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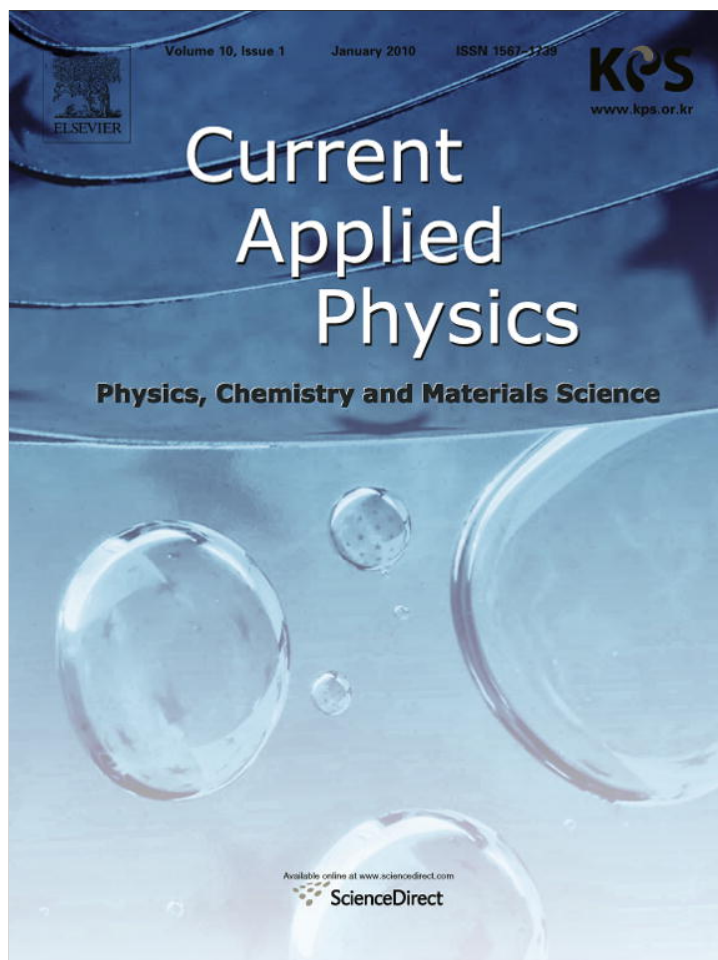


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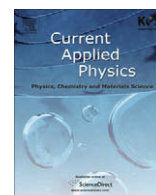
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DFT and TD-DFT study on structure and properties of organic dye sensitizer TA-St-CA

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ABSTRACT

The geometry, electronic structure, polarizability and hyperpolarizability of organic dye sensitizer TA-St-CA, which contains a π -conjugated oligo-phenylenevinylene unit with an electron donor–acceptor moiety, was studied using density functional theory (DFT), and the electronic absorption spectrum was investigated via time-dependent DFT (TD-DFT) with several hybrid functionals. The calculated geometry indicates that the strong conjugated effects are formed in the dye. The TD-DFT results show that the hybrid functional PBE1PBE and MPW1PW91 are more suitable than B3LYP for calculating electronic absorption spectra. The features of electronic absorption spectra were assigned on account of the qualitative agreement between the experiment and the calculations. The absorption bands in visible and near-UV region are related to photoinduced electron transfer processes, and the diphenylaniline group is major chromophore that contributed to the sensitization, and the interfacial electron transfer are electron injection processes from the excited dyes to the semiconductor conduction band. Compared with the similar dye D5, the good performance of TA-St-CA in dye-sensitized solar cells may be resulted from the higher energy level of the lowest unoccupied molecular orbital and the larger oscillator strengths for the most excited states with intramolecular electron transfer character.

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1. Introduction

In 1991, O'Regan and Grätzel presented a photovoltaic device that known as nanocrystalline dye-sensitized solar cell (DSSC). Since then, it has attracted a lot of attention because of the conversion of solar energy to electricity [1–5]. The main parts of DSSC are mesoporous oxide semiconductor layers that composed of nanoparticles and monolayer of dye sensitizers that attached to the surface of the semiconductor nano-films [3]. The dye sensitizers play an important role in DSSC that have a significant influence on the photoelectric conversion efficiency and transport performance of electrode [6–9]. Up to now, over thousands of dye sensitizers were synthesized and tested, only several kinds of dye sensitizers have good performance in DSSC. In metal–organic complexes, especially the noble metal ruthenium polypyridyl complexes, including N3 and black dye etc. that were presented by Grätzel et al., have proved to be the best dye sensitizers with overall energy conversion efficiency greater than 10% under air mass (AM) 1.5 irradiation [10–12]. In me-

