Materials Chemistry and Physics 196 (2017) 142–152

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

The investigation of the central metal effects on the porphyrin-based DSSCs performance; molecular approach

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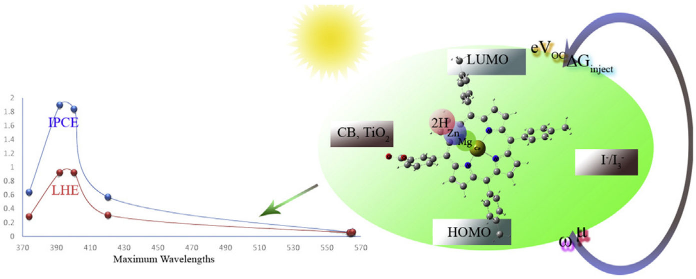
HIGHLIGHTS

- The performance of the porphyrin-based dyes in DSSC by replacing the metal inside the macrocycle cavity has been assessed.
- Based on the arrangement of energy levels of the materials involved in DSSC, we propose the dyes are proper as sensitizers.
- The behavior of the IPCE and LHE as a function of wavelength has been presented.
- Linear correlation between the DFT conceptual reactivity indices and the photovoltaic parameters has been obtained.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 November 2016
Received in revised form
3 March 2017
Accepted 28 April 2017
Available online 3 May 2017

Keywords:
Porphyrin-based sensitizer
Density functional theory
Reactivity indices
Efficiency
Absorption spectra

ABSTRACT

In this work, we have investigated the insertion of the different metal atoms, -Ca, -Mg and -Zn, into the porphyrin-based dyes for access to more efficient photovoltaic processes in the dye-sensitized solar cells. The photovoltaic processes have been described through the electronic properties of the dyes in the ground and excited states and quantum chemistry descriptors of them. The structural, electronic and spectroscopic properties of the dyes have been obtained by using the natural bond orbital, density functional theory (DFT) and time-dependent-DFT calculations. The preference of applying the metalloporphyrins, especially the Ca-porphyrin complex, in the solar cell is correlated with more proper photovoltaic properties than the free-base porphyrin. Proper photovoltaic properties of the metalloporphyrins are originated from the acceptable electronic chemical potential, electrophilicity indices and electron injection force from the dye to TiO_2.

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1. Introduction

Due to the energy crisis, the global warming and depletion of fossil fuels, the development of the energy generation technology from an unlimited source is a valuable research topic [1–4]. Among the renewable energy technologies, solar cells are considerable because of the ability of using a clean and abundant energy source of the sun and convert the solar energy into the electric energy, without carbon dioxide emission [5,6]. Since less than 0.1% of our energy needs is met through the direct conversion of sunlight, with the aim of reducing the cost and increasing the efficiency in

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http://dx.doi.org/10.1016/j.matchemphys.2017.04.054
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Nomenclature

Greek letters

μ	electronic chemical potential (eV)
ω	electrophilicity index (eV)
η	solar cell efficiency
$\Phi(\lambda)$	incident photon flux
Φ_{inject}	injection efficiency
$\eta_{collect}$	charge collection
λ_{max}	maximum wavelength (nm)

Abbreviations

DSSC	dye-sensitized solar cell
TiO_2	titanium dioxide
Zn	zinc
Ca	calcium
Mg	magnesium
DFT	Density Functional Theory
TD-DFT	Time-Dependent Density Functional Theory
NBO	Natural Bond Orbital analysis
CAM-B3LYP	Coulomb-attenuating method of Lee–Yang–Parr gradient-corrected correlation potential
UV–Vis	Ultraviolet–Visible
MATLAB	Matrix Laboratory
MLCT	Metal to ligand charge transfer
CB	conduction band (eV)
I^-/I_3^-	iodide/triiodide (eV)
Z	atomic number
LHE	light harvesting efficiency
IPCE	incident photon to current conversion efficiency
LUMO or L	lowest unoccupied molecular orbital (eV)
HOMO or H	highest occupied mnaturalolecular orbital (eV)
eV_{OC}	gap energy between the LUMO level of the dye and CB of TiO_2 (eV)
$E_{OX(dye^*)}$	excited state oxidation potential (eV)
ΔG_{inject}	free energy change for the electron injection (eV)
$E_{OX(dye)}$	ground state oxidation potentials (eV)
ΔG_{rege}	free energy change of the dye regeneration (eV)
EBE	exciton binding energy (eV)
J_{sc}	short-circuit current density (A/m^2)
Voc	open circuit photo voltage (V)
FF	fill factor
P_{inc}	incident power (W)
f	oscillator strength
$E_{0\text{-}0}$	excitation energy (eV)

conjunction with this technology, many attempts have been made to improve this technology [7,8].

