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Tuning the photovoltaic parameters of β -substituted porphyrin analogues: An experimental and theoretical approach

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ABSTRACT

Spectroscopic and theoretical techniques were used to examine the effects of adsorption solvents and electrolyte additives on the photovoltaic performance of dye sensitized solar cells of two β -substituted zinc porphyrin analogues (A1-H and A1-M), where A1-M has an added methyl group at the phenyl ring attached to the meso-position of the porphyrin macrocycle. These results showed that the different solvents used in the sensitization process affects how the dyes are aggregated and how much of the dyes are adsorbed on the semiconductor surface. The highest efficiency of 4.2% (30 min soaking time) and 4.0% (1 h soaking time) was achieved for A1-H and A1-M analogues, respectively. The hypsochromic shift observed in the UV/Vis spectra of the analogues when THF was used as a solvent was due to the partial deprotonation of the hydrogen at the carboxylic moiety of the analogues induced by the interaction of the THF molecule. Theoretical calculations at the B3LYP/6-31G(d) level of theory indicated that when THF was used as an adsorption solvent, it tends to form six- or five-coordinate complexes causing the dyes to be largely separated when attached to the semiconductor thus lowering the amount of dye. The dye molecular plane of A1-M was 13° closer to the TiO₂ surface than A1-H due to steric hindrance introduced by the methyl group. This increases the surface area occupied by the A1-M dye, as indicated by the smaller amount of dye adsorbed on the TiO₂ surface. The addition of 4-tert-butylpyridine or the replacement of lithium ions with guanidinium thiocyanate decreased the solar cell efficiency by 12 and 37%, respectively, which was attributed to a decrease in the electron injection processes.

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1. Introduction

Porphyrins, which are considered to be natural light harvesters, have long been studied for a range of material applications [1]. Currently, the focus is more on the applications of these macrocycles in photoelectric devices, particularly for solar cells [2–16]. Dye sensitized solar cells (DSSCs), which are also known as Grätzel cells, offers a viable alternative to conventional all-inorganic solar cells due to its lower production cost. There are three essential parts of DSSCs: the photoelectrode, electrolyte, and counter electrode. The photoelectrode is composed of fluorine-doped SnO₂ (FTO) glass coated with a sensitizer that is anchored chemically to the semiconducting TiO₂ surface, whereas the counter electrode is FTO coated with platinum [17]. Most studies focused on enhancing the properties of the photoelectrode, specifically the dye, which is responsible for most light absorption. Some of the important properties that need to be considered when designing sensitizers for DSSCs are the geometric structures, molecular orbital (MO) energy, absorption profiles, and aggregation states of the dye. For porphyrin

analogues, the substitution at the *meso*- or β -position of the macrocycle with electron-withdrawing or -donating groups leads to a perturbation of the MO, which affects the photophysical properties. Substitution at the β -position was reported to exert more steric and electronic effects in the porphyrin macrocycle than those at the *meso*-positions, which leads to a more nonplanar distortion of the macrocycle often resulting in a larger red-shift in the absorption spectra [18–24].

This paper reports the synthesis and application of two β -substituted Zn porphyrin analogues, one with a known photo-to-current conversion efficiency (cyano-3-(2'-5',10',15',20'-tetraphenylporphyrinato zinc(II)yl)acrylic acid (A1-H)) [3] and the other with an added electron-donating moiety (cyano-3-(2'-5',10',15',20'-tetratolylporphyrinato zinc(II)yl)acrylic acid (A1-M)) as a sensitizer in dye sensitized solar cells (Scheme 1). The photophysical properties and photovoltaic performance of these analogues were assessed with different types of soaking solutions using different spectroscopic and theoretical techniques. Porphyrins containing electron-donor and -withdrawing groups or substituents that contribute to π - π stacking of the analogues can exhibit solvatochromic behavior [25–27]. The ability of the solvent to chelate to the central metal of the porphyrin macrocycle can affect the aggregation and orientation of the porphyrin monomers

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Scheme 1. Synthesis of Zn porphyrin analogues.

in solution, which affects the packing of the analogues at the surface of the semiconductor during the sensitization process. In this study, the effect of two solvents, tetrahydrofuran (THF) and toluene, with different solvation characteristics was evaluated. THF is a common adsorption solvent in DSSCs because it can dissolve a wide range of non-polar and polar analogues. In Zn porphyrin analogues, THF has a tendency to bind to the axial position of Zn forming fiveor six-coordinate structures [28-30], which can affect the packing of the analogue at the surface of the semiconductor. On the other hand, toluene is a non-polar non-coordinating solvent. Theoretical calculations were used to better understand the effect of the solvents in the zinc porphyrin analogues. There are 3 basic ways of incorporating solvent effects into theoretical calculations. The first is using an implicit solvent model, wherein the solvent is modeled as a dielectric continuum of permittivity that forms a cavity around the solute. The most common implicit solvation frameworks are the polarizable continuum model (PCM) [31] and its variant the conductor-like PCM (C-PCM) [32]. Of these two, the C-PCM provides results that agree well with experimental data with less computational time [20,32,33]. The second method employs an explicit approach, where the number of solvent molecules is included to allow an interaction with the solute molecules [34,35]. Lastly is the hybrid (implicit-explicit) solvation model, where a small number of solvent molecules are included in the calculation together with an implicit solvent model to account for the local and long-range solvation effects [36]. Both experimental and theoretical approaches are needed to obtain insight into the effect of the solvent in the photophysical state of the dye, which affects the adsorbed amount and efficiency of the solar cell.

