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Theoretical design of highly efficient porphyrazine solar cells

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Abstract

Density functional theory and time-dependent density functional theory methodologies have been applied to design porphyrazine (tetraazaporphyrin) sensitizers. This was done by replacing the porphyrin macrocycle cavity with a porphyrazine macrocycle cavity and increasing the number of p-carboxyphenyl moieties at the macrocycle periphery so that the performances of the suggested cells could be expected to exceed the efficiency of the reference YD2-o-C8 porphyrin sensitizer with Ti\textsubscript{38}O\textsubscript{76}, (TiO\textsubscript{2})\textsubscript{60}, SiC, ZrO\textsubscript{2}, and GaP semiconductor electrodes. Macrocycle replacement assists in promoting the efficiency in the red shoulder of the spectrum more effectively than increasing the number of anchoring groups. The expected effects of the former structural modifications on cell performances are confirmed in terms of natural transition orbitals, energy gaps, semiconductor valence bands and conduction band edges, density of states, UV–visible absorption, and lifetimes of the excited states $\Phi_{LHE}$, $\Phi_{inj}$, and $\Delta G_{\text{regen}}$. The structural modifications resulted in charge-separated states, unidirectional charge transfer, narrower band gaps, increase of density of states nearby Fermi levels, delocalization of the negative charges near the anchoring groups, efficient light harvesting and electron injection, suppressing macrocycle aggregation, active dye regeneration, and inhibited dye recombination. Co-sensitizers are suggested for near-infrared sensitization.

Keywords: porphyrin, porphyrazine, density functional theory, solar cells

(Some figures may appear in colour only in the online journal)

1. Introduction

In search for efficient, stable, and low cost alternatives to the silicon-based solar cells, porphyrins and phthalocyanines have shown to be the most promising candidates. In addition to their light-harvesting properties, they are attractive sensitizers for dye-sensitized solar cells (DSSCs) due to their appropriate redox properties for the sensitization of TiO\textsubscript{2} electrode and dye regeneration by the typical (I\textsubscript{3}/I\textsubscript{2}) redox mediator. That is, the lowest unoccupied molecular orbital (LUMO) level lies above the TiO\textsubscript{2} conduction band (CB), while the highest occupied molecular orbital (HOMO) level lies below the redox potential of the electrolyte to ensure efficient dye regeneration. Several reviews concerning the utilization of porphyrins and phthalocyanines as dyes in DSSCs have been reported [1–5].

The incorporation of ‘push-pull’ porphyrin derivatives in DSSCs has led to remarkable progress in this family of sensitizers, reaching photo-to-current conversion efficiency values comparable to that of the ruthenium bipyridyl complexes. Of these, Yella \textit{et al} [6] developed a DSSC with an incorporated porphyrin dye with a cell performance that achieves the figure of merit for state-of-the-art systems. They reported that the porphyrin sensitizer YD2-o-C8 with co-sensitization of an organic dye Y123, using a cobalt-based electrolyte AY1, attained power conversion efficiencies 12.5% at light intensity $P_{in}$ (mW/cm\textsuperscript{2})=9.4, 12.7% at $P_{in}$ = 51.2, and 11.9% at $P_{in}$ = 99.5 of AM 1.5 solar light. This
success could be attributed to a compromise between suppression of dye aggregation, extension of the π-conjugated system, and enhancement of the charge transfer directionality in the extended state by introduction of an electron donating group opposite to the anchoring group, thus optimizing the system performance.

The elongation of the π-conjugated system of porphyrin monoacids produces a decrease in the band gap, and a concomitant red shift in both the Soret and Q band absorptions. It was therefore predicted that improvement of the visible light-harvesting efficiency in porphyrin dyes would lead to better photovoltaic performance. Indeed, several investigations have demonstrated this effect by comparing the photovoltaic performances of π-elongated porphyrin monoacids with respect to derivatives lacking this property [7–14]. Modification of the central metal at the macrocycle cavity has been varied to study its influence on system performance [15–22]. A stronger binding produced by a more acidic anchoring group was also expected to increase the system performance. Thus, sulfonic and phosphonic acid groups were tested as binding groups of the porphyrin dyes. However, the carboxylic acid derivative was shown to be significantly superior in solar cell sensitization over both the sulfonic and the phosphonic acid porphyrins [23–25]. More recently, we examined the combined effects of metal modification and π elongation on cell performance. We demonstrated that the broadness and red shift of the absorption bands and easy intra-molecular charge transfer of the highest record efficient cell of Gratzel [6] can be achieved by incorporating Cd instead of Zn onto the porphyrin ring and elongating the length of the π conjugation by adding an ethylene link and an anthracene unit, which eventually improved the cell performance [26].