tal-free organic dyes sensitizers, including cyanines, hemicyanines, triphenylmethanes, perylenes, coumarins, porphyrins, squaraines, indoline, and azulene-based dyes etc., have also been developed because of their high molar absorption coefficient, relatively simple synthesis procedure, various structures and lower cost [13–16]. In contrast to the numerous experimental studies of dye sensitizers, the theoretical investigations are relatively limited. Only several groups focused on the electronic structures and absorption properties of dye sensitizers [17–26], and Ru-complexes and organic dyes coupled TiO₂ nanocrystalline [27–30], as well as the electron transfer dynamics of the interface between dyes and nanocrystalline [31–35]. Until now, it remains a severe challenge for both experiment and theory to elucidate the fundamental properties of the ultrafast electron injection in DSSC [30], and to approach the satisfied efficiency of DSSC. Further developments in dye design will play a crucial part in the ongoing optimization of DSSC [36], and it depends on the quantitative knowledge of dye sensitizer. So the theoretical investigations of the physical properties of dye sensitizers are very important in order to disclose the relationship among the performance, structures and the properties, it is also helpful to design and synthesis novel dye sensitizers with higher performance.

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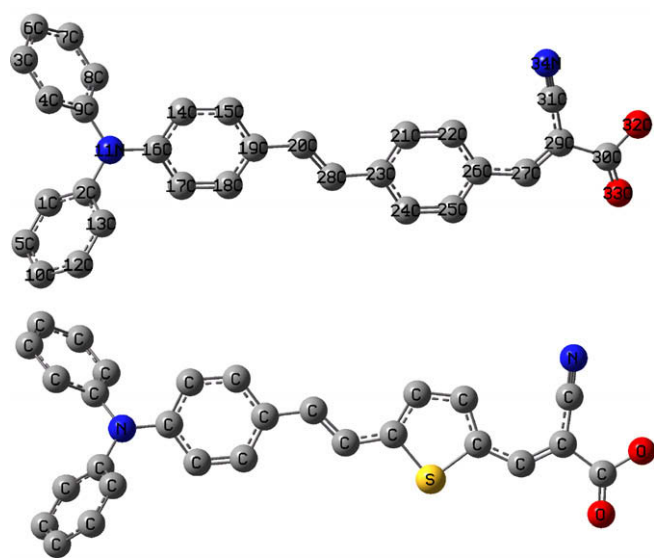


Fig. 1. Optimized geometrical structures of dye sensitizers TA-St-CA (top) and D5 (bottom). (B3LYP/6-31G*, Hydrogen atoms have been omitted for clarity, the spheres with 11 and 34: N; the spheres with 32 and 33: O; the other dark colored spheres: C).

Recently, the novel organic dye TA-St-CA, which contains a π -conjugated oligo-phenylenevinylene unit with an electron donor–acceptor moiety and a carboxyl group as anchoring group, was designed and synthesized, the overall solar-to energy conversion efficiency was achieved at 9.1%, and the frontier molecular orbitals were also calculated by using B3LYP/6-31 + G(d) [37]. However, the conversion efficiency of the very similar dye D5 (see Fig. 1) is only 5.1% [38]. Why does the similar structure induce such different conversion efficiency? What is the difference of electronic structures and absorption properties between TA-St-CA and D5? In order to answer the above mentioned questions and to understand the sensitized mechanism, the geometry, electronic structures, along with polarizabilities and hyperpolarizabilities of the dye sensitizer TA-St-CA were studied in detail via density functional theory (DFT), and the electronic absorption spectrum was investigated by using time-dependent DFT (TD-DFT) [39–41] calculations.

