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Saddle-Shaped Porphyrins for Dye-Sensitized Solar Cells: New Insight into the Relationship between Nonplanarity and Photovoltaic Properties

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We report on the theoretical and experimental studies of the new dye-sensitized solar cells functionalized with 5, 10, 15, 20-tetrakis(4-carboxyphenyl) porphyrin zinc(II) complexes bearing 2 and 8 bromo substituents at the β positions. In agreement with the results of TD-DFT calculation, the absorption maxima of di- and octa-brominated Zn(II) complexes, ZnTCPPPBr₂ and ZnTCPPPBr₈, exhibited large red-shifts compared to that of the non-brominated free base porphyrin (H₂TCPP). Furthermore, DFT calculations showed that the higher stabilization of the LUMO levels relative to the HOMO ones makes the HOMO–LUMO gaps of the brominated Zn-porphyrins models smaller compared to that of the nonbrominated counterparts, which explains the red shifted Soret and Q bands of the brominated compounds. Solar cells containing the new saddle-shaped porphyrins were subjected to analysis by a photovoltaic calibration laboratory to determine their solar to electric energy conversion. In this regard, we found that the overall conversion efficiency of ZnTCPPPBr₈ adsorbed on TiO₂ nanocrystalline films was 5 times as large as that of ZnTCPPPBr₂ adsorbed on the same films. The effect of increasing number of Br groups on the photovoltaic performance of the complexes was compared to results of computational methods by ab initio DFT molecular dynamics simulations and quantum dynamics calculations of electronic relaxation to investigate the interfacial electron transfer (IET) in TCPPBr₂/TiO₂-anatase nanostructures. Better IET for the ZnTCPPPBr₂ compared to ZnTCPPPBr₈, and for H₂TCPP was evaluated from interfacial electron transfer simulation (IETs). IET results indicate that electron injection in ZnTCPPPBr₂-TiO₂ (τ = 25 fs) can be up to 5 order of magnitude faster than ZnTCPPPBr₈-TiO₂ (τ = 125 fs). Both experimental and theoretical results demonstrate that the increasing of the number of bromo substituent at the β-pyrole position of the porphyrin macrocycle created a new class of porphyrin DSSC, which exhibits a remarkable increase in photovoltaic performance than non-brominated porphyrins.

1. Introduction:

The sensitization of semiconductors with a significant number of dyes for light harvesting has been investigated over the last 25 years for the development of efficient solar cells. Porphyrin sensitizers were among the first examined natural types of dyes, and to this day they continue to be some of the most frequently studied sensitizers. Recently, a breakthrough has been achieved in porphyrin-sensitized solar cell field when a record efficiency of 13% has been reported using a single push–pull porphyrin dye SM315 with cobalt (II/III)-based redox electrolyte. In this regards, a widely used approach is to modify the porphyrins in the hope of increasing the charge-injection and light-harvesting efficiencies. One of the most appealing aspects of these methods is that a wide variety of functionalized porphyrins with different spectroscopic properties can now be synthesized. Meanwhile, extension the light-harvesting region into the near-infra-red (NIR) is a of the main strategies for improvement of the efficiency of a DSSC. The free-base and zinc derivatives of the meso-azoic acid substituted porphyrins (TCP) are one of the most widely studied dyes due to their appropriate LUMO and HOMO energy levels. However, the nearly orthogonal orientation of the meso aryl substituent with respect to the porphyrin mean plane may limit injection from ZnTCP. In contrast, the decreased dihedral angles between the aryl substituent and the porphyrin mean plane caused by the introduction of halogen group at the β- position of ZnTCP, might allow more efficient direct charge injection from the porphyrin moiety to the semiconductor surface as well as the pushing of the Soret band to higher wavelengths, accounting for the higher performance of halogenated Zn-porphyrins. In particular, the modification of ZnTCP by substitution at the β-positions with halogen atoms decreases the splitting between the key filled or empty orbitals, and leads to the enhancement of the red-absorbing Soret and Q bands. The four orbital model states that the degeneracy of the two e₁ LUMOs and the near-degeneracy of the a₂g HOMO and a₁u HOMO-1 causes strong configuration interaction between the (a₂g e₁)⁰ and (a₂g e₁)³ excited states of e₁ symmetry. In addition, the electron-withdrawing substituent makes the macrocycle more electron deficient and consequently more stable towards oxidative degradation. Among the known β-pyrole halogenated porphyrins, β-pyrole brominated porphyrins have been a subject of intense research, because of their synthetic ease and the fact that the number of bromo substituent can be controlled with a high degree of certainty.
The Soret and visible absorption bands of porphyrins have been shown to be highly sensitive to distortion of the porphyrin ring caused by peripheral substitution of the aromatic macrocycle.\textsuperscript{16, 17} Hence, one can quantitatively prove the porphyrin geometry by measuring the wavelengths and molar absorptivities of each (TPPBr)_2Zn derivative as a function of the number of Br groups introduced onto the macrocycle. The above discussion clearly demonstrates the importance of β-pyrole halogenated porphyrins from both fundamental and applied points of view.\textsuperscript{18}