The former results provide guidelines for the design of new sensitizers based on porphyrin and phthalocyanine macrocycles. In the present study, we address a new class of intermediate macrocycles called porphyrazine (tetraazaporphyrin) macrocycles, in which an extra set of four nitrogen atoms are added to the porphyrin macrocycle. Because red shifting of Soret and Q bands provides a straightforward approach to increasing the efficiency of dyes as sensitizers, we focused our attention on the effects of structural modifications for narrowing the band gaps. By comparing dyes to a dye with known solar cell efficiency, we could identify candidate(s) ideal for DSSCs. We have therefore used density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methodologies to design five new sensitizers, considering YD2-o-C8, which has the highest record efficiency (11.9–12.7%) as the reference sensitizer. We replaced the porphyrin macrocycle cavity of YD2-o-C8 with a porphyrazine macrocycle cavity and increased the number of carboxylic acid anchoring groups. The former structural modification effects were then confirmed in terms of several photophysical and photovoltaic properties, such as natural transition orbitals (NTOs), energy gaps, semiconductor valence bands (VB), CB edges, density of states (DOS), UV–visible electronic absorption, lifetimes of the excited states, light-harvesting efficiency (ΦLHE), electron injection efficiency (Φinjection), free energy of regeneration (∆Gregen), and co-sensitization.

2. Computational details

Molecular electronic structure calculations were performed using the DFT and TD-DFT. The electrons in DFT and TD-DFT methodologies are described quantum-mechanically [27]. DFT and TD-DFT methodologies provide a modern and versatile means to investigate molecular and solid state structures, reaction pathways, thermochemistry, dipole moments, spectroscopic response, and many other properties [28].

The DFT calculations were performed using Becke’s three-parameter exchange functional (B3) with the Lee–Yang–Parr (LYP) correlation functional [29–32]. The B3LYP hybrid functional has been chosen because it provides a rather accurate description of metal interactions. A 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 [33, 34]. B3LYP correctly reproduces the thermochemistry of many compounds, including transition-metal atoms.

Full geometry optimizations of the dyes were carried out at the B3LYP/6-31g(d) level of theory. The optimal geometries obtained were then employed to calculate all photophysical and photovoltaic properties. The calculations of the UV–visible electronic absorption spectra and the related data of lifetimes of excited states were calculated using the Coulomb-attenuation method CAM-B3LYP/6-31g(d) [35]. The NTOs and the related data of ΦLHE, Edx, Edye*, ∆Gregen, ∆Ginext, and DOS were considered. The electronic absorption spectra require calculations of the allowed excitation energies. The absorptions in visible and near-UV regions are the most important regions for photo-to-current conversion. Therefore, only the singlet-to-singlet transitions of the absorption bands with modulus configuration interaction coefficients greater than 0.10, wavelengths longer than 300 nm, and oscillator strengths greater than 0.10 were considered. The electronic absorption spectra and the contributions of singly excited state configurations to each electronic transition of the dyes were calculated with the TD-DFT method in vacuum.

All calculations were carried out using a Gaussian 09 system [36] and DOS were calculated using Gauss Sum 2.2.5, which is a post-processing of Gaussian 09 code [37]. The following convergence criteria were considered: (i) convergence on RMS density matrix = 1.00D-08 within 128 cycles, (ii) convergence on MAX density matrix = 1.00D-06, and (iii) convergence on energy = 1.00D-06. The optimal geometries of molecular skeletons and molecular orbital densities were visualized using the corresponding Gauss View 5.0 software.
3. Results and discussion

Despite the complexity of the processes involved in DSSCs, there are two main ways in which the efficiency of a dye solar cell can be improved: (i) extending the light-harvesting region into the near-infrared (NIR) and (ii) lowering the redox potential of the electrolyte to increase Voc [38]. Using a dye that absorbs further into the NIR region while still managing to generate and collect the charge carriers efficiently could increase the current by over 40%. Further increasing the power-conversion efficiency beyond 14% will require improved dyes and electrolytes with smaller over-potentials to efficiently transfer charge. In general, the relatively high efficiency of the DSSC is attributed to a combination of very fast electron injection from the dye onto the semiconductor, slow back-reaction of the electron in the semiconductor to either the dye cation or the oxidized redox electrolyte, fairly fast regeneration of the dye by the redox mediator, and the electron-injection kinetic efficiency, which is related to the reorganization of electron density in the excited state close to the anchoring group. However, most of the processes involved in DSSCs are connected with the light-harvesting property. Improvement of the DSSC performance has been essentially controlled by the light-harvesting capability of the dye, particularly the strong absorption in the NIR region where the solar flux of photons is maximal.