2. Methods

For TA-St-CA, the computations of the geometry, electronic structure, polarizability, and hyperpolarizability were performed using DFT with Gaussian03 package [42]. The DFT was treated according to Becke's three parameter gradient-corrected exchange potential and the Lee-Yang-Parr gradient-corrected correlation potential (B3LYP) [43–45], all the calculations were performed without any symmetry constraints by using polarized split-valence 6-31G* basis sets. The electronic absorption spectra require calculation of the allowed excitations and oscillator strengths. These calculations have been done using TD-DFT with the same basis sets and the hybrid functionals B3LYP, PBE1PBE [46], and MPW1PW91 [47]. The non-equilibrium version of the polarizable continuum

model (PCM) was adopted for calculating the solvent effects [48,49]. TDDFT has been used to investigate the absorption spectra of clusters and molecules successfully [17–20,50,51], including Ru-polypyridine complex in water and ethanol solution [17,18], and Ru(II)L₂ [L = bis(5'-methyl-2,2'-bipyridine-6-carboxylato)] in DMF solution [19].

Solvent could affect on the geometry, electronic structures and the related properties of molecule. In order to understand how the solvent affect on the structure and properties, the deprotonated TA-St-CA and the coupled systems, including one and two ethanol molecules bind to dye molecule TA-St-CA through hydrogen bonds, were presented. The geometries and electronic structures are also investigated.

3. Results and discussion

3.1. The geometrical structure

The optimized geometries of the TA-St-CA and the similar dye molecule D5 are shown in Fig. 1, and the selected bond lengths, bond angles and dihedral angles are listed in Table 1. For TA-St-CA, the calculated distance between the C atom (in carboxyl) and the N atom (in aniline) is 1.473 nm, this value is larger about 0.038 nm than that of similar dye D5 (see Fig. 1), hence the length of conjugate bridge of TA-St-CA is slightly longer than that of D5. Furthermore, the cyanoacrylic acid group was located to be coplanar with the groups in conjugate bridge, including phenyl, vinylene, and phenyl groups. Thus, the strong conjugated effects are formed. This conjugation is very helpful for efficient electron transfer in the conjugated chains. Similar geometric characters are also appeared in the dye sensitizers D5 [38], JK-1 and JK-2 [52], JK16 and JK17 [53,54], the dyes 1 and 2 [55].

The carboxyl acid may be ionized in some solvent through deprotonation. The optimized geometry of the deprotonated TA-St-CA indicates that the bond lengths and bond angles were changed slightly, but several non-planar dihedrals were changed remarkably. This indicates that the deprotonation changed electron distribution in molecule, further affect on the atomic interaction in the molecule, especially the Coulomb interaction.

In order to investigate how much the solvent affect on the geometrical and electronic structure of dye molecule TA-St-CA, the coupled complexes, one and two solute molecules C₂H₅OH bind to TA-St-CA through hydrogen bonds, were further optimized. The hydrogen bond lengths were also labeled in Fig. 2. The optimized geometries of the TA-St-CA coupled one and two ethanol molecules suggest that the change of the bond angles and dihedrals of these two complexes are more appreciable than that of bond lengths. This indicates that the bond angles and dihedrals are more sensitive to charge distribution in the system than bond lengths. The bond lengths were mainly determined by localized interaction, but the bond angles and dihedrals were affected by stereo effect that was induced by electron distribution.

3.2. Electronic structures

Natural Bond Orbital (NBO) analysis was performed in order to analyze the charge populations of the dye TA-St-CA. The natural

Table 1
The selected bond lengths (in nm), bond angles (in degree) and dihedrals (in degree) of the dye TA-St-CA. (B3LYP/6-31G*).

Definition	Values	Definition	Values	Definition	Values	Definition	Values
11–16	0.141	9–11	0.143	2–11	0.143	26–27	0.145
23–28	0.146	19–20	0.146	16–11–9	120.5	16–11–2	120.4
23–28–20	126.7	26–27–29	132.3	2–11–16–17	34.6	9–11–16–14	33.9
25–26–27–29	–179.0	20–28–23–24	179.7				