In fact, β-pyrole halogenated porphyrins are a kind of a “missing link in the family tree” represented by porphyrin sensitizers in DSC application. Therewith, understanding the photophysics of porphyrins attached to semiconductor surfaces is essential for the design of β-pyrole halogenated porphyrins for solar energy conversion.\textsuperscript{19} In this area, there is still considerable controversy about the time scale and nature of the primary electron-transfer process in dye sensitized TiO_2 electrodes, revealing that nuclear motion cannot be the rate-determining factor in the underlying interfacial electron-transfer mechanisms. Therefore, it seems essential to develop experimental studies with realistic theoretical simulations to develop a comprehensive understanding of the underlying electron-transfer dynamics.\textsuperscript{20}

The efficiency of photon-to-current conversion thus relies upon optimal conditions for the underlying electron transfer mechanism as well as on the rational design of dyes and linker photosensitizers. Thus, in focusing on photo-injection mechanisms from the excited electronic states of new β-pyrole brominated porphyrins sensitized solar cells, this study examines the process of electron injection on and through its application to design of efficient photoactive devices.

Here, we focus on TiO_2 surfaces modified by zinc porphyrins attached to the surface by carboxylate linkers. Emphasis has been given to the characterization of the electronic excitations and injection time scales as determined by the number of the bromine atom at the β-pyrole position of carboxylated porphyrin. The simulation results described in this paper show the first direct evidence of an electron-injection mechanism and the relation of substituent atoms in porphyrins and time-dependent charge distribution during the time relaxation dynamics. The interfacial electron-transfer involves an ultrafast (τ = 25–120 fs) electron-transfer event that localizes the charge on the Ti^{4+} surface ions next to the adsorbate molecule.

2. Experimental:

2.1 Material and Instruments. All chemicals and solvents were purchased from the Batista group and performed it with considering reported conditions in literature.\textsuperscript{22} In summary, we have computed the survival probability, p(t), defined as the probability that the photoexcited electron remains in the adsorbate molecule at different times (t) after excitation of the system. Computing the time-dependent wave function \(|\Psi(t)\rangle = \sum \langle q_i | \Psi(t) \rangle |q_i\rangle\), expanded in the basis set of AOs \(|q_i\rangle\), required the propagation of the expansion coefficients \(\langle t \psi | \Psi(t) \rangle \) over time (see the initial state \(|\Psi(0)\rangle = \sum \langle q_i | \Psi(0) \rangle |q_i\rangle\). To avoid artificial recurrences in electron-transient populations, the calculations of charge injection were conducted in models consisting of a 3x3 adsorbate-anatase supercell array. Initial states are defined in terms of the excited electronic states of the adsorbate with significant electronic coupling with the semiconductor conduction band.\textsuperscript{23}

Figure 1. Nanostructure of TiO_2-anatase sensitized by Zn TCPP after geometry relaxation under vacuum conditions and electronic density in the highest occupied molecular orbital.

2.3 Synthesis of porphyrin dyes. 2.1 H_2TCPB \textsuperscript{25, 26} (300 mg, 0.38) and zinc(II) acetate (166 mg, 0.75 mmol) were dissolved in DMF (80 mL), and the solution was stirred at reflux for 45 min. The metal complex formation was monitored by UV-Vis spectroscopy in DMF. After filtration, DMF was evaporated under vacuum and the residue was washed with water to remove the excess metal salt. UV-Vis (DMF): \(\lambda_{max}(nm): 423, 556, 598\).

2.2. Bromination of ZnTCP (ZnTCPBr) (X = 2 and 8) Dibromo-meso-tetrakis-(4-phenyl carboxyl) porphyrinato Zinc(II) complex (ZnTCPBr, ZnTCPBr_2) was prepared according to the literature.\textsuperscript{27} ZnTCP (200 mg, 0.23 mmol) was dissolved in THF (40 mL). To this solution, freshly recrystallised NBS (166 mg, 0.93 mmol) was added. The reaction mixture was stirred for 24 h at room temperature and then the solution was evaporated to dryness. The solid was then dissolved in chloroform and washed several times with distilled water in a separating funnel.