An attempt has been made to improve the highest record efficiency (11.9–12.7%) of the experimental YD2-o-C8 sensitizer [6] by designing structurally related candidates. We are therefore interested in the relative measures of the photophysical and photovoltaic properties, rather than in the absolute measures. It is conceivable that the comparison of the properties obtained should provide useful indications to the performances of the designed dyes. We have focused on the effects of structural modifications on narrowing the energy gaps, and consequently, the red-shifted absorption bands. The modifications of the dye structure were performed at the macrocycle periphery by increasing the number of carboxylic acid anchoring groups and replacing the porphyrin macrocycle with the porphyrine macrocycle to tune the energy gaps. The present study helped us determine the relationship between the molecular structures of porphyrin and porphyrine sensitzers and the performances of the DSSCs. It also brought to light how the photophysical and photovoltaic properties play a key role in the DSSC efficiency. The molecular structures and optimized geometries of the dyes Zn-Por-1C or YD2-o-C8 (ZnC7H121N5O6), Zn-Pz-1C (ZnC7H128N4O8), Zn-Por-2C (ZnC106H126N4O8), Zn-Pz-2C(ZnC102H126N4O8), Zn-Por-3C(ZnC7H126N10O10), and Zn-Pz-3C(ZnC102H138N10O10) are presented in figure 1.

3.1. NTOs

Because charge-separated states are one of the main factors affecting solar cell efficiency, qualitative predictions of the efficiency of sensitzers could be made by using HOMO, LUMO, and HOMO–LUMO energy gaps of NTOs. HOMOs must be localized on the donor and LUMOs must be localized on the acceptor to create efficient charge-separated states [39]. To clarify the donor-pi-acceptor (D-π-A) nature of the present dyes, the HOMOs and LUMOs were calculated. Isosurface plots are presented in figure 2.

As can be seen while in Zn-Por-1C, Zn-Por-2C, and Zn-Por-3C, HOMOs are localized on the diphenylamine donor groups and LUMOs are localized on the carboxylic acid acceptor groups and the porphyrin chromophors constitute the π bridges. In Zn-Pz-1C, Zn-Pz-2C, and Zn-Pz-3C, HOMOs are localized on the porphyrine macrocycle donors and LUMOs+1 are localized on the carboxylic acid acceptor groups, and the ethynylene bridge constitute the π bridges. The present structures are therefore (D-π-A) type donors with electron-rich (donor) and electron-poor (acceptor) sections connected through a conjugated (π) bridge. The electron-poor section is functionalized with an acidic binding group that couples the molecule to an electrode surface, such as TiO2 anatase, to form integrated DSSCs in the presence of redox mediators.

As shown in figure 2, the π electron density distributions of HOMOs and LUMOs localize mainly at the conjugated macrocycle cavities. Because the peripheral substituents are not coplanar with the planes of the macrocycle cavities, there is diminutive charge delocalization into terminal meso-p-carboxyphenyl moieties at LUMO and LUMO+1 orbitals. Interestingly, the anchoring meso-p-carboxyphenyl moieties nearly exclusive electron density distributions at LUMO+1 of the porphyrine dyes, suggesting that the electron injection from higher excited states involving LUMO+1 should be more efficient than the lower ones involving LUMO.

The large sizes of the present dyes create barriers between holes in the redox mediator and electrons in the electrode surface, thereby inhibiting dye recombination. It is also noteworthy that the strain of a porphyrin ring is likely to cause fast nonradiative relaxation in the porphyrine singlet excited states [40]. The radiative relaxation would compete with electron injection to the CB of an oxide electrode, resulting in a decrease in cell performance. As shown in figure 2, the macrocycle cavities are not strained under the effect of replacing the porphyrine macrocycle with a porphyrine macrocycle or the addition of p-carboxyphenyl moieties, explaining the expected high cell performance of the six dyes. Moreover, for porphyrines, the additional four nitrogen atoms are placed at the macrocycle plane, indicating that the lone pairs participate in the π-conjugated system at one hand, and explain the expected higher cell performances of porphyrines relative porphyrins at the other hand.

The electron densities of the terminal p-carboxyphenyl moieties at LUMO and LUMO+1 orbitals are shown in figure 2. The increased electron densities of the anchoring groups of porphyrine candidates relative to those of porphyrin candidates are attributed to the addition of four nitrogen atoms to the porphyrin macrocycles. The larger electron densities lead to efficient electron injection from the dye singlet excited state to the CB of the electrode, owing to the strong electronic coupling between the excited adsorbed dye and the 3d-orbitals that make up the CB of the electrode surface through the carboxy group, resulting in the difference
in the cell performances between the two systems. This gives a primary indication to the enhanced cell performance of the porphyrazine dyes.

3.2. Energy gaps

The energy difference between the HOMO and LUMO is termed the HOMO–LUMO energy gap. The photovoltaic performance of a DSSC is closely associated with the energy gap of the dye, which correlates with the experimental parameters: maximum short current intensity ($J_{sc, mA/cm^2}$) and ($E_{1/2(oxidation)}$-$E_{1/2(reduction)}/V$) potentials. Developing efficient NIR dyes represents one of the basic strategies for improving the performance of the DSSCs. Natural transition orbital energy levels and energy gaps of the dyes Zn-Por-nC and Zn-Pz-nC, where $n = 1$–3, are given in table 1. As can be seen, replacing the porphyrin ring with a porphyrazine ring (and/or) adding p-carboxyphenyl moiety lead to narrowing of the band gap of the reference dye YD2-o-C8 (Zn-Por-1C). This nominates Zn-Por-2C, Zn-Por-3C, Zn-Pz-1C, Zn-Pz-2C, and Zn-Pz-3C dyes to be better candidates for DSSCs by virtue of harvesting more light in the solar spectrum. The expected order of performance is Zn-Por-1C < Zn-Por-2C < Zn-Por-3C < Zn-Pz-1C < Zn-Pz-2C < Zn-Pz-3C. This result is consistent with the theoretic maximum of $J_{sc}$ as a function of the energy gap and the achieved values in different kinds of excellent solar cells reported by Zhang et al [41].