In an effort to further improve the solar-to-electric conversion efficiency, the effect of the electrolyte composition on the photovoltaic performance of porphyrin-based DSSCs was also investigated. For most DSSCs, the electrolyte is composed mainly of imidazolium iodide, iodine, lithium iodide, guanidinium thiocyanate (GuSCN), and 4-tert-butylpyridine (4-tBP). For the N719 dye, which achieved an efficiency of 11.18% at 1 sun, an A6141 electrolyte, which has a similar composition to the electrolyte mentioned above but without Lil, was used [37]. In studies involving β -substituted porphyrins, the researchers did not consider the use of GuSCN and there is no clear correlation between the effect of 4-tBP on its photovoltaic performance [2–5]. However, in mesosubstituted porphyrins, researchers normally use 4-tBP as part of the composition of the electrolyte [7,8]. Therefore, it is essential to examine how the composition of the electrolyte can affect the efficiency of the β -substituted porphyrin-based DSSCs.

In this study, the photovoltaic performance of Zn porphyrin analogues was assessed based on the ability of the adsorption solvents to coordinate with the axial position of the metal in the porphyrin macrocycle. In addition, careful consideration is undertaken on the soaking time, addition of the co-adsorbent, and the electrolyte composition to understand its effects on the solar cell efficiency.

2. Experimental method

2.1. Materials and synthesis

Analytical reagent grade solvents and reagents were used for the synthesis of cyano-3-(2'-5',10',15',20'-tetraarylporphyrinato zinc(II)yl)acrylic acid analogues and distilled laboratory grade solvents were used for chromatographic processes. A gravity or flash chromatography using silica gel (0.040–0.063 mm) was used for compound separation and purification processes. Thin-layer chromatography (TLC) was performed using precoated silica gel (TLC silica gel 60 F254). All fractions or solutions containing a single spot in TLC with the same R_f were combined and filtered, and the solvent was removed using rotary evaporator and then dried overnight under high vacuum.

The details of the synthetic procedure shown in Scheme 1 were presented by Bonfantini et al. [38] and Officer et al. [3]. The synthesis started with the typical porphyrin condensation reaction followed by a series of Wittig reactions using the appropriate functionalized aldehydes. The introduction of the substituents at the β -position was done via the Vilsmeier reaction. The final product was obtained via a Knoevenagel condensation of the aldehyde with cyanoacetic acid followed by the addition of phosphoric acid at pH 2 to give the desired carboxylic acid. The LC–ESI-MS data for A1-M is 827.2 *m*/*z*. The ¹H and ¹³C NMR spectra of A1-M are given as supplementary data (Fig. S1 and S2), wherein it show typical peaks at about 2.6 ppm for ¹H and 21 ppm for ¹³C NMR spectra corresponding to methyl moiety on the phenyl ring attached to the *meso*-position of the porphyrin macrocycle.

2.2. Analytical measurements

All UV–visible absorption spectra were measured on a Shimadzu UV-2401PC Spectrometer. The concentration of solutions used in the absorption experiment is set at 2×10^{-6} M. ¹H and ¹³C NMR spectra were obtained using a varian VNMRS 500 MHz NMR spectrometer. The compounds were dissolved in DMSO- d_6 and chemical shifts are relative to tetramethylsilane. LC-ESI-MS data were done

using applied biosystems 3200 Q Trap at 200 $^{\circ}$ C and 19 psi with a scan range of 500–1000 *m/z*.

2.3. Cell fabrication

A paste consisting of 20 nm sized TiO₂ (CICC, PST-18NR) was doctor-bladed on a fluorine-doped SnO₂ (FTO, Pilkington TEC-8 glass, 6-90hms/sq with 2.3 mm thickness) conducting glass and then air-dried for 2 h. The electrode was gradually heated at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. Subsequently, a second scattering layer made up of a paste containing 400 nm anatase TiO₂ particles (CICC, PST-400 C) was further coated onto the first layer to form a light-scattering layer. The electrode was air-dried and then sintered in the same way as the first layer. The TiO₂-coated FTO glass plate was immersed in 40 mM aqueous TiCl₄ solution at 70 °C for 30 min and subsequently washed with water and ethanol. The electrode was then heated at 500 °C for 30 min and allowed to cool to 80 °C before dipping into 0.2 mM dye solutions. After soaking, the electrodes are kept in the dye solutions for 2 h. The dye-coated electrodes were rinsed with ethanol. To prepare the counter electrode, a small hole was drilled in an FTO glass and the Pt catalyst was deposited on the FTO glass by spin-coating drops of H₂PtCl₆ solution (2 mg Pt in 1 mL of ethanol) on the FTO plate and then sintering at 400 °C for 15 min. A sandwich cell was prepared by using the dve-anchored TiO₂ film as the working electrode and the counter Pt-electrode which were put together with a thin Surlyn polymer transparent film in between the electrodes (SX 1170-25, 25 µm). The sandwich cells were lightly compressed at 110 °C to seal the two electrodes. A thin layer of electrolyte was introduced into the inter electrode space from the counter electrode side through pre-drilled holes using vacuum backfilling method. The drilled holes were sealed with Surlyn and microscope cover slides to avoid leakage of the electrolyte solution. Three different kinds of electrolyte were used in the cells, Electrolyte A (0.6 M butylmethylimidazolium iodide (BMII), 0.05 M I₂, 0.10 M LiI in 1:1 acetonitrile/valeronitrile (CH₃CN/C₄H₉CN) solvent); Electrolyte B (0.6 M BMII, 0.05 M I2, 0.10 M GuSCN in 1:1 CH₃CN/C₄H₉CN); and Electrolyte C (0.6 M BMII, 0.05 M I₂, 0.10 M LiI, 0.5 M 4-tBP 1:1 CH₃CN/C₄H₉CN).