Octabromo-meso-tetrakis-(4-phenyl carboxyl) porphyrinato Zinc(II) complex (ZnTCPBr_4, ZnTCPBr_8) was prepared starting from m ZnTCP (150 mg, 0.175 mmol) and freshly recrystallised NBS (0.779 g, 4.489 mmol) using the same procedure as described for ZnTCPBr_2 to yield the product. The degree of bromination of ZnTCP and the purity of ZnTCPBr_4 have been determined by \(^1\)H NMR spectrometry based on the ratio of the intensities of the signals corresponding to the protons of H_3 and meso substituents (H_3/H_ortho and H_3/H_ortho ratios); in the case of ZnTCPBr_2, a value of ca. 0.75 was observed for both the H_3/H_ortho and H_3/H_ortho ratios. In the case of ZnTCPBr_8, the signal due to the β protons disappeared. Also,
ICP analysis was used to confirm the elemental composition of the brominated zinc porphyrins.

2. 4. Fabrication of DSSC. TiO$_2$ photoelectrode was prepared by screen-printing methods. TiO$_2$ photoelectrode (area: ca. 0.3 cm $\times$ 1 cm) was prepared by a similar method reported in the literature. Nanocrystalline TiO$_2$ films of 10–15 µm thickness were deposited onto transparent conducting glass (which has been coated with a fluorine-doped stannic oxide layer, thickness of 5 mm, sheet resistance of 20–25X). These films were dried at 150 °C for 30 min and then were gradually sintered at 450 °C for 30 min. The sensitizer was dissolved in ethanol at a concentration of $1\times10^{-4}$ mol L$^{-1}$. The photoelectrode was dipped into the dye solution immediately kept at room temperature for 24 h so that the dye was adsorbed onto the TiO$_2$ films. A sandwich cell was assembled by using the dye anchored TiO$_2$ films as the working electrode and conducting glass coated with Pt as the counter electrode. The two electrodes were placed on top of each other. The electrolyte was introduced into the TiO$_2$ photoelectrode (area: ca. 0.3 cm $\times$ 1 cm) was prepared by a similar method reported in the literature. The shape and the main peaks of the spectra reproduce the experimental data reasonably well.

3. Results and discussion

3.1 Absorption spectroscopy. The molecular structures of H$_2$TCPP (1), ZnTCPPBr$_2$ (2) and ZnTCPPBr$_8$ (3) are shown in Scheme 1.

![Scheme 1. Molecular structures of (1), ZnTCPPBr$_2$ (2) and ZnTCPPBr$_8$ (3).](image)

The strong absorption of porphyrins in the 400-450 nm region (Soret band) as well as absorptions in the 500-700 nm region (Q bands) make them excellent candidates as photosensitizers in solar cells. The UV–Vis absorption spectra of ZnTCPP, ZnTCPPBr$_2$ and ZnTCPPBr$_8$ in THF are shown in Fig. 2. Also, the peak positions of the Soret and Q bands of porphyrin dyes are summarized in Table 1.

![Figure 2. Absorption spectra of H$_2$TCPP, ZnTCPPBr$_x$ (X= 2 and 8) in THF solution $10^{-3}$ mol lit$^{-1}$ (solid lines).](image)

As seen in Figure 2, there is a systematic red shift in $\lambda_{\text{max}}$ of Soret band upon increasing the number of Br groups at the β positions. The UV–Vis absorption spectrum of H$_2$TCPP exhibits a strong Soret band at 417 nm and four weak Q-bands at 513, 548, 591 and 648 nm. On the other hand, the Soret and Q bands of ZnTCPPBr$_2$ appear at 435, 566 and 606 nm, respectively which are red-shifted with respect to those of H$_2$TCPP. However, ZnTCPPBr$_8$ showed a strong absorption band at 506 nm and a broad one at 675 nm, which are broader and more red-shifted compared to those of other compounds. As seen in the UV–Vis absorption spectra, the Soret band of ZnTCPPBr$_2$ and ZnTCPPBr$_8$ are red-shifted about 18 and 89 nm compared to that of H$_2$TCPP, respectively.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Soret band (d nm)</th>
<th>Q$_{\text{UV}}$ (m)</th>
<th>Q$_{\text{III}}$ (m)</th>
<th>Q$_{\text{II}}$ (m)</th>
<th>Q$_{\text{I}}$ (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$<em>2$TCPP$</em>{\text{Exp}}$</td>
<td>417</td>
<td>513</td>
<td>548</td>
<td>591</td>
<td>648</td>
</tr>
<tr>
<td>H$<em>2$TCPP$</em>{\text{Theo.}}$</td>
<td>408</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZnTCPPBr$<em>2$$</em>{\text{Exp}}$</td>
<td>435</td>
<td>565</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZnTCPPBr$<em>2$$</em>{\text{Theo.}}$</td>
<td>437</td>
<td>553</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZnTCPPBr$<em>8$$</em>{\text{Exp}}$</td>
<td>506</td>
<td>-</td>
<td>-</td>
<td>675</td>
<td>-</td>
</tr>
<tr>
<td>ZnTCPPBr$<em>8$$</em>{\text{Theo.}}$</td>
<td>495</td>
<td>-</td>
<td>-</td>
<td>740</td>
<td>-</td>
</tr>
</tbody>
</table>

The simulated absorption spectra for H$_2$TCPP, ZnTCPPBr$_x$ (X=2 and 8), obtained by the TD-DFT/(LanL2D Z) level of theory (dashed lines).

