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CONCEPTUAL DENSITY FUNCTIONAL THEORY [DFT] STUDY OF SOME ORGANIC DYES FOR THEIR USE AS SENSITIZERS IN MOLECULAR PHOTOVOLTAICS

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ABSTRACT

Solar energy can be converted to electricity by photovoltaic and photo electrochemical cells, Dye-sensitized solar cell [DSSC] has been considered as a promising next generation solar cells. In this work, we used theoretical methods to studies the properties of some metal free organic dayes our aim was to make a correlation between some new Density Functional theory derived indexes and the efficiency of the organic dyes used as sensitizers in solar cells. The Density Functional Theory (DFT) calculations were done using the B3lyp hybrid functional level of theory and the 6–31G(d,p) basis set. This level of calculation was used to find the optimized molecular structure, the molecular orbitals energies, and the global properties, derived from Conceptual DFT our results show a good correlation between the DFT derived indices and the experimental efficiencies.

Keywords: DFT, Dyes, Photovoltaiic sollar celles, Reactivity indices

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1. INTRODUCTION

1.1. Solar energy

Energy' is identified as one of the most important challenges that humanity faces over the next 50 years [1]. To overcome this problem the scientific community had already started working on various issues (to save, convert or create energy by utilizing existing resources). Actually, solar energy conversion has become one of the major alternatives to the conventional fossil fuels, considering their drastic depletion over the last few decades [2]. Indeed a very important number of both theoretical and experimental researches has greatly encouraged scientists to explore and develop renewable and environmentally friendly energy sources, particularly low cost direct use photoelectric conversion devices [3]. Inorganic semiconductor cells, especially silicone in various forms, have been developed over several decades and have important applications. However, silicone materials are not cost effective. Recently, dye sensitized solar cells [DSScS], are considered as a credible alternative to activist inorganic silicone-based solar cells, and have attracted much attention relevant to global environmental issues [4]. Recentlly, It has been found that the nature of photosensitizers, such as redox potential, structure and photophysical properties, play an important role in determining the overall cell efficiencies.

1.2 Dyes Sensitizers solar cells Very recently, two kinds of photo sensitizers ,ruthenium dyes [5,6] and metal-free organic dyes, were developed for DSSCs. Metal-free organic dyes were regarded as an alternative to ruthenium dyes because of their high molar absorption coefficient, simple synthesis procedure, and low cost. To date, various kinds of metal-free organic dyes [7] including coumarin[8], indoline[9], squaraine [10], polyene [11], hemicyanine [12], oligothiophene[13], perylene[14] porphyrin [15], carbazole [16], benzothidizole [17] and truexene [18] have been developed and attained high efficiency up to 9% [9b,19]. Our aim in this work is to elucidate theoretically by means of DFT derives indices the solar-to-electric conversion efficiencies of two groups of dye sensitizers: Coumarin and Carbazoledye and three other dyes from the same family, experimental results have been done by Mishra and all [20].

2. RESULTS AND DISCUSSIONS

2.1. Computational methods

- DFT calculations were carried out using the semi empirical PM6 method and the B3LYP exchange-correlation functional, together with the standard 6-31G[d] basis set.
- The stationary points were characterized by frequency calculations in order to verify that TSs had one and only one imaginary frequency.
- The electronic global properties derived from conceptual DFT were caring out .
- The calculations presented in this work were performed with the Gaussian 09 suite of programs

2.2. Molecular structure choice of some metal free organic dye

The molecular structure of the dye plays an important role in DSSCs. After absorption of light, charge separation is generally initiatedat the interface between the dye bond at the TiO_2 surface and the hole-transporting material. The performance of DSScS generally depends on the energy levels of the sensitizers and the kinetics of the electrontransfer processes at the interface between the dye bound to the semiconductor surface and the hole-transporting material.[21].