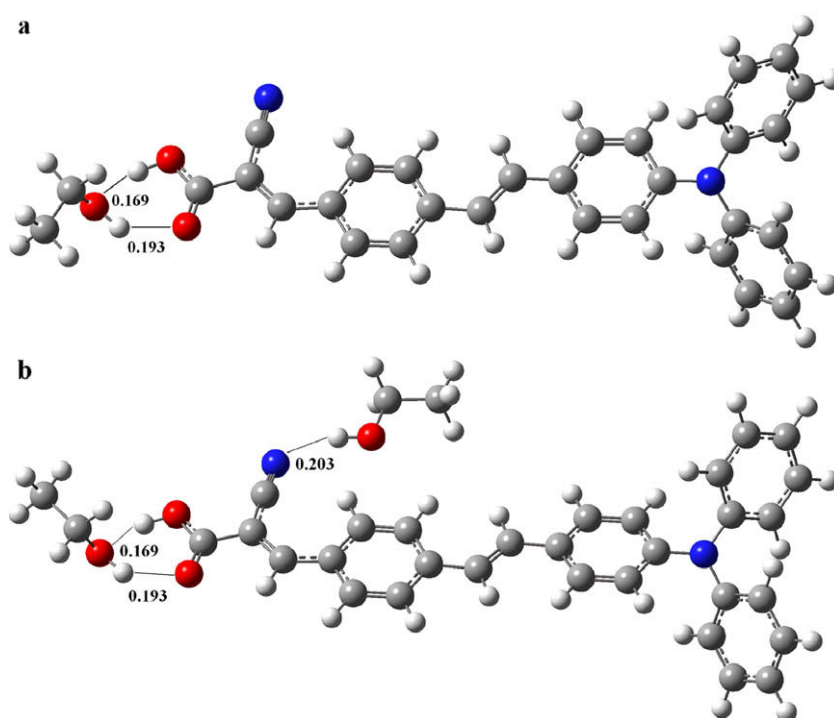


Fig. 2. Optimized geometrical structures of the complexes TA-St-CA-C₂H₅OH (a) and TA-St-CA-2(C₂H₅OH) (b) at the PBE1PBE/6-31G* level (the blue colored spheres: N; the red colored spheres: O; the larger dark colored spheres: C; the smaller grey colored spheres: H). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

charges of cyanoacrylic acid, phenyl (bridge), vinylene and diphenylamine are -0.13 , 0.03 , 0.05 , and 0.05 e, respectively. Thus, the natural charges of donor (diphenylamine group), bridge (vinylene phenyl) and acceptor (cyanoacrylic acid) are 0.05 , 0.08 and -0.13 e, respectively. While for D5, the charges of donor, bridge and acceptor are 0.06 , 0.12 and -0.18 e, respectively. This may be resulted from that the electronic structure of phenyl is more stable than that of thiophene, so the natural charges of conjugate bridge in TA-St-CA are smaller than that of D5.

The frontier molecular orbitals (MO) energies of TA-St-CA, D5, deprotonated TA-St-CA, and C₂H₅OH molecules bind to TA-St-CA complexes are shown in Fig. 3. The calculated the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO) gap of TA-St-

CA is very close to the experimental value 2.4 eV (the HOMO was estimated from the oxidation potential, and the LUMO was estimated from the edge of absorption spectrum) [37]. Furthermore, the results also indicate that the electronic structures of TA-St-CA are very similar to that of D5, but the HOMO and the LUMO levels of TA-St-CA are slightly higher than that of D5, and the HOMO–LUMO gap of TA-St-CA is larger than that of D5. The HOMO level of the dye corresponds to the oxidation potential of the dye [13], and the larger oxidation potential will increase the driving force for the reduction of the oxidized dye [56] so the driving force for the reduction of the oxidized D5 may be slight larger than that of TA-St-CA. The deprotonation destabilized the HOMO and LUMO, and it makes the HOMO–LUMO gap smaller about 0.50 eV than that of neutral TA-St-CA. Similar tendency also appeared in dye sensitizers N866 [57], N3 [20] and [Ru(H_mtcterpy)(NCS)₃]^{n−} ($m = 0, 1, 2$, and 3 ; $n = 4, 3, 2$, and 1) [9]. For one and two C₂H₅OH molecules bind to TA-St-CA, the HOMOs were also destabilized, and the electronic structures of the complexes had appreciable change. On the basis of the results of deprotonated TA-St-CA and the complexes, the solvent effects are very important to understand the experimental results quantitatively.