The simulated absorption spectra for H$_2$TCPP, ZnTCPPBr$_x$ (X=2 and 8), obtained by the TD-DFT/(LanL2D Z) level of theory reproducibly reproduce the experimental data reasonably well.

Hence, we can quantitatively probe the porphyrin geometry by measuring wavelengths of each ZnTCPPBr$_x$ derivative as a function of the number of Br groups on the macrocycle. As shown in Figure 2, the theoretical results suggest that the Soret and visible
absorption bands of the porphyrins are highly sensitive to periphe-
ral substitution. Similar spectral trends were also observed for dif-
ferent isomers of ZnTPPBr, which was suggested that the red shif-
t in absorption bands of the brominated porphyrins can be attrib-
ed to both an electron-withdrawing effect of the Br groups and a
nonplanarity of the macrocycle caused by steric factors. However,
significant red shifts in the UV-Visible spectra often serve as a
signature of porphyrins non-planarity. Nonplanar distortions in
cludes Ruffle, Saddle, Dome and Wave distortions well-estab-
lished for both synthetic porphyrins as well as for biological appli-
cations.

Figure 3. Schematic depiction of ruffled, saddled, domed and wavy
ed conformations. The black and white circles indicate displacem-
ts on opposite sides of the mean plane of the porphyrin.

The saddle conformation caused by Br groups on the nonplanarit-
y of the macrocycle is illustrated in Figure 4.

The presence of a large red shift for peripherally substituted non-
lunar porphyrins has also been proved by a number of studies wher-
ere the electronic effect of the substituents is more carefully contr-
olled for a series of porphyrins.

In addition, X-ray structure determination of the β-pyrrole bromi-
ated porphyrins proved the saddle-shaped conformation. In gen-
eral, porphyrin nonplanarity can cause the changes in the a1g and
HOMOs levels and the narrowing of the HOMO–LUMO gap by distorting D2h porphyrin complexes to those of D2 symmetry as observed for β-substituted TPFP (tetrakis (penta fluorophen-
yl)porphinato) complexes. This issue will be discussed in follo-
wing.

Figure 4. The saddle-shaped ZnTPPBr caused by Br atom substi-
ation.

These results suggest that UV-visible band red-shifts of β-pyrroli-
c substituted nonplanar porphyrins are potentially useful candi-
ates for the enhancement of light harvesting provided highly efficien-
cy dye sensitized solar cell based on Saddle-shaped porphyrins.

3. 2. DSSC measurements. Investigations into the solar energy c
ersion to electricity of the β-pyrrolic substituted porphyrins li-
ned to a semiconductor surface are rare. On the basis of eviden-
ces which mentioned in previous section, we expected the increa-
sing of overall conversion efficiency in brominated porphyrins co-
pared to non-brominated porphyrins.

Thus, DSSCs were fabricated using H2TCPP, ZnTCPPBr(X= 2 an-
d 8) as the sensitizers, with an effective area of 0.4 cm2, single-l
ayer TiO2 film with 10–15 μm thickness on FTO, and the electrol-
yte composed of 0.1 M LiI, 0.05 M I3, and 0.5 M 4-tert-butyl-pyri-
dine (TBP) in acetonitrile solvent. The photovoltaic performance
of the Zn-porphyrin-sensitized TiO2-cells was obtained. Figure 5
shows the J–V curve of DSSCs based on ZnTCPPBr.

Figure 5. J–V curve of DSSCs sensitized with H2TCPP, ZnTCPPBr,
and ZnTCPPBr.

The detailed parameters (Jsc, Voc, ff, and η) are summarized in Ta-
ble 2. The DSSCs based on brominated Zn-porphyrin dyes shows
a better comprehensive properties than DSSC based on H2TCPP
dye under AM 1.5 irradiation (100 mW cm–2).

Table 2: Photovoltaic performances of DSSCs sensitized with H2-
TCPP and ZnTCPPBr (x=2 and 8).

<table>
<thead>
<tr>
<th>Dye</th>
<th>Jsc (mA cm–2)</th>
<th>Voc (V)</th>
<th>FF (%)</th>
<th>H (%)</th>
<th>IPCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2TCPP</td>
<td>0.2</td>
<td>0.32</td>
<td>41</td>
<td>0.04</td>
<td>7.3</td>
</tr>
<tr>
<td>ZnTCPPBr2</td>
<td>0.7</td>
<td>0.50</td>
<td>57</td>
<td>0.22</td>
<td>14.1</td>
</tr>
<tr>
<td>ZnTCPPBr8</td>
<td>5.4</td>
<td>0.46</td>
<td>47</td>
<td>1.17</td>
<td>26.7</td>
</tr>
</tbody>
</table>

