FULL PAPER

# Zinc–Porphyrin Dyes with Different *meso*-Aryl Substituents for Dye-Sensitized Solar Cells: Experimental and Theoretical Studies

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Abstract: A series of new zinc-porphyrin dyes that contain different *meso* substituents (phenyl, carbazole phenyl, and carbazole thiophenyl groups) and bithiophenyl cyanoacrylic acid as the  $\pi$ -conjugated anchoring moiety were designed, synthesized, and characterized as sensitizers for dye-sensitized solar cells (DSSCs). The effects of these *meso* substituents on the properties of the porphyrin dyes were theoretically and experimentally investigated. By *meso* substitution of the porphyrin ring with carbazole-aryl moieties, the short-circuit current  $(J_{sc})$  and opencircuit voltage  $(V_{oc})$  of the DSSCs were improved as was the power conversion

**Keywords:** carbazoles • dyes/ pigments • porphyrinoids • substituent effects • zinc efficiency ( $\eta$ ) owing to the influence of both the suppression of dye aggregations and the enhanced charge separation and charge-injection efficiency of the dye to TiO<sub>2</sub> films. Among these dyes, ZnPCPA made of the carbazole phenyl *meso* substituents gave rise to the highest  $\eta$  of 6.24% ( $J_{sc}$ = 13.38 mA cm<sup>-2</sup>,  $V_{oc}$ =0.66 V, and fill factor of 0.71).

# Introduction

Dye-sensitized solar cells (DSSCs) have arisen as one of the promising technologies for renewable energy on account of their low cost, ease of assembly, and decent conversion efficiency.<sup>[1]</sup> To date, a variety of dye sensitizers including transition-metal complexes,<sup>[2]</sup> porphyrins,<sup>[3]</sup> and metal-free organic molecules<sup>[4]</sup> have been investigated to improve the ef-

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ficiency of DSSCs and to realize their structure-property relationship. The use of organic dyes is primarily attractive owing to their easy structural modifications, easy purification, and low production cost.<sup>[5]</sup> To achieve high-performance sensitizers, many studies have focused on improving the following key properties of the dye molecule: (i) enhancing the light-harvesting efficiency, (ii) subduing the trend of dye aggregations, and (iii) decreasing the charge recombination at the  $TiO_2$  and the triiodide ion  $(I_3^-)$  interfaces. Among these dyes, porphyrin has attracted a great deal of attention because of its natural role in photosynthesis, its intense absorption in the visible region, its high stability, and the relative ease with which functional groups can be attached to its basic structure.<sup>[6]</sup> Although incredible improvement has been achieved recently for porphyrin-dye-based DSSCs with a power conversion efficiency  $(\eta)$  reaching a new record of 13% for SM315 dye,<sup>[7]</sup> this still lags behind the performance of the challenging 16.7% efficiency of the DSSC that used an organometal halide perovskite (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>) as a dye sensitizer.<sup>[8]</sup>

From the Goutermann orbital model of porphyrin (Figure 1), in the ground state, the highest-occupied molecular orbitals (HOMOs)  $(a_{1u} \text{ or } a_{2u})$  have their orbital density mostly on the porphyrin *meso* positions and the nitrogen atoms with a small amount of electron density on the  $\beta$ -pyrrolic positions. In the excited state, the electrons go into the lowest-unoccupied molecular orbitals (LUMOs)  $(e_g)$ , which have their electron density on the  $\beta$ -pyrrolic and *meso* positions. This means that a porphyrin functionalized through the *meso* positions would be expected to show a strong effect on the properties of the macrocyclic core, especially

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Figure 1. The Gouterman orbital models for the HOMO and LUMOs of porphyrin.

with electron-donating arylamine or carbazole groups. Furthermore, its inherent LUMO level is situated above the conduction band of TiO<sub>2</sub>, and its 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.<sup>[9]</sup> So far, a large number of porphyrins have been developed as sensitizers for DSSCs such as carboxyphenyl metalloporphyrins ( $\eta =$ 0.2-3.6%);<sup>[10]</sup> thiophene-, olefin-, and acetylene-linked porphyrins ( $\eta = 3.6-5.1$  %);<sup>[11]</sup> quinoxaline-fused porphyrins ( $\eta =$ 5.2–6.5%);<sup>[12]</sup> zinc–zinc porphyrin dimers ( $\eta = 2.1-5.5$ %);<sup>[13]</sup> bacteriochlorin ( $\eta = 1.1-6.6\%$ );<sup>[14]</sup> 2,4-pentadienoic acid  $\beta$ pyrrolic-functionalized porphyrins  $(\eta = 3.03 - 7.47\%)$ ;<sup>[15]</sup> phe- $(\eta = 0.25 - 6.12\%);^{[16]}$ nylethynyl-substituted porphyrins meso-(diarylamino)-substituted porphyrins  $(\eta = 3.8 -$ 13%);<sup>[7,17]</sup> 4-ethynylstyryl β-pyrrolic-functionalized porphyrins  $(\eta = 4.3 - 7.1 \%)$ ;<sup>[18]</sup> and acene-modified porphyrins  $(\eta =$ 0.10-5.44%).<sup>[19]</sup> The performances of these porphyrins varied depending on the chemical structure. Hence, a further structural modification and improvement of the porphyrinbased dye is still a challenge and needs to be carried out. In this work, we therefore present the design, synthesis, characterization, and properties of new functionalized porphyrin dyes. We explore the possibility of improving the photovoltaic performance of porphyrin-based DSSCs by tuning the spectral and electrochemical characteristics of the porphyrin dyes. The target zinc-porphyrins contain bithiophenyl cyanoacrylic acid as the  $\pi$ -conjugated anchoring moiety and different meso substituents (phenyl, carbazole phenyl, and carbazole thiophenyl groups). Varying the type of the meso substituents would provide a rational study of the effect of the electron-donating properties, the bulkiness of the carbazole, and the charge-transfer properties of the phenyl and thiophenyl linkages on the properties of the dyes. The use of bithiophenyl cyanoacrylic acid would offer an effective electron-transfer bridge from the porphyrin core to the TiO<sub>2</sub> film as observed in most of the high-efficiency organic dyes.<sup>[4,20]</sup> The theoretical and experimental investigations of the optical and physical properties and their applications as sensitizers in DSSCs are also reported.



## **Results and Discussion**

# Synthesis and Characterization

The synthetic route to the design of meso-substituted zincporphyrin dyes ZnPPA, ZnPCPA, and ZnPCTA is presented in Scheme 1. We began with the synthesis of aryl aldehydes 1,<sup>[21]</sup> 6, and 7. Aldehydes 6 and 7 were prepared by the Ullmann coupling of 3,6-di-tert-butylcarbazole with bromoaryl aldehydes 5 and 2 catalyzed by Pd(OAc)<sub>2</sub>/PPh<sub>3</sub>/K<sub>2</sub>CO<sub>3</sub> in oxylene under reflux conditions, respectively. The 5-(2-bromothiophenyl)-10,15,20-triaryl-substituted zinc-porphyrins 3, 8, and 9 were then formed by the condensation of a 1:3 mixture of 5-bromothiophene-2-carbaldehyde (2) and the relevant aldehydes 1, 6, or 7 with pyrrole in the presence of trifluoroacetic acid (TFA) as the acid catalyst in CH<sub>2</sub>Cl<sub>2</sub> followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Subsequently, the mixture of mono-, di-, and tri-2-bromothiophenyl meso-substituted free-base porphyrins formed was metalated with Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub>/MeOH heated at reflux to facilitate the separation of these mixed porphyrins by column chromatography. The corresponding zinc-porphyrins 3, 8, and 9 were isolated in 5-8% yields. Coupling of 3, 8, and 9 with 5-formyl-2-thiopheneboronic acid catalyzed by  $[Pd(PPh_3)_4]/2M$  Na<sub>2</sub>CO<sub>3</sub> in THF afforded the relevant porphyrin aldehydes 4, 10, and 11 in 58-65%. Knoevenagel condensation of these aldehydes with cyanoacetic acid in the presence of piperidine in MeOH under reflux conditions gave the target zinc-porphyrin dyes ZnPPA, ZnPCPA, and ZnPCTA as dark purple solids in good yields of 76-84%. The chemical structures of the porphyrin dyes were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, IR, and MALDI-TOF mass spectrometry.