2.4. Measurement of absorption spectra in TiO₂

The preparation of TiO_2 films were done using a microscope slide and was doctor-bladed with 20 nm sized TiO_2 with a cell area of 1 cm². The glass slide coated with TiO_2 was air-dried and then sintered in the same way as the FTO coated glass. The TiO_2 -coated glass plate was immersed in 40 mM aqueous $TiCl_4$ solution at 70 °C for 30 min and subsequently washed with water and ethanol. The electrode was then heated at 500 °C for 30 min and allowed to cool to 80 °C before dipping into 0.2 mM Zn porphyrin dye solutions and were kept in the dark for 2 h. The dye-coated electrodes were rinsed with ethanol and the absorption spectra of the dyes in TiO_2 were taken.

2.5. Determination of the amount of dye

To determine the amount of dye absorbed on the TiO₂ films (using the TiO₂-coated glass used in absorption measurements on TiO₂), the dye was desorbed with 5 mL of 0.1 M KOH in CH₃OH overnight and a corresponding aliquot was further diluted with the desorption solvent. Calibration curves for A1-H and A1-M in 0.1 M KOH in CH₃OH at their corresponding λ_{max} were obtained. The amount of dye (nmol cm⁻²) was calculated according to the Beer's law based on the measured absorbance.



Scheme 2. Equivalent circuit proposed to fit the EIS data. The (A and B) labels in the circuit correspond to the counter electrode/electrolyte and TiO_2 /electrolyte interfaces, respectively. *R* corresponds to resistance, while CPE is the constant phase element.

2.6. Photovoltaic measurements

The current–voltage characteristics of the devices were carried under simulated AM 1.5G irradiation using Oriel sol 3A class AAA Solar simulator equipped with a 450 W xenon lamp attached to a Keithley 2400 source meter. The light intensity was calibrated with a crystalline silicon reference cell (VLSI standard, SRC-1000-TC-K-KG5-N). The solar cell efficiency (η) is obtained with these relations, $\eta = (J_{SC} \cdot V_{OC} \cdot FF)/P_{in}$ in which J_{SC} (mA/cm²) is the current density measured at short circuit, V_{OC} (V) is the voltage measured at open circuit, FF is the fill factor and P_{in} is the input radiation power (for 1 sun illumination (AM 1.5G), $P_{in} = 100$ mW cm⁻²). A black mask was applied to the area surrounding the TiO₂ with an illuminated active area of 0.159 cm² for all measurements. The incident photon-tocurrent conversion efficiency (IPCE) spectra were measured using the Oriel QE-PV-SI QE/IPCE measurement kit with a silicon detector.

2.7. Electrochemical impedance measurement

The electrochemical impedance spectroscopy (EIS) for DSSCs with a forward bias of -0.5 V under dark condition was measured with Princeton Applied Research VersaStat MC. The spectra were scanned in a frequency range of 10⁻¹–10⁵ Hz at room temperature. The alternate current amplitude was set at 10 mV. The device was connected in a three-electrode configuration: the sensitized porous electrode was connected as working electrode and the counter and reference electrodes were connected at the Pt counter electrode making it a pseudo-reference electrode. The resulting curves were fitted to an appropriate equivalent circuit comprising a series of two Randles-type circuits with series resistance shown in Scheme 2. Each circuit represent one electrode interface: circuit A is the redox charge transfer response at the counter electrode/electrolyte interface and circuit B is electron transfer and recombination kinetics at the TiO₂/electrolyte interface. R_S is the series resistance accounting for the transport resistance of the FTO glass and contact resistance of the cell.

2.8. Theoretical calculations

The ground state geometries of the analogues using B3LYP [39,40] exchange correlation (xc) functional with 6-31G(d) basis set were recovered from reference [41]. Solvation effect was done using the C-PCM framework [32]. The calculation of singlet state excitation energies based on time-dependent density functional theory was done with CAM-B3LYP [42]. xc functional, since B3LYP normally fails to describe valence, Rydberg, and charge transfer state transitions [43–46].

