DFT and TD-DFT Study of (e)-3-(5-(anthracen-3-yl)- Hexahydrothieno [3,4-b][1,4]Dioxin-7-yl)-2-Cyanoacrylic Acid Dye for Dye Sensitized Solar Cell Application

P. M. Anbarasan[1,2,*], A. Priyadharsan[1], A. Arunkumar[1], M. Prakasam[1,2] and D. Nicksonsebastin[1]

[1]Department of Physics, Periyar University, Salem - 636 011, India.

[2]Centre for Nanoscience and Nanotechnology, Periyar University, Salem - 636 011, India.

ABSTRACT

In this study, the optimized geometries, electronic structures, polarizability, hyper polarizability and dipole moment of the chosen (E)-3-(5-(anthracen-3-yl)-hexahydrothieno[3,4-b][1,4]dioxin-7-yl)-2-cyanoacrylic acid (E-3-2- CYANOACRYLIC ACID) dye sensitizer has been analyzed by using Density Functional Theory (DFT) and Time Dependent Density Functional Theory (TD-DFT) calculations (based on hybrid functional B3LYP). The HOMO and LUMO energies of the dye (E-3-2- CYANOACRYLIC ACID) are -4.84 and -2.22 eV respectively based on DFT calculations. To understand the conversion efficiency of the chosen dye architecture unit we selected TiO_2 as a model for semiconductor. Results reveal that the selected dye sensitizer exhibits large dipole moment difference between the ground and excited state which is comparable to that of metal based dye sensitizers. Results concluded that intramolecular energy transfer is occurring in (E-3-2-CYANOACRYLIC ACID) and further the large dipole moment would be expected to give high photo-current conversion efficiency in practical Dye sensitizer solar cells (DSSC) besides promising candidate as a sensitizer for DSSC applications.

Introduction

New technologies for direct solar energy conversion have gained more attention in the last few years. In particular, Dye Sensitized Solar Cells (DSSCs) are promising in terms of efficiency and low cost [1-3]. The leading feature of DSSC consists in a wide band gap nanocrystalline film grafted with a quasi-monolayer of dye molecules and submerged in a redox electrolyte. This elegant architecture can synchronously address two critical issues of employing organic materials for the photovoltaic applications: (i) efficient charge generation from the Frenkel excitons and (ii) long-lived electron-hole separation up to the millisecond time domain. The latter attribute can often confer an almost quantitative charge collection for several micrometer-thick active layers, even if the electron mobilities in nanostructured semiconducting films are significantly lower than those in the bulk crystalline materials. Benefited from systematic device engineering and continuous material innovation, a state of the art DSC with a ruthenium sensitizer has achieved a validated efficiency of 11.1%[4] measured under the Air Mass 1.5 Global (AM1.5G) conditions. In view of the limited ruthenium resource and the heavy-metal toxicity, metal-free organic dyes have received surging research interest in recent years [5-21]. Because of their high molar absorption coefficient, relatively simple synthesis procedure, various structures and lower cost in contrast to a ruthenium dye and the flexibility in molecular tailoring of an organic sensitizer provides a large area to explore. [22-24]. In addition, recently a rapid progress of organic dyes has been witnessed reaching close to 10.0% efficiencies in combination with a volatile acetonitrile-based electrolyte [25]. In the present work we introduce (E-3-2- cyanoacrylic acid) and investigate its quantum chemical properties.

Computational methods

Computational calculations of (E-3-2- cyanoacrylic acid) were performed with the use of Gaussian09w package [26]. DFT calculations were based on hybrid functional Becke's three parameter and the Lee–Yang–Parr (B3LYP)[27-29], and all calculations were performed without any symmetry constraints by using polarized triple-zeta 6-311G(d,p) basis sets. The Natural Bonding Orbital (NBO) analysis was performed using restricted Hartree–Fock (RHF) with 6-311G(d,p) basis set. The electronic absorption spectrum involves calculation of the allowed excitations and oscillator strengths. These calculations were performed by using TD-DFT with the same basis sets and exchange–correlation functional in solution, and the non-equilibrium version of the polarizable continuum model (PCM) [30, 31] was adopted for calculating the solvent effects.

