Molecular Modelling of Organic Sensitizer 3-chloro-4-methoxybenzonitrile for Dye-Sensitized Solar Cell Applications

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ABSTRACT

Based on theoretical calculations, we studied 3-chloro-4-methoxybenzonitrile (3C4MBN) 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. This kind of 3C4MBN based metal free organic dye sensitizer is a promising sensitizer for practical DSSCs applications.

Keywords: Electrochemical, Density Functional Theory, Organic dye.

1. 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 [1−4]. 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 [5-8]. Two general classes of dyes exist: 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 [9-10]. Typically, metal-free sensitizers belong to a class of dyes commonly referred to as 3-chloro-4-methoxybenzonitrile dyes, and consist of the 3-chloro-4-methoxybenzonitrile which also serves to chemically bind the dye to the surface of the TiO_2. The Dye 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 [11,12], hemicyanines [13,14], triphenylamine [15-18], porylenes [19-21], comarins [22-24], phorphyrins [25,26] and indoline-based[27-29] dyes have been developed and exhibited satisfactory performance. Hence, the present study we have chosen the effective of the selected dye Shown Fig 3.1. Based on the theoretical calculation geometric, electronic structure and absorption properties are studied.

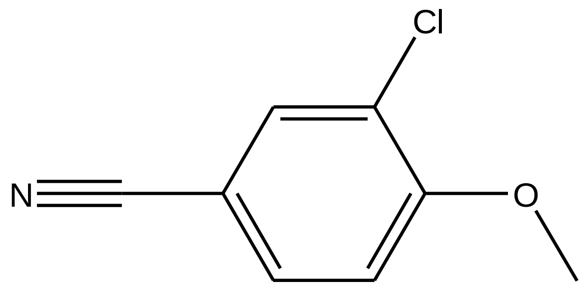

Fig. 3.1. Chemical structure of the 3-chloro-4-methoxybenzonitrile

2. Computational Details

All the calculations were performed Gaussian 09w package [30]. 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 6-311++G(d,p) basis set. To compute the excited state geometries calculation using Time Dependent-DFT (TD-DFT) theory method and same basis set. In this work, the polarizable continuum model (PCM)[31] was used for solvent medium (Acetonitrile) and Gas phase effects dye molecule [32].

3. Results and Discussion

3.1 The ground state geometries

The optimized gruond state geometries structure of the 3C4MBN dye molecule are analysied by DFT for hybrid functional B3LYP/6-311++G (d,p) level of theory, as well as in acetonitrile medium. Optimized stucture shown Fig. 3.2. Table 3.1. Shown the bond length, bond angle and dihedral angle.

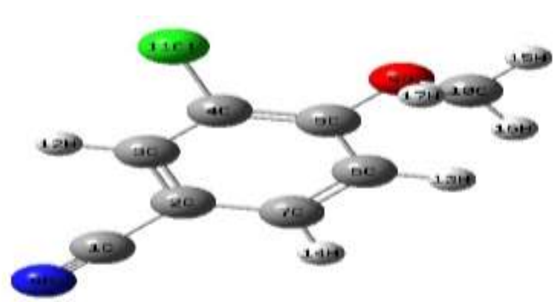

Fig.3.2. Optimized geometrical structure of dye 3-chloro-4-methoxybenzonitrile.

Table 3.1 Bond lengths (in nm), bond angles (in degree) and dihedral angles (in degree) of the dye 3-chloro-4-methoxybenzonitrile.