In accordance with UV-Vis results, linear relationship is observed
between photovoltaic performance of each compound and the nu-
ber of bromo substituent at the β-pyrrolic position of macrocycle.
It is easy to see that the Voc of H2TCPP dye is lower than that of
the brominated Zn-porphyrins. To a large extent, the two bromin-
ed Zn-porphyrin dyes display higher Jsc than H2TCPP. The differ-
et η values of the three porphyrin-sensitized primarily result from
the difference of Jsc. The biggest difference in Jsc values, between
the brominated dyes and non-brominated dye is because the effici-
ent injection of electrons into TiO2 conduction band. This subject
will be discussed in following.
Action spectrum, incident photon-to-electron conversion efficiency (IPCE) as a function of wavelength, was measured to evaluate the photoresponse of photoelectrode in the whole spectral region. Figure 6 shows the IPCE spectra of DSCs based on H₂TPPP, Zn(II)TPPPBr₆ and Zn(II)TPPPBr₈ dyes onto TiO₂. Three dyes can convert visible light to photocurrent in the range of 400-700 nm. Zn(II)TPPPBr₈ anchored TiO₂ gave broader spectra and higher photoresponse in the long wavelength region (>500 nm) than other dyes, which was consistent with the corresponding absorption spectra. IPCE performance clearly indicated that bromine substitution on porphyrin macrocycle makes the red-shift of IPCE spectra. FT-IR spectroscopy has been shown to be a powerful tool for extracting structural information of the molecules adsorbed onto a TiO₂ surface. Figure 7 shows FT-IR spectra of H₂TPPP, Zn(II)TPPPBrₓ and their complexes adsorbed onto TiO₂ films. Figure 7 shows spectra of dyes with a strong adsorption at 1702 cm⁻¹ attributable to the ν(C=O) stretching mode of the carboxylic acid group.

Figure 6. IPCE spectra of nanocrystalline TiO₂ films sensitized by H₂TPPP, Zn(II)TPPPBrₓ, X=2 and 8.

The FT-IR spectra of the adsorbed porphyrins onto TiO₂ film do not exhibit typical carboxylic acid vibrational modes, but they all show the presence of carboxylate asymmetric ν(-COO⁻) and symmetric ν(-COO⁻) bands at ~1625 and 1417 cm⁻¹, respectively. This indicates binding of the porphyrins to the TiO₂ rather than aggregation of the porphyrins on the surface. The difference between νas(COO⁻) and νs(COO⁻) (Δν), compared to the corresponding values in ionic (218 cm⁻¹), is currently used to determine the corresponding mode of the carboxylate group. The possible binding modes for porphyrins containing carboxylic acid groups on a TiO₂ surface are shown in Figure 8.

Figure 8. Possible coordination modes for carboxylate anions in the TiO₂ solid state.

On the basis of the FT-IR measurements, the difference between these bands in the ionic value (=218 cm⁻¹) and the adsorbed porphyrins (=208 cm⁻¹), together with other evidence that suggests that the carboxylate groups are bound to the TiO₂ surface via a bridging bidentate mode (III).

3. DFT and TD-DFT calculations. Initial calculations were performed on the synthesized porphyrins to determine the HOMO and LUMO levels of the Zn-porphyrins independently. After the initial calculations, the HOMO and LUMO levels were calculated and compared. These have known cell efficiencies of 0.04, 0.22 and 1.41 for (H₂TPPP), (Zn(II)TPPPBr₂), (Zn(II)TPPPBr₈), respectively (See Table. 3). Figure 9 shows the four highest and four lowest m
molecular orbital energy levels of the synthesized Zn-porphyrins. It is noteworthy that the HOMO and LUMO energy levels of the brominated Zn-porphyrins are relatively lower than those of the non-brominated porphyrin. However, higher stabilization of the LUMO levels relative to the HOMO ones makes the HOMO–LUMO gaps of the brominated Zn-porphyrins models smaller compared to that of the nonbrominated counterparts. This observation seems to be a good explanation for the enhancement of solar cell efficiency of the brominated Zn-porphyrins compared to the nonbrominated ones, as was evident by the experimental results. For the acceptor moieties, carboxylic acid is the main functional group, and it is a good anchoring functional group for titanium dioxide. 43