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Scheme 1. Synthesis of the zinc-porphyrin dyes. Reagents and conditions: (i) a) pyrrole, TFA,  $CH_2Cl_2$ , room temperature, then DDQ; b) Zn-(OAc)\_2-2H\_2O, CH\_2Cl\_2/MeOH, heat; (ii) 5-formyl-2-thiopheneboronic acid, [Pd(PPh\_3)\_4], 2M Na\_2CO\_3 (aqueous), THF, heat; (iii) 3,6-di-*tert*-butylcarbazole, Pd(OAc)\_2, PPh\_3, K\_2CO\_3, o-xylene, heat; and (iv) cyanoacetic acid, piperidine, MeOH, heat.

They exhibit good solubility in most organic solvents to allow dye adsorption onto the  $TiO_2$  film, and thus fabrication of DSSCs could be performed.

#### **Optical, Electrochemical, and Thermal Properties**

Optical properties of the zinc-porphyrin dyes ZnPPA, ZnPCPA, and ZnPCTA in a dilute solution of  $CH_2Cl_2$  and adsorbed onto  $TiO_2$  films are shown in Figure 2a, b, and the relevant data are summarized in Table 1. In solutions, the

UV/Vis absorption spectra of the dyes display characteristic absorptions due to the zinc-porphyrin, which consist of two sets of bands, namely, an intense Soret band that appears between 400 and 450 nm in each case and two much weaker Q bands (Q(1,0) and Q(0,0)) that appear between 550 and approximately 600 nm (Figure 2a). These characteristic absorption peaks arise on account of the configurational interaction of two porphyrin  $\pi$ - $\pi$ \* electronic transitions  $a_{1u}(\pi)$ and  $a_{2u}(\pi) \rightarrow e_g(\pi^*)$ . The constructive interaction corresponds to a strong allowed transition that gives rise to the Soret



Figure 2. Plots of UV/Vis absorption spectra of the dyes a) in  $CH_2Cl_2$  and b) adsorbed on  $TiO_2$  films. c) CV curves of the dyes measured in  $CH_2Cl_2$  with  $nBu_4NPF_6$  as a supporting electrolyte at a scan rate of 50 mV s<sup>-1</sup>.

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Table 1. Photophysical, physical, and electrochemical data of the zinc-porphyrin dyes.

Compound	$\lambda^{ m sol}_{ m abs}\left(arepsilon ight) \ \left[{ m nm}\left(10^5{ m m}^{-1}{ m cm}^{-1} ight) ight]^{[{ m a}]}$	$\lambda^{ m sol}_{ m abs} \ [nm]^{[b]}$	$\lambda_{em}^{sol}$ $[nm]^{[b]}$	$T_{5d}$ [°C] <sup>[c]</sup>	$E_{1/2}$ vs Ag/AgCl $[V]^{[d]}$	$E_{ m g}^{ m opt}/E_{ m g}^{ m ele}/E_{ m g}^{ m cal} \ [ m eV]^{ m [e]}$	HOMO/LUMO [eV] <sup>[f]</sup>
ZnPPA	418 (2.97), 546 (0.26), 590 (0.12)	424, 557, 600	607	510	-1.39, 0.77, 1.04	2.01/1.98/2.07	-5.13/-3.12
ZnPCPA	298 (0.76), 430 (2.34), 553 (0.25), 597 (0.11)	429, 560, 605	614	521	-1.38, 0.84, 1.10, 1.24	1.99/1.97/2.10	-5.22/-3.23
ZnPCTA	297 (0.72), 438 (1.68), 561 (0.20), 609 (0.09)	434, 564, 611	626	518	-1.39, 0.84, 1.30	1.98/1.95/2.10	-5.19/-3.21

[a] Measured in CH<sub>2</sub>Cl<sub>2</sub>. [b] Measured as dyes adsorbed on TiO<sub>2</sub>. [c] Obtained from TGA measured at 10 °C min<sup>-1</sup> under N<sub>2</sub>. [d] Obtained from CV measured in CH<sub>2</sub>Cl<sub>2</sub> at a scan rate of 50 mV s<sup>-1</sup> and  $nBu_4NPF_6$  as electrolyte. [e] Calculated from  $E_g^{opt} = 1240/\lambda_{onset}$ ;  $E_g^{ele} = E_{onset}^{ee} - E_{onset}^{oas}$ ;  $E_g^{ela}$  calculated with the TD-B3LYP/6-31G(d,p) basis set in CH<sub>2</sub>Cl<sub>2</sub> solvent by the C-PCM model. [f] Estimated from HOMO =  $-(4.44 + E_{onset}^{oas}; LUMO = E_g^{opt} + HOMO)$ .

band, whereas the destructive interaction corresponds to a weak disallowed transition that gives rise to the Q bands at longer wavelength. In most porphyrins, in response to the absorption of light, rapid population of the lowest-energy excited singlet state occurs owing to fast nonradiative transitions. In the cases of ZnPCPA and ZnPCTA, the additional absorption peak due to the  $n-\pi^*$  transition of carbazole peripheries is observed at approximately 298 nm. These dyes exhibit high molar extinction coefficients ( $\varepsilon = 2.97 - 1.49 \times$  $10^5 \,\mathrm{M^{-1} \, cm^{-1}}$ ) at the Soret bands. Upon replacement of the phenyl meso substituents of ZnPPA with the carbazole-aryl units, the Soret bands shifted toward longer wavelengths from 418 to 430 and 438 nm for ZnPCPA and ZnPCTA, respectively (Table 1). A similar pattern is observed for the Q bands: the Q(0,0) bands redshift from 590 nm for ZnPPA to 597 and 609 nm for ZnPCPA and ZnPCTA, respectively. These spectral shifts are consistent with literature reports.<sup>[22]</sup> thus indicating that there is electronic coupling between the carbazole substituent and the porphyrin ring, and the  $\pi$  conjugation of ZnPCPA and ZnPCTA becomes extended. The spectral features of ZnPCPA and ZnPCTA with broad Soret band and redshifted Q bands serve to increase the harvesting of solar energy in a DSSC device, as explained in the next section.

The absorption spectra of ZnPPA, ZnPCPA, and ZnPCTA adsorbed on TiO<sub>2</sub> films show broader absorption peaks than those in solution (Figure 2b). Such a phenomenon is commonly observed in the spectral response of other organic dyes, which might be ascribed to the interaction of the anchoring groups of the dyes with the surface of TiO<sub>2</sub>.<sup>[23]</sup> The wide absorption spectrum is an advantageous spectral property for light harvesting of the solar spectrum. For the fluorescence spectra (see the Supporting Information), major emission bands of the porphyrins were observed at 607, 614, and 626 nm for ZnPPA, ZnPCPA, and ZnPCTA, respectively. The trend for the ZnPCPA and ZnPCTA emissions redshifted from that of ZnPPA is similar to the trend of the Soret and Q-band absorption spectra.