Parameters	HF/6-311G(d,p)	DFTB3LYP/6-311G(d,p)
Bond length(Å)		
C1-C2	1.4418	1.4289
C1-N8	1.1308	1.156
C2-C3	1.387	1.4041
C2-C7	1.3888	1.3984
C3-C4	1.3804	1.3827
C3-H12	1.073	1.0819
C4-C5	1.3904	1.41
C5-1C11	1.7366	1.7463
C5-C6	1.3879	1.4003
C5-C9	1.3449	1.3473
C6-C7	1.379	1.3893
C6-H13	1.0742	1.0812
C7-H14	1.0739	1.0827
O9-C10	1.4146	1.4264
C10-H15	1.0796	1.0878
C10-H16	1.0854	1.0943
C10-H17	1.084	1.0943
Bond Angle(°)		
C1-C2-C3	119.6622	120.0577
C1-C2-C7	120.1236	120.5266
C3-C2-C7	120.2139	119.4157
C2-C3-C4	119.6679	120.0616
C2-C3-H12	120.4683	120.3219
C4-C3-H12	119.8634	119.6164
C3-C4-C5	120.6646	120.9523
C3-C4-1C11	119.1012	119.5774
C5-C4-1C11	120.231	119.4704
C4-C5-C6	119.0318	118.4965
C4-C5-C9	121.1838	116.896
C6-C5-C9	119.7344	124.6075
C5-C6-C7	120.8094	120.7457
C5-C6-H13	118.4471	120.1191
C7-C6-H13	120.7392	119.1352
C2-C7-C6	119.6098	120.3281
C2-C7-H14	120.0194	119.7931
C6-C7-H14	120.3699	119.8788
C5-O9-C10	116.4766	119.159

O9-C10-H15	106.3655	105.4405
O9-C10-H16	110.6054	111.1789
O9-C10-H17	110.9022	111.1693
H15-C10-H16	109.6473	109.5009
H15-C10-H17	109.5934	109.515
H16-C10-H17	109.6692	109.9294
C2-C1-N8-C3-(-C1	180.1622	180.157
C2-C1-N8-C3-(-C2	180.1871	180.1103
Dihedral Angle (°)		
C1-C2-C3-C4	179.9294	179.9936
C1-C2-C3-H12	-0.2862	-0.0028
C7-C2-C3-C4	-0.2965	-0.0025
C7-C2-C3-H12	179.4879	-179.9989
C1-C2-C7-C6	179.9777	-179.9952
C1-C2-C7-H14	0.3296	0.0046
C3-C2-C7-C6	0.2046	0.0008
C3-C2-C7-H14	-179.4435	180.0006
C2-C3-C4-C5	-0.0402	0.0068
C2-C3-C4-1C11	179.3132	-179.9922
H12-C3-C4-C5	-179.8259	-179.9968
H12-C3-C4-1C11	-0.4725	0.0041
C3-C4-C5-C6	0.4616	-0.0092
C3-C4-C5-O9	177.8834	179.985
1C11-C4-C5-C6	-178.8845	179.9898
1C11-C4-C5-O9	-1.4627	-0.016
C4-C5-C6-C7	-0.5556	0.0075
C4-C5-C6-H13	178.6999	-179.9881
O9- C5-C6-C7	-178.0155	-179.9862
O9- C5-C6-H13	1.24	0.0182
C4-C5-O9- C10	91.7182	-180.0127
C6-C5-O9- C10	-90.8779	-0.0189
C5-C6-C7-C2	0.2262	-0.0034
C5-C6-C7-H14	179.873	-180.0032
H13-C6-C7-C2	-179.0122	179.9922
H13-C6-C7-H14	0.6347	-0.0076
C5-O9-C10-H15	-179.2184	179.9603
C5-O9-C10-H16	61.783	61.3778
C5-O9-C10-H17	-60.1222	-61.4455

3.2 Electrons transfer process

Extensive knowledge about the frontier molecular orbital (FMO) of organic molecule is important while studying the optoelectronic properties of the molecule. The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) energies the energy gap between the 5.27 eV. An efficient sensitizer should have a small HOMO – LUMO (E_{H-L}) gap. From Fig. 3 it can be observed design in the molecule, the LUMO energy of the dye molecule are above the conduction band of TiO_2 (-4.0 eV) [33] and the HOMO energies are below the redox couple of I^-/I^{3-} (-4.8 eV) [34].