Although the addition of a p-carboxyphenyl moiety to either a porphyrin or a porphyrazine macrocycle periphery marginally decreases the corresponding band gap, the replacement of the porphyrin macrocycle itself with a porphyrazine macrocycle sharply decreases the corresponding band gap. The decrease in the HOMO–LUMO energy gap mainly comes from destabilizing (raising) the HOMO. The macrocycle replacement and/or addition of a p-carboxyphenyl moiety to either a porphyrin or a porphyrazine macrocycle periphery negligibly affects the level of LUMO. The effect of ring replacement on cell performance is therefore more significant than that of the addition of the p-carboxyphenyl moiety. In other words, ring replacement leads to harvesting more light in the domains of UV–visible and NIR. Moreover, the molecular structures of the present dyes with elongated peripheral side chains and p-carboxyphenyl moieties help suppress the macrocycle aggregations on the electrode surface.

To calibrate our present calculations with the available experimental and theoretical results, we consider the frontier molecular orbital (FMO) energy gaps. The band gap (2.325 eV) of the present Zn-Por-1C dye obtained from full geometry optimization at the B3LYP/6-31G(d) level is very close to the band gap (2.334 eV) of the identical YD2-o-C8...
dye calculated at the same B3LYP/6-31g (d) level by Yella et al [6]. The band gap (2.325 eV) of the present Zn-Por-1C dye may also be correlated with the experimental value $[E_{1/2}(oxidation)-E_{1/2}(reduction) = 2.690 \text{ V}]$ of YD2-o-C8 reported by Yella et al [6] where $[E_{1/2}(oxidation)/\text{V}]$ is related to the irreversible process $E_{pa}$.

### 3.3. Electrode surfaces

The present DSSCs are based on p-type organic dye donors and n-type inorganic semiconductor acceptors, namely, DSSCs using semiconductor electrodes and redox mediators. In solid-liquid junction solar cells, the voltage is attributed to the energy gap between the Fermi level (near conduction-band level for an n-type semiconductor) of the semiconductor electrode and the redox potential of the mediator in the electrolyte. The HOMOs, LUMOs, and energy gaps of Zn-Por, Zn-Pz, H2-Por, and H2-Pz dyes, as well as (TiO2)302, Ti53O76, ZrO2, GaP, and SiC semiconductor electrodes [42–44], are presented in figure 3. An efficient electron injection into an electrode surface is required to enhance photo-to-current conversion efficiency of a DSSC. Inspection of figure 3 reveals that the LUMOs of the dyes are noticeably higher than the lower edges of the CBs, and HOMOs are noticeably higher than the upper edges of VBs of the semiconductor surfaces. This indicates that all of the present dyes should be capable of injecting electrons into the present semiconductor electrodes upon excitation. Furthermore, all HOMOs of the dyes fall within the (HOMO–LUMO) energy

![Figure 2. NTOs isosurface plots (isodensity contours = 0.02 a.u) of the dyes Zn-Por-nC and Zn-Pz-nC (n = 1–3) computed at the CAM-B3LYP/6-31G(d) level of theory.](image)

![Figure 3. NTOs occupied and virtual (HOMOs and LUMOs) and energy gaps of the dyes Zn-Por-nC and Zn-Pz-nC (n = 1–3) computed at the CAM-B3LYP/6-31G(d) level of theory, as well as those of semiconductor acceptors. All energies are given in eV.](image)
moieties—this is in contrast to HOMOs, which are significantly affected by ring replacement. Ning et al [45] speculated that the increased $E_{\text{LUMO}}$ might produce deep electron injection for retarded charge recombination. Because the lowest edge of CBs for oxide semiconductor electrodes is assigned to the Ti$_{35}$O$_{76}$ oxide semiconductor, the electron injection processes may be the most favorable into this oxide. However, a comparison between the lower edges of the CBs of the other semiconductors reveals that the pair (TiO$_2$)$_{60}$ and SiC, as well as the pair ZrO$_2$ and GaP, exhibit approximately identical electron injection behavior. Solvent effects should also be considered, because the maximum for the lower edge of the CB in an oxide semiconductor electrode surface such as TiO$_2$ using saturation photo voltage measurements ($\sim$4.45 eV) shifts to ($\sim$3.90 eV) when immersed in a solvent with an electrolyte [46].