The supermolecular method was used to calculate the binding energies (adsorption energies) of the system based on the following relation:

 $E_{ads} = E_{complex} - \sum (E_{analogue} + nE_{solvent})$ The $E_{complex}$ is the energy of the complex, $E_{analogue}$ and $E_{solvent}$ are the energies of the isolated Zn porphyrin analogue and the THF molecule, respectively,

Analogue	Condition	Solvent/soaking solution	Absorption peaks	Absorption peaks, nm ($\epsilon \times 10^4$, $M^{-1}~cm^{-1}$)		
			B-band Q2-band THF 436(17.4) 567(1.37) Toluene 454(10.4) 568(0.81) TUE 460 570		Q1-band	
A1-H	In solution	THF	436(17.4)	567(1.37)	612(0.75)	
		Toluene	454(10.4)	568(0.81)	616(0.75)	
	In film	THF	460	570	620	
		Toluene	461	570	621	
A1-M	In solution	THF	438(14.8)	568(1.32)	616(0.85)	
		Toluene	456(8.6)	569(0.70)	617(0.63)	
	In film	THF	460	572	622	
		Toluene	461	572	523	

 Table 1

 Absorption spectral data of A1-H and A1-M in different solvents.

and *n* is the number of solvent molecules explicitly included in the formation of the complex.

All theoretical calculations were performed using the Gaussian 09 software package [47]. Natural bond orbital (NBO) analysis was performed with NBO version 3.1 incorporated in the Gaussian package using ground state structures.

3. Results and discussion

3.1. Absorption profile of Zn porphyrin analogues

The absorption spectra of the zinc porphyrin analogues (A1-H and A1-M) were recorded in two solvents: (a) tetrahydrofuran, a polar coordinating solvent, which has a capability to coordinating with the axial position of the metal in the porphyrin macrocycle and also undergoes hydrogen bonding interaction with the carboxylic acid moiety of the analogue that may induce partial deprotonation; and (b) toluene, a non-polar non-coordinating solvent. The relative intensities and wavelengths of the Soret or B-band and Q-bands for the analogues are presented in Table 1 and their corresponding spectra are shown in Fig. 1.

Between the analogues, A1-M exhibited a more red-shifted spectra as compared to A1-H in both solvents indicating the addition of methyl groups to the *meso*-substituted phenyl rings in A1-M, contributes to the increased electron-donating capacity of the porphyrin macrocycle, which increases the electron charge-transfer from the donor to the acceptor group.

All of the analogues exhibit negative solvatochromism, especially at the Soret band region, wherein both analogues are blue-shifted by 18 nm when THF (ε = 7.43) was used as a solvent as compared to toluen (ε = 2.38). The blue-shifting was also observed in free-base porphyrin compounds which suggest that the metalcenter of the porphyrin macrocycle has a minor influence on the solvatochromatic character of the analogues [48,49]. Moreover, this negative solvatochromatic behavior was even seen in phthalocyanines [50,51] and fluorene-based organic dyes [52].

To properly identify the cause of the spectral shifts, an implicit method was first used to calculate the excited state energies using the C-PCM framework at different solvent conditions with the TD-CAM-B3LYP/6-31G(d)//B3LYP/6-31G(d) theoretical method. This method represents the solvent as a continuous medium and normally accounts for the electrostatic nature of the solvent. As shown in Table 2, all of the excitation energies were all underestimated compared to the experimental data. A slight blue-shift at the B-band region was observed going from toluene to THF, which was observed in the experimental data. Contrary to experimental results, all the excitation energies at the Q-bands are red-shifted.

One theory of the observed blue-shift of the absorption spectra of the analogues is probably due to the hydrogen bond interaction of the oxygen of the tetrahydrofuran and the hydrogen of the carboxylic acid of the analogue. In order to prove this theory, we explicitly modeled A1-H analogue and THF to interact through Hbonding. As shown in Fig. 2a, the O–H bond undergoes elongation of 2.63 pm when interacted with THF. An analysis of the second



Fig. 1. Absorption spectra of A1-H (a and c) and A1-M (b and d) in the THF (solid lines) and toluene (dashed lines) solvents. The insets show an enlarged version of the absorption spectra at the Q-band regions.

Table 2

The	four	lowest excitation	energies (nm)) with its o	corresponding	oscillator	strengths (f	f) of A1-H and A1-M.
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State	Excitation ener	Excitation energies/nm (f)							
	A1-H			A1-M	A1-M				
	Gas	Toluene	THF	Gas	Toluene	THF			
1	561.0 (0.0400)	569.0 (0.0841)	571.8 (0.0851)	564.0 (0.0523)	572.3 (0.1013)	575.0 (0.1020)	Q ₁		
2	556.8 (0.0182)	562.5 (0.0229)	563.4 (0.0289)	557.9 (0.0144)	563.3 (0.0240)	564.1 (0.0223)	Q ₂		
3	386.8 (1.6702)	412.9 (2.0878)	411.9 (2.0049)	389.5 (1.7286)	415.3 (2.1477)	414.0 (2.0700)	B1		
4	378.2 (1.0010)	399.8 (1.3175)	398.8 (1.1840)	380.9 (0.9956)	401.4 (1.3176)	400.3 (1.1878)	B ₂		

order perturbation theory of the Fock matrix based in NBO basis indicated that the stabilization energy at the $n_{01} \rightarrow n_{\rm H}$ interaction before and after the THF association decreased by 70.56 kcal mol⁻¹. A $n_{02} \rightarrow n_{\rm H}$ interaction with a 34.87 kcal mol⁻¹ stabilization energy was observed when THF was explicitly added to A1-H which corresponds to the H-bond formation. These resulted in the elongation of the O—H bond supporting the partial deprotonation theory.