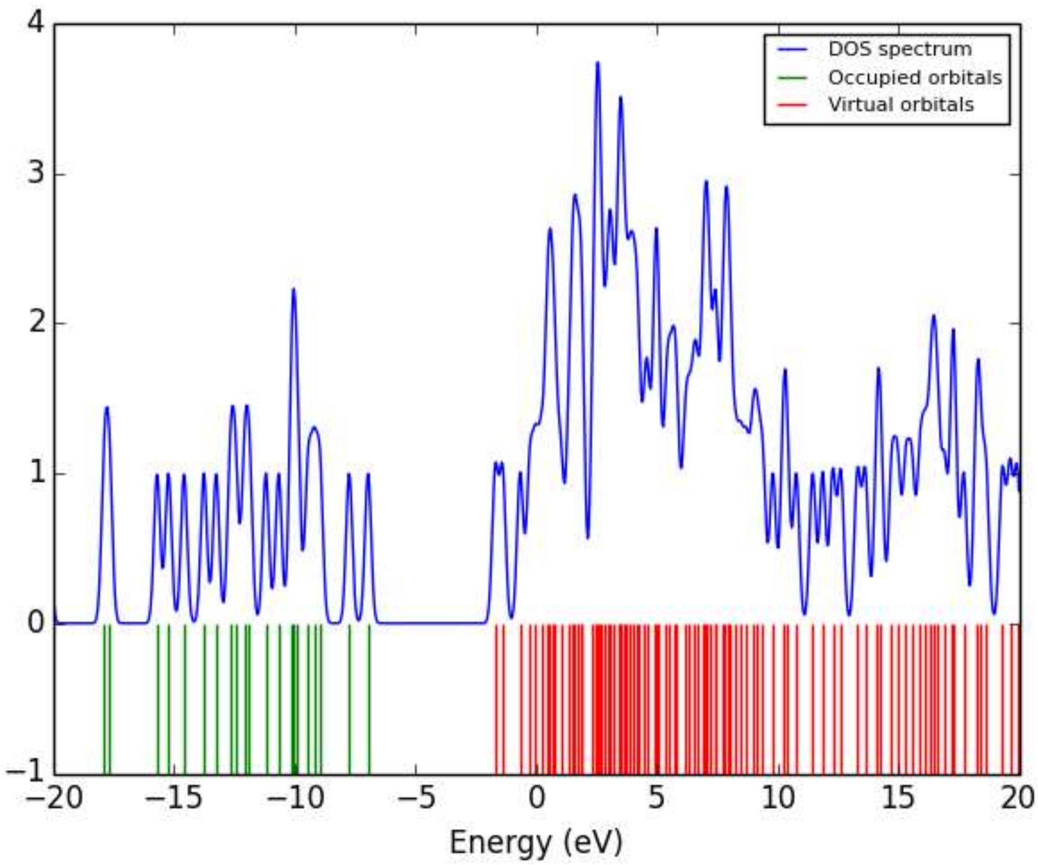

Fig. 3.3. The frontier molecular orbital energies and corresponding DOS spectrum of the dye 3-chloro-4-methoxybenzonitrile,