To explain the relationship between band gap reduction due to a particular modification of the dye and the conversion efficiency of the solar cell, suppose that the situation in which HOMO of the sensitizer is lower enough than the redox potential of the electrolyte and the LUMO is higher enough than the CB of the semiconductor electrode, which indicates the open circuit voltage $V_{\text{oc}}$ of the solar cell, will not be influenced by the HOMO and LUMO variations. In this case, as the HOMO–LUMO gap decreases, more photons at the longer-wavelength side would be absorbed to excite the electrons into the unoccupied molecular orbital, which increases the short current intensity $I_{\text{sc}}$ and the conversion efficiency $\eta$ of the solar cell. The former data therefore suggest the sensitized mechanism of the present dye-semiconductor couple to be an interfacial electron transfer between the semiconductor electrode and the dye, such that the electron injection process occurs from the excited dye to the semiconductor CB. This is a type of typical interfacial electron transfer reaction [47].

As shown in table 1, the gaps are narrowed by replacing the porphyrin macrocycle with porphyrazine. This explains the expected higher solar cell efficiencies of the Zn-Pz-nC dyes relative to the Zn-Por-nC dyes and implies that the DOS becomes more abundant near Fermi levels of Zn-Pz-nC sensitizers. Consequently, explanation of the differences in photo-to-current conversion efficiency due to the replacement of the macrocycle cavity is sought in the DOS. The DOS of a system describes the number of states per interval of energy at each energy level available to be occupied by electrons. A high DOS at a specific energy level means that there are many states available for occupation, and therefore scales linearly with the photovoltaic conversion efficiency. In figure 4, the calculated DOS of the dyes is presented to clarify the effects of replacing the macrocycle cavity and increasing the number of p-carboxyphenyl moieties. As shown, the DOS becomes more abundant near Fermi levels in both cases, where the overall features of DOS change and deep vales develop on both sides near Fermi levels.

### 3.4. UV–visible absorption

To understand the electronic transitions of the present dyes, TD-DFT calculations of the electronic absorption spectra in a vacuum were performed. The 15 lowest spin-allowed singlet–singlet transitions were calculated. The early theoretical interpretations of the spectra of various metalloporphyrins have been made by Gouterman [48], who initially used the four orbital model to interpret the Q and B bands, which assumes that the HOMO and LUMO–1 are almost degenerate in energy and well separated from the other levels, and a similar assumption is made for the LUMO and LUMO–1. As shown in table 1, non-negligible separations between the two highest occupied orbitals and the two lowest unoccupied orbitals result in the fact that the four orbital model no longer holds for these molecules. The $\lambda_{\text{max}}$/nm (581.87) corresponding to the transition energy/eV (2.13) of the present Zn-Por-1C dye obtained from the full optimized geometry of the dye at the B3LYP/6-31g(d) level of theory, considering the range separated hybrid functional CAM-B3LYP/6-31g(d), may be compared with $\lambda_{\text{max}}$/nm (581) of the identical YD2-o-C8 dye measured in tetrahydrofuran (THF) at 23 °C by Yella et al [6].

As shown in table 2, the maximum absorption bands are red shifted under the effect of either replacing the macrocycle or increasing the number of p-carboxyphenyl moieties. However, the effect of replacing the macrocycle on light harvesting is more significant than that of increasing the number of p-carboxyphenyl moieties. The maximum absorption bands result from the electronic transitions that occur from the initial states, which are mainly contributed by HOMOs, to the final states, which are mainly contributed by LUMOs. The other absorption bands result from the electronic transitions that occur from the initial states, which are contributed by HOMOs+n, to the final states, which are contributed by the HOMOs+n+n. These absorption bands in the visible region are typical $\pi$–$\pi^*$ transitions. The maximum absorption bands in a vacuum are red shifted by 166.46, 197.42, and 243.04 nm under the effect of replacing...
is the redox potential of the ground state and the calculated oscillator strength of the dye associated to the electron transition. It can be estimated from the light-harvesting efficiency (\(\Phi_{\text{LHE}}\)) and the coefficient of effectual electron injection (\(\Phi_{\text{inject}}\)) and charge collection efficiency (\(\Phi_{\text{CC}}\)) and can be expressed as [49]:

\[
\text{IPCE} = \Phi_{\text{LHE}} \Phi_{\text{inject}} \Phi_{\text{CC}}
\]

(1)

The efficiency of the electron density movement is related to both optical absorption intensity and the available electron transition. It can be estimated from the light-harvesting efficiency (\(\Phi_{\text{LHE}}\)) and the coefficient of effectual electron transition. The equation used for the calculation of \(\Phi_{\text{LHE}}\) is [50]:

\[
\Phi_{\text{LHE}} = 1 - 10^{-f}
\]

(2)

where \(f\) is the oscillator strength of the dye associated to the \(\lambda\). The calculated \(\Phi_{\text{LHE}}\) values of the present dyes at \(\lambda_{\text{max}}\) are listed in table 4. Obviously, replacing macrocycles (and/or) increasing the number of p-carboxyphenyl moieties leads to an increase \(\Phi_{\text{LHE}}\) of the Zn-Por-1C (YD2-o-C8) sensitizer.