A hybrid solvation model was used to calculate the excited state energies of A1-H with an H-bonded THF moiety, while only the implicit model was applied when toluene was used as a solvent. The schematic spectrum of the corresponding solvents of A1-H is shown in Fig. 2b. The transition energies at both bands (B- and Qbands) were consistent with the blue-shift in the absorption spectra in solution when THF was used as a solvent as compared to toluene. This confirms the theory of partial deprotonation when THF was used as a solvent.

3.2. Influence of the adsorption solvent on DSSCs performance

The soaking solvent plays a vital role in the efficiency of the solar cells which influences the coverage of the dye on the TiO₂ surface and also plays an active role in the formation of dyesolvent-TiO₂ complex [53]. The solar cell performances of the zinc porphyrin analogues using THF and toluene as adsorption solvents are presented in Table 3. It was observed that all the photovoltaic parameters, such as the short circuit photocurrent density (I_{SC}) , open circuit voltage (V_{OC}) and fill factor (FF), were affected by the soaking solvent. Toluene produced a lower photovoltaic values as compared to THF under standard AM 1.5 solar conditions. The TiO₂ surface concentration of A1-H sensitized in THF and toluene were determined to be 37 and 41 nmol cm⁻², respectively, while 23 and 27 nmol cm⁻² for THF and toluene, respectively, was observed for A1-M. For both analogues the increase in the absorbed amount when toluene was used as a solvent resulted in lower photovoltaic efficiencies which could be due to the aggregation of the dye at the TiO₂ surface.

The aggregation of the dye when toluene was used as a solvent was even supported with the analysis of the full width at half maximum (FWHM) at the Soret band (Fig. 1c and d) indicating that toluene has a wider FWHM compared to THF (A1-H: toluene (FWHM = 2088 cm^{-1})>THF (FWHM = 1828 cm^{-1}); A1-M: toluene (FWHM = 2145 cm^{-1})>THF (FWHM = 2144 cm^{-1})). This shows that toluene is more aggregated in film as compared to THF.

To determine why THF has a smaller amount of dye adsorbed in the semiconductor, different interactions of THF in A1-H were explicitly modeled to account for the solute-solvent interactions in solution. THF has a tendency to chelate to the central metal atom of the porphyrin macrocycle, acting as a donor solvent, and at the same time has the ability to bind to carboxylic acid through H-bonding. Fig. 3 shows the optimized geometry of the A1-H(THF)_{n(+1)} complex calculated at B3LYP/6-31G(d), where the +1 in the subscript indicates THF bonding to the carboxylic acid. The most favored conformation is A1-H binding with three THF molecules with a binding energy of -36.14 kcal mol⁻¹, where two THF molecules form a six-coordinate Zn complex and the other THF interacts with the carboxylic acid of the acceptor group through H-bonding (Fig. 3a). The mean Zn–O bond distance of this complex was 2.392 Å, which was only 1.2 pm larger than the experimentally determined crystal structure of ZnTPP(THF)₂ [43]. The five-coordinate Zn porphyrin structures with another THF Hbonded to the carboxylic acid (Fig. 3b and c) has about 6 kcal mol⁻¹ higher binding energy than the six-coordinate counterpart. A1-H(THF)₁₊₁ undergoes out-of-plane distortion of the macrocycle forming a square pyramidal configuration as shown in Fig. 3b and c. The conformation of the five-coordinate Zn porphyrin structure is similar to that observed with high-spin iron(II) porphyrins [54]. The presence of either six- or five-coordinate complexes in solution makes the dye far apart from each other hence lowers the amount of dye adsorbed in the semiconductor. This multi-coordinated porphyrin complex could also be the reason for the increase of V_{OC} when THF was used as a solvent (Table 3) as compared to toluene due to the minimization of the interaction between the redox species and the TiO₂ surface.

A comparison of the two analogues using the same adsorption solvent showed that the A1-M analogue produced a lower solar-to-electric conversion efficiency than A1-H. Assuming that



Fig. 2. (a) A truncated view of A1-H analogue showing the H-bond interaction with THF together with the selected bond lengths (bond length before interaction with THF is enclosed in parenthesis). (b) Comparative schematic spectrum of A1-H in THF (solid line, hybrid solvation model) and toluene (dashed line, explicit solvation model).

Table 3	
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Photovoltaic p	erformances of Zn	porph	vrin analog	ues at different	soaking solutions. ^a

Analogue	Adsorption solvent	$V_{\rm OC}({ m mV})$	J _{SC} (mA/cm ²)	FF (%)	η (%)
А1-Н	THF	452	12.9	64.1	3.73
	Toluene	424	13.6	62.7	3.62
A1-M	THF	448	12.2	66.6	3.65
	Toluene	433	11.3	63.8	3.12

^a Photovoltaic performance were measured at AM 1.5 irradiation with 0.159 cm² working area. Soaking time was 2 h. Electrolyte A: 0.6 M BMII, 0.05 M I₂, 0.10 M Lil in 1:1 CH₃CN:C₄H₉CN.