The electrochemical properties of solutions of ZnPPA, ZnPCPA, and ZnPCTA were examined by cyclic voltammetry (CV) in CH<sub>2</sub>Cl<sub>2</sub> with  $nBu_4NPF_6$  as a supporting electrolyte (Figure 2c and Table 1). Their CV traces exhibit a single process of quasi-reversible reduction at the same potential ( $E_{1/2}$ ) of -1.39 V associated with the reduction of the zincporphyrin ring to form the anion radical. Dyes ZnPPA and ZnPCTA exhibit two quasi-reversible oxidation processes, whereas ZnPCPA displays three quasi-reversible oxidation processes. The first oxidation wave is attributed to removal of electrons from the zinc-porphyrin center to result in porphyrin radical cations. It is noteworthy that the first oxidation potential of ZnPPA ( $E_{1/2}=0.77$  V) occurs at a lower potential than that of ZnPCPA and ZnPCTA ( $E_{1/2}=0.84$  V), thus supporting the notion that the porphyrin moiety is perturbed by the meso substitution with carbazole, as observed in the optical properties. Multiple CV scans of ZnPPA, ZnPCPA, and ZnPCTA display unchanged CV curves that indicate electrochemically stable molecules. The HOMO and LUMO energy levels of ZnPPA, ZnPCPA, and ZnPCTA calculated from their oxidation onset potentials  $(E_{\text{onset}}^{\text{ox}})$  and optical energy gaps  $(E_{\text{g}}^{\text{opt}})$  are listed in Table 1. Their HOMO levels are -5.13 eV for ZnPPA, -5.22 eV for ZnPCPA, and -5.19 eV for ZnPCTA, which are lower than the redox potential of the  $I^{-}/I_{3}^{-}$  electrolyte (-4.80 eV). Hence, dye regeneration should be thermodynamically favorable and could compete efficiently with recapture of the injected electrons by the dye radical cations. The LUMO levels of the dyes estimated from the relevant HOMOs and energy gaps  $(E_g^{opt})$  obtained from the optical onset are -3.12 eV for ZnPPA, -3.32 eV for ZnPCPA, and -3.21 eV for ZnPCTA. The LUMOs are less negative than the conduction band (CB)-edge energy level of the TiO<sub>2</sub> electrode (-4.00 eV versus vacuum),<sup>[24]</sup> thus promising effective charge injection from the excited dyes to the conduction band of TiO<sub>2</sub>. Therefore, all new zinc-porphyrin dyes have enough energetic driving force for efficient  $TiO_2$  and  $I^-/I_3^-$ -based DSSCs. On the basis of the CV data, the energy gaps  $(E_{\alpha}^{\text{ele}})$  of these dyes are also calculated to be in the range of 1.95-1.98 eV, which are close to those estimated from their corresponding UV/Vis absorption spectra ( $E_{a}^{opt} = 1.98$ -2.01 eV), thus indicating that the LUMO and HOMO levels obtained by the electrochemical measurements are reliable (Table 1).

The thermal properties of the zinc-porphyrin dyes ZnPPA, ZnPCPA, and ZnPCTA were investigated by thermogravimetric analysis (TGA), and the results suggested that they are thermally stable materials, with temperature at 5% weight loss ( $T_{\rm 5d}$ ) well over 510°C (Table 1). The high thermal stability of the dye is essential for the lifetime of the solar cells.<sup>[25]</sup>

#### **Quantum Chemical Calculations**

To gain insight into the geometrical, electronic, and optical properties of ZnPPA, ZnPCPA, and ZnPCTA, we carried

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Figure 3. Structures of porphyrins ZnPPA and ZnPCTA optimized by B3LYP/6-31G(d,p).

out quantum chemical calculations. The ground-state geometries of these dyes were fully optimized by the B3LYP/6-31G(d) method<sup>[26]</sup> and are displayed in Figure 3 and the Supporting Information. In all cases, the calculated groundstate geometries reveal that the meso-substituted aryl rings are twisted nearly perpendicular to the planar macrocyclic zinc-porphyrin core; the dihedral angles are in the range of approximately 68-88°. The end-capped carbazoles of ZnPCPA and ZnPCTA are twisted from the phenyl and thiophenyl rings by about 36-44° and bent out of the plane of the porphyrin ring, thus creating bulky substituents around the porphyrin core. This could influence the  $\pi$ - $\pi$  stacked aggregation of the dye molecules and the amount of dye loading on TiO<sub>2</sub> films, the photoelectron injection efficiency from the dye to the  $TiO_2$  electrode, and thereby the overall conversion efficiency. As depicted in Figure 3, ZnPCPA and ZnPCTA have bulkier molecular structures than ZnPPA. As

an electron donor, the end-capped carbazole can pump the electron into the porphyrin and push the excited electrons spatially in the direction of the TiO<sub>2</sub> film. Considering the conformation of the aryl rings that connect between the carbazole and porphyrin ring, the dihedral angles ( $\varphi$ ) between these moieties will have a direct influence on such electron transfers. As shown in Figure 4, the dihedral angles ( $\varphi$ ) between the phenyl linkage and porphyrin ( $\varphi_1$ =68.42°) and carbazole ( $\varphi_2$ =36.12°) units of ZnPCPA are smaller than those of the thiophenyl linkage and porphyrin ( $\varphi_1$ =87.74°) and carbazole ( $\varphi_2$ =44.05°) units of ZnPCTA. These findings imply that delocalization or injection of the  $\pi$  electron from the *meso*-substituted carbazole into the porphyrin core in ZnPCTA would be less efficient than in ZnPCPA.

It is very useful to determine the electronic distribution of the HOMO and LUMO of the dyes, as these can offer a sensible qualitative indication of the charge-separated state of sensitizers. To generate an efficient charge-separated state, the HOMO should be localized on the donor subunit and the LUMO on the acceptor moiety.<sup>[27]</sup> The electron-density distributions of ZnPPA, ZnPCPA, and ZnPCTA calculated at the B3LYP/6-31G(d,p) level are illustrated in Figure 5. The frontier molecular orbital shows that in the LUMOs of all dyes, the excited electrons localize on the entire  $\pi$ -conjugated anchoring moiety of bithiophenyl cyanoacrylic acid. The electron-density distribution of LUMOs around an anchoring group is known to influence the electronic coupling between the excited adsorbed dye and 3d orbital of TiO<sub>2</sub>.<sup>[28]</sup> In the HOMO of ZnPPA,  $\pi$  electrons are mainly delocalized on the porphyrin ring, whereas in the HOMOs of ZnPCPA and ZnPCTA,  $\pi$  electrons are delocalized over the  $\pi$  system of the porphyrin ring as well as the carbazole aryl meso substituents. During photoexcitation, electrons are transferred from the donor carbazole through the bithiophene cyanoacrylic acid to the surface-bound carboxylate. The HOMO



Figure 4. The selected bond lengths [Å] and dihedral angles [°] of the dyes calculated at the B3LYP/6-31G(d,p) level. R=bithiophenyl cyanoacrylic acid.

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Figure 5. The electronic distribution of the frontier molecular orbitals (HOMO and LUMO) computed at the B3LYP/6-31G(d,p) level.

and LUMO of all dyes were thoroughly separated, which favors a facile charge migration from the donor to acceptor upon irradiation. This is confirmed by the charge-density difference between ground and excited states as shown in Figure 6. Yellow and blue colors symbolize the decreased



Figure 6. A contour plot of the transition density difference  $(\rho S_1 - \rho S_0)$  calculated with the TD-PBE0/6-31G(d) basis set in CH<sub>2</sub>Cl<sub>2</sub>, The contour threshold is 0.004 a.u.

and increased electron contributions of the lowest-energy excitation ( $\rho S_1 - \rho S_0$ ), respectively. The density-difference plots of ZnPPA, ZnPCPA, and ZnPCTA exhibit an affectedly strong charge-separation character. Charge gained on the acceptor group after excitation is found in all cases. On the basis of these calculations, the dipolar structure present in the porphyrins of this study was expected to facilitate an efficient and rapid electron injection from the porphyrin excited state into the conduction band of TiO<sub>2</sub>. Moreover, within the present series of dyes, the charge-transfer effects were expected to be enhanced for ZnPCPA and ZnPCTA (which bear three carbazole aryl substituents) relative to ZnPPA.

