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

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ABSTRACT

In this study, the optimized geometries, electronic structures, polarizability, hyperpolarizability 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 TiO2 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.

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

<table>
<thead>
<tr>
<th>Bond Length</th>
<th>In Angstroms</th>
<th>Bond Angle</th>
<th>In Degree</th>
<th>Dihedral Angle</th>
<th>In Degree</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>DFT</td>
<td>HF</td>
<td>DFT</td>
<td>HF</td>
<td>DFT</td>
</tr>
<tr>
<td>1C-2C</td>
<td>1.365</td>
<td>1.343</td>
<td>121.4</td>
<td>121.2</td>
<td>14C-1C-2C-3H</td>
</tr>
<tr>
<td>1C-14C</td>
<td>1.436</td>
<td>1.435</td>
<td>118.2</td>
<td>120.4</td>
<td>4C-5C-6C-7C</td>
</tr>
<tr>
<td>4C-33H</td>
<td>1.086</td>
<td>1.073</td>
<td>121.1</td>
<td>118.2</td>
<td>4I-H-1C-9C-19C-20C</td>
</tr>
<tr>
<td>6C-7C</td>
<td>1.401</td>
<td>1.388</td>
<td>119.2</td>
<td>120.5</td>
<td>24C-25C-270-46H</td>
</tr>
<tr>
<td>6C-34H</td>
<td>1.085</td>
<td>1.073</td>
<td>120.5</td>
<td>119.0</td>
<td>43H-21C-22C-44H</td>
</tr>
<tr>
<td>7C-12C</td>
<td>1.446</td>
<td>1.423</td>
<td>120.5</td>
<td>119.0</td>
<td>4C-5C-14C-13C</td>
</tr>
<tr>
<td>19C-45H</td>
<td>1.093</td>
<td>1.080</td>
<td>122.5</td>
<td>118.1</td>
<td>5C-6C-7C-8C</td>
</tr>
<tr>
<td>21C-22C</td>
<td>1.945</td>
<td>1.911</td>
<td>118.7</td>
<td>119.2</td>
<td>16C-17C-22C-44H</td>
</tr>
<tr>
<td>21C-46H</td>
<td>1.092</td>
<td>1.079</td>
<td>118.8</td>
<td>121.5</td>
<td>18C-17C-22C-21C</td>
</tr>
<tr>
<td>29O-30N</td>
<td>1.165</td>
<td>1.140</td>
<td>119.3</td>
<td>119.3</td>
<td>18C-17C-22C-44H</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th></th>
<th>αSX</th>
<th>αSY</th>
<th>αSZ</th>
<th>αXY</th>
<th>αYZ</th>
<th>αZZ</th>
<th>α</th>
<th>Δαα</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/6-311G(d,p)</td>
<td>-171.377</td>
<td>3.9931</td>
<td>-184.242</td>
<td>5.4652</td>
<td>2.6122</td>
<td>-180.528</td>
<td>178.71</td>
<td>(2.648x10^-12 esu)</td>
</tr>
<tr>
<td>DFT/6-311G(d,p)</td>
<td>-158.467</td>
<td>-7.4211</td>
<td>-188.351</td>
<td>-2.9496</td>
<td>10.2815</td>
<td>-166.307</td>
<td>171.03</td>
<td>(2.534x10^-12 esu)</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th></th>
<th>βXXX</th>
<th>βXY</th>
<th>βYX</th>
<th>βYY</th>
<th>βYZ</th>
<th>βZX</th>
<th>βZY</th>
<th>βZZ</th>
<th>β</th>
<th>Δβββ</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/6-311G(d,p)</td>
<td>-10.038</td>
<td>-96.865</td>
<td>-36.407</td>
<td>73.501</td>
<td>-2.2122</td>
<td>-13.883</td>
<td>36.705</td>
<td>-8.035</td>
<td>-18.785</td>
<td>47.91</td>
</tr>
<tr>
<td>DFT/6-311G(d,p)</td>
<td>-69.588</td>
<td>-103.179</td>
<td>-63.475</td>
<td>127.513</td>
<td>28.2161</td>
<td>-3.2006</td>
<td>16.198</td>
<td>11.727</td>
<td>-2.509</td>
<td>124.35</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Dye Molecule</th>
<th>Gas phase</th>
<th>Solvent (methanol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Energy (eV)</td>
<td>Wavelength (nm)</td>
</tr>
<tr>
<td>(E-3-2 cyanocrylic acid)</td>
<td>2.2067</td>
<td>561.86</td>
</tr>
<tr>
<td></td>
<td>2.4894</td>
<td>498.05</td>
</tr>
<tr>
<td></td>
<td>3.0492</td>
<td>406.61</td>
</tr>
</tbody>
</table>

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- cyanocrylic 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 TiO2 cluster as a model for semiconductor to evaluate the performance of the dye sensitizer.

The HOMO and LUMO energies of the bare Ti3O12 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].
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 TiO₂ 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 (∆E₉) of the conduction band edge of the TiO₂ 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 Vₛₑ 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 increases 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)](image)

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 \(\Delta G^{\text{inject}}\), (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].

\[
\text{LHE}=\frac{\text{λ}_{\text{max}}}{1-10^{\Delta G^{\text{inject}}}}
\]

Where λₘₐₓ is the absorption (oscillator strength) of the dye associated to the λₘₐₓ. 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 \(\Delta G^{\text{inject}}\) and \(E_{\text{exc}}\) 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)](image)
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 TiO2. This electron injection generates charge separated states in the interface results photo induced charge transfer processes takes place from the dye sensitizer to TiO2 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, $J_{sc}$ 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 (Dπ-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 $\Delta G^{inj}$ 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.

Acknowledgement
The authors acknowledge with thank the Periyar university providing financially supported the form of by University research fellow (URF) and The Department of Physics, Periyar university salem.

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