For TA-St-CA, the HOMO, lying at -5.32 eV, is a delocalized π orbital over the cyano group through diphenylamine. The HOMO-1, lying 1.03 eV below the HOMO, is a delocalized π orbital over the entire molecule. While the HOMO-2 and HOMO-3, lying 1.88 , 1.92 eV below the HOMO, respectively, are π orbitals that localized in phenyl group of diphenylamine. The LUMO, lying at -2.51 eV, is π^* orbital that localized in cyanoacrylic acid, vinylene phenyl, and phenyl in aniline. The LUMO+1, lying about 1.41 eV above the LUMO, is also a π^* orbital that is similar to LUMO. The MOs that calculated with B3LYP/6-31 + G* are very similar to the present calculations [37]. While the calculated HOMO and LUMO energies of the bare Ti₃₈O₇₆ cluster as a model for nanocrystalline are -6.55 and -2.77 eV, respectively, resulting in a HOMO–LUMO gap of 3.78 eV, the lowest transition is reduced to 3.20 eV according to

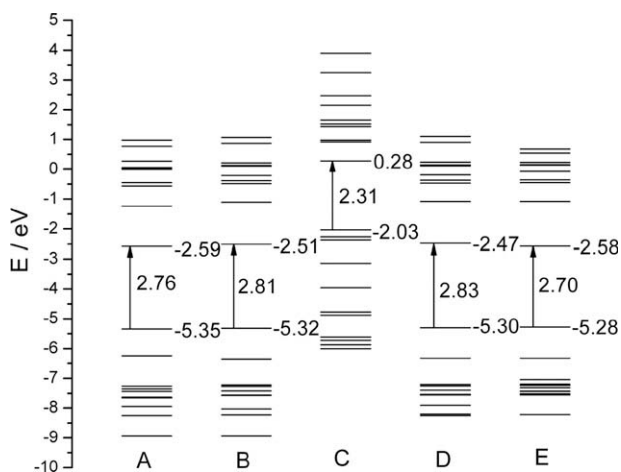


Fig. 3. The calculated frontier molecular orbitals energies at PBE1PBE/6-31G* level (A: D5; B: TA-St-CA; C: deprotonated TA-St-CA; D: TA-St-CA-C₂H₅OH; E: TA-St-CA-2(C₂H₅OH)).

Table 2
Polarizability (α) of the dye TA-St-CA (in a.u.)

α	XX	XY	YY	XZ	YZ	ZZ
	348.3	62.3	686.1	123.5	338.5	446.7

TDDFT, and this value is slightly smaller than typical band gap of TiO_2 nanoparticles [20]. Through the calculated HOMO, LUMO and gap of TA-St-CA and $\text{Ti}_{38}\text{O}_{76}$ cluster, we can find that the HOMO energy of TA-St-CA fall within the TiO_2 gap. These data reveal the sensitized mechanism: the interfacial electron transfer between semiconductor TiO_2 electrode and dye sensitizer TA-St-CA is electron injection process from the excited dyes as electron donor to the semiconductor conduction band. This is a kind of typical interfacial electron transfer reaction [58].

3.3. Polarizability and hyperpolarizability

Polarizabilities and hyperpolarizabilities could determine not only the strength of molecular interactions (such as the long-range intermolecular induction, dispersion forces, etc.) as well as the cross sections of different scattering and collision processes, but also the nonlinear optical properties (NLO) of the system [59]. It has been reported that dye sensitizer hemicyanine system, which has good NLO property, usually possesses good photoelectric conversion property [60]. In order to investigate the relationships among photocurrent generation, molecular structures and NLO, the polarizabilities and hyperpolarizabilities of TA-St-CA were calculated.

The polarizabilities and hyperpolarizabilities could be computed via finite field method (FF), sum-over states method based on TDDFT (SOS), and coupled-perturbed HF (CPHF) method. In order to make a comparative study with D5 and taking account of computational cost, we compute the polarizability and the first hyperpolarizabilities as a numerical derivative of the dipole moment using B3LYP/6-31G(d). The definitions of the isotropic polarizability α , polarizability anisotropy invariant $\Delta\alpha$ and the average hyperpolarizability $\beta_{||}$ are as follows [59]:

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}),$$

$$\Delta\alpha = \left[\frac{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2}{2} \right]^{\frac{1}{2}},$$

$$\beta_{||} = \frac{1}{5} \sum_i (\beta_{iiz} + \beta_{izi} + \beta_{zii}).$$

Tables 2 and 3 list the values of the polarizabilities and hyperpolarizabilities of TA-St-CA. In addition to the individual tensor components of the polarizabilities and the first hyperpolarizabilities, the calculated isotropic polarizability, polarizability anisotropy invariant and hyperpolarizability are 493.7, 300.9 and 23765.8 (in a.u.), respectively. The calculated isotropic polarizability of TA-St-CA is slightly less than that of D5 (510.6 a.u. [61]). This may be resulted from that the aromaticity of the phenyl group in conjugate bridge of TA-St-CA is stronger than that of thiophene group in D5, and then the electronic structure of phenyl group is more stable than that of thiophene group, thus the response of external field for TA-St-CA is weaker than that for D5.