To confirm the efficient electron injection from the porphyrin excited state into the CB of  $TiO_2$  in the device, the prototype system was modeled by dyes ZnPPA and ZnPCPA adsorbed onto the  $(TiO_2)_{38}$  cluster. The optimizations were carried out by means of the Perdew–Burke–Ernzerhof (PBE)/double-numeric polarized (DNP) method implemented in the DMol<sup>3</sup> program.<sup>[29]</sup> The detail of the method is the same as in our previous work.<sup>[27,30]</sup> By using the bidentate binding mode of the carboxyl group (– COOH) on a TiO<sub>2</sub> anatase (101) surface, the two Ti–O bonds of the zinc–porphyrin–(TiO<sub>2</sub>)<sub>38</sub> complexes were found to be 2.16 Å with the calculated adsorption energy ( $E_{ads}$ ) of –12.79––13.14 kcalmol<sup>-1</sup> (see the Supporting Information), thus indicating strong chemical binding. The HOMO and LUMO orbitals of ZnPPA–(TiO<sub>2</sub>)<sub>38</sub> and ZnPCPA–(TiO<sub>2</sub>)<sub>38</sub> complexes are illustrated in Figure 7. The electron distribu-



Figure 7. The HOMO and LUMOs of ZnPPA– $(TiO_2)_{38}$  and ZnPCPA– $(TiO_2)_{38}$  calculated by PBE/DNP using DMol<sup>3</sup>.

tions in the HOMO orbital of the ZnPPA– $(TiO_2)_{38}$  complex are mainly localized on the porphyrin core, whereas in the HOMO of the ZnPCPA– $(TiO_2)_{38}$  complex, they are localized on both the porphyrin core and carbazole phenyl substituents. In the LUMO orbital of both complexes the entire excited electrons are distributed on the TiO<sub>2</sub> cluster. The results indicate that excited electrons efficiently transfer from the dye sensitizer to the conduction band of the TiO<sub>2</sub> cluster when the dye is absorbed onto the TiO<sub>2</sub> film under illumination. This character is defined as an interfacial direct charge-transfer injection mechanism.<sup>[27,30]</sup> This behavior of the electron transfer is highly consistent with the chargetransfer transition of isolated dyes, which is contributed by 67-69% (H $\rightarrow$ L). The above results imply that dyes ZnPPA and ZnPCPA with bithiophene as the conjugated bridge and

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cyanoacrylic acid as the anchoring moiety have sufficient potential to inject an electron from the porphyrin core into the conduction band of  $TiO_2$  film.

#### **Photovoltaic Properties**

To investigate the effects of the meso substituents on the photovoltaic performances of the porphyrin dyes, the DSSCs using the newly synthesized dyes ZnPPA, ZnPCPA, and ZnPCTA as sensitizers were fabricated and their performances were measured under AM 1.5G conditions at 100 mW cm<sup>-2</sup>. The solar cells with an effective area of  $0.25 \text{ cm}^2$  were composed of TiO<sub>2</sub> film with 14 µm (9 µm transparent+5 µm scattering) thickness, the adsorbed dye (from  $6 \times 10^{-4}$  M solutions), a redox electrolyte (Z960 electrolyte: 1.0м 1,3-dimethylimidazolium iodide (DMII), 0.1м guanidinium thiocyanate (GuSCN), 0.03 M I<sub>2</sub>, 0.05 M LiI, and 0.5 M tert-butypyridine (4-TBP) in the mixed solvent of acetonitrile (CH<sub>3</sub>CN) and valeronitrile (VN) (85:15 v/v)), and a platinum on fluorine-doped SnO<sub>2</sub> (FTO) counter electrode. To evaluate the photovoltaic performance, five cells were prepared and measured under the standard conditions for each dye. The incident monochromatic photon-to-current conversion efficiency (IPCE) spectra and current-density-voltage (J-V) characteristics are plotted in Figure 8. The relevant photovoltaic parameters (average values) of the short-circuit current  $(J_{sc})$ , open-circuit voltage  $(V_{oc})$ , fill factor (ff), and power conversion efficiency ( $\eta$ ) are listed in Table 2. According to these results, it is clear that the photovoltaic performances of the DSSCs can be clearly affected by the modifications on the meso positions of the porphyrin ring. Solar cells fabricated with the dyes ZnPCPA and ZnPCTA that contain carbazole-N-yl benzene or carbazole-N-yl thiophene as the meso substituents, respectively, show significantly higher power conversion efficiencies than the cell fabricated with pristine zinc-porphyrin ZnPPA. The overall performances of the DSSCs are in the order of ZnPCPA ( $\eta = 6.25\%$ )>ZnPCTA ( $\eta = 5.09\%$ )>ZnPPA ( $\eta =$ 2.51%). The ZnPCPA-based cell exhibits the best performances (highest  $\eta$ ), clearly due to its high  $J_{\rm sc}$  (13.38 mA cm<sup>-2</sup>),  $V_{\rm oc}$  (0.66 V), and IPCE efficiency (>70% in the range 360– 510 nm with a maximum of 94% at 442 nm), whereas the low  $\eta$  value of the ZnPPA-based cell derives from its low  $J_{sc}$ (6.23 mA cm<sup>-2</sup>),  $V_{oc}$  (0.57 V), and low IPCE value. The  $J_{sc}$  of the ZnPPA-based DSSC is lower than ZnPCPA and



Figure 8. a) J-V characteristics and b) IPCE spectra of the DSSCs.

ZnPCTA, which can be attributed to the poor charge-injection efficiency of the dye toward the TiO<sub>2</sub> film. The  $V_{oc}$  values of ZnPCPA- and ZnPCTA-based solar cells ( $V_{oc}$ = 0.66 V) are higher than ZnPPA ( $V_{oc}$ =0.57 V), thereby suggesting that charge-recombination processes of the injected electrons in TiO<sub>2</sub> and triiodide (I<sub>3</sub><sup>-</sup>) in the electrolyte of those cells are very diminished.<sup>[31]</sup> These observations could be explained by the effect of dye aggregation and electron-donating carbazole group attached at the *meso* positions of the porphyrin core.

The analyses of the optimum dye adsorption amounts on the TiO<sub>2</sub> films by the desorption method<sup>[32]</sup> reveal that the amount of dye loading on the TiO<sub>2</sub> photoanode of the ZnPCPA- and ZnPCTA-based DSSCs (1.33–1.50×  $10^{17}$  molecule cm<sup>-2</sup>) are lower than that of the ZnPPA-based cell ( $2.35 \times 10^{17}$  mol cm<sup>-2</sup>), thus confirming that the former dyes possess more bulky molecular structures (Table 2). Accordingly, the DSSC fabricated with ZnPPA dye as sensitiz-

Table 2. Photophysical, physical, and electrochemical data of the zinc-porphyrin dyes.

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Dye	Amount of dye adsorbed [molecule cm <sup>-2</sup> ] <sup>[a]</sup>	$J_{\rm sc}  [{\rm mA cm^{-2}}]$	$V_{ m oc} \left[ { m V}  ight]$	ff	η [%]	$R_{\rm CT}$ [ $\Omega$ ] at $-0.65$ V	$\tau$ [ms] at $-0.65$ V				
ZnPPA	$2.35 \times 10^{17}$	6.28	0.57	0.70	2.51	25.26	5.51				
ZnPCPA	$1.50 \times 10^{17}$	13.38	0.66	0.71	6.25	79.95	16.52				
ZnPCTA	$1.33 \times 10^{17}$	11.02	0.66	0.70	5.09	81.96	17.64				
ZnPPA+CDCA (1:2)	$1.97 \times 10^{17}$	7.93	0.63	0.70	3.50	_	_				
ZnPCPA+CDCA (1:2)	$1.02 \times 10^{17}$	12.66	0.67	0.71	5.99	-	-				
ZnPCPA+CDCA (1:5)	$8.91 \times 10^{16}$	11.99	0.66	0.69	5.51	-	-				
N719 <sup>[b]</sup>	$6.85 \times 10^{16}$	15.54	0.77	0.68	8.19	162.44	17.22				

[a] Measured by the desorption method.<sup>[32]</sup> [b] Electrolyte: A6141 electrolyte (0.6 M butylmethylimidazolium iodide (BMII), 0.03 M I<sub>2</sub>, 0.5 M 4-TBP, 0.1 M GuSCN in CH<sub>3</sub>CN/VN (85:15 v/v).