Fig. 3. Structures of the different interactions of THF with A1-H: (a) A1-H(THF)₂₊₁, (b) A1-H(THF)_{1a+1} and (c) A1-H(THF)_{1b+1}, calculated at B3LYP/6-31G(d). Also shown are the adsorption energies and the Zn—O and H-bond distances.

both analogues bind to the semiconductor through the carboxylic group of the cyanoacrylic acid in bidentate mode, the lower efficiency of A1-M might be due to the coupling orientation of the acceptor group to the surface of the TiO₂. A previous study already established the geometry of A1-H [41] in that the acceptor group is slightly co-planar with the porphyrin macrocycle and should assume a bent configuration to obtain bidentate bridging to the surface of the semiconductor. The Ti₃O₁₀H₁₂ structure for TiO₂ was used to analyze the bending configuration of the dyes in relation to the TiO₂ surface, wherein only the atoms that are responsible for attaching the dye to the TiO₂ were optimized, while the remaining atoms remain fixed. The additional methyl group in A1-M introduces steric hindrance when it is attached to TiO₂, which bends the dye molecular plane to approximately 13° more than A1-H (Fig. 4). This also increases the adsorption energy of A1-M to 22 kcal mol⁻¹, which makes the binding of A1-H to the

semiconductor thermodynamically stable. The larger bending of A1-M increases the surface area of the dye thus adsorbing only a smaller amount, hence the lower solar cell efficiency. Aside from the dye coverage, there are also a number of other possible reasons which makes A1-M lower in efficiency compared to A1-H. Due to the close proximity of the porphyrin macrocycle with the TiO₂ surface the electron injection process could involve a transition from the porphyrin macrocycle to the TiO₂ surface without going through the π -spacer group; it could be a result of the piling of multiple porphyrin analogues resulting in higher dye-dye interactions; or the lower dye coverage could result in the penetration of the electrolyte species in to the TiO₂ surface [53,55].

The incident photon-to-charge carrier efficiency action spectra for DSSCs based on A1-H and A1-M in THF is shown in Fig. 5 (Electrolyte A: 0.6 M BMII, 0.05 M I₂, 0.10 M LiI in $1:1 \text{ CH}_3 \text{CN}: \text{C}_4 \text{H}_9 \text{CN}$). The IPCE at the maximum absorption of the Soret band reaches 63%



Fig. 4. Possible adsorption configurations of (a) A1-H and (b) A1-M. The inset shows the bidentate adsorption of the dye in Ti₃O₁₀H₁₂. C1-C2-O3 determines the dye molecular angle against the TiO₂.

Table	4
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Analogue	Soaking time (h)	$V_{\rm OC}({ m mV})$	$J_{\rm SC}$ (mA/cm ²)	FF (%)	η (%)
A1-H	0.5	478	13.0	67.5	4.19
	1.0	461	12.7	66.6	3.91
	2.0	452	12.9	64.1	3.73
	3.0	450	12.9	63.5	3.68
A1-M	0.5	439	13.2	65.3	3.77
	1.0	465	12.8	67.5	4.03
	2.0	448	12.2	66.6	3.65
	3.0	439	11.9	66.4	3.46

^a Photovoltaic performance were measured at AM 1.5 irradiation with 0.159 cm² working area. Concentration of dye = 0.2 mM in THF. Electrolyte A: 0.6 M BMII, 0.05 M I₂, 0.10 M Lil in 1:1 CH₃CN:C₄H₉CN.



Fig. 5. Spectra of monochromatic incident photon-to-current conversion efficiency (IPCE) for DSSCs based on A1-H (solid line) and A1-M (dotted line) with electrolyte A.

at 460 nm with A1-H analogue, while for A1-M, 56% was observed at the same wavelength as A1-H. This is also consistent with the observed photovoltaic parameters wherein A1-H has a higher J_{SC} values than A1-M.

3.3. Effect of soaking time and co-adsorbent on DSSCs performance

As mentioned in the previous section, the analogues in consideration tend to form aggregates on the surface of the semiconductor. By varying the soaking or immersing time or the amount of 3α , 7α dihydroxy-5 β -cholanic acid (chenodeoxycholic acid, CDCA), which acts as a co-adsorbent in the dye solutions, can control the degree of aggregation in porphyrin analogues. The photovoltaic performances of the zinc porphyrin analogues at different immersing time using THF as solvent and at different concentration of CDCA are presented in Tables 4 and 5.

It was shown that A1-H has a larger amount of dye $(37 \text{ nmol cm}^{-2})$ than A1-M $(23 \text{ nmol cm}^{-2})$ in THF due to the wider angle of the dye with respect to the semiconductor surface (Fig. 4) thus A1-H is more aggregated at the surface than A1-M. This premise is also supported by the data presented in Table 4, wherein the most efficient soaking condition for A1-H is 30 min which could control the amount of dye adsorbed at the TiO₂ surface, while A1-M having a smaller adsorbed amount needed 1 h

Table 5 Photovoltaic performances of A1-H analogue at CDCA content.^a

Dye:CDCA ratio	$V_{\rm OC}({ m mV})$	$J_{\rm SC}$ (mA/cm ²)	FF (%)	η (%)
1:0	452	12.9	64.1	3.73
1:1	510	10.8	69.1	3.79
1:10	515	6.9	69.9	2.49

^a Photovoltaic performance were measured at AM 1.5 irradiation with 0.159 cm^2 working area. Concentration of dye = 0.2 mM in THF. Soaking time = 2 h. Electrolyte A: 0.6 M BMII, 0.05 M I₂, 0.10 M LiI in 1:1 CH₃CN:C₄H₉CN.

to attain the highest photovoltaic performance. We also performed different soaking time of A1-M analogue in toluene. As shown in Table S1 (supporting data), the solar-to-electric cell efficiency trend in soaking time is the same as with the data when THF was used as a soaking solvent. This is probably due to the small difference between the amount of dye between solvents. Based on these findings, we could also expect that A1-H in toluene would have an optimal soaking condition nearing 30 min.

