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Effects of π-linker, anchoring group and capped carbazole at *meso*-substituted zinc-porphyrins on conversion efficiency of DSSCs

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ABSTRACT

A series of zinc-porphyrin based sensitizers, **F1**–**F6**, has been studied using theoretical calculations to investigate their performances in dye-sensitized solar cells (DSSCs). Three effects; (i) π-Linker, (ii) anchoring group and (ii) capped carbazole at *meso*-substituted porphyrin core on the energy conversion efficiency of the DSSCs were evaluated. The results reveal that the increased conjugation length in π-linker and use of cyanoacrylic acid as an anchoring group can enhance charge transfer ability from donor to acceptor group and further to TiO_2 which leads to increasing of the current density of the devices. Capped carbazole unit does not significantly affect the electronic properties of the dyes but crucially helps in suppressing aggregation of the dyes on the TiO_2 surface, then leads to higher conversion efficiency of the device. Therefore, we predict that **F6** designed by taking advantages of all positive key parameters would be a promising sensitizer for higher efficient photovoltaic cell.

1. Introduction

The energy demands have led to attempt to find renewable energy which comes from natural resources such as sunlight by solar cells. The first generation solar cells were produced from silicon. However, the processing of silicon purification is so complicated and highly cost, which brings to expensive silicon solar cells. Since dye sensitized solar cells (DSCs) was introduced by Grätzel in 1991 [1], there are a lot of attention in their abilities for converting solar light into electricity based on low cost solar cell. The highly efficient metal-organic dye based on ruthenium (Ru) sensitizer has shown very impressive solar light-to-electric power conversion efficiencies, reached 11% at standard AM 1.5 sunlight [2]. Although Ru-complexes are suitable as photosensitizers, the limited availability and environmental issues would limit their extensive applications. On the contrary, alternative organic dyes exhibit high molar extinction coefficients and are easily modified due to short synthetic and economical processes. Among the organic dyes, the porphyrin dyes have shown promising properties to be a good sensitizer in DSSCs [3]. There are many reports about various kinds of unsymmetrical zinc-porphyrin in recent years [4–6]. The ability to modify and tune the photophysical properties of synthetic porphyrins via the introduction of specific substituents has led to the design and synthesis of a number of porphyrin dyes.

In general, porphyrins dyes show a high intense Soret band (B-band) at 400–450 nm and lower intense of Q-bands at 500–650 nm. To extend the absorption of porphyrin dyes to the near infrared region and increase light harvesting efficiency (LHE), the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels must be reduced [7]. Karthikeyan and Lee have reported that energy gap of Zn-porphyrins can be tuned by modifying the π-spacer of porphyrin based dyes [8]. Moreover, molar extinction coefficient and absorption ability of the dyes strongly depends on the chemical composition of their structures. The insertion of the

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linker at β- and *meso*-positions of the porphyrin, in which the substituent on *meso*-position was found to inhibit the molecular aggregation and also decrease recombination between the photo-injected electrons at the TiO_2 electrode and the electrolyte (Iodide) [9]. For the metal ions in the porphyrin core, Bessho and co-workers [10] reported the ability of best-performing zinc-porphyrin dyes which compose of zinc macro porphyrin core connected to diarylamino moiety as an electron donating group and ethynylbenzoic acid moiety as an anchoring group (YD2), in which a porphyrin chromophore itself contains the π-linker in the donor–π–acceptor motif. Later this YD2 was slightly modified into YD2-*o*-C8 and a power conversion efficiency of 12.3% was reported [11], which is so far the best reported porphyrin dye. These zinc-porphyrin compounds showed the Q-band spectrum in near infrared region and exhibited the conversion efficiency in the range of Ru-complexes on a double layer TiO_2 film under standard illumination test conditions. However, these porphyrin dyes show relatively less absorption intensity in the near infrared region, which dramatically reduces the light-harvesting ability. Recently, Santhanamoorthi and co-workers [12] have molecularly designed the porphyrin dyes by varying the electron-donating and withdrawing substituents at the *meso* position. They found that the new designed dyes gave more broadened absorption spectra and shifted to longer wavelength compared to YD2-*o*-C8.