However, an exception is noticed for the Zn-Pz-3C sensitizer, where the \(\Phi_{\text{LHE}}\) value was smaller than that of Zn-Pz-2C.

Figure 4. FMOs, HOMOs, LUMOs, and DOS of the dyes Zn-Por-nC and Zn-Pz-nC (n = 1–3).

The electron injection efficiency (\(\Phi_{\text{inject}}\)) is closely related to the driving force (\(\Delta G_{\text{inject}}\)) of the electron injection from the photo-induced excited states of the sensitizer to the CB of the semiconductor. A larger driving force is desirable for more rapid and efficient electron injection and then higher photocurrent of DSSCs. Preat et al [51] proposed a theoretical scheme to quantify the electron injection onto a TiO2 surface. The free energy change (\(\Delta G_{\text{inject}}\)) in eV for the electron injection can be expressed by the following equation [52]:

\[
\Delta G_{\text{inject}} = E_{\text{OX}}^{\text{dye}} - E_{\text{CB}}^{\text{exc}}
\]

(3)

where \(E_{\text{OX}}^{\text{dye}}\) is the oxidation potential of the dye in the excited state and \(E_{\text{CB}}^{\text{exc}}\) is the reduction potential of the semiconductor CB (2.77, 2.97, 3.60, and 3.00 eV for Ti35O76, (TiO2)60, ZrO2, and SiC, respectively). Note that the CB values of SiC and GaP are identical. Assume that the electron injection occurs from the unrelaxed excited state, \(E_{\text{OX}}^{\text{dye}}\), and can be expressed as:

\[
E_{\text{OX}}^{\text{dye}} = E_{\text{OX}}^{\text{exc}} - E_{\text{exc}}^{\text{dye}}
\]

(4)

where \(E_{\text{exc}}^{\text{dye}}\) is the redox potential of the ground state and \(E_{\text{exc}}^{\text{dye}}\) is the vertical transition energy (in eV) at \(\lambda_{\text{max}}\). The calculated \(E_{\text{exc}}^{\text{dye}}\), \(E_{\text{OX}}^{\text{dye}}\), \(E_{\text{OX}}^{\text{exc}}\), and \(\Delta G_{\text{inject}}\) for Ti35O76, (TiO2)60, ZrO2, and SiC semiconductor electrodes are also listed in table 3. As can be seen, while the \(\Delta G_{\text{inject}}^{\text{exc}}\) increases (more negative) with macrocycle replacement, it decreases (less negative) with an increase in the number of p-carboxyphenyl moieties, implying more favorable electron injections from the excited-states macrocycles, and by 17.8, 3.93, 48.76, and 42.95 nm under the effect of increasing the number of p-carboxyphenyl moieties. Usually, if the absorption bands are close to the infrared region, it is expected that the dyes have a higher photo-to-current efficiency. On this basis, the dyes Zn-Por-nC (n = 2,3) and Zn-Pz-nC (n = 1–3) are expected to have higher photo-to-current conversion efficiencies than the dye Zn-Por-1C (YD2-o-C8), which is characterized by (11.9–12.7%) efficiencies.

A measurement of the performance of a DSSC is called incident photon to current conversion efficiency (IPCE). Simply, it is a function of light-harvesting efficiency (\(\Phi_{\text{LHE}}\)), electron injection efficiency (\(\Phi_{\text{inject}}\)), and charge collection efficiency (\(\Phi_{\text{CC}}\)) and can be expressed by the following equation [52]:

\[
\Delta G_{\text{inject}} = E_{\text{OX}}^{\text{dye}} - E_{\text{CB}}^{\text{exc}}
\]

\[
\Delta G_{\text{inject}} = E_{\text{OX}}^{\text{exc}} - E_{\text{exc}}^{\text{dye}}
\]
of Zn-Pz-nC dyes to the semiconductors CBs. The results also indicate that the efficiency of electron injection depends on the type of the semiconductor electrode, and may be ordered as follows: ZrO2(GaP) > SiC > (TiO2)60 > Ti35O70. Moreover, despite the fact that the previous ΦLHE value of Zn-Pz-3C is smaller than that of Zn-Pz-2C, the Φinject value of Zn-Pz-3C is greater than that of Zn-Pz-2C so that the product (ΦLHE × Φinject) of Zn-Pz-3C is greater than that of Zn-Pz-2C, implying greater contribution to IPCE. The efficiency of dye regeneration or the free energy change of dye regeneration

---

**Table 2.** Computed excitation energies, oscillator strengths (f), and molar extinction coefficients (ε) for the optical transitions of the absorption bands in the UV–visible regions (involving HOMOs) of the dyes Zn-Por-nC and Zn-Pz-nC (n = 1–3) in vacuum computed at the CAM-B3LYP/6-31g(d) level of theory.