The relative positions of the LUMO levels for the donor and acceptor moieties are very important for charge transport to be effective. 44 The acceptor moieties cited above have a LUMO acceptor difference that ranges from approximately 0.21 to 0.75 eV, which is sufficient for charge transport. Figure 10 shows the HOMO and LUMO orbital spatial orientation of the brominated Zn-porphyrins and non-brominated porphyrin. Mizuseki et al. 45 suggested that the charge transport was related to the spatial distribution of the frontier orbitals. The HOMO should be localized in the donor moiety and the LUMO in the acceptor moiety. 39 In our calculations, in all porphyrin complexes their HOMO localized in the α and β positions of macrocycle ring region and their HOMO-1 localized in the pyrrolic ring nitrogens and meso-positions that adapted to frontier molecular orbitals (FMOs) of Gouterman’s four-orbital model. ZnTCPPBr$_{8}$ complex have eight bromine groups in their structure, which caused the more localization of the LUMO on the acceptor groups. The presence of zinc metal might be responsible for or the delocalization of both the HOMO and LUMO, suggesting the presence of a metal-to-ligand charge transfer (MLCT) or metal-centered transitions from both the metal and the ligand π-orbitals in the LUMO. 46 The electron-withdrawing substituents seem to localize the HOMO on their sides. The charge-separated state is on one of the main factors affecting solar cell efficiency. Based on our DFT calculations, brominated Zn-porphyrins generally have smaller HOMO–LUMO gaps than their nonbrominated counterparts. These results may provide structural guidelines for selecting the candidate porphyrin complexes to be used for higher-level calculations, which could provide actual electronic and structural information about the interface between the dye molecule and semiconductor. The result could also help as a qualitative selection process to synthesize porphyrins for developing an efficient DSSC.

As well as performed TD-DFT calculation in THF solution for these porphyrins. According to the Figure 2, there are two main transitions for the ZnTCPPBr$_{8}$ complex, in wavelengths 437 and 560 nm with f 1.71 and 0.07 respectively. In λ = 430 nm, electron transfer from HOMO-1 (e$_{a}$) to LUMO (e$_{g}$), which having percentage %38. When occur the electron transition from HOMO to LUMO, appear Q band at 553 nm in UV/Vis spectrum. Finally, there are two absorption bands at 495 and 740 nm for Zn TCPPBr$_{8}$ complex. In wavelength of 495 nm, electron transfer occurred from HOMO-1 (a$_{π}$) to LUMO+1 (e$^{*}_{π}$). In continuing, at λ = 740 nm, electrons transferred from HOMO-1 to LUMO with percentage % 49.1 that leads to appearance of the Q band. According to the calculations, through introduction any bromine atom on β-positions red-shifted Soret band about 5 nm. 47-50 H. J. Carillo et al. reported the first observation of a red shift of the Soret band upon β-pyryl bromination. 47 The decreased HOMO-LUMO gap and the multitudes of configuration interactions caused by the introduction of substituent at the periphery of the porphyrin ring have been suggested to explain the observed red shifts. 29, 30, 48-50

**3.4. Interfacial Electron Transfer Simulation.**

In focusing on photoinjection mechanisms from the excited electronic states of porphyrin, herein, improvement in the electron injection process to TiO$_{2}$ induced by the substitution of bromine atoms at the beta positions of H$_{2}$TCPP and the likely application to the design of an efficient ZnTCPPBr$_{8}$-sensitized solar cell are examined. The Soret and Q bands of porphyrins are associated with an electronic displacement towards the periphery of the aromatic macrocycle. 41 Accordingly, in the excited states of porphyrins, the meso substituents may be considered as the donor part of the macrocycle. Also, upon the coordination of H$_{2}$TCPP and ZnTCPPBr$_{8}$ to the surface of TiO$_{2}$, the Ti(IV) centre acts as the acceptor part, due to the Lewis acid strength of the Ti(IV) centre.
cation. It should be noted that the oxygen atoms of the –COOH groups, can form strong bonds with the Ti(IV) atom. Surface sensitization involves the adsorption of a porphyrin to TiO₂ surface and the formation of a porphyrin-TiO₂ surface complex. Photoexcitation of the surface complex will lead to interfacial electron transfer when there is appropriate energy match between the photoexcited electronic state in the surface complex and the electronic states in the conduction band of the TiO₂ semiconductor. Injection times as short as a few femtoseconds have been investigated for various systems whereas charge recombination in the micro to millisecond time scale. This result is a sign of the nuclear motion cannot be the rate-determining factor in the underlying IET mechanisms. Therefore, the results of simulations of IET allow us to predict the net rates and probabilities of IET into TiO₂ semiconductor. To investigate the interaction between the sensitizer LUMO orbital and the substrate conduction band, we have made a detailed investigation of the adsorbate LUMO DOS. The density of states (DOS) obtained by the extended Hückel (eH) method for all porphyrin adsorbed on TiO₂ is presented in Figure 11.

![Density of states](image)

Figure 11. Density of states (DOS) calculated by the extended Hückel theory for functionalized TiO₂ anatase nanostructures with H₂TCPP (a), ZnTCPPBr₂ (b) and ZnTCPPBr₈ (c) adsorbed to the (101) surface of TiO₂ and a bare TiO₂ anatase nanostructure.