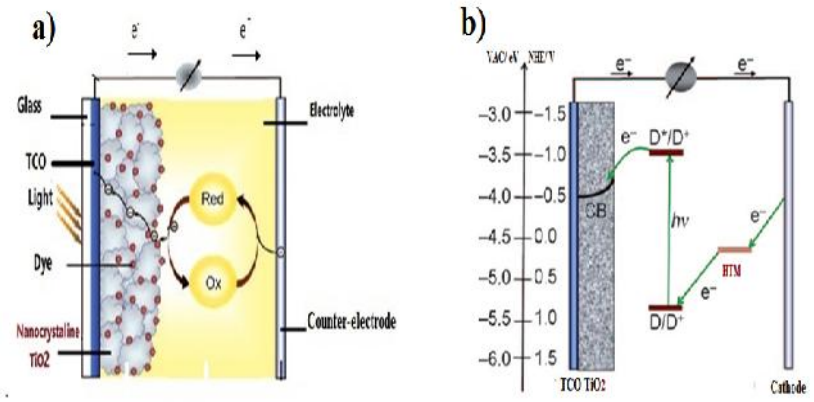

Fig.1. a) fundamental processes in a dye-sensitized solar cell.
b) Energy-level diagram of a DSSC. TCO= transport conducting oxide.[21]

In fig. 2, 3 and 4 we represent for each family the molecular structurewhich we have chosen in our study and DFT calculation.

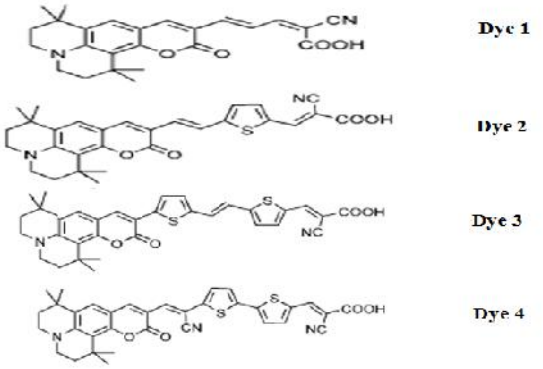

Fig.2. Coumarin molecularstructure

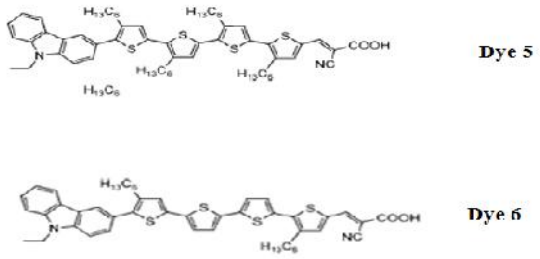

Fig.3. Carbazole molecular structure

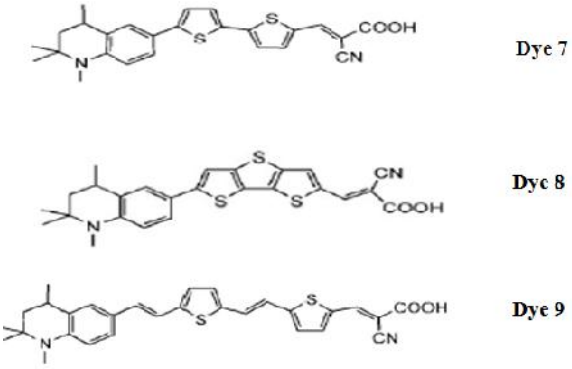

Fig.4. Other family of sensitizers

Table 1. Experimental results [21]

Dye family	*Dye n°*	J_{sc}	v_{oc}	*FF*	*n%*
Coumarin	***1***	14.0	0.60	0.71	6.0
	2	14.7	0.67	0.73	7.2
	3	15.9	0.69	0.75	8.2
	4	18.8	0.53	0.65	6.5
Carbazole	***5***	14.0	0.74	0.74	7.7
	6	10.2	0.67	0.64	4.4
Other	***7***	12.0	0.60	0.63	4.5
	8	8.8	0.52	0.63	2.9
	9	7.2	0.54	0.59	2.3

With

[Jsc]:represent theshort-circuit photocurrent density

[Voc]: open-circuit photovoltage

[ff]: The fill factor is identified

[η]: it is solar-to-electric conversion efficiencies

2.3. DFT Results

To rationalize result resumed in table. 1, we have calculate the global properties namely: namely, electronic chemical potential ‘μ’, global hardness ‘ η’ , global electrophilicity, ‘ω’ , and global nucleophilicity, ‘Nu’, and global charge transfer , ΔN_{max},results are reported in table 2,3 and 4

Table 2. The global properties of coumarin metal free organic dye.