Results and discussion

The geometric structure

To optimize the structure of (E)-3-(5-(anthracen-3-yl)-hexahydrothieno[3,4-b][1,4]dioxin-7-yl)-2-cyanoacrylic acid we have used HF/B3LYP/6-311G(d,p) method and shown in Figure 1. From these calculations we can find the bond lengths, bond angles and dihedral angles in table 1. Since the crystal structure of the mentioned compound is not available till now. However, we can compare the optimized structure with other similar systems for which the crystal structures have been solved.

From the optimized geometry we can find the most of the optimized bond lengths, bond angles and dihedral angles theoretically. The geometrical data reported in the present work mainly characterizes the donor and acceptor part of the sensitizers which is the primary requirement of practical DSSCs.

Tele: +91-0427-2345766, 2345520
E-mail addresses: anbarasanpm@gmail.com

Table 1. Selected bond lengths (angstroms), bond angles and dihedral angles (degrees) of (E-3-2- cyanoacrylic acid)

Bond Length	In Angstroms		Bond Angle	In Degree		Dihedral Angle	In Degree	
	DFT	HF		DFT	HF		DFT	HF
1C-2C	1.365	1.343	2C-1C-14C	121.4	121.2	14C-1C-2C-31H	180.0	180.1
1C-14C	1.436	1.435	14C-1C-30H	118.2	120.4	4C-5C-6C-7C	-180.0	-179.9
4C-33H	1.086	1.073	1C-2C-3C	121.1	118.2	41H-18C-19C-20C	178.0	179.8
6C-7C	1.401	1.388	10C-9C-35H	119.2	120.5	24C-25C-27O-46H	-180.0	-180.0
6C-34H	1.085	1.073	9C-10C-11C	120.5	119.0	43H-21C-22C-44H	180.0	179.5
7C-12C	1.446	1.423	1C-14C-5C	118.1	119.4	4C-5C-14C-13C	0.001	0.001
19C-45H	1.093	1.080	1C-14C-13C	122.5	118.1	5C-6C-7C-8C	-0.003	-0.002
21C-22C	1.945	1.911	20C-19C-42HH	118.7	119.2	16C-17C-22C-44H	-175.3	-176.2
21C-46H	1.092	1.079	17C-22C-44H	118.8	121.5	18C-17C-22C-21C	179.0	179.8
29O-30N	1.165	1.140	21C-22C-44H	119.3	119.3	18C-17C-22C-44H	-176.5	-176.9

Table 2. Polarizability (α) of the (E-3-2- cyanoacrylic acid) (in a.u.)

| *	α_{XX}	α_{XY}	α_{YY}	α_{XZ}	α_{YZ}	α_{ZZ}	α	$\Delta\alpha$
HF/6-311G(d,p)	-171.377	3.9931	-184.242	5.4652	2.6122	-180.528	178.71 (2.648×10^{-12}esu)	11.47 (1.699×10^{-12}esu)
DFT/6-311G(d,p)	-158.467	-7.4211	-188.351	-2.9496	10.2815	-166.307	171.03 (2.534×10^{-12}esu)	26.84 (3.977×10^{-12}esu)

Table 3. Hyperpolarizability (β) of the dye (E-3-2- cyanoacrylic acid) (in a.u.)

*	β_{XXX}	β_{XXY}	β_{XYY}	β_{YYY}	β_{XXZ}	β_{YYZ}	β_{XZZ}	β_{YZZ}	β_{ZZZ}	β
HF/6-311G(d,p)	-10.038	-96.865	-36.407	73.501	-2.2122	-13.883	36.705	-8.035	-18.785	47.91 (4.139×10^{-30}esu)
DFT/6-311G(d,p)	-69.588	-103.179	-63.475	127.513	28.2161	-3.2006	16.198	11.727	-2.509	124.35 (1.07×10^{-30}esu)

Table 4. Excitation energy (E) and Light Harvesting Efficiency (LHE) of dyes at B3LYP/6-311G(d,p) level of theory

| Dye Molecule	Gas phase			Solvent (methanol)		
	Energy (eV)	Wavelength (nm)	LHE	Energy (eV)	Wavelength (nm)	LHE
(E-3- 2 cyanoacrylic acid)	2.2067	561.86	0.0011	2.4458	506.93	0.0048
	2.4894	498.05	0.0050	2.6443	468.88	0.0082
	3.0492	406.61	0.1040	2.9398	421.74	0.1474

