DOI:10.7598/cst2016.1296
ISSN:2278-3458

Chemical Science Transactions
2016, **5(4),** 1107-1113

RESEARCH ARTICLE

Theoretical Investigations of 1,5-Diaminoanthraquinone Organic Dye Sensitizer for Dye Sensitizer Solar Cell

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Received 2 July 2016 / Accepted 14 August 2016

Abstract: Based on theoretical calculations, we have studied quinine based dye for the application of Dye Sensitized Solar Cells (DSSCs). The effects of the electron donor-deficient units on the spectra and electrochemical properties have been investigated by Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) approaches. Further, the semiconductor TiO_2 is used as a model to evaluate the photo conversion efficiency of the chosen dye architecture. Results show that amino group acts as a donor and quinine group acts as an electron acceptor. Here, the group combination gives rise to large difference in dipole moment at excited state dipole moment than the ground state. This kind of quinine based metal free organic dye sensitizer is a promising sensitizer for practical DSSCs applications.

Keywords: Dye sensitizer, Density functional theory, Electronic structure, Electronic absorption spectra

Introduction

Since the report by O'Regan and Gratzel in 1991, Dye Sensitized Solar Cells (DSSCs) have merged as a potential low-cost alternative energy solution, compared to the silicon-based p-n junction solar cell[1,2]. In the particular case, there are four factors that can affect the performance of the DSSCs; there are photosensitive dyes, electrodes (anode and cathode) and electrolyte[3,4]. Two general classes of dyes exist are: metal-based and metal-free. Metal-free dyes are advantageous because of their high molar extinction coefficients, ease of modification and engineering, lower cost and environmental impact and increased performance in DSSC[5].

Typically, metal-free sensitizers belong to a class of dyes commonly referred to as D-π-a dyes and consist of three groups: an electron donor (D); an electron-rich conjugated bridging group (π) and an electron acceptor (A), which also serves to chemically bind the dye to the surface of the TiO_2. D-π-A structure motif exhibit several advantages over the coordination complex: high molar coefficient, low cost production and an extraordinary diversity. The metal-free organic dye sensitizers, such as cyanines[6], hemicyanines[7], triphenylamine[8], porylenes[9], comarins[10], phorphyrins[11] and indoline-based[12] dyes have been developed and exhibited satisfactory performance. Hence, in the present study, we performed first-principles quantum chemistry calculations on properties of 1,5-diaminoanthraquinone (1,5 DAQ) based D-π-A organic dyes for potential use as DSSCs. Based on the theoretical calculate geometric, electronic structure and absorption properties analyzed new design D-π-a molecules systems.

Computational methodology

All the calculations were performed Gaussian 09w package[13]. The ground state geometries of the molecules were optimized by the density functional theory (DFT) using Becke's three parameters and the Lee-Yang-Parr (B3LYP) and all the calculation were performed without any symmetry constrains by using polarized triple-zeta in the 6-31G(d,p) basis set. To compute the excited state geometries calculation was done using Time Dependent-DFT (TD-DFT) theory method and same basis set. In this work, the polarizable continuum model (PCM)[14] was used for solvent medium (Acetonitrile) and Gas phase effects dye molecules[15].

Results and Discussion

The ground state geometries

The optimized gruond state geometries structure of the 1,5-diaminoanthraquinone (1,5 DAQ) molecules are analysied by DFT for hybrid functional B3LYP/6-31G (d,p) level of theory, optimized stucture is shown in Figure 1.