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er will experience a greater tendency to form  $\pi$ - $\pi$ -stacked dye aggregates on the TiO<sub>2</sub> surface than that of ZnPCPA and ZnPCTA. It has been known that dye aggregation can directly affect photoelectron injection efficiency of the dye and thereby the overall conversion efficiency.<sup>[33]</sup> The breakup of  $\pi$ -stacked aggregates might improve electron injection yield and thus  $J_{sc}$  values. The influence of dye aggregation on TiO<sub>2</sub> surfaces for ZnPPA and ZnPCPA dyes was therefore further investigated by coadsorption of ZnPPA and ZnPCPA with chenodeoxycholic acid (CDCA) (Table 2). The cell performance of ZnPPA improved upon addition of CDCA at a dye/CDCA ratio of 1:2, whereas that of ZnPCPA decreased in the presence of CDCA. The addition of CDCA increased both the  $J_{sc}$  and  $V_{oc}$  of the ZnPPA/ CDCA-based cell. This improvement in  $J_{sc}$  would take place through the coadsorbed CDCA to hinder the formation of dye aggregates and increase the electron injection yield and modify the TiO<sub>2</sub> electrode surface to increase electron interception,<sup>[34]</sup> whereas the increase in  $V_{oc}$  would be attributed to the decrease in charge recombination. The  $J_{sc}$  of the device has a maximum value at a dye/CDCA ratio of 1:2. The existence of CDCA, however, systematically decreases the amount of dye loading on the TiO<sub>2</sub> surface and reduces electron injection from dye to TiO<sub>2</sub>, thereby resulting in the lower  $J_{sc}$  in the case of ZnPCPA. The coadsorption of CDCA thus fails to improve the cell performance of ZnPCPA, unlike for ZnPPA and other organic sensitizers.<sup>[35]</sup> The overall performance of a porphyrin-based DSSC is thus a subtle balance between these factors. It is noticeable that the efficiency of the ZnPPA/CDCA-based solar cell ( $\eta =$ 3.50%) is still lower than that of ZnPCPA- and ZnPCTAbased cells ( $\eta = 5.09-6.24\%$ ), which suggests that the higher efficiencies of the latter devices might not only result from lower dye aggregations on TiO<sub>2</sub> owing to bulky carbazole substituents but also come from an electron-donating property of the carbazole.

The large J<sub>sc</sub> values of ZnPCPA- and ZnPCTA-based solar cells relative to that of the ZnPPA-based cell might arise from the effect of the broadly covering IPCE spectra. The IPCE spectra (Figure 8b) of the DSSCs that replicate absorption features of zinc-porphyrin are consistent with the measured  $J_{sc}$ ; they increase in the order of ZnPCPA  $(J_{sc} = 13.38 \text{ mA cm}^{-2}) > \text{ZnPCTA}$   $(J_{sc} = 11.02 \text{ mA cm}^{-2}) >$ ZnPPA ( $J_{sc} = 6.23 \text{ mA cm}^{-2}$ ). All three electron-donating carbazole groups attached at the meso positions of the zincporphyrin core of ZnPCPA and ZnPCTA not only extend the absorption spectrally to a region of greater wavelength but also push the excited electrons spatially toward the TiO<sub>2</sub> film for an enhanced charge separation, charge-injection efficiency of the dye, and thus  $J_{\rm sc}$ , as observed in the DFT calculations. The N-carbazole substituents in ZnPCPA and ZnPCTA can also reduce a recombination reaction between conduction-band electrons in TiO<sub>2</sub> and electron-accepting  $I_3^-$ , thus leading to the  $I_2^-$  radical anion, because  $I_3^-$  might attach to the positively charged N atom of the carbazole moiety far from the TiO<sub>2</sub> surface.<sup>[36]</sup> This process manifests itself as a dark current in limiting the photovoltage of the DSSCs. Moreover, the bulkiness of the molecular structures of ZnPCPA and ZnPCTA due to the carbazole substituents might be beneficial in retarding the electron transfer from TiO<sub>2</sub> to the oxidized dye or electrolyte, which would enhance the  $V_{oc}$  value. The slightly larger  $J_{sc}$  of the ZnPCPAbased cell than ZnPCTA can be tentatively attributed to a better electron transfer from the carbazole phenyl group to the acceptor moiety than that of the carbazole thiophenyl group as described in quantum chemical calculations.

The effect of the *meso* substituent of carbazoles on the essential interfacial charge-transfer processes in the DSSCs was also evaluated by electrochemical impedance spectroscopy (EIS) analyses. In general, the  $V_{\rm oc}$  of a DSSC is related to the electron transport at the interfaces or the electron lifetime in the cell.<sup>[37]</sup> The EIS was measured in the dark to describe the correlation between  $V_{\rm oc}$  and the molecular structure of a dye. The equivalent circuit is shown in Figure 9. The Nyquist plots of the DSSCs are shown by two semicircles (Figure 10a).



Figure 9. Equivalent circuit for the DSSCs.

The small and large semicircles, separately located in the high- and middle-frequency regions, are assigned to the charge transfer at the Pt counter electrode/electrolyte and the TiO<sub>2</sub>/electrolyte interface, respectively.<sup>[38]</sup> The charge-recombination resistance  $(R_{CT})$  at the TiO<sub>2</sub> surface can be deduced by fitting curves from the middle-frequency range using ZMAN software (Figure 10c and Table 2). The value of  $R_{\rm CT}$  is related to the charge-recombination rate between the injected electron and electron acceptor  $I_3^-$  in the electrolyte, estimated by radius of the larger semicircle. The ZnPCPA- and ZnPCTA-based DSSCs ( $R_{CT} = 79.26$  and 81.96  $\Omega$ ) exhibit significantly larger  $R_{\rm CT}$  values than the ZnPPA DSSC ( $R_{\rm CT}$ =25.26  $\Omega$ ), thus implying the slow rate of charge recombination or minor charge recombination at the TiO<sub>2</sub>/electrolyte interface, with a consequently high  $V_{\rm oc}$ for these cells. The  $R_{\rm CT}$  values of these DSSCs appear to agree with their  $V_{\rm oc}$  values. The decrease in  $R_{\rm CT}$  indicates the high charge loss in the TiO2/electrolyte interface and consequently a lower  $V_{\rm oc}$  value. The difference in  $V_{\rm oc}$  of these DSSCs can also be elucidated by the electron lifetime. Figure 10b shows the Bode plot for the DSSCs based on these three dyes. The position of the lower frequency peaks, which correspond to the large semicircle (Figure 10a, right) in the Nyquist plots, can be related to the electron lifetime  $(\tau)$  of the DSSCs. The electron lifetime can be extracted from the angular frequency  $(\omega_{\min})$  at the mid-frequency peak in the Bode phase plot using  $\tau = 1/\omega_{min}$  (Figure 10d and Table 2).<sup>[39]</sup> The  $\tau$  values of ZnPCPA- and ZnPCTA-based

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Figure 10. a) Nyquist plots and b) Bode-phase plots of the DSSCs. Plots of c)  $R_{CT}$  and d)  $\tau$  at different bias voltages ( $V_{bias}$ ) of the DSSCs.

solar cells ( $\tau$ =16.52 and 17.64 ms) are higher than that of ZnPPA ( $\tau$ =5.51 ms), which is consistent with the trend of their  $V_{oc}$  values. The high  $\tau$  values for ZnPCPA- and ZnPCTA-based solar cells support more effective suppression of the recombination of the injected electrons with  $I_3^-$  in the electrolyte by alternation of HOMO of the sensitizer, which leads to the enlargement of the photocurrent and photovoltage and to considerable improvement of the cell efficiency.

