The role of the electronic structure and solvent in the dye-sensitized solar cells based on Zn-porphyrins: Theoretical study

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A B S T R A C T

In this work, using the density functional theory (DFT) and time-dependent DFT (TD-DFT), we have theoretically studied the electronic structures, quantum reactivity parameters and absorption spectra of the several dyes based on Zn-porphyrin derivatives in the gas phase, methanol (MeOH) and tert-buthanol (t-BuOH). Also, open-circuit photovoltage (V_{OC}), exciton binding energy (EBE), light harvesting efficiency (LHE), the free energy change of regeneration ($\Delta G_{regen \cdot (dye)}$), and the free energy change of electron injection (ΔG_{inject}) have been investigated. The studied dyes in the presence of the solvents showed a smaller gap of the highest occupied molecular orbital (HOMO) − the lowest unoccupied molecular orbital (LUMO) and lower EBE, a higher intensity and oscillator strength and red shift in the absorption spectra. These changes facilitate the charge transfer (CT) phenomena in the nano-structures of the dyes and improve the solar cell efficiency. Chemical modifications of the dyes by electron donor groups or conjugated system extension, improve the incident photon to current conversion efficiency (IPCE), the energy gap between the LUMO of the dye and the conduction band (CB) of the TiO_2 (eV_{OC}), and the LHE of these dye-sensitized solar cells (DSSCs). Finally, some correlations between the molecular descriptors and solar cell parameters were analyzed.

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1. Introduction

Due to the environmental problems such as global warming, depletion of fossil fuels, and the growth of the energy request, efforts to develop the environmental friendly renewable energy technologies are an urgent duty for human life [1]. Among all of the renewable energy technologies, solar cells are important photovoltaic devices for using the solar energy.

The dye-sensitized solar cell (DSSC) is a new type of the solar cells with efficient performance for the direct conversion of light into electrical power [2], which has been introduced by Grätzel and co-workers [3] and is the proper alternative for the p-n junction photovoltaic devices [4]. It has attracted considerable interest due to low-cost [5], flexibility [6] and environmentally-friendly properties [7] and facile fabrication process [8]. A general DSCC consists of the different components stacked in serial, including transparent conducting glass substrate, transparent conducting layer, TiO_2 nanoparticles, dyes, electrolyte, and the counter electrode [9]. The working principle of a DSSC is based on the electron excitation from the ground state to the higher-energy excited states of the sensitizer [10]. It is arisen through the photon absorption and followed by the injection of the excited electron from the photo-excited sensitizer to the conduction band (CB) of the semiconductor [11]. TiO_2 transports the injected electrons into the conductive contact [12]. On the other hand, electrolyte reduces the oxidized dyes [13], and transports the holes to the counter electrode [14].

To date, developments in the cell efficiencies have been pertained to three main components of the DSSCs: dye, redox shuttle and the semiconductor electrode [15]. Since electric charge is generated through the light harvesting by a sensitizer, finding a reasonable relationship between the electronic structure of the sensitizers and the performance of the solar cells is important [16].

Porphyrin derivatives are considerable as the sensitizers in DSSCs. They show tunable visible absorption properties possessing a conjugated system of pyroles. Also, there is a possibility of the metal ion insertion at the center of these systems, yielding the organometallic complexes [17]. Moreover, other properties such as their proper redox potentials for sensitization of the large band-gap semiconductors (e.g. TiO_2), low cost, relatively simple synthesis

procedure [18], a high molar absorption coefficient, excellent chemical and thermal stability make them ideal sensitizers [19].

Some processes such as an efficient injection of electrons from the dye into a semiconductor, the regeneration of the oxidized dye by the electrolyte [20], losses resulting from charge transports and recombination are important in determining the efficiency of the DSSCs [21]. In an efficient DSSC, the lowest unoccupied molecular orbital (LUMO) energy level of a sensitizer should be higher than the CB edge of the semiconductor and it's the highest occupied molecular orbital (HOMO) energy level should be lower than the redox potential level of the electrolyte. Moreover, the absorption spectrum of a dye should overlap efficiently with the solar spectrum [22]. In addition to these factors, the performance of a solar cell can be developed through the proper modification of the sensitizer electronic structure and solvent effects [23].

The porphyrin system shows a wide and intense optical absorption band which arises from the appropriate HOMO and LUMO energy levels. This band consists of strong absorption in the region of 350–500 nm (Soret or B-band) and 550–700 nm (Q-band) [24]. In the past few years, studies have shown an abrupt improvement in the efficiency of DSSCs [25]. Most of these studies are on the basis of changes in the molecular geometries of the sensitizers and their effect on the solar cell efficiency. Therefore, such studies are helpful to interpret the optical properties and electron transfer phenomena in the DSSCs and designing of the new efficient sensitizers.

Although, numerous experimental efforts have been done on the improvement in the energy conversion of the DSSCs, but in order to have a meaningful insight into the solar cell efficiency, a molecular approach is necessary for investigation of the photophysical and photochemical properties of the applied materials [26]. Also, a knowledge of the possible correlations between the quantum chemistry descriptors and solar cell efficiency enables us to predict the best price/efficiency ratio in the DSSCs [27].