Table 3. The percent of electron injection from adsorbates to TiO₂ anatase crystal at first 25fs after photoexcitation

<table>
<thead>
<tr>
<th>Time(fs)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂TCPP</td>
<td>0%</td>
<td>0.50%</td>
<td>1.85%</td>
<td>0.86%</td>
<td>2.22%</td>
<td>2.49%</td>
</tr>
<tr>
<td>ZnTCPPBr₂</td>
<td>0%</td>
<td>3.04%</td>
<td>6.17%</td>
<td>4.03%</td>
<td>5.00%</td>
<td>8.75%</td>
</tr>
<tr>
<td>ZnTCPPBr₈</td>
<td>0%</td>
<td>4.83%</td>
<td>17.32%</td>
<td>35.68%</td>
<td>51.06%</td>
<td>65.69%</td>
</tr>
</tbody>
</table>
Figure 12. Panels a, b, and c show nanostructures extended along the [101], [010], and [-101] directions in the anatase crystal.

Figure 13. Time-dependent survival probability in sensitized nanostructures extended along the [-101], [010] and [101] crystallographic direction in the TiO$_2$ anatase crystal.
The filled solid curve at the bottom of the graph represents the projected density of states on the H₂TCPP, ZnTCPBPBr₂ and ZnTCPBPBr₈ basis functions. The DOS plot shows the presence of energy levels from the ZnTCPBPBrₓ-adsorbate in the band gap of TiO₂. Moreover, Figure 11 clearly shows that the investigated systems differ both in the exact position of the LUMO level and the degree to which the sensitizer LUMO orbital mixes with the substrate conduction band. Additionally, there is a number of virtual orbitals (LUMOs) positioned within the conduction band.

Table 3 shown The percent of electron injection from adsorbates ount the distance of 2 Å.

A good overlap of these orbitals is mandatory for efficient charge injection. The better overlap between energy levels of LUMO of dye (donor) and the conduction band of TiO₂ (acceptor) is believed to play a crucial role making more favorable the electron injection. In Fig. 6, the energy levels of LUMO of ZnTCPBPBr₂ , ZnTCPBPBr₈ and the conduction band potential of TiO₂ lies at 3.11, 3.64 and 4.2 eV, respectively . It is clear that electron injection from the excited dyes molecules into the conduction band of the semiconductor is possible, as the driving force for charge displacement into the oxide is about 1.0 eV for the ZnTCPBPBr₂ dyes, whilst for ZnTCPBPBr₈ it is only 0.46 eV. The excited state of ZnTCPBPBr₂ dye matches better the lower bound of the conduction band of the semiconductor than the LUMOs of the H₂TCP and ZnTCPBPBr₂ dyes, thus minimizing the energetic losses during the electron transfer process. It is important to investigate the convergence properties of the simulation results with respect to the size of the system. This is accomplished by checking convergence in the electron injection times in nanostructures extended along the [-101], [010], and [101] crystallographic directions.

Figure 12 shows extended structures generated by replicating nanostructures along the three [-101], [010], and [101] crystallographic directions.

Smith and Nozik have investigated 1-dimensional and 3-dimensio nal model systems in an effort to understand the central aspects of interfacial electron transfer as well as the limitations of theoretical approaches such as the Landau-Zener approximation 4 and the Anderson Hamiltonian approach. 22, 66 The distance bond length bet

ween the carboxylic groups of formic acid and TiO₂ anatase (101) surfaces represents approximately 2.10, 2.08, 30, 67, 68 As earlier reports on porphyrin adsorbed on TiO₂ surface and FT-IR results, w e connect the four dyes under identical conditions to take into acc ount the distance of 2 Å.

Table. 3 shown The percent of electron injection from adsorbates to TiO₂ anatase crystal at first 25 fs after photoexcitation for initial model system. The result as well as shown porphyrin structure substitution of bromine atoms at β pyrrole positions, electron injection is much better and because of the increased efficiency in this category of porphyrins clearly indicates. Figure 13 shows results for the survival probability p_{surv}(t) obtained from simulations of electron injection in nanostructures extended along the[101], [-101] and [010] directions. Exponential fitting curves to p_{surv}(t) define the approximate characteristic times for the two electron-injection steps in nanostructures extended along the [-101] [010], and [101] direction. The IET rates, >450, ~125, and 25 fs, are observed for the H₂TCP, ZnTCPBPBr₂ and ZnTCPBPBr₈, respectively. On the basis of our IET simulations, the excited states of ZnTCPBPBrₓ x=2 and 8 will lead to the electron injection into TiO₂, since they have significant electron population on the phenyl (COOH) ligand attached to the nanoparticle.

Figure 14. Evolution of time-dependent charge distribution during the early time relaxation dynamics after instantaneously populating the ZnTCPBPBrₓ-LUMO. The individual frames show snapshots of an electronic density isosurface at intervals of 125 fs.