Therefore here we can found the most of the geometrical data from the optimized structures.
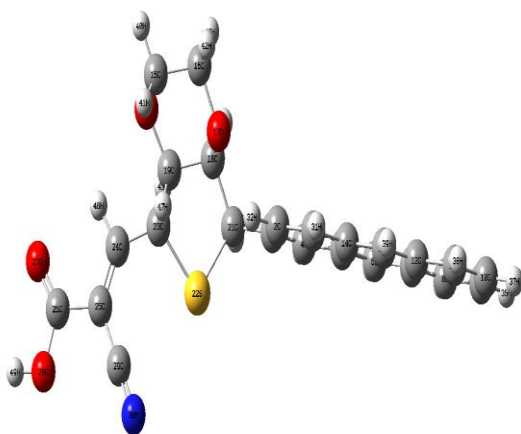
Figure 1. Optimized geometry structure of the (E-3-2-cyanoacrylic acid)

Electronic structures and molecular orbitals

In order to examine the charge population of the (E-3-2-cyanoacrylic acid) we performed the natural bonding orbital analysis (NBO) of the dye (E-3-2- cyanoacrylic acid) shown in Figure 2.

The HOMO and LUMO energies of (E-3-2- cyanoacrylic acid) is -4.84 eV and -2.22 eV respectively in the figure 3.
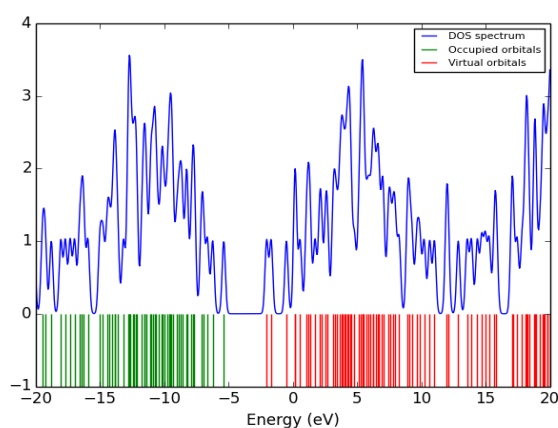
Figure 2. The frontier molecular orbital energies and corresponding density of state (DOS) Spectrum of (E-3-2-cyanoacrylic acid)

The HOMO–LUMO band gap energy of the sensitizer is 2.62 eV. Here we take the TiO_2 cluster as a model for semiconductor to evaluate the performance of the dye sensitizer.

The HOMO and LUMO energies of the bare $Ti_{38}O_{76}$ cluster as a model for nanocrystalline are 6.55 and -2.77 eV respectively and the HOMO–LUMO band gap is 3.78 eV according to TD-DFT calculations [32].

This indicates that the chosen dye architecture unit possesses sufficient driving force for electron injection according to Hara et al [33].
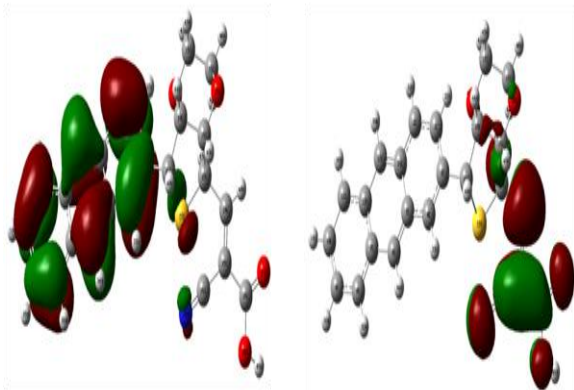
Figure 3. Isodensity plot (isodensity contour = 0.02 a.u.) of the frontier orbitals of of (E-3-2- cyanoacrylic acid) and corresponding orbital energies (in eV)

The band gap energy of the semiconductor falls within the band gap energy of dye sensitizer; further the LUMO and LUMO + 1 energies of sensitizer are well above the conduction band edge of the $Ti_{38}O_{76}$ semiconductor which indicates that favorable electron injection takes place from the sensitizer to conduction band of the semiconductor. Charge recombination kinetics of the sensitizer can be determined by the difference in energy level (ΔE_R) of the conduction band edge of the TiO_2 and HOMO of the dye sensitizer. In the present case it is around 1.41 eV. This confirms that the charge recombination kinetics becomes sluggish and hence we could expect that the sensitizer will exhibit large V_{oc} in practical DSSCs [34].