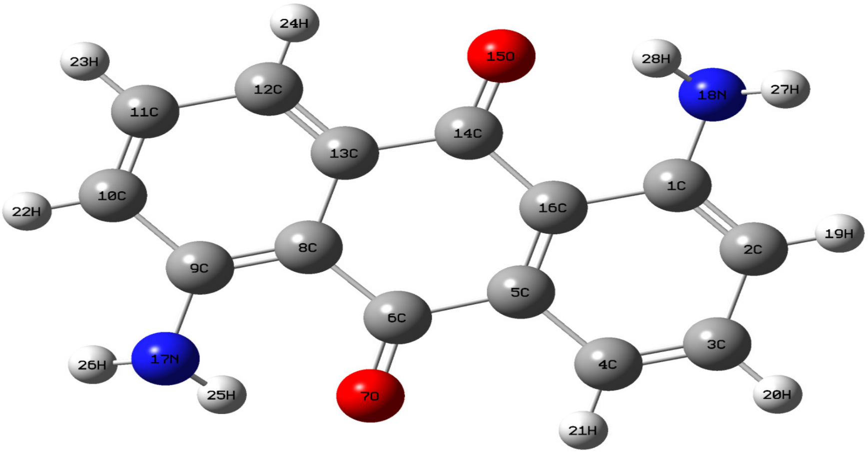

Figure 1. Optimized structure of the studied 1, 5 DAQ dye calculated by B3LYP/6-31G (d,p) level of theory

Table 1 shows bond, bond angle and dihedral angle. For the donor and acceptor moieties are fully conjugated through the π bridge as demonstrated by the coplanarity between the amino and quinone group.

Table 1. The selected bond length (Å), bond angle (in degree) and dihedral angle (in degree) for optimized structure the 1,5 DAQ dye calculated at the B3LYP-6-31G (d,p) level of theory

Bond length (Å)	
1C-2C	1.41
1C-18N	1.35
2C-19H	1.07
6C-7O	1.23
18N-28H	0.99
Bond angle(˚)	
2C-1C-16C	118.28
2C-1C-18N	118.63
5C-6C-7O	118.65
7O-6C-8C	122.08
27H-18N-28H	119.81
Dihedral angle(˚)	
16C-1C-2C-19H	179.99
18N-1C-2C-3C	-179.99
5C-6C-8C-9C	180.01
8C-9C-17N-26H	-180.00
15O-14C-16C-5C	179.94

Electrons transfer process

Extensive knowledge about the frontier molecular orbital (FMO) of organic molecules is important while studying the optoelectronic properties of the molecules. The energy gap between the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) has calculated as 2.99 eV. An efficient sensitizer should have a small HOMO – LUMO (E_{H-L}) gap. From Figure 2 it can be observed that the LUMO energy of the dye molecules above the conduction band of the TiO_2 (-4.00)[16] and the HOMO energies below the redox couple of the I^- / I_3^- (-4.80)[17]

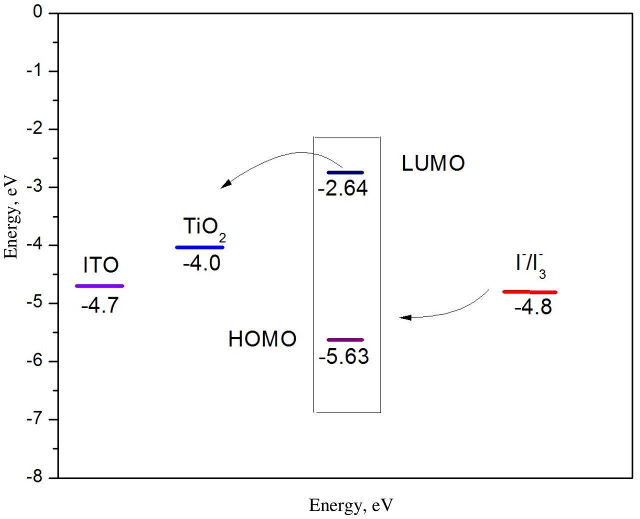

Figure 2. Schematic energy diagram of the 1, 5 DAQ-based dye TiO_2 and electrolyte (I^-/I_3^-)

The HOMOs are dominated by delocalized π orbital spread over the entire amino moiety and partial quinine moiety, whereas LUMOs are acceptor orbitals located from amino to quinine moieties predominantly. The distributions of HOMO and LUMO are separate, which can cause the possibility of electrons transfer from the amino moiety to the quinine moiety. Furthermore, these features could also reduce the chance of recombination between the injected electrons in conduction band of TiO_2 and the oxidized dyes.