# Conclusion

In summary, we have demonstrated the design strategy and synthesis of novel meso-substituted zinc-porphyrin dyes that contain arylenes (benzene, phenyl carbazole, and thiophenyl carbazole) as donor and bithiophenyl cyanoacrylic acid as a  $\pi$ -linkage acceptor. The influence of the arylene substituents is clearly observed by the redshift in UV/Vis absorption spectra (both Soret and Q bands) and the shift of the redox potentials of the dyes. The DSSCs made of porphyrins with electron-donating carbazole substituents (ZnPCPA and ZnPCTA) show better performance than the ZnPPA reference cell. The superlative power conversion efficiencies of the ZnPCPA and ZnPCTA solar cells are due to their large  $J_{\rm sc}$  and  $V_{\rm oc}$  values. The large  $J_{\rm sc}$  values in ZnPCPA and ZnPCTA arise from their much broader and redshifted IPCE spectra because of the effective electronic coupling between the carbazole aryl groups and the porphyrin core. The electron-donating properties of the carbazole also pushes the excited electrons spatially toward the TiO<sub>2</sub> film for an improved charge separation, whereas the large  $V_{\rm oc}$ ZnPCPA values in and ZnPCTA come from the bulky structure of the carbazole aryl groups that can effectively suppress the porphyrin aggregations on the surface of the  $TiO_2$ films to result in the increase of the injected electrons and modification of the TiO<sub>2</sub> electrode surface to increase electron interception, and thus diminish a recombination between  $I_3^-$  and conduction-band electrons. Among the three syndye molecules, thesized ZnPCPA that contains carbazole phenyl as the meso substituent shows the maximum power conversion efficiency of  $(J_{\rm sc} = 13.38 \,\mathrm{mA\,cm^{-2}},$ 6.24%  $V_{\rm oc} = 0.66$  V, ff = 0.71) under simulated AM 1.5G irradiation  $(100 \text{ mW cm}^{-2})$ . Our results

thus indicate that the design of porphyrin dyes with bulky or/and electron-donating groups to avoid dye aggregation and improve the charge injection is effective in promoting cell performance for future porphyrin-based DSSC.

#### **Experimental Section**

#### Materials and Methods

All chemicals were purchased from Aldrich, Acros, or Thai companies and used as received. THF and CH2Cl2 for CV measurements were distilled according to the standard methods. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker AVANCE 300 MHz spectrometer. IR spectra were measured with a Perkin-Elmer FTIR spectrum RXI spectrometer. UV/Vis spectra were recorded in CH2Cl2 with a Perkin-Elmer UV Lambda 25 spectrometer. Diffuse reflectance spectra of dye adsorbed on TiO<sub>2</sub> were measured at room temperature with a Shimadzu UV-3101 spectrophotometer. BaSO4 was used as a standard. The measured reflectance spectra were then converted into absorption spectra by the Kubelka-Munk method. Thermogravimetric analysis (TGA) was performed with a Rigaku TG-DTA 8120 thermal analyzer with heating rate of 10°Cmin<sup>-1</sup> under an N<sub>2</sub> atmosphere. CV measurements were performed with an Autolab potentiostat PGSTAT 12 with a three-electrode system (platinum counter electrode, glassy carbon working electrode, and Ag/ AgCl reference electrode) in CH2Cl2 under an Ar atmosphere with  $nBu_4NPF_6$  as a supporting electrolyte at scan rate of 50 mV s<sup>-1</sup>. The concentration of analytical materials and the electrolyte were 10-3 M and 0.1 M, respectively. Melting points were measured with an Electrothermal IA 9100 series digital melting-point instrument and are uncorrected. MALDI-TOF mass spectra were recorded with a Bruker Daltonics (Bremen, Germany) Autoflex II matrix-assisted laser desorption/ionization/time-of-flight mass spectrometer (BIFEX).

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#### Synthesis of Zinc-Porphyrins 3, 8, and 9

Aryl aldehydes 1, 6, or 7 (15.70 mmol), 5-bromothiophene-2-carbaldehyde (2) (5.23 mmol), and pyrrole (20.93 mmol) were places in a dry round-bottomed flask and dissolved in CH22Cl2 (600 mL). The solution was degassed with N2. TFA (5.23 mmol) was added, and the reaction mixture stirred in the dark under an N2 atmosphere for 3 h. DDQ (7.851 mmol) was added, and the mixture was stirred for 1 h. Na<sub>2</sub>CO<sub>3</sub> (2.0 g) was added, and the mixture was filtered through a plug of silica by eluting with CH2Cl2. The solvent was reduced, and Zn(OAc)2·2H2O (7.851 mmol) and MeOH (50 mL) were added. The reaction mixture was heated under reflux conditions for 1 h. The solvents were removed to dryness, and the crude product was purified by column chromatography over silica gel by eluting with a mixture of CH<sub>2</sub>Cl<sub>2</sub>/hexane (20:80) and recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to give 3 as a purple solid (8%). M.p. > 250 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.54$  (s, 54 H), 7.48 (d, J =3.6 Hz, 1 H), 7.68 (d, J = 3.6 Hz, 1 H), 7.81–7.82 (m, 3 H), 8.10 (d, J =1.6 Hz, 6 H), 9.02 (s, 4 H), 9.03 (d, J=4.7 Hz, 2 H), 9.21 ppm (d, J= 4.7 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 31.45, 31.50, 31.76, 35.06, 109.79, 113.46, 120.91, 123.01, 123.72, 129.08, 129.56, 129.69, 131.16, 132.15, 132.82, 133.13, 141.64, 141.68, 145.82, 148.58, 148.64, 150.26, 150.51, 150.79, 150.92 ppm; IR (KBr):  $\tilde{\nu}$ =2963, 1592, 1475, 1363, 1248, 801, 713 cm<sup>-1</sup>; HRMS (ESI-TOF): m/z calcd for C<sub>66</sub>H<sub>73</sub>BrN<sub>4</sub>SZn [M]<sup>+</sup>: 1096.4031; found: 1096.4064.

Compound **8** was yielded as a purple solid (6%). M.p. > 250°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.56 (s, 54H), 7.52 (s, d, *J* = 3.6 Hz, 1 H), 7.64 (d, *J* = 8.7 Hz, 6H), 7.73 (d, *J* = 3.6 Hz, 1 H), 7.81 (d, *J* = 8.4 Hz, 6H), 8.01 (d, *J* = 8.1 Hz, 6H), 8.28 (s, 6H), 8.45–8.49 (m, 6H), 9.17–9.23 (m, 6H), 9.32 ppm (d, *J* = 4.8 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 32.09, 34.85, 109.50, 116.47, 121.04, 123.75, 123.86, 124.63, 129.28, 131.93, 132.26, 132.48, 133.47, 135.71, 138.00, 139.34, 141.03, 141.17, 143.25, 150.18, 150.44, 150.64, 151.26 ppm; IR (KBr):  $\tilde{\nu}$  = 2961, 1592, 1477, 1360, 1249, 807 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>102</sub>H<sub>94</sub>BrN<sub>7</sub>SZn [*M*]<sup>+</sup>: 1591.5766; found: 1592.1220.

Compound **9** was yielded as a purple solid (5%). M.p. >250°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =1.54 (s, 54H), 7.52–7.57 (m, 2H), 7.62–7.72 (m, 9H), 7.87 (d, *J*=9.0 Hz, 6H), 8.00 (t, *J*=3.9 Hz, 3H), 8.22 (s, 6H), 9.25 (d, *J*=4.5 Hz, 1H), 9.29 (d, *J*=4.8 Hz, 1H), 9.40 (t, *J*=5.1 Hz, 2H), 9.46–9.47 ppm (m, 4H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ =29.71, 32.06, 34.87, 109.89, 116.42, 123.17, 123.79, 124.15, 132.27, 140.38, 140.72, 143.89, 151.56 ppm; IR (KBr):  $\bar{\nu}$ =2961, 1591, 1478, 1362, 1251, 802 cm<sup>-1</sup>; HRMS (ESI-TOF): *m*/*z* calcd for C<sub>96</sub>H<sub>88</sub>BrN<sub>7</sub>S<sub>4</sub>Zn [*M*]<sup>+</sup>: 1609.4459; found: 1609.4583.

