

Theoretical Investigation of Carbazole-Based D-D- π -A Organic Dyes for Efficient Dye-Sensitized Solar Cell

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Abstract—In this paper, four carbazole-based D-D- π -A organic dyes code as CCT₂A, CCT₃A, CCT₁PA and CCT₂PA were reported. A series of these organic dyes containing identical donor and acceptor group but different π -system. The effect of replacing of thiophene by phenyl thiophene as π -system on the physical properties has been focused. The structural, energetic properties and absorption spectra were theoretically investigated by means of Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TD-DFT). The results show that nonplanar conformation due to steric hindrance in donor part (cabazole-carbazole unit) of dye molecule can prevent unfavorable dye aggregation. By means of the TD-DFT method, the absorption spectra were calculated by B3LYP and BHandHLYP to study the affect of hybrid functional on the excitation energy (E_g). The results revealed the increasing of thiophene units not only resulted in decreasing of E_g , but also found the shifting of absorption spectra to higher wavelength. TD-DFT/BHandHLYP calculated results are more strongly agreed with the experimental data than B3LYP functions. Furthermore, the adsorptions of CCT₂A and CCT₃A on the TiO₂ anatase (101) surface were carried out by mean of the chemical periodic calculation. The result exhibit the strong adsorption energy. The calculated results provide our new organic dyes can be effectively used as dye for Dye Sensitized Solar Cell (DSC).

Keywords—Dye-Sensitized Solar cell, Carbazole, TD-DFT, D-D- π -A organic dye

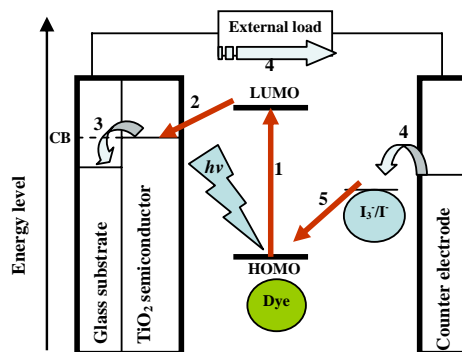
I. INTRODUCTION

THE Dye-sensitized Solar Cell (DSC) have attracted a great deal of interest rapidly in the attention of many research groups during the recent years [1]. Since the first developed and reported by M. Grätzel *et al* in the 1991 [2], this DSC technology is one of the most promising alternatives to compete with the traditional silicon solar cell because of organic dye molecules in DSC shown distinguished advantages such as their high optical absorption extinction coefficient, adjustable spectral wavelength response, low cost materials, and their environmental friendly [3, 4]. The mechanism of

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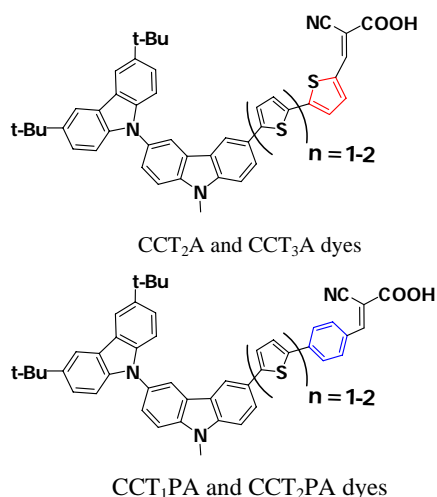
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Scheme. 1 Principle operations of DSC: (1) photon excitation; (2) electron injection; (3) electron collection; (4) electron transportation; (5) charge recombination