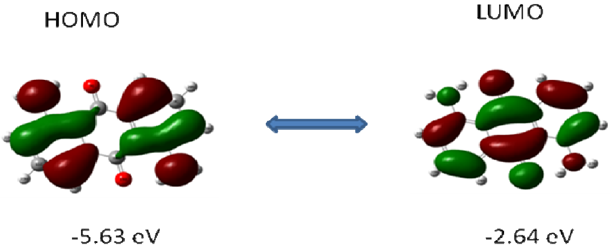

Figure 3. The frontier molecular orbitals of 1,5 DAQ HOMO (left) and LUMO (right)

Static Polarizability and Hyperpolarizability

The polarizability (α) and hyperpolarizability (β) of the 1,5 DAQ molecule were calculated using the formula

$$\alpha_{tot} = \frac{1}{3}\left[\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right] \tag{1}$$

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

$$\beta = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{xxy} + \beta_{yyy} + \beta_{yzz}\right)^2 + \left(\beta_{xxz} + \beta_{zyy} + \beta_{zzz}\right)^2\right]^{1/2} \tag{3}$$

and values are summarized in Table 1. The 1,5 DAQ molecule has the maximum polarizability of 1.72×10^{-23} e.s.u. The static polarizability is directly proportional to the dipole moment. The first hyperpolarizability is inversely proportional to the transition energy[19]. Accordingly, the 1,5 DAQ molecule is minimum transition energy (2.99 eV obtained from TD-DFT calculation) exhibits the maximum β value of 2.35×10^{-30} e.s.u. compared to urea higher than that 6 times.

Table 2. The calculated polarizability (α), isotropic polarizability (Δα) hyperpolarizability (β) and dipole moment (μ) of the 1, 5 DAQ dye

α (esu) ×10^{-23}		Δα (esu)×10^{-24}		β (esu) ×10		μ	
HF	DFT	HF	DFT	HF	DFT	HF	DFT
1.72	1.69	2.82	2.68	2.35	2.40	11.20	12.36

A higher value of first hyperpolarizability is important for active non linear optical (NLO) performance and the present results inculcate that 1,5 DAQ molecule can be used for NLO applications. The dipole moment of the designed quinone based molecules is calculated using the following formula:

$$\mu_{tot} = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2} \tag{4}$$

Where $\mu_x, \mu_y, \mu_z\, and\, \mu_{tot}$ are tensor component.

The dipole moment of design molecules ground state and excited state are 12.36 and 15.12 Debye. The dipole moment is one of the important parameters which provide information about the electronic charge distribution in the molecule[20]. The knowledge about the dipole moment of the organic molecule is important while designing the materials for optoelectronic applications.

Absorption properties

The absorption spectra of the 1,5 DAQ molecules calculated at the TD-B3LYP/6-31G (d,p) level of theory in gas phase and acetonitrile medium are summarized in Table 3. It can be observed that the absorption spectra of the designed molecules have significantly red shifted with respect to the 1,5-diaminoanthraquinone dye molecule. The dominant absorption band of 1,5-diaminoanthraquinone molecule is observed at 490 and 480 nm solvent and gas phase medium respectively. The dominant and is associated with HOMO-LUMO transition. As shown in Figure 4, the dominant absorption spectra of the 1,5-diaminoanthraquinone dye molecules lie in the visible region of the spectrum. The molecular orbital analysis has showed that the dominant absorption bands of the dye molecule is due to n→π* transition.

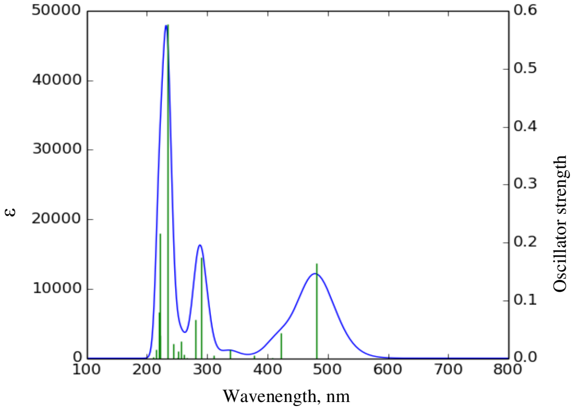

Figure 4. The calculated UV-Vis spectra of 1,5 DAQ dye using TD-B3LYP/631G (d,p) model in solvent medium