Figure 14 and 15 show a quantitative description of the survival probability as a function of time after instantaneously populating the ZnTCPBPBrₓ (x=2 and 8)-(LUMO) in nanostructures extended along the [-101] directions in the TiO₂-anatase crystal. Note that the frames in Figure 14 describe the electron injection at first 0, 5, 10, 15, 20 and 25 fs. As our calculation results and previous experimen tal evidences, the electron injection from excited porphyrin dyes to TiO₂ conduction band usually occurs very rapidly in the femtosecond–picosecond time domain, therefore natural decay of excited porphyrin dyes cannot compete kinetically with charge-transfer processes.

According to classical theory of electronic transfer developed by Marcus and Hush, the rate of electron transfer, k₉₇ between discrete donor and acceptor levels under non-adiabatic conditions is given by 24, 69

\[
k = \frac{2\pi}{\hbar} \frac{H^2}{\sqrt{4\pi\lambda K_BT}} \exp\left[-\frac{(\lambda_t + \Delta G_0)}{4\lambda_t K_BT}\right]
\]

Where H² is the electronic coupling between donor and acceptor state, ΔG₀ the free energy driving force for electron transfer, λₜ the total reorganization energy, T the absolute temperature and h and K_B the radial Planck and Boltzmann constants respectively. The electronic coupling decreases exponentially with increasing distance, d, between the donor and the acceptor as

\[
H^2 = H^2_0 \exp(-\beta d)
\]

Where β is related to the properties of the medium between donor and acceptor, and H₀² is the coupling at distance d=0. Therefore, the distance between eg* of porphyrin and conduction band of TiO₂ has an important effect on the rate of electron transfer (k₉₇) and the shortest distance between eg* of porphyrins and CB of TiO₂ is realized in ZnTCPBPBr₈. As shown in Table 3, the electron-injection mechanism from ZnTCPBPBr₈ involves ultrafast interfacial processes where the initial population in the
excited electronic state of the molecular adsorbate decays to about 66% in about first 25 fs. At the same time, the initial population for the excited-state interfacial electron transfer in ZnTCPPBr₂ and H₂TCPP decay about 8% and 2%, respectively.

The analysis of the time-dependent charge distribution also indicates that the population of the ZnTCPPBr₂ adsorbate depends on the number of substituted bromine atom, which decays during the different first time scale of dynamics due to a primary electron-injection event. This process concentrates the injected charge in δₓ, orbitals, next to the surface complex, including the hexa coordinated Ti⁴⁺ ion and the Ti⁴⁺ ions that anchor the photoexcited ZnTCPPBr₂ adsorbate. The following relaxation mechanism involves charge diffusion and surface-charge separation. Interestingly, the electron injection at first 10 fs is slower than second 10 fs in ZnTCPPBr₂ (Table 3). IET results of ZnTCPPBr₂ indicate that the time relaxation can be investigated by an ultrafast (τ=25 fs) electron-injection event that involves a population decay in the molecular adsorbate to about 67% during the first 25 fs of dynamics. Therefore, IET simulation is clearly demonstrated that the increasing of charge distribution is one of accounts for higher conversion efficiency in ZnTCPPBr₂.

Figure 15. Evolution of time-dependent charge distribution during the early time relaxation dynamics after instantaneously population for the excited-state interfacial electron transfer in ZnTCPPBr₂-LUMO. The individual frames show snapshots of an electronic density isosurface at intervals of 5 fs.

We expected that the various fundamental properties elaborated in this study would be beneficial to the future development of halogenated-porphyrin sensitizer for use as DSSCs.

The authors wish to thank the University of Zanjan for financial supports.

4. Conclusion

We have shown that the substitution of bromine atoms at β-pyrrolic positions in 5, 10, 15, 20-tetraakis(4-carboxyphenyl) porphyrin zinc(II) complexes has an effect on the photovoltaic performance a nd life times of the excited electronic states, which, in turn, can influence the electron transfer process between the dyes and the conduction bands of the TiO₂. In addition, the dramatic red-shift in excitation energies observed experimentally and theoretically upon β-bromination of the porphyrin are qualitatively reproduced by the calculations using H₂TCP, ZnTCPBB₃ and ZnTCPBB₂. The results of DFT and TD-DFT calculations suggest that the changes in the electronic absorption spectra of the fully β-brominated porphyrin can be attributed to nonplanarity of the porphyrin macrocycle caused by steric factors. Finally, this view that the large red shifts seen in the UV-visible absorption bands of β-pyrylic substitut ed nonplanar porphyrins are the result of saddle-shaped deformation of the porphyrin macrocycle has been employed for enhancement in the harvesting in DSSCs.

Although this work does not decide to show an easy rationalization of various parameters, it is clear that bromo substituents at β-pyrrolic positions in porphyrins affect its light harvesting ability in dye sensitized solar cells. This paper opens the way for a more in depth investigation of this new approach.

References


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Graphical abstract: