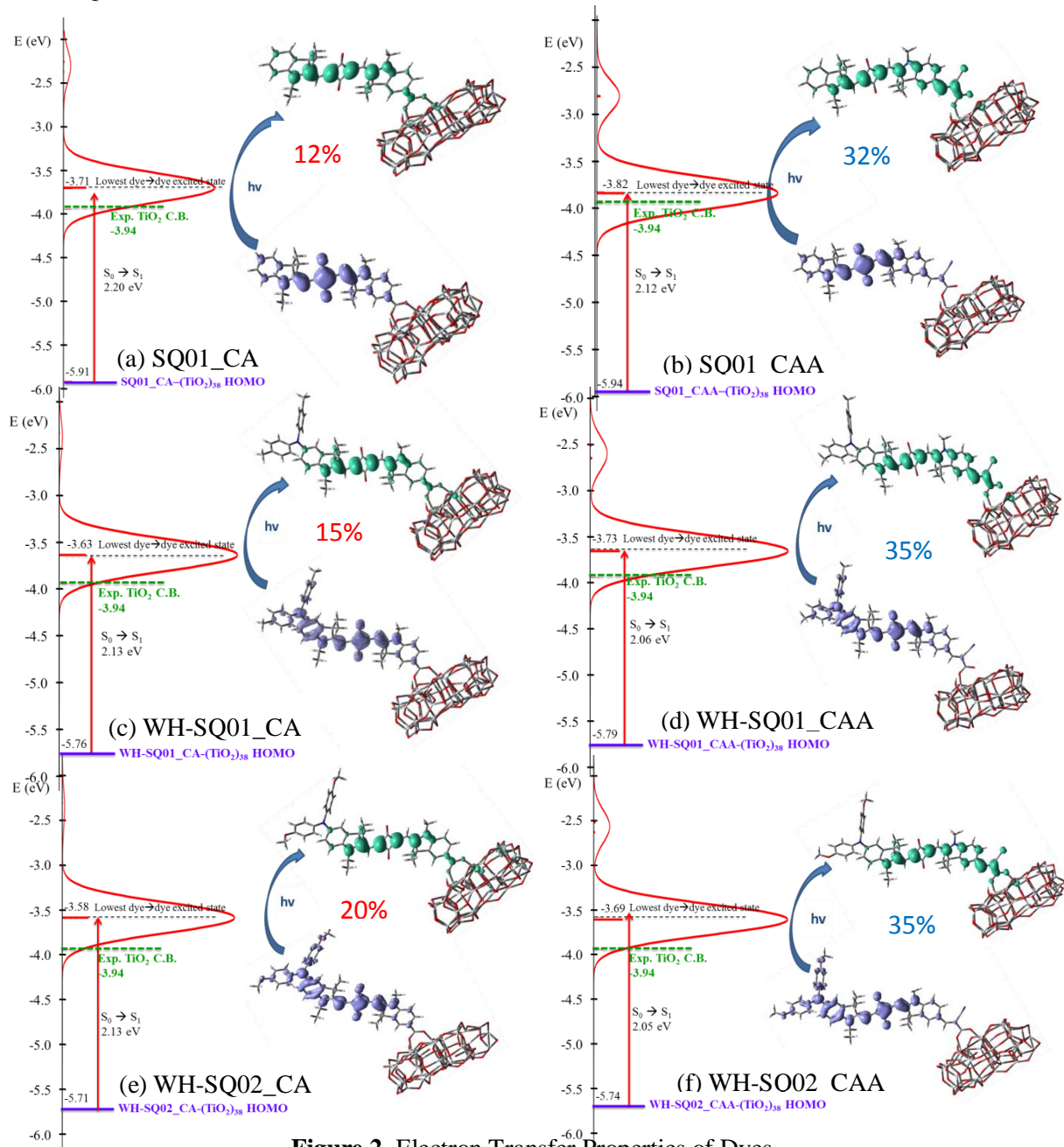


Figure 2. Electron Transfer Properties of Dyes

4. Conclusion

Our calculations show additional diarylamines in donor tail, the SQ dyes have red-shifted absorption and have slightly larger probability of electron density transferred to TiO_2 moiety. Moreover, the additional donor does not effectively push electron from donor to acceptor of TiO_2 . Moreover, an additional $-\text{CN}$ group as electron withdrawing group in the acceptor exhibits more red-shifted absorption even though $-\text{CN}$ group attract electrons to itself and some electron density transfer to TiO_2 .

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