DSC (shown in scheme 1.) is start when electrons in dye molecules absorb the sun light and go to the excited state (LUMO). The excited electrons are then injected into the conduction band (CB) of TiO₂ via anchoring group in quickly time. These electrons were collected and flow through the external load to the counter electrode, at the same time the oxidized dyes are neutralized to ground state via I₃⁻/I⁻ system. The efficiency of DSC is based on the injection of electrons from dye molecules into the conduction band of TiO₂. Until now, the highest efficiency of DSC reported by M.Grätzel in the early 1990s, which is the ruthenium (Ru) complex coded as N3 dye was recorded about 11% under AM1.5 irradiation and it has used as general reference for standard efficiency of dye [5]. However, the Ru dyes are limited with the problem of manufacturing cost and toxicity issues. Therefore, many research teams have attempted to increase the performance of organic dyes not only in the synthesis laboratory, but also in the field of theoretical investigation based on computational study for understanding mechanism of electron transfer. In recent years, numerous organic dyes, such as coumarin [6], indoline [7], triarylamine [8], perylene [9], and hemicyanine [10] derivatives, have been investigated as dyes in DSC. The efficiency of DSC based on organic dyes is in range of 5-9% that lower than the Ru dyes. One choice for increasing the efficiency of organic dye is the design with Donor- π -conjugated-Acceptor (D- π -A) system [11]. Generally, organic dyes used for efficient DSC are required to broaden spectral absorption with high intensity to get most of sunlight.

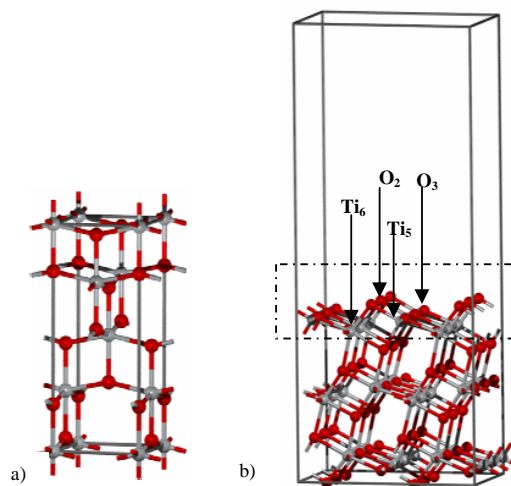


Scheme 2 Chemical structures of dyes under study

And should have suitable energy level by the highest occupied molecular orbital (HOMO) of the dye must lower than iodine/iodide redox potential and the lowest unoccupied molecular orbital (LUMO) must higher than the conduction band of TiO₂. In order to rationalize the experimentally observed properties of known materials as well as predict and design those of unknown efficient-dyes, theoretical studies using accurate quantum mechanical methods are very essential to provide the energetic properties and geometry of the target dye molecules. At present, numbers of papers have been proposed in the theoretical studies of organic dyes for dye-sensitized solar cell [12]. In this study, we reported four carbazole-based D-D- π -A organic dyes CCT₂A, CCT₃A, CCT₁PA and CCT₂PA (show in scheme 2.) which have been synthesized by our group using a combination of bromination, Suzuki coupling and Knoevenagel condensation reaction. Carbazole dimer acts as electron donor and cyanoacrylic acid as electron acceptor linked by thiophene and phenyl thiophene units as π -spacer. The photophysical properties of dyes, such as structures, and electronic properties, in term of HOMO, LUMO involve the absorption spectra were studied to reveal mechanism of electron transfer and discuss about the efficiency of these dyes. In addition, excitation states and frontier molecular orbitals of dyes were also analyzed. We have also studied the adsorption of CCT₂A and CCT₃A on the TiO₂ anatase (101) surface were carried out by mean of the chemical periodic calculation and analyzed on the adsorption energy.

II. COMPUTATIONAL METHODS

The calculated results of all organic dyes, CCT₂A, CCT₃A, CCT₁PA and CCT₂PA, have been obtained using Gaussian 03 *ab initio* DFT quantum chemical package. The ground-state geometries were fully optimized using Density Functional Theory (DFT) method combined with Becke's three-parameter hybrid functional and Lee-Yang-Parr's gradient-corrected

Fig. 1 TiO₂ vacuum slab used for the adsorption studies of the dyes.