The relatively high efficiency of the incident solar light to electricity conversion and low cost of production are two prominent properties of the dye-sensitized solar cells (DSSCs) which were presented by O'Regan and Grätzel in 1991 [9]. They are new type of the solar cell which attracted considerable attention in the recent years not only because of the main properties mentioned above, but also because their environmentally friendly components, flexibility in manufacture and employments [10–12]. DSSCs are formed of a transparent conducting glass substrate, transparent conducting layer, electrolyte, counter electrode, mesoporous oxide semiconductor layer (such as TiO_2 nanoparticles) and a dye sensitizer anchored on the TiO_2 surface. After the absorption of the sun light by the sensitizer, electrons are injected from the excited dye into the conduction band (CB) of TiO_2, making an electric current. The excited dye is then regenerated by the electron transfer from the electrolyte (commonly; iodide/triiodide (I^-/I_3^-)) [13,14].

Since the dye is responsible in the light absorption and generation of the electric charges, for investigation of the photovoltaic properties through the molecular dye structure, developing the new dyes and finding the optimal working conditions to improve the performance of the DSSCs seem essential [15,16]. Among a wide variety of the studied sensitizers, novel complexes such as the porphyrins are forefront to be applied in the DSSCs [17,18] due to their availability in the natural sources and relatively simple synthesis procedure [19]. They have a low cost, high molar absorption coefficient and good energy conversion efficiency [20,21]. However, there are some challenges related to the porphyrin, such as light-harvesting ability, that limited the performance of porphyrin-based solar cells. Such limitations can be eliminated by the loss of the symmetry of the porphyrin structures through the structural changes [22]. Therefore, studying the structure and its related properties can be helpful to improve the performance of DSSCs.

The absorption spectrum of the porphyrin appears in the near-ultraviolet and visible region. It consists of a Soret absorption band at 350–500 nm which followed by a Q absorption band at higher wavelengths of 550–700 nm [23].

By metallation of the porphyrin-based dyes, especially, by the inexpensive and nontoxic metals, an opportunity is provided to control the redox potential, the location, separation of electron and hole inside the molecule. It is also possible to change the electronic coupling between the porphyrin core and the TiO_2 surface and tune the level of the excited state [25,26]. Moreover, the insertion of a metal into the porphyrin cavity or protonation of the inner nitrogen atoms and symmetry changes of the porphyrins alter the absorption spectra [27].

Since applying the 4d-transition metals porphyrin derivatives with high atomic number (Z), such as ruthenium in DSSCs is prohibitive, so the characterization of the DSSCs based on the 3d-transition metal porphyrin such as Zn-porphyrin is considered, here. Another type of the metalloporphyrin derivatives investigated in this work is alkaline earth metals such as Ca- and Mg-porphyrins. The latter is the most plenty cyclic-tetrapyrrole-based molecule on the earth and is a main factor in the natural photosynthesis [28,29]. Since the elimination of the metals in the center of the porphyrins significantly reduces the cost of an environmentally friendly DSSC, this type of free-base derivative has been considered, too [29]. Generally, porphyrins would be better materials than some organic compounds.

Since, in the previous study, the performance of a series of the porphyrin-based sensitizers have been analyzed by the solvent effects and the position of the anchoring and alkyl side groups [30,31], it was a great of interest to know, what occurs in their electron-transfer dynamics by the insertion/change of the metal ion into the porphyrin ring. Also, there are other various studies about the photovoltaic properties of the solar cells [32–35]. With this in mind and because of the importance of quantum chemistry in providing a molecular approach of the electronic processes and DSSC performance, a theoretical study was designed.

For the most efficient metal-based dyes, the computational methodologies based on density functional theory (DFT) and time-dependent density functional theory (TD-DFT) [36] give accurate results along with the ground and excited state oxidation potentials

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