Performance of metalloporphyrin malonic acids as dye sensitizers for use in dye-sensitized solar cells assessed by density functional theory

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ABSTRACT

The performance of metallo (Zn, Cd, Hg) tetra (4-methylphenyl) porphyrin malonic acids as dye sensitizers for use in dye-sensitized solar cells (DSSCs) is assessed by means of ab initio molecular electronic structure calculations. The results reveal that malonic acid side chain cannot be described as an acceptor moiety, and the photo-to-current conversion efficiencies of the DSSCs that are based on organic semiconducting Cd and Hg tetra (4-methylphenyl) porphyrin malonic acid donors and a series of oxide semiconducting acceptors are expected to be greater than the reference porphyrin dye Zn tetra (4-methylphenyl) porphyrin malonic acid under standard global AM 1.5 solar conditions. This result is confirmed and characterized in terms of charge transfer, band gaps, density of states, polarizabilities, dipole moments, molecular electrostatic potential contours, electronic absorption energies, and infrared vibrational frequencies. The study emphasizes the role of metal centers, and provides alternatives to DSSCs with expensive materials.

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1. Introduction

In TiO$_2$ based dye sensitized solar cells, efficiencies of up to 11% have been obtained using Ru dyes. However, the limited availability of these dyes has led to the search for cheaper organic based dyes [1–3]. Of these, porphyrin has attracted a great deal of attention because of its natural role in photosynthesis and the relative ease with which functional groups can be attracted to its basic structure [4–7]. Furthermore, porphyrin – as well as other organic dyes – has inherent lowest unoccupied molecular orbital (LUMO) level is situated above the conduction band of TiO$_2$ and its highest occupied molecular orbital (HOMO) level is below the redox couple of the electrolyte solution required for charge separation at the semiconductor-dye-electrolyte surface, which makes it a good donor moiety [8].

The first requirement of a potential DSSC is the harvesting of a significant fraction of the solar spectrum. Porphyrins possess an intense S band at 400 nm and moderate Q bands at 600 nm. Additional absorption at longer wavelengths can gain additional efficiencies up to a point; the theoretical optimum band gap is at about 1.1 eV (1100 nm) and the maximum efficiency is about 33% [9]. Although a smaller band gap allows for harvesting a larger fraction of the solar spectrum, there are diminishing returns caused by the effects of degrading high energy photons to the level of the decreasing band gap. Thus an ideal solid absorber would appear black—absorbing all the ultraviolet and visible and into the near infrared [10].

In 2007, Officer and co-workers [11] reported a 7.1% efficient porphyrin, which consisted of a tetraphenylporphyrin with a conjugated bridge to a dicarboxylic acid. This

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work included a series of porphyrin dyes, all of which are over 5% efficient. However, the 7.1% efficient porphyrin gives an efficiency of 3.6% in a solid state cell with *spiro*-MeOTAD as the hole transporting component, comparable to solid state cells incorporating the best performing Ru dyes. Since 2007 report on β-linked porphyrins, Officer and co-workers have used β-linked derivatives to study several aspects of solar cell design and performance. The aspects of design under study included the use of a post adsorbed phosphinic acid blocking moiety to improve efficiencies by minimizing recombination events at the electrode surface [12]. They also studied the use of ionic liquid electrolyte as a replacement for volatile organic solvents in typical liquid electrolytes [13]. The Officer group has also studied the open circuit voltage and electron injection dynamics using β-substituted porphyrin and have suggested that the reason for limitations to the V_{oc} and J_{sc} are related to reduced electron life time and less favorable electron injection dynamics [14,15]. More recently, Irfan et al. [16–18] carried out quantum chemical calculations towards modeling of highly efficient DSSCs.

To improve the photovoltaic performance of Officer and co-workers cell [11] Zn tetra (4-methylphenyl) porphyrin malonic acid with photo-to-current conversion efficiency ($\eta=7.1\%$) we attempted to extend the absorbance window to the red shoulder of the spectrum. This was done through replacing Zn by the higher group IIB elements, Cd and Hg. The structural nature of the present metallo (Zn, Cd, Hg) tetra (4-methylphenyl) porphyrin malonic acids (i.e., donor moieties or donor–acceptor dyads) was identified, and the role of metal centers is emphasized. It is conceivable that the comparison of the photo physical and photo voltaic properties obtained with the same assumption should give a useful clue to the performances of dyes. We have therefore attempted to examine a series of properties that determine the efficiency and compared Zn and Cd/Hg metalloporphyrins, hopefully to provide alternatives to DSSCs with expensive materials (notably Pt and Ru) and liquid electrolytes (if fullerenes are employed as acceptors).