Table 3
Hyperpolarizability (β) of the dye TA-St-CA (in a.u.)

β	XXX	XXY	XYX	YYY	XXZ	XYZ	YYZ	XZZ	YZZ	ZZZ
	−42.7	1489.9	9015.2	33756.7	863.4	6234.9	25430.7	4169.2	18653.9	13315.6

3.4. Electronic absorption spectra and sensitized mechanism

The UV–vis spectrum of the dye TA-St-CA was measured in ethanol solution, and it is found that the first absorption band centered at 386 nm [37]. In order to understand electronic transitions, TD-DFT calculations on electronic absorption spectra in vacuum and solvent were performed, the 30 lowest spin-allowed singlet–singlet transitions were taken into account. In vacuum, two kinds of hybrid functional B3LYP and PBE1PBE were adopted, while in solvent, three kinds of hybrid functional B3LYP, MPW1PW91, and PBE1PBE were used to calculate the spectrum. These calculations were based on the optimized geometry of B3LYP. In the simulation of UV–vis spectra, assuming each transition is Gaussian distribution with full width at half maximum (fwhm) of 3000 cm^{-1} . The calculated results are shown in Fig. 4. It is seen that the calculated relative strength and line shape agree well with that of experiment, and the hybrid functional PBE1PBE and MPW1PW91 are more suitable than B3LYP for calculating electronic absorption spectra of TA-St-CA. Compared with the results of experiment [37], the results of TDDFT have appreciable red-shift, and the degree of red-shift in solvent is more significant than that in vacuum. Similar results are also found for several dye sensitizers [19,62–64]. The discrepancy between experiment and TD-DFT calculations may be attributed to DFT and solvent effects [61]. Though the discrepancy is existed, the TD-DFT calculations are capable of describing the spectral features because of the qualitative agreement of line shape and relative strength as compared with experiment.

In order to obtain the microscopic information about the electronic transitions, we check the corresponding MO properties. The absorption in visible and near-UV region is the most important region for photo-to-current conversion, so only the singlet \rightarrow singlet transitions of the absorption bands with the oscillator strength larger than 0.01 and the wavelength longer than 300 nm were listed in Table 4. Fig. 5 shows the isodensity plots of the frontier MOs of the TA-St-CA. The absorption bands near 552 nm resulted from the electron transitions from the initial states that is mainly contributed by the HOMO (No: 116) to final states that is mainly contributed by the LUMO (No: 117). The HOMO is π orbital that composed of the cyano group through diphenylaniline, and HOMO-1 is a delocalized α orbital over the entire molecule, whereas the LUMO is π^* orbital that localized in cyanoacrylic acid, vinylene phenyl, and phenyl in aniline group. As to the absorption bands near-UV region, the initial states are composed of α orbitals that are mainly related to 115 MO (HOMO-1), whereas the final states are composed of LUMO.

On the basis of the above analysis of transitions and MOs, the absorption bands of the TA-St-CA in visible and near-UV region are typical $\pi \rightarrow \pi^*$ transitions. Furthermore, the 12 transitions with the lowest excited energies except the transitions that mainly contributed by HOMO \rightarrow LUMO + 2 does not generate effective charge separated state, the initial states of other transitions are mainly related to the MOs that localized in electron donor groups, while the final states are mainly related to the MOs that localized in electron acceptor groups. This indicates that the absorptions are photoinduced electron transfer processes, thus the excitations generate charge separated states. It is worthy to be noted that the HOMO-6 \sim HOMO are all related to the diphenylaniline group, so this group is major chromophore that contributed to the sensitization