Table 2 and table 3 list the polarizability and hyperpolarizabilities of (E-3-2- cyanoacrylic acid) was calculated by DFT calculations. The polarizability and hyperpolarizability quantities of (E-3-2- cyanoacrylic acid) dye sensitizer are 171.03 and 124.35 a.u. respectively. The highest molecular polarizability leads to increase the NLO property of the system results good photoelectric conversion efficiency according to Z. S. Wang et al [35].

Dipole Moment
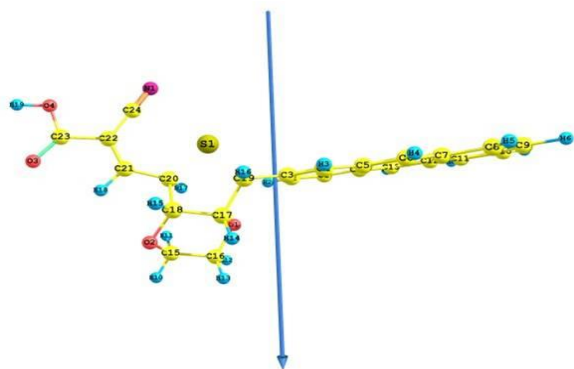
Figure 4. Dipole Moment of (E-3-2- cyanoacrylic acid)

The figure 4 shows that the dipole moment optimized structure. It is one of the important parameters which provide information about the electronic charge distribution in the molecule. The knowledge about the dipole moment of the organic molecules is important while designing the materials for optoelectronic applications. The calculated ground state dipole moments of the studied dye molecules in the ground and excited state dipole moments are 5.3454 and 6.9766 Debye respectively. This is because of the additional dipole moment induced by the solvent reaction field. The reduced dipole moment is due to the donor part of the sensitizer has long side chain which may decrease the distance between the charge centers results the decrease of electron delocalization [36]

Light Harvesting Efficiency (LHE) and Oscillator Strength

In the present section, we propose structural modifications improving the electron injection efficiency of the (E-3-2-cyanoacrylic acid) based DSSCs. Of course, all modifications are theoretically possible and a large panel of new structure can be tested. We focus on three properties that can be optimized
(i) The free energy of injection ΔG^{inject}.

(ii) The oxidation potential of the dyes must be more positive,
(iii) The light harvesting efficiency (LHE) of the dye has to be as high as possible to maximize the photocurrent response. More precisely, LHE is expressed as [37].
$$LHE = 1 - 10^{-A} = 1 - 10^{-f}$$

Where A(f) is the absorption (oscillator strength) of the dye associated to the λ_{max}. It is known that TDDFT is less efficient for the evaluation of transition probabilities than for transition energies. For the sake of computational consistency, the LHE criterions have therefore to be underweighted in our classification, as our estimates of ΔG^{inject} and E_{ox}^{dye} are

probably more reliable.

The light harvesting efficiency (LHE) is the efficiency of dye in responding to light. It is another factor which indicates the efficiency of DSSC. The light harvesting efficiency (LHE) of the dye should be as high as possible to maximize the photocurrent response. The value of LHE of the dyes has to be as high as possible to maximize the photocurrent response. The LHE has to be underweighted for the calculation. These values are important for charge transfer process in DSSC. So the LHE is regarded to underweight in this work. The LHE of the dyes are calculated and listed in table 4.

Electronic absorption spectra

The figure 5 presents the electronic absorption spectra of (E-3-2- cyanoacrylic acid) is performed in vacuum and solvent (methanol) using TD-DFT (B3LYP)/6-311G(d,p) calculations. The major absorption bands are observed in solvent are 506, 468 and 421 nm. This is attributed to the fact that the polar solvents usually stabilize or destabilize the molecular orbitals of the sensitizer either in the ground state or excited state. The results of TD-DFT have an appreciable red – shift in vacuum and solvent, and the degree of red – shift in solvent is more significant than that in vacuum.
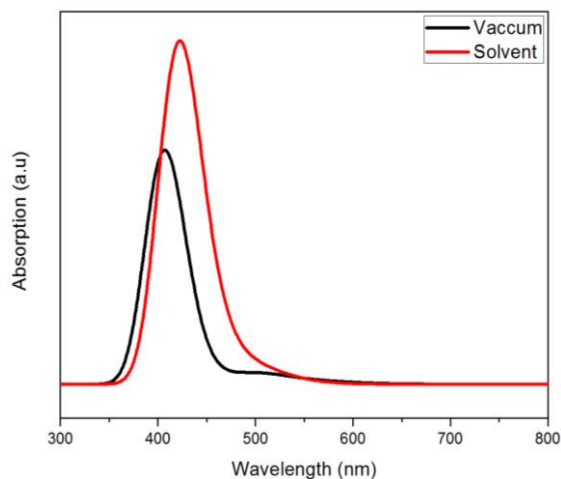
Figure 5. Electronic absorption spectra of (E-3-2-cyanoacrylic acid)