<table>
<thead>
<tr>
<th>State</th>
<th>The weight of the single excitation in the excited state expansion</th>
<th>Excitation energy (eV nm⁻¹)</th>
<th>f</th>
<th>ε/(M⁻¹ Cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn-Por-1C State</td>
<td>&gt;0.1 (corresponding transition orbitals)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>−0.37 (407 →410); 0.58 (408 →409)</td>
<td>2.13/581.87</td>
<td>0.23</td>
<td>9866</td>
</tr>
<tr>
<td>3</td>
<td>0.53 (406 →409); −0.15 (406 →411); 0.10 (406 →412); −0.31 (407 →410); −0.25 (408 →409)</td>
<td>2.90/426.15</td>
<td>0.33</td>
<td>13 881</td>
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<td>HOMO is No. 408 orbital</td>
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<tr>
<td>Zn-Por-2C State</td>
<td>&gt;0.1 (corresponding transition orbitals)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1</td>
<td>0.71(410 → 411); −0.12 (411→ 410)</td>
<td>1.65/748.33</td>
<td>0.56</td>
<td>55 870</td>
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<tr>
<td>2</td>
<td>0.71(409 → 411)</td>
<td>1.76/703.36</td>
<td>0.88</td>
<td>56 579</td>
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<td>HOMO is No. 410 orbital</td>
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<tr>
<td>Zn-Por-3C State</td>
<td>&gt;0.1 (corresponding transition orbitals)</td>
<td></td>
<td></td>
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<tr>
<td>1</td>
<td>0.11(444 →446); −0.34 (444 →447); 0.57 (445 →446)</td>
<td>2.06/599.67</td>
<td>0.23</td>
<td>12 098</td>
</tr>
<tr>
<td>3</td>
<td>0.54 (443 →446); −0.13 (443 →449); 0.29 (444 →447); 0.23 (445 →446)</td>
<td>2.83/436.80</td>
<td>0.38</td>
<td>16 037</td>
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<td>HOMO is No. 445 orbital</td>
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<tr>
<td>Zn-Por-4C State</td>
<td>&gt;0.1 (corresponding transition orbitals)</td>
<td></td>
<td></td>
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<tr>
<td>1</td>
<td>0.71 (447 →448); −0.12 (448 →447)</td>
<td>1.56/797.09</td>
<td>0.52</td>
<td>53 253</td>
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<tr>
<td>2</td>
<td>0.70 (446 →448)</td>
<td>1.73/714.30</td>
<td>0.98</td>
<td>56 720</td>
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<tr>
<td>HOMO is No. 447 orbital</td>
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<tr>
<td>Zn-Por-5C State</td>
<td>&gt;0.1 (corresponding transition orbitals)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1</td>
<td>−0.10 (480 →483); −0.35 (481 →474); 0.58 (482 →483)</td>
<td>2.05/603.60</td>
<td>0.19</td>
<td>10 190</td>
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<tr>
<td>3</td>
<td>0.50 (480 →483); −0.12 (480 →487); 0.33 (481 →484); 0.28 (482 →483)</td>
<td>2.82/439.02</td>
<td>0.56</td>
<td>23 285</td>
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<td>HOMO is No. 482 orbital</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Zn-Por-6C State</td>
<td>&gt;0.1 (corresponding transition orbitals)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1</td>
<td>0.70 (484 →485); −0.11 (485 →484)</td>
<td>1.47/840.04</td>
<td>0.50</td>
<td>49 556</td>
</tr>
<tr>
<td>2</td>
<td>0.70(483 →485)</td>
<td>1.70/726.32</td>
<td>1.00</td>
<td>55 521</td>
</tr>
<tr>
<td>HOMO is No. 484 orbital</td>
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</table>
\( \Delta G_{\text{redox}}^{\text{gen}} \) can affect the rate constant of redox process between the oxidized dyes and electrolyte. Considering the ideal redox potential (3.5 eV vs vacuum), \( \Delta G_{\text{redox}}^{\text{gen}} \) can be calculated from the relation

\[
\Delta G_{\text{redox}}^{\text{gen}} = E_{\text{redox}}^{\text{ox}} - E_{\text{redox}}^{\text{red}}
\]

Where \( E_{\text{redox}}^{\text{red}} \) is the redox potential of electrolyte. The free energy changes of the present dyes are listed in table 3. As shown, replacing the porphyrin macrocycle with a porphyrine macrocycle generates a considerable reduction of \( \Delta G_{\text{redox}}^{\text{gen}} \). In general, the UV-visible absorption is attributed to the process of electron transfer from the ground to the excited state of the dye. This, in turn, implies that the corresponding excitations generate charge-separated states and contribute to the sensitization of photo-to-current conversion processes. In other words, replacing macrocycles and increasing the number of p-carboxyphenyl moieties shift the absorption bands to longer wavelengths, and make the dyes Zn-Por-nC (n = 2, 3) and Zn-Pz-nc (n = 1–3) good potential candidates for harvesting more light in the UV-visible region of the solar spectrum for photovoltaic applications.

