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THEORETICAL STUDY OF DITHIAPORPHYRIN AS SENSITIZER FOR DYE-SENSITIZED SOLAR CELLS APPLICATION

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Abstract - Dye-sensitized solar cells (DSSCs) have gained significant attention because of their low production costs, ease of fabrication and tunable aesthetic features. Here, we have designed a zinc dithiaporphyrin structure based on D-π-A strategy and studied its optoelectronic properties and then compared it with the YD2-o-C8 of porphyrin asreference dye.Properties ofthis sensitizerwas investigated using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations. Our calculation results indicated that the new structure has the reasonable optical propertiesas a sensitizer for DSSCs applications.

1. Introduction

Today, replacement of fossil fuels with renewable and clean fuels such as biofuels, wind, geothermal and solar energy are one of the essential requirements for civilization [1].Dye-sensitized solar cells (DSSCs) have showed great potential as a low cost alternative to silicon-based inorganic cells. Dye molecules play a fundamental role in DSSC, they are involved in light capturing and electron injection to the titania, therefore a large part of the final efficiency is associated to them [2]. In photosynthesis, porphyrins act as antennae to capture photons for the efficient capture of sunlight [3].Inspired by nature, porphyrinsand their derivatives are considered as asuitable alternative to the expensive Ru complexes in the fabrication of DSSCsbecause of their good electron donating/accepting nature, rigid macrocyclic structuresandhaving strong absorption in the visible region [4].

Modification of the porphyrin core by replacing one or more of the pyrrolic nitrogens in the porphyrin ring with heteroatoms like oxygen, sulphur, selenium and tellurium result in an altered electronic structure with interesting optical, chemical, photochemical and electrochemical properties [5]. For applications in organic photovoltaics, core-modified dithiaporphyrins, for example, have shown enhanced visible light absorption and facile redox properties compared to their nitrogen equivalent [6]. In this study, we designed a sensitizer based on dithiaporphyrin to obtain improved light absorption properties at Soret and Q bandsand the HOMO–LUMO energy gap.The electrondonors and π-bridge system are substituted in meso positions of the basic dithiaporphyrin dye.

2. Computational methods

Molecular structure was optimized in the gas phase at CAM-B3LYP method and the 6-311+G (d) basis set using Gaussian 09 program package.Vibrational frequency calculations at the same level of theory was carried out to ensure of the minima. To gain insight into the electronic properties of dyes, their HOMO and LUMO energies were calculated.The electronic and optical properties and absorption spectra of dyes were calculated using time-dependent density functional theory (TD-DFT) calculationsat the same level of theory.

3. Results and discussion

We constructed a structure of dithiaporphyrin-based sensitizer and studied its intrinsic optical properties and then compared it with the YD2-o-C8 of porphyrin as reference dye.We selected YD2-o-C8 for the reference dye because of have recently been studied experimentallyand considered to be an efficient dye [7].The investigated structureof dithiaporphyrinin this study is illustrated in Fig.1.

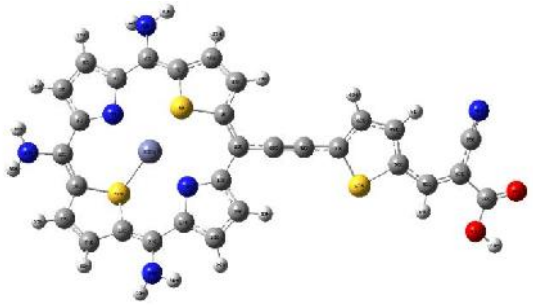

Fig. 1. Molecular structure of the investigated dithiaporphyrin sensitizer.(yellow :sulphur,red: oxygen, violet: zinc, gray: carbon)

This structure have designed based on D-π-A strategy in which the amine moieties were substituted with a basic zinc-dithiaporphyrin structure acts as electron donors, 2 ethynylthiophene bridge is π-spacer and

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carboxylic acid and cyanoacrylic acid are selected as acceptor and the anchoring groups.

In the design of dye molecules, HOMO, LUMO, and the HOMO-LUMO energy gap are among the most important parameters dominating the dye performance in DSSCs[8]. Generally, the HOMO and LUMO orbitals of solar cell sensitizers should match the corresponding energy levels of the electrolyte and the conduction band (CB) of the TiO_2 electrode. An efficient sensitizer should have a small HOMO-LUMO (E_{H-L}) gap, LUMO energy level above the conduction band of the semiconductor of TiO_2 (-4.0 eV) and HOMO energy level below the redox couple of I^-/I_3^- (-4.8 eV)[9]. Molecular orbital energy levels of our molecule were compared with Yd2-o-C8 in Table 1.

Table 8 Molecular orbital energy levels (eV) for the investigated dithiaporphyrin dye calculated at CAM-B3LYP level of theory

structure	E_{HOMO}	E_{LUMO}	E_{gap}
dithiaporphyrin	-5.6	-2.1	3.5
Yd2-o-C8*	-5.6	-1.5	4.1

* Taken from Ref.7

As shown in Table 1, the energy gap between the HOMO and LUMO is 3.5 for our Dye that is smaller than the reference dye YD2-o-C8.