Since, in our previous study, the performance of a series of the porphyrin-based sensitizers have been investigated as a function of the position of the anchoring and alkyl side groups [28], it is a great of interest to know, what occurs during the electron-transfer dynamic of the other porphyrin derivatives in the solvent media. Here, with this in mind and using the quantum chemistry approach, we theoretically investigate another type of porphyrins with different structures as the light-harvesting units within a carboxylic acid as an anchoring group in the gas and solution phases, for the first time. To better understand the electron-transfer dynamics in the porphyrin derivatives, we have analyzed the quantum reactivity parameters such as the electrophilicity index (ω), the electronic chemical potential (μ_e), the chemical hardness (η_q) and charge transfer. Since the transition metal complexes are often used as the photoactive compounds in the sunlight-based technologies, Zn (II) polyphyrin derivatives [29] have been investigated in this work.

2. Theory and computational details

To optimize the ground state structures, the density functional theory (DFT)/B3LYP/6-31G(d,p) level of the theory was used [30]. Furthermore, to consider the excited states and optical properties, the time-dependent DFT (TD-DFT) calculations [31] with the larger basis set of 6–311++G(d,p) [32] within the B3LYP/CAM-B3LYP functionals were applied [33].

In order to have an accurate representation of the excitation energies in the realistic environment, the solvent effects of methanol (MeOH; CH_3–OH) and tert-butanol (t-BuOH; $C(CH_3)_3$–OH) have been evaluated by the non-equilibrium version of the conductor-like polarizable continuum (CPCM) model [34]. Also, to describe the diffusion of electrons into the atomic and molecular orbitals, natural bond orbital (NBO) analysis, has been carried out

[35]. Through this analysis, it is possible to have insight into the various stabilizing interactions in the ground state of the dye-sensitizers [36]. Based on the data obtained from the orbital analysis, it is possible to be described the photon-to-electric conversion efficiencies [37].

Within the conceptual framework of the DFT [38], μ_e, η_q, and ω, have been evaluated using the Koopman's theorem [39]. μ_e shows the escape tendency of an electron from an equilibrium state. η_q and ω represent the resistance to the charge transfer (CT) and the stabilization energy of the saturated systems by electrons of the surroundings, respectively [40]. These parameters can represent the role of the structure and medium on the performance of a sensitizer. For example, the chemical hardness or softness arises from HOMO-LUMO energy difference, which is affected by the geometrical parameters of the chemicals and their interactions with the solvent. Also, ω is an intrinsic property of atoms and molecules which measures the stabilization in energy when the system gains an additional electronic charge from the media. Gaussian 09 program [41] has been used for all calculations.

3. Results and discussion

3.1. Electronic structures and photovoltaic parameters

Fig. 1 shows the optimized structures of the porphyrin-based dyes named as BP; 5-(biphenyl-4-carboxylic acid)- 10,15,20-tris(2,4,6-trimethyphenyl)porphyrinatozinc (II), CNBP; 5-(biphenyl -4-carboxylic acid)-10,20-di(2,4,6-trimethyphenyl)-15-phenylnitr-ileporphyrinatozinc (II), CNMP; 5-(4-carboxylphenyl)-10,20-di(2,-4,6-trimethyphenyl)-15-phenylnitrileporphyrinatozinc (II) and MP; 5-(4-carboxyphenyl)-10,15,20-tris(2,4,6-trimethyphenyl)porphyrinatozinc (II) in the gas phase. We have reported the corrected energies by the thermal and zero point vibrational energies in Table 1 for all of the studied dyes in the gas and solvent phases.

Comparison between the total energies of the dyes in the gas phase and solvents shows the solvent media can stabilize the dye structures through the intermolecular interactions of the dye and the solvent.

Sunlight-to-electricity conversion efficiency, η in Eq. (1), of the solar cell is described by the open-circuit photovoltage (V_{OC}), short-circuit current density (J_{SC}), and fill factor (FF), as compared to the incident solar power (P_{inc}) [42]:

$$\eta = \frac{J_{sc}V_{OC}FF}{P_{inc}} \tag{1}$$

where, J_{SC} in DSSCs is determined by the Eq. (2) [43]:

$$J_{SC} = \int_{\lambda_1}^{\lambda_2} q \cdot IPCE(\lambda) \cdot \phi(\lambda) d\lambda \tag{2}$$

where, $\phi(\lambda)$ is the incident photon flux at a given wavelength. Usually, this integrated current is used to cross-check with the J-V experimental data. The incident photon to current conversion efficiency ($IPCE$) reflects a series of the basic processes within a DSCC; the amount of absorbed photons (LHE), injection efficiencies (ϕ_{inj}) and collecting electrons (η_{coll}), (Eq. (3)) [44].

$$IPCE = LHE(\lambda) \cdot \Phi_{inject} \cdot \eta_{collect} \tag{3}$$

where, $LHE(\lambda)$ is the light harvesting efficiency at a given wavelength, Φ_{inject} shows the electron injection efficiency, and η_{coll} defines the charge collection efficiency. In the systems which are only different in sensitizers, $\eta_{collect}$ can be wisely considered to be