Journal of Molecular Structure 1134 (2017) 112–120

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Photophysics, TiO_2 sensitization and photovoltaic performance of Zn-ProtoporphyrinIX

Venkatesan Srinivasan [a], Nagaraj Pavithra [b], Sambandam Anandan [b], Madhavan Jaccob [c], Arunkumar Kathiravan [a, *]

[a] National Centre for Ultrafast Processes, University of Madras, Taramani Campus, Chennai, 600 113, Tamil Nadu, India
[b] Nanomaterials and Solar Energy Conversion Laboratory, Department of Chemistry, National Institute of Technology, Tiruchirappalli, 620 015, Tamil Nadu, India
[c] Department of Chemistry & Computational Chemistry Laboratory, Loyola Institute of Frontier Energy (LIFE), Loyola College, Chennai, 600 034, Tamil Nadu, India

ARTICLE INFO

Article history:
Received 10 September 2016
Received in revised form
10 December 2016
Accepted 12 December 2016
Available online 13 December 2016

Keywords:
Porphyrin
Density functional theory
XPS
Dye adsorption
DSCs

ABSTRACT

Chlorophylls are playing an important role in natural photosynthesis. Hence, in the present investigation, a chlorophyll analogue Zn-Protoporphyrin IX (ZnPPIX) was selected for dye sensitized solar cell applications. The properties of ZnPPIX were fully investigated by optical spectroscopy, attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), density functional theory (DFT) calculations, electrochemical and photovoltaic measurements. The optical and electrochemical HOMO-LUMO gaps were consistent with those estimated by PBE functional. The nature of the binding of ZnPPIX onto the TiO_2 surface was investigated using ATR-FTIR and XPS measurements. The amount of adsorbed ZnPPIX on TiO_2 surface was reasonably fit using the Langmuir adsorption isotherm, with a binding constant value of 25,800 M^{-1}. The power conversion efficiency of ZnPPIX is smaller than those of reference cell under the optimized conditions (η = 0.6% for ZnPPIX; η = 6.3% for N3).

1. Introduction

Chlorophylls are amazing compounds as a photosensitizer in the visible region. They play an important role not only for light harvesting and also energy and electron transfer processes in natural photosynthesis [1,2]. Inspired by natural photosynthesis [3], scientists utilized artificial chlorophylls – the porphyrins – as efficient centres to harvest visible light for solar cells sensitized with porphyrin. The intrinsic advantages of porphyrin-based dyes are their rigid molecular structures with large absorption coefficient in the visible region and their many reaction sites, i.e., four *meso* and eight β positions, available for functionalization: fine tuning of the optical, physical, electrochemical and photovoltaic properties of porphyrins thus becomes feasible. Due to these characteristics, porphyrins are promising candidates for dye sensitized solar cells (DSCs). The typical DSC consists of dye-sensitized photoanode (TiO_2) and platinum counter electrode sandwiching an electrolyte that contains redox mediator [4]. The photocurrent of DSCs is generated through the following processes. First, the photoexcited dye (S^*) upon illumination injects an electron into a conduction band (CB) of TiO_2 (−0.5 V vs. NHE). Then, the resultant oxidized dye ($S^{\bullet+}$) is reduced by redox shuttle in the electrolyte (dye-regeneration). The injected electrons move through an external circuit to the counter electrode. Finally, the I^- ion is regenerated by the reduction of an I_3^- ion at the surface of the counter electrode, and the circuit is completed.

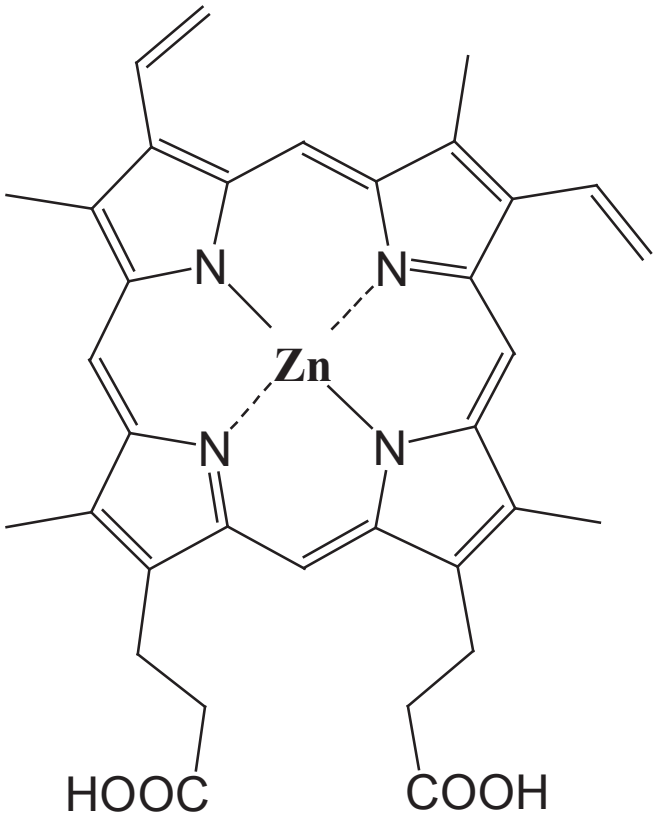
The first use of porphyrin sensitizers in DSCs was reported in 1993 for β-substituted chlorophyll derivatives and related natural porphyrins [5], reaching a maximum power conversion efficiency (PCE) of 2.6%. Since then, the performance of DSCs based on β-substituted porphyrins had not progressed well. In 2004, Grätzel and co-workers reported β-porphyrins dyes [6] reaching PCE between 4.8 and 5.6%. In 2007, the same group reported porphyrin sensitizers [7] with PCE of 7.1%, opening a great opportunity for the development of various porphyrin sensitizers to enhance the