The characteristic absorption band n–π* transition of (E-3-2- cyanoacrylic acid) molecule are observed around 506, 468 and 421 nm. Molecular orbital properties of (E-3-2-cyanoacrylic acid) are investigated to understand about the microscopic transitions of electronic states. The absorption in the UV–Visible region is one of the most important regions for

photo–current conversion region. The electronic transition take place from donor anthracene group through pi conjugation to cyanoacrylic acid acceptor group involves 20 singlet–singlet transitions (Figure 5. and the electronic transitions listed in Table 4). Here the cyanoacrylic acid acceptor group injects the electron from its LUMO to the conduction band of the TiO_2. This electron injection generates charge separated states in the interface results photo induced charge transfer processes takes place from the dye sensitizer to TiO_2 semiconductor surface [38].

The remarkable solar to electricity conversion efficiency (η) of the (E-3-2- cyanoacrylic acid) can be calculated from the following formula:

$$\eta(\%) = \frac{J_{SC}[mAcm^{-2}]V_{OC}[V]ff}{I_0[mWcm^{-2}]} \times 100$$

Where I_0 is the photon flux, Jsc is the short-circuit photocurrent density, and V_{oc} is the open-circuit photovoltage, and ff represents the fill factor [39]. We can obtain these quantities by experiment however, the relationship among these quantities and the electronic structure of dye is still unknown. The band gap of the investigated dye is 2.62 eV results smaller short circuit current density leads to larger V_{oc} in the practical cells.

As per single electron and single state approximation and also basing on sensitized mechanism i.e electron injected from the dye sensitizer to semiconductor conduction band there is a relationship [40] between V_{oc} and semiconductor band edge is

$V_{oc} = (E_{LUMO} - E_{CB})/e$

It induces that the higher the E_{LUMO}, the larger the V_{oc}. The results of organic dye sensitizer JK16 and JK17 [94], D-ST and D-SS also proved the tendency [41]

Certainly, this formula expects further test by experiment and theoretical calculation. 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 effect on the redox processes is very complex, and it is not taken into account in the present calculations. This indicates that most of excited states of (E-3-2- cyanoacrylic acid) have larger absorption coefficient, and then with shorter lifetime for the excited states, so it results in the higher electron injection rate which leads to the larger J_{sc} of (E-3-2- cyanoacrylic acid). On the basis of above analysis, it is clear that the (E-3-2- cyanoacrylic acid) has better performance in DSSC.

Conclusions

The geometries, electronic structures, polarizabilities, and hyperpolarizabilities of   (E-3-2- cyanoacrylic acid) dye was studied by density functional theory with hybrid functional B3LYP, and the UV-Vis spectra were investigated by using TD-DFT methods. The NBO results suggest that (E-3-2- cyanoacrylic acid) is a (D-π-A) system. The ground and excited state dipole moments are 5.3454 and 6.9766 Debye respectively and the polarizability and hyperpolarizability quantities of (E-3-2- cyanoacrylic acid) dye sensitizer are 171.03 and 124.35 a.u. respectively based on DFT/B3LYP/6-311G(d,p) calculations. This confirms that the designed dye sensitizer has high NLO property and exhibits good conversion efficiency. The light harvesting efficiency (LHE) of the dye should be as possible to maximize the photocurrent response. However we suggest that the further chemical modification of the dye such as adding high effective electron acceptor and donor could raise the ΔG^{inject}

and LHE of the DSSC with these photo sensitizers. Electronic absorption spectra of (E-3-2- cyanoacrylic acid) is performed in

vacuum and solvent (methanol) using TD-DFT (B3LYP)/6-311G(d,p) calculations. The major absorption bands are observed in solvent are 506, 468 and 421 nm. The characteristic absorption band n–π* transition of (E-3-2- cyanoacrylic acid) molecule is observed around 506, 468 and 421 nm whereas it is slightly red shifted to longer wavelength. So it indicates that the choice of the appropriate conjugate bridge in dye sensitizer is very important for improve the performance of DSSC.

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