Motivated by the superior performance of YD2-*o*-C8 and the work by Santhanamoorthi and co-worker, here in our group, we are interested in developing the zinc-porphyrin dye due to its ease of synthesis and structural modification as a sensitizer in DSSC. Recently, we have synthesized the zinc-porphyrin dyes, **F1**–**F4**, and have fabricated them as sensitizers in the photovoltaic devices [13]. The structure of compounds **F1** and **F2** contains phenyl ring as an electron-donating group at the *meso* position of porphyrin core and the carboxylic acid as an anchoring group. **F1** has one thiophene unit connecting to ethynylene-phenylene as a π-linker. **F2** is modified from **F1** by adding one more thiophene unit next to the first thiophene in π-linker. **F3** also contains two thiophene units as a π-linker but has cyanoacrylic acid as an anchoring group. **F1** and **F2** dyes are systemically synthesized to study the effect of conjugation length of the π-linker, while **F2** and **F3** are compared to study the effect of anchoring group. Moreover, to study the effect of capping carbazole on phenyl ring moieties at *meso*-substituent position of porphyrin core, **F4** is synthesized by modifying from **F1** (see Fig. 1). In this work, the computational methods with quantum chemical calculation were used as a useful tool for investigating the electronic structure, optical property, molecular energy level diagram, light harvesting efficiency, dipole moment of the dye perpendicular to the surface of TiO_2, to determine the effects of varying the (i) π-linker, (ii) anchoring group, and (iii) having capped carbazole units on the energy conversion efficiency of DSSCs. These calculated results are compared with our experimental data and photovoltaic devices based on **F1**–**F4** sensitizers [13]. Then **F5** and **F6** were designed and calculated to seek for higher efficient sensitizer in photovoltaic device. The important key parameters affecting to the efficiency of the device are also presented.

2. Computational details

The hybrid functional Becke3LYP (B3LYP) [14] has been proved as a suitable method for the geometry optimization of porphyrins, as well as their various analogues [15–19]. Thus, in the present study B3LYP was employed for conducting the geometry optimization of our synthesized zinc-porphyrin analogues, **F1**–**F6**. For the calculations, the tertiary-butyl group is adopted by H atom since it does not affect to the electronic and optical properties of the molecules. All geometries were optimized in *vacuum* using B3LYP with standard 6-31G(d) basis set.

The excitation energies (E_{ex}) were computed based on time-dependent density functional theory (TD-DFT) formalism on the optimized ground state geometry. The effect of solvation by dichloromethane (CH_2Cl_2) was considered using the conductor-like polarized continuum model (C-PCM) framework [20]. The PBE0 hybrid functional, which was successful used for reproducing UV spectrum of porphyrin analogues in various reports [21–23], was first used to evaluate the absorption spectra of our zinc-porphyrin dyes in the present work. Their calculated results shows that the absorption wavelengths of B and Q bands calculated at PBE0 level agree well with experimentally observed absorption maxima. However, the evaluation of PBE0 hybrid functional has been compared with the increasing amount of Hartree-Fock (HF) exchange fraction and long range-corrected version of B3LYP using the Coulomb-attenuating method (CAM-B3LYP), to find a more proper method. Thus, **F1** compound was selected and its absorption wavelength was calculated by three functionals; TD-B3LYP, TD-PBE0 and TD-CAM-B3LYP, the calculated results and corresponding experimental values are listed in Table S1 and Fig. 2. As a result, the TD-PBE0 and TD-B3LYP hybrid functionals give the discrepancies of 0.12 and 0.18 eV compared with experimental results, respectively. On the other hand, the long-range-corrected CAM-B3LYP, which has been widely used to describe the intramolecular charge-transfer states of organic dyes, provides a discrepancy of 0.26 eV. Furthermore, TD-PBE0 and TD-B3LYP functionals also show high ability to exhibit the Q-band spectra than CAM-B3LYP as can be seen in Fig. 2. Hence, PBE0 functional with 6-31 + G(d) basis set was adopted to further simulate the excitation properties of the dyes since it provided the agreeable results compared with experimental data. Simulated UV–Vis spectra and the contribution of molecular orbitals to each electronic transition were derived from a Gaussian output file using the GaussSum [24] and Gabedit programs [25]. Electron density difference between ground and excited states was evaluated to see a direction of charge transfer when dye absorbs light. All starting geometries were constructed in GaussView 3.0 and calculated using the Gaussian09 suit of program [26]. The calculated results of this work were compared with our experimental data [13].

3. Results and discussion

3.1. Ground state geometry

It is well-known that the structural modification changes the optical and electronic properties of molecules. The ground state geometries of targeted zinc-porphyrin analogues, **F1**–**F6**, were fully optimized by B3LYP/6-31G(d) method and are displayed in Fig. 3, while the selected bond distances and dihedral angles are listed in Table 1.

The calculated ground state geometries show that all structures exhibit planarity at macro porphyrin ring. The *meso*-substituted phenyl rings are nearly perpendicular to the porphyrin core; the dihedral angles are in the range of ~68–112°, the C–C bond distances between C-Phenyl and C-Porphyrin are ~1.5 Å. The dihedral angles between porphyrin and thiophene (P-T) units of the dyes are nearly perpendicular with macro porphyrin which are similar to the phenyl ring (107–111°). However, the extension of π-linker by adding one more thiophene unit on **F2** and **F3** increased these dihedral angles from 104.63° (**F1**) to 109.04° (**F2**) and 110.59° (**F3**); this feature occurs in **F4**, **F5** and **F6** in the same way. Considering the carbazole capped porphyrins, the carbazole moieties of **F4**–**F6** are twisted from phenyl ring around 54–55°. In experiment we also found that non-planarity within donor units of **F4** was helpful in