#### Synthesis of Zinc-Porphyrin Aldehydes 4, 10, and 11

A mixture of 3, 8, or 9 (0.090 mmol), 5-formyl-2-thiopheneboronic acid (0.091 mmol),  $[Pd(PPh_3)_4]$  (4.50  $\mu mol),$  and  $2\, M$   $Na_2CO_3$  (aqueous, 5 mL) in THF (15 mL) was degassed with N2 for 5 min. The mixture was stirred under reflux conditions for 18 h. After cooling, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2×50 mL), washed with water (50 mL) and brine solution (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub> anhydrous, and filtered. The solvent was removed to dryness, and the crude product was purified by column chromatography over silica gel by eluting with a mixture of CH<sub>2</sub>Cl<sub>2</sub>/hexane (30:70) and recrystallization from  $CH_2Cl_2\!/MeOH$  to give 4 as a purple solid (65%). M.p. > 250 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.54$  (s, 54H), 7.44 (d, J = 5.6 Hz, 1H), 7.73 (d, J = 3.9 Hz, 1H), 7.76 (d, J =3.5 Hz, 1H), 7.81 (s, 3H), 7.87 (brs, 1H), 8.10 (s, 6H), 9.02 (s, 4H), 9.05 (d, J=4.8 Hz, 2H), 9.26 (d, J=4.7 Hz, 2H), 9.87 ppm (s, 1H); <sup>13</sup>C NMR  $(75 \text{ MHz}, \text{CDCl}_3)$ :  $\delta = 31.75, 35.06, 120.95, 124.25, 125.14, 129.66, 131.07,$ 132.20, 132.56, 132.89, 137.50, 141.71, 147.47, 148.65, 150.57, 182.53 ppm; IR (KBr):  $\tilde{\nu} = 2963$ , 1647, 1460, 1220, 1004, 796 cm<sup>-1</sup>; HRMS (ESI-TOF): m/z calcd for C<sub>71</sub>H<sub>76</sub>N4OS<sub>2</sub>Zn [M]<sup>+</sup>: 1128.4752; found: 1128.4786.

Compound **10** was yielded as a purple solid (58%). M.p. > 250°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =1.56 (s, 54H), 7.49 (d, J=3.9 Hz, 1H), 7.64 (d, J=8.7 Hz, 6H), 7.76 (d, J=3.9 Hz, 1H), 7.81–7.84 (m, 7H), 7.96 (d, J=3.6 Hz, 1H), 8.01 (d, J=8.1 Hz, 6H), 8.28 (s, 6H), 8.47–8.51 (m, 6H), 9.20–9.22 (m, 6H), 9.37 (d, J=4.8 Hz, 2H), 9.90 ppm (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ =29.73, 32.12, 34.88, 109.53, 110.72, 116.50, 121.11, 121.66, 123.82, 123.88, 124.22, 124.66, 125.26, 131.87, 132.29, 132.67, 134.62, 135.75, 137.37, 138.08, 183.21, 139.38, 141.06, 141.09, 141.65, 143.30, 145.84, 147.22, 150.27, 150.46, 150.69, 151.03, 182.37 ppm; IR (KBr):  $\tilde{\nu}$ =2955, 1702, 1585, 1512, 1489, 1473, 1364, 1262, 999, 808 cm<sup>-1</sup>; HRMS (ESI-TOF): *m*/*z* calcd for C<sub>107</sub>H<sub>97</sub>N<sub>7</sub>OS<sub>2</sub>Zn [*M*]<sup>+</sup>: 1623.6487; found: 1623.8261.

Compound **11** was yielded as a purple solid (62%). M.p. > 250°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.56$  (s, 54H), 7.39 (s, 1H), 7.64–7.76 (m, 11H), 7.89–7.93 (m, 6H), 8.00–8.04 (m, 4H), 8.24 (s, 6H), 9.35 (d, J =4.6 Hz, 2H), 9.43 (d, J = 4.6 Hz, 2H), 9.49 (s, 4H), 9.65 ppm (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 29.74$ , 32.10, 32.31, 34.90, 109.94, 112.16, 113.25, 113.35, 116.47, 123.19, 123.27, 123.86, 124.19, 125.26, 132.23, 132.31, 132.54, 134.72, 137.40, 138.28, 140.40, 140.44, 140.87, 141.42, 141.59, 143.95, 145.40, 147.15, 151.07, 151.53, 151.60, 151.62, 182.26 ppm; IR (KBr):  $\tilde{\nu} = 2946$ , 1633, 1558, 1488, 1365, 1286, 1166, 973, 788 cm<sup>-1</sup>; HRMS (ESI-TOF): m/z calcd for C<sub>101</sub>H<sub>91</sub>N<sub>7</sub>OS<sub>3</sub>Zn [M]<sup>+</sup>: 1641.5180; found: 1641.5194.

#### Synthesis of Zinc-Porphyrin Dyes ZnPPA, ZnPCPA, and ZnPCTA

A mixture of 4, 10, or 11 (0.25 mmol), 2-cyanoacetic acid (5.03 mmol), and piperidine (0.25 mmol) in MeOH (20 mL) was heated under reflux conditions for 3 h. After cooling, the mixture was added to water (50 mL), extracted with  $CH_2Cl_2$  (2×50 mL), washed with water (50 mL), brine solution (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and filtered. The solvent was removed to dryness, and the crude product was purified by column chromatography over silica gel by eluting with a mixture of CH2Cl2/MeOH and recrystallization from CH2Cl2/MeOH to give ZnPPA as a purple solid (70%). M.p. > 250 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta =$ 1.59 (s, 54 H), 6.07 (s, 1 H), 7.06 (d, J=2.9 Hz, 1 H), 7.53 (d, J=2.9 Hz, 1 H), 7.84 (s, 3 H), 8.17 (d, J = 7.2 Hz, 6 H), 9.04 (s, 6 H), 9.27 ppm (d, J =4.4 Hz, 2 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 29.76, 31.83, 31.84, 35.11, 110.05, 120.71, 122.59, 122.63, 122.76, 13.30, 123.68, 129.47, 129.72, 129.88, 131.14, 132.02, 132.35, 132.63, 133.16, 133.99, 138.19, 140.83, 142.16, 144.76, 148.45, 148.50, 150.19, 150.46, 150.63, 150.82, 161.62 ppm; IR (KBr):  $\tilde{\nu} = 3425$ , 2962, 2220, 1592, 1462, 1362, 1247, 1218, 1132, 1002, 798 cm<sup>-1</sup>; HRMS (ESI-TOF): m/z calcd for  $C_{74}H_{78}N_5O_2S_2Zn [M+H]^+$ : 1196 4888 · found · 1196 4882

Compound ZnPCPA was yielded as a purple solid (68%). M.p. > 250°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =1.54 (s, 54H), 7.43 (brs, 1H), 7.63 (d, *J*=7.8 Hz, 7H), 7.80 (d, *J*=8.1 Hz, 7H), 7.99–8.04 (m, 8H), 8.28 (s, 6H), 8.43–8.51 (m, 6H), 9.17 (d, *J*=6.6 Hz, 6H), 9.35 ppm (d, *J*=3.9 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ =29.72, 32.08, 34.84, 109.51, 110.56, 116.47, 121.09, 121.64, 123.76, 123.85, 124.60, 125.81, 131.78, 132.24, 132.50, 132.66, 134.91, 135.73, 137.96, 138.02, 139.31, 140.94, 141.03, 143.25, 150.20, 150.36, 150.61, 150.87, 166.45 ppm; IR (KBr):  $\tilde{v}$ =3450, 2955, 2221, 1702, 1585, 1512, 1489, 1473, 1364, 1262, 999, 808 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>110</sub>H<sub>99</sub>N<sub>8</sub>O<sub>2</sub>S<sub>2</sub>Zn [*M*+H]<sup>+</sup>: 1691.6624; found: 1691.6512.