Further increasing immersing time leads to the decrease in the solar cell efficiency which was attributed to increased dye aggregation thus increasing the recombination effect or exciton annihilation [56], as observed with the decreasing J_{SC} values. It was also observed with other porphyrin analogues that the longer sensitization time could lead to quenching of the absorbed light energy through radiationless process such as intramolecular relaxation leading to the decrease in efficiency [53].

To know the effect of CDCA on the photovoltaic efficiency, different concentration of CDCA was added to the dye (0.2 mM concentration) as presented in Table 5. As shown in Table 5, the value of the short circuit current density (J_{SC}) decreased as the concentration of the CDCA increased. Since CDCA undergoes competitive adsorption with the dye, the decrease in the photocurrent with increasing amount of CDCA is due to the decreased amount of dye at the semiconductor surface thus limiting the photoinduced collection. The addition of CDCA improved the V_{OC} values as compared to the dye without the addition of the co-adsorbent. At 1:1 dye/CDCA ratio, it achieved the highest efficiency of 3.79%, due to the 58 mV increase of the V_{OC} . The improvement of the open-circuit voltage with CDCA could be due to the prevention of the electron recombination between the redox species and the injected electrons on the TiO₂ surfaces [57].

3.4. Influence of electrolyte composition on DSSCs performance

Lithium ions (Li⁺), a common electrolyte additive, can improve J_{SC} but at the same time often results in a decrease in V_{OC} . The decrease in V_{OC} was often attributed to the positive shift of the CB of TiO₂, which eventually leads in a decrease in photovoltaic performance due to the irreversible surface intercalation of these ions at the surface of the TiO₂ films [58-60]. An alternative compound is to replace inorganic ions with guanidinium thiocyanate, which improves the solar cell performance of the N3 dye by slowing the rate of surface recombination thus reducing the dark current [61]. To determine how Li⁺ affects the photovoltaic parameters, the DSSCs using Li⁺ and guanidinium ions as additives in the electrolytes were compared, as presented in Table 6. The replacement of 0.1 M Li⁺ with 0.1 M of GuSCN increased the V_{OC} by 22%, however decreased the J_{SC} by one-half. This suggests that the use of GuSCN negatively shifts the CB of the semiconductor giving a much higher V_{OC} . This is probably due to the possible adsorption of thiocyanate ion through its nitrogen side on the unoccupied positions of the semiconductor. The lower J_{SC} could be due to



Fig. 6. (a) Nyquist and (b) Bode phase plots of A1-H using various electrolyte composition measured in the dark at forward bias of -0.5 V. (i) Electrolyte A: 0.6 M BMII, 0.05 M I₂, 0.10 M LiI in 1:1 CH₃CN:C₄H₉CN; (ii) Electrolyte B: 0.6 M BMII, 0.05 M I₂, 0.10 M GuSCN in 1:1 CH₃CN:C₄H₉CN; (iii) Electrolyte C: 0.6 M BMII, 0.05 M I₂, 0.10 M LiI, 0.5 M 4-tBP in 1:1 CH₃CN:C₄H₉CN.

Table 6
Photovoltaic performances of A1-H analogue using different electrolyte.

Electrolyte	$V_{\rm OC}~({\rm mV})$	$J_{\rm SC}$ (mA/cm ²)	FF (%)	η (%)	$R_1(\Omega)$	$CPE_1 (\times 10^{-5} \text{ F})$	$R_2(\Omega)$	$CPE_2 \; (\times 10^{-5} \; \text{F})$	τ_2 (ms)
А	452	12.9	64.1	3.73	5.0	1.2	57.1	28.8	16.4
В	552	6.5	66.4	2.36	68.1	0.7	314.8	2.7	8.6
С	576	8.1	70.4	3.29	24.5	0.9	386.6	9.6	37.1

^a Photovoltaic performance were measured at AM 1.5 irradiation with 0.159 cm² working area. Concentration of dye = 0.2 mM in THF. Soaking time = 2 h. Electrolyte A: 0.6 M BMII, 0.05 M I₂, 0.10 M GuSCN in 1:1 CH₃CN:C₄H₉CN. Electrolyte G: 0.6 M BMII, 0.05 M I₂, 0.10 M GuSCN in 1:1 CH₃CN:C₄H₉CN. Electrolyte C: 0.6 M BMII, 0.05 M I₂, 0.10 M GuSCN in 1:1 CH₃CN:C₄H₉CN. Electrolyte C: 0.6 M BMII, 0.05 M I₂, 0.10 M Lil, 0.5 M 4-tBP in 1:1 CH₃CN:C₄H₉CN.

the suppression of the electron injection process brought by the bulkiness of the GuSCN and the possibility of the thiocyanate ion to chelate with the Zn metal of the porphyrin macrocycle similar to the THF chelation discussed in Section 3.2.