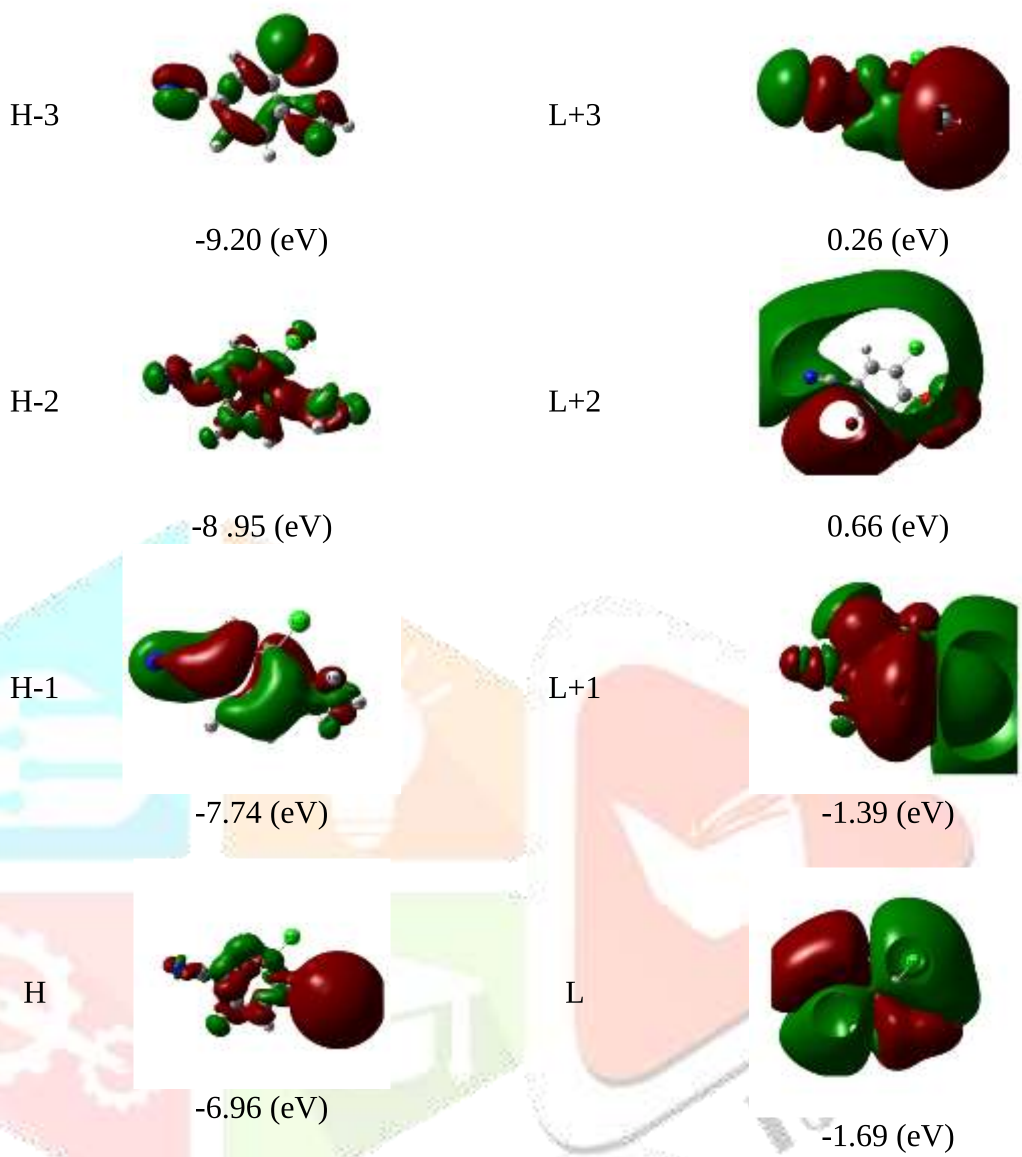

Fig.3.4.Isodensity plots (isodensity contour = 0.02 a.u.) of the frontier orbitals of 3-chloro-4-methoxybenzonitrile.

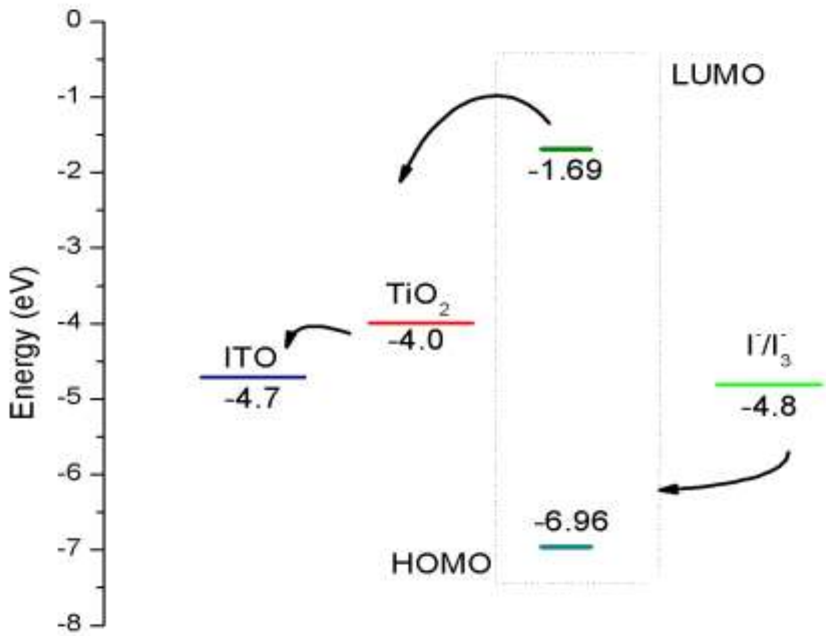

Fig.3.5 Energy level diagram of 3-chloro-4-methoxybenzonitrile

The HOMOs are dominated by delocalized the electron, whereas LUMOs are acceptor orbital located from the electron. The distributions of HOMO and LUMO are separate, which can cause the possibility of electrons transfer from the molecule. Furthermore, these features could also reduce the chance of recombination between the injected electrons in conduction band of TiO_2 and the oxidized dyes.

3.3.3 Static Polarizability and Hyperpolarizability

The polarizability (α) and hyperpolarizability (β) of the 3C4MBN Dye molecule were calculated using the equation (1) [35]: and values are summarized in Table 2

$$\alpha_{tot} = \frac{1}{3}\left[\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right] \qquad (3.1)$$

$$\beta_0 = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{xxy} + \beta_{yyy} + \beta_{yzz}\right)^2 + \left(\beta_{xxz} + \beta_{zyy} + \beta_{zzz}\right)^2\right]^{\frac{1}{2}} \qquad (3.2)$$

Whereas $\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \beta_{xxz}, \beta_{zyy}, \beta_{zzz}, \beta_{xxx}, \beta_{xyy}, \beta_{xzz}, \beta_{xxy}, \beta_{yyy} and \beta_{yzz}$ tensor comments.

The 3C4MBN molecule has the maximum polarizability of 23.70 a.u. The static polarizability is directly proportional to the dipole moment. The first hyperpolarizability is inversely proportional to the transition energy [36]. Accordingly, the 3C4MBN molecule is minimum transition energy exhibits the maximum β value of 13.38 a.u. A higher value of first hyperpolarizability is important for active

Table 3.2 The Polarizability (α) in a.u , Hyperpolarizability (β) in a.u and Dipole moment (μ) in Debye calculated at B3LYP level using 6-31G(d,p) basis set by GAUSSIAN 09 for selected dye at the ground state

Polarizability		Hyperpolarizability		Dipole Moment	
α_{xx}	-89.48	β_{xxx}	179.15	μ_x	4.95
α_{xy}	-6.582	β_{xxy}	-17.83	μ_y	-3.19
α_{yy}	-62.40	β_{xyy}	12.00	μ_z	0.30
α_{xz}	0.007	β_{yyy}	-9.063		
α_{yz}	-0.019	β_{xxz}	1.728		
α_{zz}	-72.45	β_{yyz}	0.950		
		β_{xzz}	9.390		
		β_{yzz}	2.140		
		β_{zzz}	0.720		
α	23.70 a.u.	β	13.38 a.u	μ	5.90 Debye

Non Linear Optical (NLO) performance and the present results inculcate that 3C4MBN molecule can be used for NLO applications. The dipole moment of the designed 3C4MBN Dye molecule to calculate following the formula:

$$\mu_{tot} = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2} \qquad (3.3)$$

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

The dipole moment value of 3C4MBN Dye molecule is 5.90 Debye. The dipole moment is one of the important parameters which provide information about the electronic charge distribution in the molecule [37]. The knowledge about the dipole moment of the organic molecule is important while designing the materials for optoelectronic applications.