correlation functional (B3LYP) at 6-31G(d,p) level. All calculations were performed without any symmetry constraints only in gas phase. These optimized structures were calculated the first excitation energy (E_g), maximal absorption wavelength and oscillator strengths (f) for the 10 states by using Time-Dependent Density Functional Theory (TD-DFT). To investigate the affect of hybrid functional on the E_g , TD-DFT with B3LYP and BHandHLYP hybrid functional were calculated at 6-31G(d,p) level. Subsequently, the TD-DFT results were entered in to the SWizard program for the simulation of absorption spectra of these dyes. Furthermore, these results are also discussed on electronic transition and its character which related to the absorption wavelength. These calculated results were compared with the experimental data in our group. To model the adsorption modes of the dyes on TiO₂ anatase (101) surface, the periodic density functional theory calculation have been carried out using the Dmol³ package as implemented in Material Studio (version 4.3). The TiO₂ anatase crystal cell as show in Figure 1.a was cleaved into the (101) surface to form TiO₂ periodic slab as show in Figure 1.b. In TiO₂ relaxation, the two lower layers of TiO₂ were fixed to keep their bulk structures and 20 Å vacuum regions between the slab to avoid the surface interaction. For these calculations we used the generalized gradient approximation (GGA) functional with Perdew and Wang (PW91) formulation. The electronic properties of core electron were treated with DFT semi-core pseudopotentials in term of DNP basis set. The convergence energy tolerance, gradient, and displacement convergences were 1.0×10^{-5} Ha, 0.004 Ha/Å, and 0.005 respectively.

III. RESULTS AND DISCUSSION

A. Optimal ground-state electronic structures

To gain insight into the effect of differing π -conjugated bridge on geometrical properties of the dye molecules,

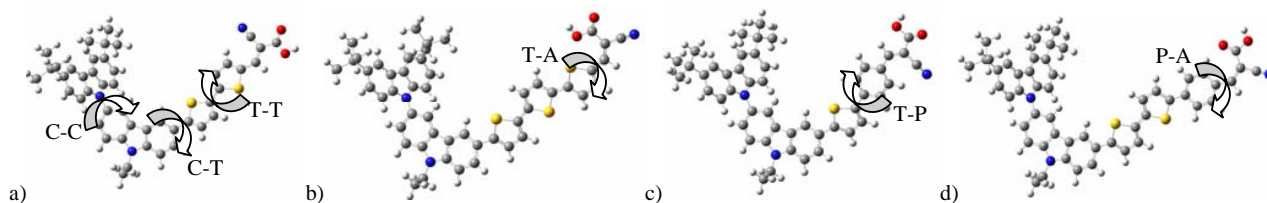


Fig. 2 The optimized conformation of CCT₂A (a), CCT₃A (b), CCT₁PA (c) and CCT₂PA (d) dyes obtained at the B3LYP/ 6-31G(d,p) level.

TABLE I
THE CALCULATED DIHEDRAL ANGLE CORRESPONDING TO THE OPTIMIZED CONFORMATION

Dyes	Dihedral angle (°)							
	C ₁ -C ₂	C ₂ -T ₁	T ₁ -T ₂	T ₂ -T ₃	T ₁ -P	T ₂ -P	T-A	P-A
CCT ₂ A	58.859	26.677	6.817	-	-	-	0.427	-
CCT ₃ A	58.493	27.962	11.538	6.538	-	-	0.131	-
CCT ₁ PA	59.057	28.433	-	-	16.204	-	-	0.075
CCT ₂ PA	56.913	26.862	7.387	-	-	15.245	-	0.105

C = Carbazole, T = Thiophene, P = Phenyl, A = Anchoring group

these four dyes have been optimized using DFT at B3LYP/6-31G(d,p) level of theory, the ground state structures are shown in Fig 2. and the selected dihedral angles are also summarized in Table I. Owing to a major factor for the low conversion efficiency of many organic dyes in the DSC is the formation of dye aggregates on the semiconductor surface [13]. Therefore, we designed carbazole dimer as donors to perform steric hindrance part of molecules which expect to reduce this dye aggregation phenomenon. For the optimized conformation, we found that dihedral angle between carbazole-carbazole units (in C-C column) of all four dyes were twisted out-of-plane fashion about 58 – 59 degree. These results show that nonplanar conformation due to steric hindrance in dye molecule can prevent unfavorable dye aggregation. Comparing between dyes with two different π -system, one contains only thiophene unit and another one contains phenyl-thiophene moieties, we found that dihedral angle are about 6-7° (T-T column) for the former and 15-16° (T-P column) for the latter. These results indicate that when phenyl ring was introduced to the dyes, the flat conformation on π -system were decreased respect to adjacent ring probably due to steric hindrance with H atom in phenyl ring. This causes the delocalization of π -electrons from donor to acceptor part cannot perform smoothly and may not increase the conjugation length. In addition, dihedral angle between π -spacer and anchoring group (in T-A and P-A column) of CCT₃A, and CCT₂PA are 0.131 and 0.105 degree, respectively, it reveal that replacing thiophene unit by phenyl ring does not significantly affect coplanarity on π -spacer respect to anchoring group of these dyes, consequently the injection of excited electron from thiophene or phenyl thiophene unit into the neighboring cyanoacrylic acid group are conveniently performed which is considered as an intramolecular charge transfer (ICT) process.