Another common electrolyte additive, 4-*tert*-butylpyridine, can be adsorbed via a Ti–N bond on the unoccupied positions on the semiconductor. This bonding shifts the conduction band in the negative direction thereby increasing the open circuit voltage of the DSSC. This also decreases the recombination effect between the TiO₂ and redox couple [58,62–66]. Table 6 shows that the V_{OC} increases by ~ 27%, however, J_{SC} decreases by ~ 37% when 4-tBP was added to the electrolyte. The decrease in the J_{SC} value offsets the gains of V_{OC} and FF resulting in a decrease in the overall conversion efficiency from 3.73% to 3.29%. A similar trend was observed for the phthalocyanine and Ru-based DSSCs dyes [58,64–66]. One possible reason for the decrease in efficiency was credited to the suppression of electron injection of the dye due to decreasing the density of acceptor states caused by the negative shift in the conduction band [66].

To further analyze the differences in the photovoltaic performances of the different electrolyte solution, an electrochemical impedance spectroscopy was performed. Fig. 6 shows the electrochemical impedance spectra of A1-H analogue in different electrolyte solutions measured in the dark at a forward bias of -0.5 V. All impedance spectra were fitted using the circuit presented in Scheme 2. In Fig. 6a, Nyquist plots consisting of two semicircles are shown. The smaller semicircle occurring at higher frequencies represents the redox charge transfer response at the counter electrode (CE)/electrolyte interface (R_1 and CPE₁, Scheme 2). The larger circle at the intermediate frequencies represents the electron transfer and recombination kinetics at the TiO₂/electrolyte interface (R_2 and CPE₂, Scheme 2).

Based on the EIS results, R_2 is the charge recombination resistance at the TiO₂ surface that is related to the charge recombination rate, such that a smaller R_2 means a larger recombination rate. As shown in Table 6 and Fig. 6a, the R_2 values were estimated

to be 57.1, 314.8, and 386.6 Ω for electrolytes A, B, and C, respectively, which are consistent with the increase in V_{OC} . The chemical capacitance is directly proportional to the distribution of electronic states below the conduction band. A higher chemical capacitance indicates a higher density of states of electrons at the semiconductor surface [67]. This agrees with the increasing trend of the short circuit current density values (electrolyte B < electrolyte C<electrolyte A). However, the increase of density of electronic states below the CB of the TiO₂ surface can also introduce an increase in recombination rate as seen in Table 6 for electrolyte A. The electron lifetime increases in the order of electrolyte B < electrolyte A < electrolyte C. Although A1-H in electrolyte C produced the longest electron lifetime and lower recombination rate, it does not contain enough density of electronic states at the semiconductor surface leading to the lower J_{SC} value hence lower in efficiency compared to A1-H in electrolyte A. The higher charge transfer resistance at the counter electrode ($R_1 = 68.1 \Omega$) when using GuSCN as compared to electrolyte A ($R_1 = 5.0 \Omega$) indicated that there is a longer regeneration of the I₃⁻ species, since GuSCN provides an insulating barrier that prevents the oxidation of I⁻ as evidenced by the decrease in the J_{SC} value from 12.9 to 6.5 mA/cm² [68]. However, the device with GuSCN in its electrolyte produced the shortest electron lifetime which indicates the need for inorganic cations such as Li⁺ in the electrolyte to assist in the injection dynamics and facilitates the charge separation of the dye due to its high density of ions at the semiconductor surface [66,69].

4. Conclusion

Two Zn porphyrin sensitizers, A1-H and A1-M, were synthesized. Their photovoltaic performances were found to be influenced by the dye bath condition in terms of the sensitization process and composition of the electrolyte. The solar-to-electric conversion efficiency was related directly to the amount of dye adsorbed to the semiconductor. When THF was used as a solvent it produced 3 and 17% higher solar-to-electric conversion efficiency as compared to toluene for A1-H and A1-M analogues, respectively, based on the results of 2h soaking time without CDCA. The results from theoretical calculations indicated that the use of THF as a sensitizing solution interacted with the porphyrin analogue producing a six- or five-coordinate Zn complexes making it more dispersed when sensitized on the semiconductor minimizing dye aggregation, hence the higher efficiency. The trend in the absorption spectra in solution was well depicted through theoretical calculations when the A1- $H(THF)_{0+1}$ complex was used to calculate the excited state energy supporting the partial deprotonation theory. The difference in the photovoltaic properties between A1-H and A1-M was caused by the amount of tilting of the molecular dye plane toward the dye surface. The A1-M molecular plane was closer to the TiO₂ surface due to the increased steric effect caused by the addition of a methyl group. This increases the surface area of the dye adsorbed in the TiO₂, resulting a much lower dye concentration. The amount of aggregation of the dye can be controlled by the soaking condition and the use of co-adsorbents giving a much higher photovoltaic performances. The use of 4-tBP or GuSCN as an additive in the electrolyte composition does not improve the efficiency of the resulting solar cell, which is due mainly to the suppression of the electron injection process, as shown by the decreased J_{SC} values. This study will help guide researchers in optimizing DSSCs to achieve high solar-to-electric efficiency by efficiently designing the proper sensitizer and by proper assessment of the dye adsorption solvent and electrolyte composition.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2012.08.011.

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