In order to create an efficient charge-separated state and improved efficiency, HOMOs must be localized on the donor subunit, and LUMOs must be localized on the acceptor and anchoring groups. Fig.2 illustrates the electron density distribution of the HOMO and LUMO for dithiaporphyrin sensitizer that is built using the CAM-B3LYP level of theory. From Fig.2, it can be seen that the electron densities of HOMO of this sensitizer is mainly localized on the dithiaporphyrin unit, and the LUMO is delocalized through the cyanoacrylic acid fragment which is suitable for a sensitizer dye.

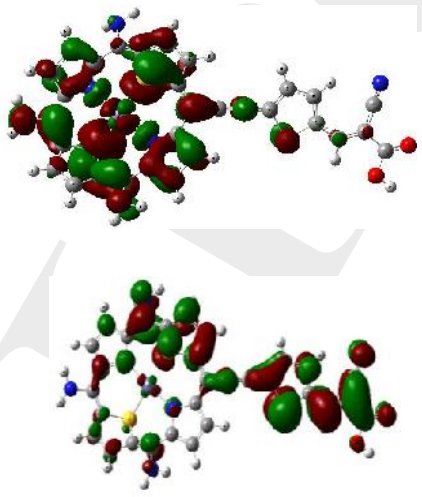

Fig. 2. Frontier molecular orbital distributions for dithiaporphyrin sensitizer, HOMO (above) and LUMO (below).

Table 2 The absorption energy of dithiaporphyrin and reference dye (YD2-o-C8)

structure	Method and basis set	Absorption energy(nm)	
		Q band	B band
dithiaporphyrin	CAM-B3LYP 6-311+G(d)	644.8	408.5
Yd2-o-C8(Exp)*	-	645	448

*Taken from Ref.7

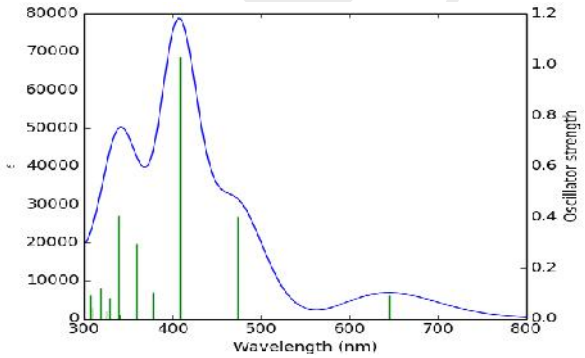

Fig. 3. The simulated absorption spectra of dithiaporphyrin sensitizer.

The simulated UV−Vis spectra is shown in Fig.3. As it can be seen from Fig.3 andTable 2, dithiaporphyrin shows strong Soret (B) and moderate Q bands in the absorption spectra, which are similar to the absorption spectra of Yd2-o-C8dye that experimentallyreported for the fabrication of DSSCs.

The calculated transition energies, oscillator strength, and molecular orbital excitations for the most relevant transitions of the electronic absorption bands of dithiaporphyrin and reference dye (YD2-o-C8) are given in Table 3.

Table 3 The calculated absorption energies (λ), oscillator strengths (*f*) and electronic transition configurations for dithiaporphyrin sensitizer and reference dye (YD2-o-C8) calculated at CAM-B3LYP/6-311+G(d)

structure	band	λ (nm)	f	MO Character
dithiaporphyrin	Q	644.8	0.09	HOMO → LUMO (46%) HOMO → L+1 (46%) H-1 → LUMO (2%)
	B	408.5	1.03	H-3 → LUMO (11%), H-1 → LUMO (62%), H-1 → L+1 (11%) H-2 → LUMO (3%), HOMO → LUMO (9%)
Yd2-o-C8*	Q	642.6	0.51	H-0→L+0(90%) H-1→L+1(7%)
	B	437.2	1.67	H-1→L+1(50%) H-0 →L+2(29%) H-2→L+0(9%) H-0→L+0(8%)

* Taken from Ref.4

From Table 3, it can be observed that the data obtained for dithiaporphyrin is similar to the resulting

data of reference dye.This indicates that our selected structure can bean appropriate candidate as a dye molecule in DSSCs.

4. Conclusion

In this work, we have presented a computational study of zinc dithiaporphyrin (a new molecule) based on D-π-A as sensitizer for dye sensitized solar cells applications. In this molecule, donor and acceptor groups attached at the meso-positions of dithiaporphyrin and optical properties of the structure were investigatedand then results compared with the YD2-o-C8 as reference dye. The results obtained from the frontier molecular orbital analysis and the absorption spectra indicatethe selected structure is a suitable candidate as a dye molecule in dye-sensitized solar cells. Furthermore,we hopefurther studies andsubstituting different donor and acceptor groups improve optical properties of this structure.We propose this molecule for synthesis by organic chemists for DSSC applications.

5. References

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