B. Effect of intramolecular charge transfer (ICT)

The molecular orbitals contribution is very important in determining the charge-separated states of organic dyes. To

create an efficient charge-separated state, HOMO should be localized on the donor subunit, and LUMO should be localized on the acceptor subunit [14]. In order to obtain ICT effect, the density of state (DOS) was performed, the molecular orbitals contribution of four organic dyes were shown in Table 2. and the contour plots of HOMO, LUMO and other molecular orbitals of these dyes are displayed in Fig 3. As listed in Table II., we divided the dye molecule into 4 parts, D1, D2, π and A. D1 and D2 represent carbazole units, π represent thiophene or phenyl thiophene units and A represent cyanoacrylic acid moiety, we found that electron density of the HOMO were located over the carbazole dimer which are calculated to be 96% (D1-D2), 89% (D1-D2), 97% (D1-D2) and 89% (D1-D2) for CCT₂A, CCT₃A, CCT₁PA and CCT₂PA, respectively. These results show the electron density of HOMO remains delocalized on the donor part. Whereas, the LUMO were located mainly across the π -system and anchoring group which are calculated to be 73% (π), 24% (A) for CCT₂A, 73% (π), 26% (A) for CCT₃A, 67% (π), 31% (A) for CCT₁PA and 73% (π), 26% (A) for CCT₂PA. As shown in Fig 3., molecular orbitals analysis confirmed that the HOMO of all dyes was delocalized over the carbazole dimer and the LUMO was delocalized across the π -system and anchoring group. This distribution of the HOMO and LUMO is separated in the molecule, indicating that the HOMO→LUMO transition can be considered as an intramolecular charge-transfer (ICT) transitions. From TD/BHandHLYP calculated results in Table III., we found that CCT₂A and CCT₁PA show electronic transitions from both of HOMO and HOMO-1 to LUMO. The main character of these transitions can be assigned as ICT corresponding to the counter plotted of electron density in Fig 3. When thiophene unit of CCT₂A was replaced by phenyl ring in CCT₁PA dye, we found that the electron density in HOMO-1 is delocalized through over the donor and π -system. This results indicating that when electron was excited from HOMO-1→LUMO is composed both of ICT and π - π^* transitions, see in Fig. 3. For CCT₃A and CCT₂PA show similar trend but they also show the composition of HOMO-3

which is ICT character. In addition, the orbitals energies of

Dye	Electronic level	Orbital energies	The percent contribution (%)			
			D1	D2	π	A
CCT ₂ A	LUMO	-1.85	0	3	73	24
	HOMO	-6.08	76	20	3	0
	HOMO-1	-6.41	13	35	45	7
CCT ₃ A	LUMO	-1.94	0	1	73	26
	HOMO	-6.05	64	25	11	0
	HOMO-1	-6.25	23	21	53	3
	HOMO-3	-7.01	8	51	35	6
CCT ₁ PA	LUMO	-1.70	0	2	67	31
	HOMO	-6.07	76	21	3	0
	HOMO-1	-6.44	14	43	40	3
CCT ₂ PA	LUMO	-1.79	0	1	73	26
	HOMO	-6.01	63	26	11	0
	HOMO-1	-6.22	23	23	52	2
	HOMO-3	-7.00	3	31	56	10

TABLE II

MOLECULAR ORBITALS CONTRIBUTION OF 3 HIGHEST OCCUPIED AND LOWEST UNOCCUPIED MOLECULAR ORBITALS OF CARBAZOLE D-D- π -A ORGANIC DYES D1, D2 = Carbazole, π = Thiophene or Phenyl thiophene, A = Cyanoacrylic acid

LUMO are -1.85, -1.94, -1.70 and -1.79 eV for CCT₂A, CCT₃A, CCT₁PA and CCT₂PA respectively. These energies level are located above the conduction band (CB) of TiO₂ (2.77 eV) [14] which indicated a good property of dye-sensitizer. Therefore, these CCT_nA organic dyes have sufficient driving force for electron injection into CB of TiO₂.