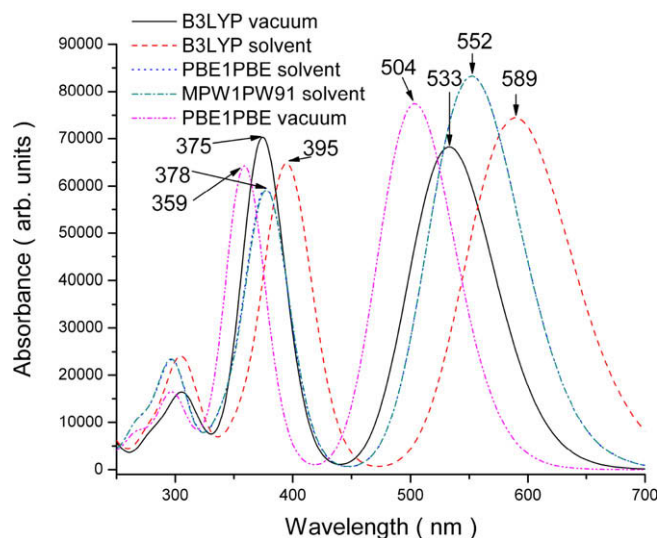


Fig. 4. Calculated electronic absorption spectra of TA-St-CA.

of photo-to-current conversion processes, and it should favor the electron injection from the excited states to semiconductor surface.

The solar energy to electricity conversion efficiency (η) under AM 1.5 white-light irradiation can be obtained from the following definition:

$$\eta(\%) = \frac{J_{sc}[\text{mA cm}^{-2}]V_{oc}[\text{V}]ff}{I_0[\text{mW cm}^{-2}]} 100,$$

where I_0 is the photon flux, J_{sc} is the short-circuit photocurrent density, and V_{oc} is the open-circuit photovoltage, and ff represents the fill factor [13]. At present, the J_{sc} , the V_{oc} , and the ff are only obtained by experiment, the relationship among these quantities and the electronic structure of dye is still unknown. In order to find the correlation between the photovoltaic performance and electronic structure parameters, the data of TA-St-CA and D5 are listed

in Table 5. Compared to D5, the carboxyl group and the similar geometry of TA-St-CA determine the similar adsorbed properties at TiO_2 surface, and then it results in the ff of TA-St-CA is very close to that of D5. Furthermore, the difference of V_{oc} is about 0.08 V, and the difference of E_{LUMO} is about 0.08 eV. The analytical relationship between V_{oc} and E_{LUMO} may be existed. According to the sensitized mechanism (electron injected from the excited dyes to the semiconductor conduction band) and single electron and single state approximation, there is an energy relationship:

$$eV_{oc} = E_{\text{LUMO}} - E_{\text{CB}},$$

where, E_{CB} is the energy of the semiconductor's conduction band edge. So the V_{oc} may be obtained from the following formula:

$$V_{oc} = \frac{E_{\text{LUMO}} - E_{\text{CB}}}{e},$$

It induces that the higher the E_{LUMO} , the larger the V_{oc} . The results of organic dye sensitizer JK16 and JK17 [54], D-ST and D-SS also proved the tendency [61] (JK16: $\text{LUMO} = -2.73$ eV, $V_{oc} = 0.74$ V; JK17: $\text{LUMO} = -2.87$ eV, $V_{oc} = 0.67$ V; D-SS: $\text{LUMO} = -2.91$ eV, $V_{oc} = 0.70$ V; D-ST: $\text{LUMO} = -2.83$ eV, $V_{oc} = 0.73$ V). Certainly, this formula expects further test by experiment and theoretical calculation. As to the J_{sc} , the J_{sc} of TA-St-CA is larger than that of D5. The J_{sc} is determined by two processes, one is the rate of electron injection from the excited dyes to the conduction band of semiconductor, and the other is the rate of redox between the excited dyes and electrolyte. Electrolyte affect on the redox processes is very complex, and it is not taken into account in the present calculations. On the basis of the analysis of excitation energies, electronic transition configurations, oscillator strengths and molecular orbitals of TA-St-CA and D5 in UV–vis region, we find that most oscillator strengths for the excited states with intramolecular electron transfer character of TA-St-CA are larger than that of D5. This indicates that most of excited states of TA-St-CA have larger absorption coefficient, and then with shorter lifetime for the excited states, so it results in the higher electron injection rate of the TA-St-CA, then it lead to the larger J_{sc} of TA-St-CA. On the basis of above analysis, the TA-St-CA has better performance in DSSC than that of D5.

Table 4

Computed excitation energies (eV), electronic transition configurations and oscillator strengths (f) for the singlet \rightarrow singlet transitions of the absorption band in visible and ultraviolet region for TA-St-CA in ethanol. (PBE1PBE/6-31G).