* Corresponding author.
E-mail address: akathir23@gmail.com (A. Kathiravan).

http://dx.doi.org/10.1016/j.molstruc.2016.12.031
0022-2860/

efficiency of a DSC. In 2011, Ishida et al. reported the β-functionalized zinc porphyrins with a diarylamino group [8] exhibits the best performance with η = 7.5% that is comparable to the performance of a N3 dye (η = 7.7%) under the same conditions. On the other hand, Cherian and Wamser reported in 2000 the first meso-substituted porphyrin [9] with η = 3.5%. In 2011, Grätzel and collaborators reported the meso-porphyrin dye YD2-o-C8 achieving a PCE of 11.9% in conjunction with the cobalt(III/II) tris(2,2′-bipyridine)-based redox electrolyte and the record efficiency of 12.3% was achieved when cosensitized with another organic dye [10]. This record was broken with the dye SM315 reported by Nazzeruddin and co-workers [11,12], achieving an unprecedented PCE of ~13%. This report is superior to the devices based on ruthenium complexes, stimulating research on the development of further porphyrin sensitizers to endorse the device performance.

The main objective of this work is to elucidate the fundamental processes of Zn-ProtoporphyrinIX (ZnPPIX, a chlorophyll analogue, Scheme 1). Therefore, we have performed DFT and time-dependent density functional theory (TD-DFT) calculations to provide a detailed description of the structural, electronic and optical properties of Zn-ProtoporphyrinIX. Attenuated total reflectance-Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy were employed to study the adsorption processes. Electron injection dynamics of ZnPPIX/TiO_2 was studied by time resolved fluorescence spectroscopy. Finally the results were correlated to photovoltaic performance.



ZnPPIX

Scheme 1. Structure of Zn-protoporphyrin IX.

2. Experimental section

2.1. Materials

Zn-Protoporphyrin IX (≥95%), $TiCl_4$, Acetyl acetone (99%), Triton-X (95%) and Poly(ethylene glycol) (PEG, MW = 10,000) were purchased from Sigma-Aldrich. TiO_2 paste (Ti-Nanoxide HT/SC series) was purchased from Solaronix SA, Switzerland. The solvents used for photophysical studies were HPLC grade.

2.2. Methods

The electronic absorption spectra of the samples were recorded using CARY 100 Bio UV–visible spectrophotometer. The fluorescence spectral measurements were carried out using Fluoromax-4P spectrofluorometer (Horiba Jobin Yvon). Time resolved picosecond fluorescence decays were obtained by the time-correlated single-photon counting (TCSPC) technique with microchannel plate photomultiplier tube (Hamamatsu, R3809U) as detector and femtosecond laser as an excitation source. The second harmonics (400 nm) output from the mode-locked femtosecond laser (Tsunami, Spectra physics) was used as the excitation source. The instrument response function for TCSPC system is ~50 ps. The data analysis was carried out by the software provided by IBH (DAS-6), which is based on deconvolution technique using nonlinear least-squares methods. Transient absorption experiments were carried out using nanosecond laser flash photolysis (Applied Photophysics, UK). The third harmonic (355 nm) of a Q-switched Nd: YAG laser (Quanta-Ray, LAB 150, Spectra Physics, USA) with 8 ns pulse width and 150 mJ pulse energy was used to excite the samples. The transients were probed using a 150 W pulsed xenon lamp, a Czerny-Turner monochromator, and Hamamatsu R-928 photomultiplier tube as detector. The transient signals were captured with an Agilent infiniium digital storage oscilloscope, and the data were transferred to the computer for further analysis. Infrared spectrometer (IR) spectra were recorded on BRUKER VERTEX 70 Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) spectrometer. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were recorded using a CHI-620B Electrochemical Analyzer, CH Instruments Inc. A three-electrode single-compartment cell system which comprises a glassy carbon working electrode, a platinum wire counter electrode and Ag/AgCl reference electrode were employed for the experiments. The glassy carbon electrode was polished with Al_2O_3 paste, cleaned thoroughly in an ultrasonic water bath, and washed with ethanol before each measurement. The oxidation potential of ZnPPIX was measured in dimethyl formamide using tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. About 10 ml of 1×10^{-3} M ZnPPIX in dimethyl formamide is charged with tetrabutyl ammonium hexafluorophosphate was taken in an electrochemical cell and degassed by bubbling research grade nitrogen for 15 min for each measurement. X-ray photoelectron spectra of ZnPPIX were recorded in an ESCA-3 Mark II spectrometer (VG Scientific Ltd., England) using Al Kα (1486.6 eV) radiation as the source. All spectra were referenced to the C1s major peak at 284.5 eV.

Fluorescence quantum yield (ϕ_F) of the ZnPPIX were calculated by using following equation (1)

$$\varphi_F = (A_R/A_S)(I_S/I_R)(\eta_S/\eta_R)^2\varphi_R \quad (1)$$

where, the subscripts S and R refers to the samples and the reference, respectively. *A* is the absorbance at the excitation wavelength, *I* is the integrated emission area, and η is the solvent refractive index. ZnTPP ($\phi = 0.03$) in Benzene was used as a standard [13].