C. Absorption spectra

To gain insight into the excited states giving rise to the absorption spectra of D-D- π -A organic dyes, TD-DFT calculations were employed with the B3LYP/6-31G(d,p) level in gas phase. It is well known that the failure of TD-DFT/B3LYP in highly delocalized/CT molecules is attributed to the fact that the exchange-correlation potentials generated by the current approximate exchange-correlation function decay too rapidly in the asymptotic region [15]. Therefore, the BHandHLYP functional has been employed to correct asymptotic behavior of the charge transfer (CT) states. The maximal absorption wavelengths from computational results are listed in Table IV. The TD-DFT results were entered into the SWizard program for the simulation of absorption spectra as show in Fig 4. These calculated results were compared with the experimental data in our group. As shown in Table IV. Absorption maximal wavelength of CCT₂A and CCT₃A dye using B3LYP functional are located at 573.40 and 597.46 nm, respectively. It has been shown that when increasing thiophene up to 3 units the adsorption wavelength were red-shifted. The similar trend has been found for the BHandHLYP results, the absorption spectra were located at 405.6 and 423.7

nm for CCT₂A and CCT₃A, respectively, the red-shifted was also performed. However the B3LYP results tended to overestimate the experimental absorption wavelength whereas BHandHLYP can

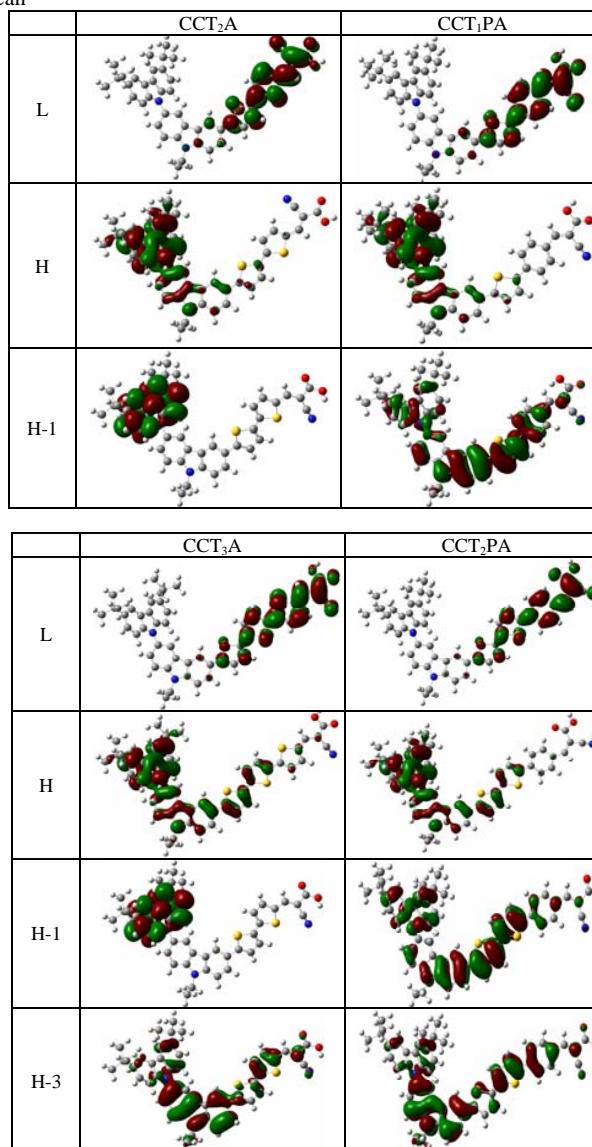


Fig 3 The counter plotted of HOMO, LUMO and others molecular orbitals of D-D- π -A organic dyes