2. Computational details

Molecular electronic structure calculations were performed by using the density functional theory (DFT) and (TD-DFT) in which the electrons are described quantum-mechanically, while the much heavier nuclei are treated classically [19]. DFT provides a modern and versatile means to investigate molecular and solid state structures, reaction pathways, thermo chemistry, dipole moments, spectroscopic response, and many other properties [20]. Since full geometry optimization of the present metallo tetra (4-methyl phenyl) porphyrin malonic acids by using the B3LYP exchange-correlation functional and the large SDD basis set size was difficult to obtain, full geometry optimizations were carried out first at the Hartree–Fock (HF) level of theory and the LANL2MB basis set. The optimal geometries obtained were then used in single point energy calculations at the B3LYP/SDD level of theory to calculate all structure and energetic properties, in addition to the ^{1}H-NMR chemical shifts and UV–vis. electronic absorption spectra in vacuum at the TD-DFT level. The smaller HF/LANL2MB level was used to calculate

the polarizabilities, hyperpolarizabilities, dipole moments, and infrared IR frequencies because of several numerical problems encountered in the computational calculations at the B3LYP/SDD level.

The DFT calculations were performed by using Becke's three-parameter exchange functional B3 with LYP correlation functional [21–24]. The B3LYP hybrid functional has been chosen since it provides a rather accurate description of metal interactions. Hybrid functional such as B3LYP provides a fair indication of the relative energies, and in some cases the resulting differences between the experimental values and the calculated ones can be considered a systematic error [25]. B3LYP correctly reproduces the thermo chemistry of many compounds including transition metal atoms [26–28]. We have opted to use hybrid functional (B3LYP) over Hartree–Fock (HF) method, as it can account for correlation effects also. Although HF describes exchange effects exactly, it results in unbound LUMO states. We also investigated the localization of frontier orbitals since spatial distribution of frontier orbitals HOMO and LUMO provides a strategy by which the photovoltaic performance of the donor can be understood. Several successful applications using hybrid functionals have been reported [29]. Therefore, the use of hybrid functional in DFT formalism is justified.

The electronic absorption spectra require calculations of the allowed excitation energies. The electronic absorption spectra and the contributions of singly excited state configurations to each electronic transition of the current metalloporphyrins were calculated and simulated with the time dependent density functional theory (TD-DFT) method in vacuum at the B3LYP/SDD level of theory. The (SDD) basis set places Dunning/Huzinaga full double zeta D95 up to Ar, and Stuttgart/Dresden ECPs on the remainder of the periodic table. The density of states (DOS) as well as Fermi levels were calculated by using the Gauss Sum 2.2.5 program [33] at the B3LYP/SDD level of theory. All calculations were carried out by using Gaussian 09 system [34] and the optimal geometries of molecular skeletons and molecular orbital densities were visualized by using the corresponding Gauss View software.

3. Results and discussion

In principle, the strategies employed to improve the performance (η, %) of a DSSC depend on the type of the donor and acceptor moieties. Two types of DSSCs are identified: (1) DSSCs based on organic semiconducting donors and π-conjugated acceptors (2) DSSCs based on organic semiconducting donors and oxide semiconducting acceptors. For both types of solar cells, the basic strategies include: (i) the narrowest $(HOMO)_{donor}$–$(LUMO)_{donor}$, $(HOMO)_{acceptor}$–$(LUMO)_{acceptor}$, and $(HOMO)_{dyad}$–$(LUMO)_{dyad}$ energy gaps. $(HOMO)_{donor}$–$(LUMO)_{donor}$ corresponds to the experimental parameter of maximum short current intensity J_{sc}, mA/C m^2 (ii) the HOMO of the dyad is close to the HOMO of the donor, and LUMO of the dyad is close to the LUMO of the acceptor (iii) HOMOs are localized on the donor moiety, and LUMOs on the acceptor moiety of the dyad (iv) the $(LUMO)_{donor}$–$(LUMO)_{acceptor}$ energy gap, which corresponds to the experimental parameter of maximum open circuit voltage