Overall efficiency

The solar-to-electricity conversation efficiency of the DSSC is calculated from the following equation:

$$\eta = \frac{J_{SC} V_{OC} FF}{P_{IN}} \tag{5}$$

Where J_{SC} short-circuit current density, V_{OC} is the open-circuit photo voltage; FF is the fill factor, and P_{IN} the intensity of the incident light. The open-circuit photo voltage, V_{OC} is calculated by the energy difference between the semiconductor conduction band edge (CBE) and the redox electrolyte potential. The J_{SC} is determined by the interaction betweenTiO_2 and sensitizer and the absorption coefficient of the sensitizer. J_{SC} can be expressed by Eq. 6

$$J_{SC} = \int LHE(\lambda) \Phi_{INJ} \eta_{coll} d\lambda \tag{6}$$

Whereas LHE (λ) is the light harvesting efficiency at a given wavelength, Φ_{inj} is the electron injection efficiency and η_{coll} is the charge collection efficiency.

In the same background of DSSCs systems, the similar sensitizers with only different π bridge fragment have same efficiency of charge collection and injection of the electron efficiency were assumed and it will be treated a constant to the similar structure in semiconductor interface. According to Eq. 6, to get large J_{SC}, the LHE of the sensitizer should be high. If only one absorption occurs for the electron injection and LHE can be presented[21] by Eq. 7:

$$LHE = 1 - 10^{-f} \tag{7}$$

Where f is the oscillator of the dye associated to the λ_{max}. From Table 3, we can calculate LHE vales in gas phase and solvent medium 0.37, 0.17, 0.79 and 0.43, 0.27, 0.80 for the 1,5 DAQ molecules respectively.

Table 3. Calculated absorption wavelengths (λ_{max}) in eV/nm, oscillator strength and major transition assignment of at TD-B3LYP/6-31G (d,p) level of theory in acetonitrile medium

Medium	Electronic Transitions	λ_{abs}		f	LHE	Major Transition Assignment
		Energy eV	Wavelength nm			
Solvent	62 → 63	2.582	480	0.1642	0.4362	H→L (99%)
	60 → 63	2.935	422	0.0438	0.2765	H1→L (94%)
	58 →64	3.039	408	0.0012	0.801	H2→L (92%)
	62 → 63	2.582	480	0.1642	0.4362	H→L (99%)

H: HOMO; L: LOMO

V_{OC} is calculated by the difference energy in the Fermi level of the injected electron in conduction band of TiO_2 and the redox potential of electrolyte. We can take the electrolyte redox potential as a constant, because the solution I^-/I^-_3 usually used as the electrolyte. Upon the adsorption of dyes onto the semiconductor, the shift of CBE can be expressed[22] as Eq. 8:

$$\Delta CBE = -\frac{q\mu_{normal}\gamma}{\varepsilon_0 \varepsilon} \tag{8}$$

Where q is the elementary charge, c is the molecular surface concentration, μ_{normal} is the component of the dipole moment of the individual molecular perpendicular to the interface of the semiconductor (the negative direction is defined as the dipole moment pointing toward the TiO_2 film), ε_0 and ε are the permittivity of the vacuum and the dielectric constant of the organic monolayer.

Thus, according to Eq. 8, it is obvious that a dye with a large normal μ will lead to more shift of CBE of TiO_2 film toward the vacuum energy level, which will result in large V_{OC}. The dipole moment calculated results are shown in Table 2. However, the 1,5 DAQ dye molecule has the largest LHE and dipole moment, so it maybe performance to the best conversion efficiency.

Conclusion

The geometric and electronic properties of the new designed uinine based organic dye molecule have been studied the DFT and TD-DFT methods. The results obtained from the frontier molecular orbital analysis, electron injection and electron recombination of the designed dye molecule uinine based donor molecule is suitable for DSSC applications. The 1,5 DAQ dye shows hyperpolarizability is greater than urea in gas phase. The dipole moment, static polarizability and hyperpolarizability values shows, 1,5 DAQ based donor molecule possess good NLO properties. These results suggest that the 1,5 DAQ the based dye molecules are most promising that candidates the high-performance photo sensitizers.

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