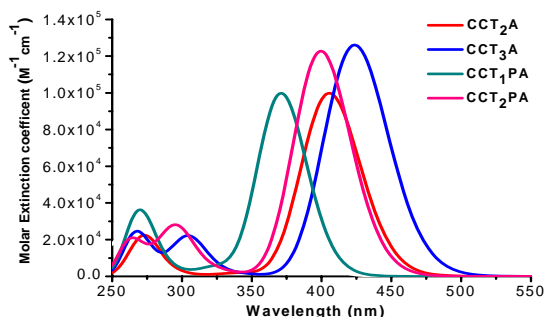


Fig 4 Computational absorption spectra obtained with TD-DFT/BHandHLYP at 6-31G(d,p)

TABLE III
CALCULATED TD-DFT EXCITATION ENERGY, OSCILLATOR STRENGTH AND ELECTRONIC PROPERTIES OF DYES BY BHANDHLYP/6-31G(D,P)

Dye	State	Excitation energy (eV, nm)	Oscillator strength (<i>f</i>)	Assignment	Character
CCT ₂ A	S1	3.06 (405.6)	1.3781	H-1 → L+0 (+64%)	ICT
				H-0 → L+0 (+14%)	ICT
CCT ₃ A	S1	2.93 (423.7)	1.7405	H-1 → L+0 (+53%)	ICT
				H-0 → L+0 (+19%)	ICT
				H-3 → L+0 (+8%)	ICT, π-π*
CCT ₁ PA	S1	3.34 (371.7)	1.3763	H-1 → L+0 (+59%)	ICT, π-π*
				H-0 → L+0 (+18%)	ICT
CCT ₂ PA	S1	3.10 (399.6)	1.6933	H-1 → L+0 (+59%)	ICT, π-π*
				H-0 → L+0 (+20%)	ICT
				H-3 → L+0 (+7)	ICT, π-π*

TABLE IV
COMPUTATIONAL AND EXPERIMENTAL ABSORPTION MAXIMA WAVELENGTH

Dye	Calculation		Experiment
	B3LYP	BHandHLYP	
CCT ₂ A	573.40	405.6	N.A.
CCT ₃ A	597.46	423.7	443
CCT ₁ PA	550.32	371.1	420
CCT ₂ PA	570.64	399.6	425

reasonably improve the calculated results to be more accurate. It has been found that BHandHLYP result is in excellent agreement with experimental data compared with B3LYP results. Furthermore, in Fig 4., the dyes exhibit wide absorption wavelength in range of 250 – 500 nm. For organic dyes with thiophene as π-system CCT₂A and CCT₃A not only show higher absorption wavelength but also exhibit higher molar extinction coefficient compared to dyes with phenyl-thiophene as π-system (CCT₁PA and CCT₂PA). In addition, when the number of thiophene unit were increased the increasing of the molar extinction coefficient were found in both of thiophene and phenyl thiophene as π-system.

A. Adsorption of dyes on TiO₂ anatase (101) surface

From the above results, it is clear that many properties of CCT_nA dyes with thiophene units as π-system show appropriate more than CCT_nPA dyes which replaced π-system by phenyl ring. For example, CCT_nA dyes show less dihedral angle on conjugated part than the CCT_nPA dyes, low excitation energy, provide good ICT character and also show broaden absorption spectral with high intensity. Therefore, only CCT_nA dyes were used to study the possible adsorption configuration of dyes on the metal oxide due to the strong adsorption configuration play a key role in improving the efficiency of the cell. The adsorption energy, E_{ads} is calculated using the expression

$$E_{ads} = E_{(slab+dye)} - E_{slab} - E_{dye}$$

where E_{slab} represent the energy of the clean slab, E_{dye} represent the anchor dye in the gas phase, and $E_{(slab+dye)}$ is the total energy of the complex of the slab with anchor dye. A negative value of $E_{ads} < 0$ indicates stable adsorption. To reduce the computational cost model molecules have been used for the dye-TiO₂ adsorption study by cutting the cabarazole dimer at the first time to calculated all possible adsorption configuration. These configuration include that molecular, dissociative, monodentate via CN-group and bidentate via CN-group and OH-group adsorption mode as show in Fig 5.a, b, c and d, respectively. The values of adsorption energy for possible mode are summarized in Table V, along with important structure parameter. From the table, it is observed that the

