

# Quantum Chemical Simulation of Molecular Structures for high efficiency solar cells

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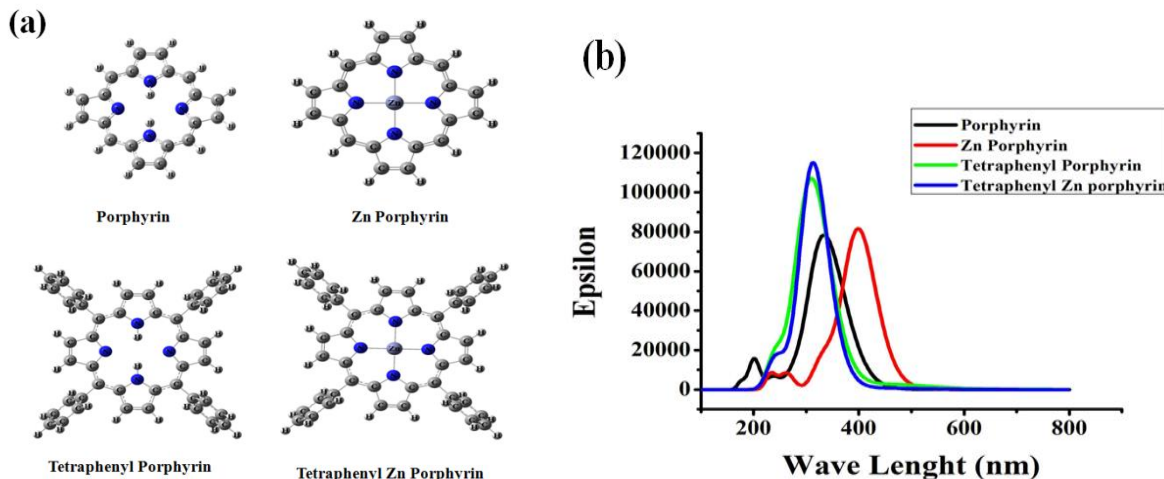
## Abstract

Organic fluorophores are important component in the present day optical and photo electronic devices such as displays, solar cells, light emitting diodes, etc due to several characteristics including large choice of emission and absorption wavelengths window, high absorption cross section, and possibility of synthesizing them from abundant renewable sources. Various dyes such as xanthenes, azo, porphyrins, indolines, Ru complex dyes are evaluated for the above applications. Among them, renewable energy devices under the photovoltaic protocol have become particularly interesting due to its potential to be fabricated at lower cost. Dyes are the important component of dye-sensitized solar cells (DSSCs), in which the dyes are the primary absorbers of solar energy. Upon light excitation, the photoexcited electrons in the dyes are injected to a metal oxide semiconducting nanostructure from where it is collected. A large choice of dyes is tested for the DSC application; however, the state-of-the-art DSC employs a porphyrin dye conjugated to mesoporous TiO<sub>2</sub> particles. Photovoltaic conversion efficiency as high as ~12% and open voltage above 1 V has been typically achieved in DSCs employing porphyrin dyes in mesoporous TiO<sub>2</sub> and CuI/ tri iodide electrolyte. Compared to the conventional ruthenium based bipyridyl dicarboxylic acid dyes, porphyrin dyes are attractive because of their low cost and extended absorption wavelength window.

A survey of literature shows that there are little study on understanding deeply the structure and properties of porphyrin dyes using quantum chemical methods. We studied the properties of different porphyrin dyes to enhance the efficiency of DSSC using ab-initio quantum chemical methods. Quantum chemical calculations under the framework of DFT were employed to study the difference in ground and excited state properties of porphyrin dyes. DFT calculations were performed with the use of Becke's three parameter hybrid methods [Becke, 1993] with the Lee, Yang and Parr (B3LYP) gradient corrected correlation functional [Lee *et al.*, 2008] using the Gaussian 09W program packages [Frisch, *et al.*, 2009]. Geometry optimizations were carried out using the standard double- $\zeta$  quality lanl2dz basis sets [Hay and Wadt, 1985] followed by harmonic frequency calculations and simulating their IR spectra. Discrete spectra of excitation energies and corresponding oscillator strengths were obtained by the time-dependent DFT (TDDFT) method including  $n$  energy singlet transitions [Scalmani, *et al.*, 2006]. Molecular volumes of molecules were obtained from the Gaussian output file of the optimized geometry. Additional TDDFT single point energy calculation is used to map the electron density of the ground and excited states of the dyes.

The porphyrin molecules were modeled with and without Zn as central atom and phenyl groups as a meso substituent. Fig.1a summarizes the results of the calculations. Porphyrin, Zn porphyrin complex, tetraphenyl porphyrin, and tetraphenyl Zn porphyrin complex were considered in this study. All these molecules were experimentally found in literature. The reliability of the optimized geometry was further checked by harmonic frequency calculations at the B3LYP/lanl2dz level of DFT. The simulated IR

spectrum of the optimized structure showed only real frequencies thereby confirming a minimum energy structure. Absorption wavelength windows and oscillator strengths of these dyes were obtained by the time-dependent DFT (TDDFT) method. UV-Vis spectrum show light absorption range is almost from 200-600, shown in fig 1b.



**Fig.1 (a) Optimized geometries of porphyrin dyes molecules and (b) UV-Vis spectra of porphyrin dyes molecules**

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