3.4 Absorption properties

The absorption spectra of the 3C4MBN Dye molecule calculated at the TD-B3LYP/6-311++G (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 molecule have significantly red shifted with respect to the 3C4MBN dye molecule. The dominant absorption band of 3C4MBN molecule is observed at 600 and 573 nm solvent and gas phase medium respectively. In the studied molecule, the dominant band is associated with HOMO-LUMO transition.

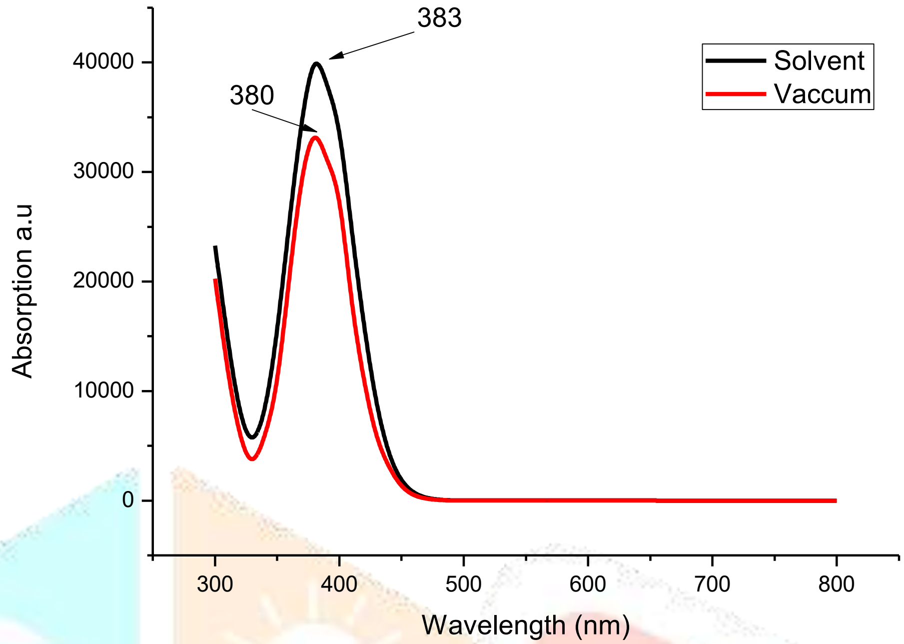

Fig.3.6 calculated electronic absorption spectra of the dye 3-chloro-4-methoxybenzonitrile.

As shown in Fig. 4, the dominant absorption spectra of the 3C4MBN dye molecule lie in the visible region of the spectrum. The molecular orbital analysis showed that the dominant absorption bands of the dye molecule are either due to $n \rightarrow \pi^*$ transition.

Table 3.3

Computed excitation energies, electronic transition configurations and oscillator strengths (f) for the optical transitions with f > 0.01 of the absorption bands in visible and near- UV region for the dye 3-chloro-4-methoxybenzonitrile in acetonitrile.

State	Configurations composition (corresponding transition orbitals)	Excitation energy (eV/nm)	oscillator strength (f)	LHE
1	HOMO->LUMO (65%)	5.7699 / 555.80	0.0004	0.0009
2	H-1->LUMO (88%)	5.7987/ 398.48	0.2608	0.4514
3	HOMO->L+1 (95%)	7.1185/ 382.88	0.2876	0.4842
4	H-2->LUMO (71%)	7.1486/362.71	0.1933	0.3592
5	H-3->LUMO (11%), H-1->L+1 (76%)	7.2241 /340.01	0.0164	0.0370
6	H-8->LUMO (89%)	7.3474/339.03	0.0001	0.0002