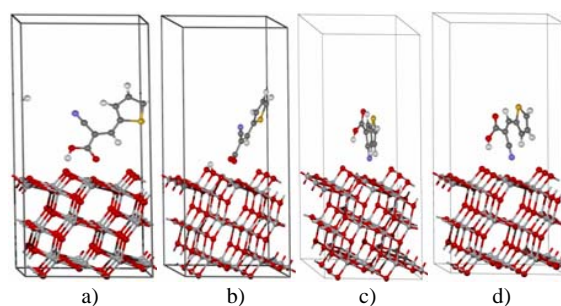


Fig 5 Different possible adsorption modes of anchor dye

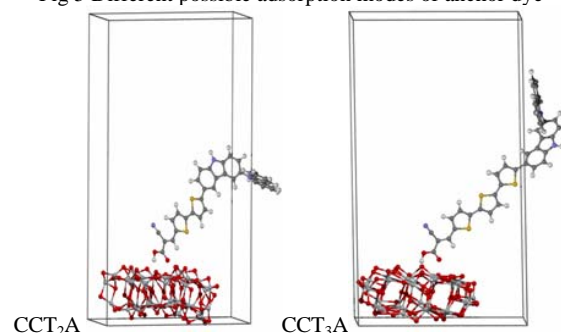


Fig 6 Molecular adsorption mode of organic dyes on TiO₂ surface

TABLE V
 IMPORTANT OPTIMIZED BOND LENGTH (Å) AND ADSORPTION ENERGY FOR THE DIFFERENT ADSORPTION CONFIGURATION OF ORGANIC DYES

Configuration mode	E_{ads} (kcal/mol)	Distance (Å)					
		Ti _{5c} -O	Ti _{5c} -OH	O _{2c} -H	C-OH	C-O	Ti _{5c} -N
a	-25.73	2.182	-	1.508	1.314	1.261	-
b	-22.07	2.029	2.01	0.97	1.275	1.288	-
c	-16.97	-	-	2.947	1.361	1.212	2.251
d	-14.60	-	-	3.892	1.354	1.214	2.308
CCT ₂ A	-26.11						
CCT ₃ A	-26.94						

molecular adsorption mode is the most stable by adsorption energy of 25.73 kcal/mol. And then optimized structure for the most stable configuration was extended to perfect molecule as show in Fig 6. These model were reduce TiO₂ in two raw. And we found that both of dyes-TiO₂ complexes show strong adsorption energy by CCT₃A tend to much than CCT₂A dyes.

IV. CONCLUSION

In summary, the theoretical study of carbazole-based D-D- π -A organic dyes were investigated. To gain a better understanding of the role of its electronic structure, absorption and electron transport properties, we performed DFT and TD-DFT calculation. From the present study, we can infer that CCT₃A dye showed the appropriate donor steric hindrance with coplanarity of π -spacer and anchoring group. It also exhibited the best absorption characteristics in maximum wavelength and highest molar extinction coefficient as well as, performing a good ICT character. Furthermore, it has strong binding energy on TiO₂ surface. This theoretical CCT₃A results show that it could greatly possible to use as potential sensitizer for highly efficient Dye-Sensitized solar cell (DSC). And we found that making use of functional using a larger percentage of exact exchange (BHandHLYP) provided better results for highly delocalized/CT molecules compared to the hybrid B3LYP density functional which tends to overestimate the transition energies. Interestingly, the experimental results obtained from our lab showed that CCT₃A dye performed high efficiency up to 5.76% which is slightly higher than N3 dye 4.11% (DSCs using these four dyes and N3 reference dye as sensitizers with TiO₂ nanoparticle and the electrolyte system of 0.5 M LiI/0.05 M 12/0.4M pyridine in mixture of γ -butyro-lactone (GBL) N-methylpyrrolidone (NMP) (7:3) were assembled and characterized).

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