Dye family	*Dye n°*	*Homo*	*Lumo*	«
Coumarin	***1***	-0,13908	-0,10182	-0,12045
	2	-0,18941	-0,10497	-0,14719
	3	-0,18706	-0,10383	-0,14545
	4	-0,19415	-0,11526	-0,15471

Table 2. [Continued]

Dye n°	¦	µ	***Nu***	ΔNmax	***S***
1	0,03726	0,19468	0,20971	3,23	26,838
2	0,08444	0,12828	0,159	1,743	11,842
3	0,08323	0,12709	0,161	1,747	12,01
4	0,07889	0,15169	0,154	1,954	12,67

Table 3. The global properties of carbazole metal free organic dye.

Dye family	***Dye n°***	***Homo***	***Lumo***	«
Carbazole	***5***	-0,19755	-0,0989	-0,14823
	6	-0,19352	-0,10013	-0,146825

Table 3. [Continued]

Dye n°	¦	µ	***Nu***	ΔNmax	***S***
5	0,09865	0 ,111	0,151	1,502	10,136
6	0,09339	0,115	0,155	1,57	10,707

Table 4. The global propertiesof dye 7,8,9.

Dye familly	***Dye n°***	***Homo***	***Lumo***	«
Other	***7***	-0,18177	-0,09761	-0,13969
	8	-0,18475	-0,0983	-0,14153
	9	-0,1754	-0,10372	-0,13956

Table 4. [Continued]

Dye n°	¦	µ	***Nu***	ΔNmax	***S***
7	0,08416	0,115	0,167	1,659	11,88
8	0,08645	0,115	0,160	1,638	11,567
9	0,07168	0,135	0,173	1,946	13,95

With: $\chi \approx \frac{\varepsilon_{HOMO} + \varepsilon_{LUMO}}{2}$ (1)

$\eta \approx \varepsilon_{HOMO} - \varepsilon_{LUMO}$ (2)

$\omega = \frac{\mu^2}{2\eta}$ (3)

$Nu = \varepsilon_{HOMO(Nuc)} - \varepsilon_{HOMO\ (TCE)}$ (4)

$S = 1/\eta$ (5)

$\Delta N\ max = -\frac{\chi}{\eta}$ (6)

2.4. DISCUSSIONS

- Our calculations indicate that:

The maximum global electrophilicity value is obtained for dye 1 and dye 3 in coumarin dye family and the highest values of this same quantity areidentified for dye 5 in the carbazole dye family and for the dye 9 in the last family dye.

The following order of global propertiesfor each family dye is gettingou :

- Coumarin family dye.

- $\omega_{Dye1} > \omega_{Dye3} > \omega_{Dye2} > \omega_{Dye4}$, and the order to the hardness and softness values are as:

- $\eta_{Dye\ 4} > \eta_{Dye\ 2} > \eta_{Dye\ 3} > \eta_{Dye\ 1}$

- $S_{Dye1} > S_{Dye\ 4} > S_{Dye\ 3} > S_{Dye\ 2}$

- $Nu_{Dye3} > Nu_{Dye2} > Nu_{Dye4}$ and $\mu_{Dye3} > \mu_{Dye2} > \mu_{Dye4}$.

- Carbazole family dye.

- $\omega_{Dye6} > \omega_{Dye5}$, and Nu dye 6> Nu dye 5,

- η dye5> η dye 6, $\Delta N_{max Dye6} > \Delta N_{max\ Dye5}$ and $\mu_{Dye6} > \mu_{Dye5}$ the same order for the softness values.

- Other family sensitisers

- $\omega_{Dye9} > \omega_{Dye8,7}$, and $\Delta N_{max Dye9} > \Delta N_{max\ Dye7} > \Delta N_{max Dye8}$ and $\mu_{Dye9} \sim \mu_{Dye7} > \mu_{Dye8}$.

- The hardness and the softness S order did not provide the same order.

3. CONCLUSIONS

From our DFT calculation we conclude that the carbazoleobeyed to the same order in her global properties wish indicate that the highest level of stability molecular structure is obtained for the second kind of family metal organic dye.

The best correlation of theoretical computation and experience results is identified for the same family.

Indeed we can observed that global global properties obtained in the comarun family dye molecules who's posed the thiophane molecule can correspond to the results experiences.

For the last classification we can say that the last kind of metal free organic dye there is a lowest correspondence between the dft calculation and experience results

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