### 3.5. The lifetimes of the excited states

The lifetime of the excited state is an important factor for considering the efficiency of charge transfer of the dyes. A dye with a longer lifetime in the excited state is expected to be more facile for charge transfer. An accurate prediction of an excited state lifetime needs to account for all deactivation channels of the excited states. To roughly estimate the lifetime of the excited state, an assumption was made by Yang et al. [53] that spontaneous deactivation is the main competing deactivation process with electron injection and other deactivation channels can be omitted. Although the assumption is very speculative and it could not be expected to obtain accurate lifetimes close to the real values, it is conceivable that the comparison of the lifetimes obtained with the same assumption should give a clue to the performances of dyes at the relative measure. The lifetime of an excited state was estimated using the formula [54]:

\[
\tau = \frac{1}{A_{kk}^{\ast}} A_{kk} = \frac{4e^2\Delta E_{kk}^{\ast}|\mu_{kk}|^2}{3\hbar^4c^3}
\]

where \( A_{kk}^{\ast} \) is the Einstein coefficient for spontaneous emission, \( e \) is the elementary charge, \( \hbar \) is the reduced Planck’s constant, \( c \) is the speed of light in vacuum, and \( \Delta E_{kk} \) and \( \mu_{kk} \) represent the transition energy and dipole moment from the first excited state.

### Table 4. Lifetimes for the first excited states (s) of dyes Zn-Por-nC and Zn-Pz-nC (n = 1–3)

<table>
<thead>
<tr>
<th>( \Delta G_{\text{inject}} )</th>
<th>( \Delta G_{\text{redox}}^{\text{gen}} )</th>
<th>( \Delta E )</th>
<th>( f^* )</th>
<th>( \mu_{kk}^2 )</th>
<th>( \tau (10^{-9}s) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn-Por-1C</td>
<td>2.1308</td>
<td>1.2333</td>
<td>4.469</td>
<td>21.73</td>
<td></td>
</tr>
<tr>
<td>Zn-Por-2C</td>
<td>2.0675</td>
<td>0.2373</td>
<td>4.684</td>
<td>22.70</td>
<td></td>
</tr>
<tr>
<td>Zn-Por-3C</td>
<td>2.0541</td>
<td>0.1957</td>
<td>3.888</td>
<td>27.88</td>
<td></td>
</tr>
<tr>
<td>Zn-Pz-1C</td>
<td>1.7627</td>
<td>0.8798</td>
<td>13.712</td>
<td>8.42</td>
<td></td>
</tr>
<tr>
<td>Zn-Pz-2C</td>
<td>1.5555</td>
<td>0.5165</td>
<td>13.553</td>
<td>18.42</td>
<td></td>
</tr>
<tr>
<td>Zn-Pz-3C</td>
<td>1.4759</td>
<td>0.5020</td>
<td>13.883</td>
<td>21.05</td>
<td></td>
</tr>
</tbody>
</table>

4. Conclusions

By comparing dyes to a dye with known solar cell efficiency, we could identify candidates ideal for DSSCs. We have performed an extensive set of theoretical calculations employing state-of-the-art DFT and TD-DFT methodologies to design a new set of porphyrin sensitizers able to compete with the reference YD2-o-C8 sensitizers.

Several photovoltaic and photophysical properties were calculated to provide the electronic information about the roles played in dominating the performances. In our attempt to design the new set of porphyrin sensitizers, we focused on macrocycle replacement and increasing the number of p-
carboxyphenyl moieties, in addition to testing several semiconductor electrodes. We interpreted the reasons that the present suggested sensitizers are expected to obtain high photo-to-current conversion efficiencies. The expected high efficiencies are ascribed to rich charge separation, unidirectional charge transfer, light-harvesting efficiency in the longer wavelength range, increasing DOS nearby Fermi levels, deep electron injection, suppressing macrocycle aggregation, active dye regeneration, longer lifetimes of the excited states, and inhibited dye recombination. Structural modifications, in particular, the replacement of porphyrin with porphyrazine, lead to desirable properties related to increasing the photo-to-current conversion efficiency. It may be concluded that the addition of four nitrogen atoms to the porphyrin macrocycle creates a potential good sensitizer, namely porphyrazine or a tetraaza porphyrin derivative. However, to exert the latent ability of the present porphyrinases, it is also necessary to incorporate a suitable redox electrolyte.

The present results possibly provide a nontraditional theoretical model and lead us to suggest that an optimization of both the D-π-A structures of the dyes and the semiconductor electrodes could lead to DSSCs with yet improved efficiencies. The present methods and techniques are applied equally well to both of the reference and designed sensitizers, so that they can be well predictive. However, the experimental verification of the former predictions is imperative.

References