State	Configurations composition with CI coeff. > 0.2 (corresponding transition orbitals) ^a	Excitation energy (eV/nm)	f
1	0.672(116 \rightarrow 117)	2.25/552	1.1497
2	0.644(115 \rightarrow 117)	3.28/378	0.8051
3	0.639(116 \rightarrow 118)	3.61/343	0.1414
4	0.548(116 \rightarrow 119); 0.364(113 \rightarrow 117)	3.96/313	0.0153
5	0.641(109 \rightarrow 117)	4.06/306	0.0152
6	0.486(113 \rightarrow 117); -0.380(116 \rightarrow 119); -0.231(114 \rightarrow 117)	4.11/301	0.0472
7	0.653(114 \rightarrow 117)	4.13/300	0.0115

^a HOMO is No. 116 orbital.

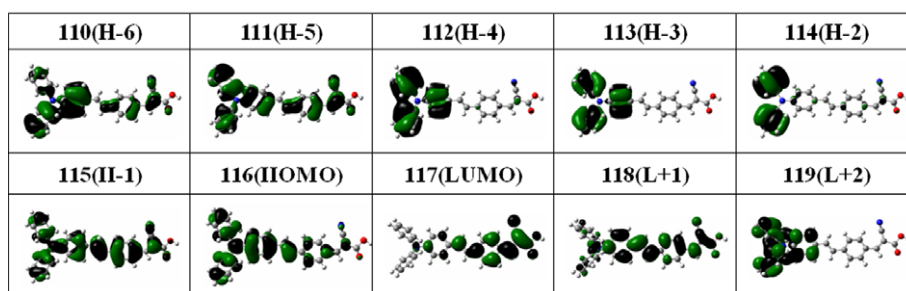


Fig. 5. Isodensity plots (isodensity contour = 0.02 a.u.) of the frontier orbitals and orbital energies (in eV) of the dye TA-St-CA.

Table 5
Photovoltaic performance and electronic structure parameters of TA-St-CA and D5.

Dye	J_{sc}/mAcm^{-2}	V_{oc}/V	ff	η %	Solvent ^c			Vacuum ^d		
					HOMO/eV	LUMO/eV	Gap/eV	HOMO/eV	LUMO/eV	Gap/eV
TA-St-CA	18.1 ^a	0.743 ^a	0.675 ^a	9.1 ^a	−4.95	−2.60	2.35	−5.32	−2.51	2.81
D5	11.9 ^b	0.66 ^b	0.68 ^b	5.1 ^b	−4.96	−2.68	2.28	−5.35	−2.59	2.76

^a Experiment value [37].

^b Experiment value [38].

^c B3LYP/6-31G*.

^d PBE1PBE/6-31G*.

4. Conclusions

The geometry, electronic structure, polarizability and hyperpolarizability of the dye sensitizer TA-St-CA was studied by using DFT, and the UV–vis spectra were investigated by using TD-DFT methods. The calculated geometric characters indicate that the strong conjugated effects across the phenyl-cyanoacrylate groups are formed. The NBO results suggest that TA-St-CA is a D- π -A systems, and diphenylaniline group is electron donor, cyano acrylic acid is electron acceptor, vinylene phenyl groups are the conjugate π bridge. The features of electronic absorption spectra in visible and near-UV region were assigned, and the absorptions are all ascribed to $\pi \rightarrow \pi^*$ transitions according to the qualitative agreement between the experiment and the TD-DFT calculations. The absorption bands in visible region are all photoinduced electron transfer processes, thus the excitations generate charge separated states, and the diphenylaniline group in TA-St-CA is the main chromophore that contributed to the sensitization of photo-to-current conversion processes, the interfacial electron transfer between semiconductor TiO_2 electrode and the dye sensitizers TA-St-CA is electron injection processes from excited dyes to the semiconductor conduction band.

In virtue of the comparative analysis of geometries, electronic structures and spectra properties between the dyes TA-St-CA and D5, the smaller isotropic polarizability of TA-St-CA may be resulted from that the electronic structure of phenyl group is more stable than that of thiophene group; the similar ff may be induced by the carboxyl group and the similar geometry; the larger the V_{oc} of TA-St-CA may be deduced by the higher E_{LUMO} ; the larger J_{sc} of TA-St-CA may be determined by the larger oscillator strengths for the most excited states with intramolecular electron transfer character. So the organic dye sensitizer with good performance for DSSC must be based on a donor- π -conjugation-acceptor structure that is required for good absorption properties with intramolecular electron transfer character in UV–vis region and the higher E_{LUMO} .

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