7	H-3->LUMO (10%), H-1->L+2 (11%), HOMO->L+2 (60%)	7.4852/318.76	0.0001	0.0001
8	H-4->LUMO (11%), H-3->LUMO (68%), H-1->L+1 (10%)	7.7604/308.88	0.0922	0.1912
9	H-4->LUMO (73%), HOMO->L+2 (10%)	7.9258/ 305.67	0.0369	0.0814
10	H-5->LUMO (82%)	8.0196/293.88	0.0025	0.0057
11	H-6->LUMO (19%), H-1->L+2 (56%)	8.0659/292.02	0.2673	0.4596
12	H-6->LUMO (73%), H-1->L+2 (12%)	8.1522/286.35	0.0076	0.0173
13	H-1->L+3 (34%), HOMO->L+3 (61%)	8.3017 /281.39	0.0123	0.0279
14	H-2->L+1 (25%), H-1->L+4 (16%), HOMO->L+4 (43%)	8.4957/279.31	0.0204	0.0458
15	H-2->L+1 (59%), H-1->L+4 (12%), HOMO->L+4 (18%)	8.5862/272.41	0.0035	0.0080
16	H-7->LUMO (79%)	8.6083/266.48	0.0002	0.0004
17	H-3->L+1 (66%)	8.6717/266.41	0.0084	0.0191
18	H-1->L+3 (44%), HOMO->L+3 (30%)	8.8072/261.32	0.0009	0.0002
19	H-4->L+1 (39%), HOMO->L+5 (16%)	8.9259/257.93	0.0247	0.0552
20	H-6->LUMO (73%), H-1->L+2 (12%)	9.4589/252.37	0.0183	0.0412

3.5. Overall Efficiency

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

$$\eta = \frac{J_{SC} V_{OC} FF}{P_{IN}} \tag{3.4}$$

Where J_{SC} short-circuit current density, V_{OC} is the open-circuit photo voltage; FF is the fill factor, and Pin the intensity of the incident light.

The open-circuit photo voltage, V_{OC}, is determined by the energy difference between the semiconductor CBE and the electrolyte redox potential. The short-circuit current density, 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. (3.5)

$$J_{SC} = \int LHE(\lambda)\Phi_{INJ}\eta_{coll}d\lambda \quad (3.5)$$

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 external environment of DSSCs systems, the similar sensitizers with only different π bridge fragment have same charge collection efficiency and electron injection efficiency were assumed and it will be treated a constant due to the similar structure in the dye semiconductor interface. According to Eq. (3.5), to get large J_{SC}, the LHE of the sensitizer should be as high as possible. If only one absorption occurs for electron injection, LHE can be presented by Eq. (3.6) [38,39]:

$$LHE = 1 - 10^{-f} \quad (3.6)$$

Where f is the oscillator of the dye associated to the $\lambda_{\max}$. From Table 3, we can calculate LHE values in Gas phase and Solvent medium 0.45, 0.48, 0.35 for the 3C4MBN Dye molecule respectively.

V_{OC} is determined by the energy difference between 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. Therefore, we paid close attention to the semiconductor CBE. Upon the adsorption of dyes onto the semiconductor, the shift of CBE can be expressed as Eq. (3.7) [38, 40, 41].

$$\Delta CBE = -\frac{q\mu_{normal}\gamma}{\varepsilon_0\varepsilon} \quad (3.7)$$

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 e ε are the permittivity of the vacuum and the dielectric constant of the organic monolayer. Thus, according to Eq. (3.7), it is obvious that a dye with a large μ_{normal} 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 3.2. The results show designed dye own larger dipole moment. From above, design dye molecule have largest LHE and dipole moment, so it maybe performance the best conversion efficiency.

4. Conclusions

The geometric and electronic properties of the 3C4MBN organic dye molecule have been studied Using DFT and TD-DFT methods. The results obtained from the frontier molecular orbital analysis, electron Absorption properties of the 3C4MBN dye molecule is suitable for DSSC applications. The dipole moment, static polarizability and hyperpolarizability values shows, 3C4MBN Dye molecule possess good NLO properties. These results suggest that the 3C4MBN dye molecule are most promising candidates the high-performance photo sensitizers.

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