Compound ZnPCTA was yielded as a purple solid (59%). M.p. > 250°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>/[D<sub>3</sub>]pyridine):  $\delta$  = 1.49 (s, 54H), 7.44–7.82 (m, 23H), 8.14 (d, *J* = 10.2 Hz, 6H), 9.24–9.31 ppm (m, 8H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 29.72, 32.03, 34.75, 109.86, 116.28, 123.77, 124.10, 132.21, 140.14, 141.41, 143.71, 150.84, 162.00 ppm; IR (KBr):  $\tilde{\nu}$  = 3411, 2952, 2222, 1619, 1555, 1482, 1362, 1258, 1116, 973, 791 cm<sup>-1</sup>; HRMS (ESI-TOF): *m*/*z* calcd for C<sub>104</sub>H<sub>93</sub>N<sub>8</sub>O<sub>2</sub>S<sub>5</sub>Zn [*M*+H]<sup>+</sup>: 1709.5316; found: 1709.5298.

#### Quantum Chemical Calculations

All calculations were performed by the Gaussian 09 software in  $CH_2Cl_2$  solvent by the conductor-like polarizable continuum model (C-PCM).<sup>[26]</sup> The energy or geometry optimizations were carried out by the B3LYP/6-31G(d,p) method. The ground- to excited-state excitation energies were calculated at the TD-B3LYP/6-31G(d,p) level in  $CH_2Cl_2$ . The orbitals of the dye-(TiO<sub>2</sub>)<sup>[38]</sup> complex were calculated by PBE0 with the 6-31G(d) basis set for C, O, S, Ti, N, and H atoms and LANL2DZ for the Zn atom using DMol<sup>3</sup>.<sup>[29]</sup>

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#### Fabrication and Testing of DSSC Devices

The TiO<sub>2</sub> photoanodes were prepared by using a previously reported procedure.<sup>[40]</sup> Fluorine-doped SnO<sub>2</sub> (FTO) conducting glasses (15  $\Omega$  sq<sup>-1</sup>, TEC15, Pilkington) were used for transparent conducting electrodes. The double nanostructured thick films ( $\approx 9+5 \,\mu m$  thickness) that consisted of a transparent (PST-18NR, JGC Catalysts and Chemical Ltd.) and scattering (PST-400C, JGC Catalysts and Chemical Ltd.) TiO2 layers were screen-printed on TiCl4-treated FTO. The thickness of the TiO2 film was controlled by selection of screen mesh size and repetition of printing. Prior to dye sensitization, the TiO<sub>2</sub> electrode with cell geometry of  $0.5 \times$  $0.5\ \text{cm}^2$  were treated with an aqueous solution of  $4 \times 10^{-2}\mbox{\,M}\ \text{TiCl}_4$  at  $70\ \text{^{o}C}$ in a water saturation atmosphere, heated to 450 °C for 30 min, and then cooled to 80 °C. The TiO<sub>2</sub> electrodes were immersed in the dye solution (  $\approx 6 \times 10^{-4}$  M in EtOH) in the dark at room temperature for 24 to 48 h to stain the dye onto the TiO2 surfaces. Excess amounts of dye were removed by rinsing with an appropriate solvent. To ensure maximum dye adsorption on TiO<sub>2</sub> film, higher dye concentrations (>10-fold) than that used for the dye adsorption experiments were used. The Pt counter electrode was prepared on a predrilled 8  $\Omega$  sq<sup>-1</sup>, TEC8, FTO glass (Pilkington) by means of the thermal decomposition of  $7 \times 10^{-3}$  M H<sub>2</sub>PtCl<sub>6</sub> in isopropanol solution at 385°C. The dye-adsorbed TiO<sub>2</sub> photoanode and Pt counter electrode were assembled into a sealed cell by heating a Meltonix 1170-25 film (25 µm thickness, Solaronix) gasket as a spacer between the electrodes. An electrolyte solution of Z960 electrolyte that comprised 1.0 M 1,3-dimethylimidazolium iodide (DMII), 0.1 M guanidinium thiocyanate (GuSCN), 0.03 M I<sub>2</sub>, 0.05 M LiI, and 0.5 M tert-butypyridine (4-TBP) in a mixed solvent of acetonitrile (CH<sub>3</sub>CN) and valeronitrile (VN) (85:15 v/v) was filled through the predrilled hole by a vacuum backfilling method. The hole was capped by using hot-melt sealing film (Meltonix 1170-25, 25 µm thickness, Solaronix) and a thin glass cover. Finally, conducting tape (Scotch 3M) and silver paint (SPI supplies) were coated on the electrodes to enhance the electric contact. The reference cell with N719 dye as the sensitizer was prepared for comparison. For each dye, five devices were fabricated and measured for consistency, and the averaged cell data was reported. The J-V of the DSSCs was measured with a Keithley 2400 source meter unit in a four-terminal sense configuration. The data were averaged from forward and backward scans with a bias step and a delay time of 10 mV and 40 ms, respectively, according to the method of Koide and Han.<sup>[41]</sup> Simulation of sunlight was provided by a Newport sun simulator 96000 equipped with an AM 1.5G filter. To minimize the error of measurements, the irradiation intensity of  $100 \; mW \, cm^{-2}$  was approximated with a calibrated BS-520 Si photodiode (Bunnkoukeiki Co., Ltd., Japan); its spectral response was very similar to that of the DSSCs. The spectral output of the lamp was also matched to the standard AM 1.5G solar spectrum in the region of 350-750 nm with the aid of a KG-5 filter with a spectral mismatch less than 2% as reported by Ito et al.<sup>[42]</sup> IPCE of the device under short-circuit conditions were performed with an Oriel 150 W Xe lamp fitted with a Cornerstone TM 130 1/8 m monochromator as a monochromatic light source, a Newport 818-UV silicon photodiode as power density calibrator, and a Keithley 6485 picoammeter. All measurements were performed using a black plastic mask with an aperture area of 0.25 cm<sup>2</sup> and no mismatch correction for the efficiency conversion data. Electrochemical impedance spectra (EIS) were analyzed with an EA163 eDAQ potentiostat integrated with an ERZ100 eDAQ Z100 electrochemical impedance analyzer at a bias potential of -0.65 V in the dark. Nyquist plots of all DSSCs were recorded over a frequency range of 50 mHz-100 kHz with an amplitude of 10 mV and fitted using ZMAN software (WonTech Co. Ltd.) and an equivalent circuit  $R_{\rm s} - R_{\rm Pt} | |Q_{\rm Pt} - R_{\rm CT}| |Q_{\rm CT}$ . The  $R_{\rm s}$  denotes the ohmic series resistance of the cell, R<sub>Pt</sub> stands for charge resistance at the Pt/electrolyte electrode, and  $R_{\rm CT}$  represents the charge-recombination resistance at the  $TiO_2$ /electrolyte interface. The Q parameters are the constant phase elements.

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# FULL PAPER

# **Solar Cells**

Kanokkorn Sirithip, Narid Prachumrak, Rattanawalee Rattanawan, Tinnagon Keawin, Taweesak Sudyoadsuk, Supawadee Namuangruk, iporn Jungsuttiwong, Vinich Promarak\* \_\_\_\_\_

Zinc-Porphyrin Dyes with Different meso-Aryl Substituents for Dye-Sensitized Solar Cells: Experimental and Theoretical Studies



To dye for: A series of new zinc–porphyrin dyes that contain different *meso* substituents (phenyl, carbazole phenyl, and carbazole thiophenyl groups) and bithiophenyl cyanoacrylic acid as the  $\pi$ -conjugated anchoring moiety were designed, synthesized, and characterized as sensitizers for dye-sensitized solar cells (see scheme).