



Asymmetric phthalocyanine derivatives containing 4-carboxyphenyl substituents for dye-sensitized solar cells



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ABSTRACT

The synthesis of two asymmetrical zinc (II) phthalocyanines (ZnPcs) containing 4-carboxyphenyl and 3-thienyl or 5'-hexyl-2,2'-bithiophene substituent was described. These Zinc Phthalocyanines were synthesized by a statistical condensation reaction between two different phthalonitriles. Each of the phthalonitrile precursors was accomplished by the Suzuki-Miyaura cross-coupling reactions with the aryl iodide and corresponding boronic acids. The ZnPc dyes were characterized by MALDI-MS, FT-IR, ¹H NMR, UV–Vis, fluorescence and cyclic voltammetry methods. Compared with 3-thienyl substituted ZnPc-1 dye, the Q-band absorption of 5'-Hexyl-2,2'-bithiophene substituted ZnPc-2 was red-shifted by 13 nm because of the extension of π -system. The ZnPc dyes were used as sensitizers in dye-sensitized solar cells (DSSCs). ZnPc-2 sensitized solar cell devices using a 7 (transparent) + 5 (scattering) μm thin TiO₂ layer yielded a short-circuit photocurrent density of 3.81 mA/cm², an open-circuit voltage of 500 mV, and a fill factor of 0.59, corresponding to an overall conversion efficiency of 1.12% under standard AM 1.5 sun light.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have received increasing attention due to their high incident to photon efficiency, easy fabrication and low production cost [1]. Tremendous research efforts have been devoted to the development of new and efficient sensitizers suitable for practical use. In TiO₂-based DSSCs, efficiencies of up to 11.4% under simulated sunlight have been obtained with ruthenium–polypyridyl complexes [2–4]. However, the main drawback of ruthenium complexes is the lack of absorption in the red region of the visible light and the high cost. For this reason, dyes with large and stable π -conjugated systems such as porphyrins and phthalocyanines are important classes of potential sensitizers for highly efficient DSSCs. Recently, the porphyrin dyes YD2-oC8 and SM315 showed the highest power conversion efficiencies of 12.3% and 13%, respectively, which broke the ruthenium based DSSCs record [5,6].

Among the various synthetic dyes being investigated for application in DSSCs, phthalocyanines (Pcs) have been considered to be promising candidates because of their unique optical and electrical properties [7]. These dyes are well known chromophores for their strong absorption around 300 and 700 nm, as well as for their excellent electrochemical, photochemical and thermal stability [8,9]. Moreover, the redox properties of Pcs are suitable for the sensitization of wide band gap semiconductors such as TiO₂ [10]. Therefore, Pcs are excellent alternative materials for DSSC applications and considerable research efforts have been made on the synthesis of various Pcs and ZnPcs. Furthermore, to achieve higher efficiency, researchers have focused on extension of the π -system and lowering the symmetry of the macro-cycle, which can result in a broadened Soret band and a red-shifted Q band absorption [11,12]. Recently, several groups have synthesized unsymmetrical phthalocyanines to improve the efficiency of DSSC [13–15]. In order to move the Q-band absorption of phthalocyanine to longer wavelength, the π -electron conjugation system can be extended by using various substituents [16–18]. In this study, we have designed two new unsymmetrical phthalocyanines (Fig. 1) containing 4-carboxyphenyl, 3-thienyl and 5'-hexyl-2,2'-bithiophene substituent and investigated their performance in DSSC. 4-Carboxyphenyl

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group was selected as an anchoring moiety to the TiO₂ surface. Substitution of 3-thienyl and 5'-hexyl-2,2'-bithiophene groups at the β -positions of the Pc ring could result in the extension of the π -system. We reported the efficiencies of zinc phthalocyanines using nanoporous TiO₂. ZnPc-2 sensitizer exhibited an efficiency of 1.12% using nanocrystalline 7 (transparent) + 5 (scattering) μm TiO₂ layers.

2. Experimental

2.1. Materials

4-Aminophthalonitrile, 3-thienylboronic acid, 5'-hexyl-2,2'-bithiophene-5-boronic acid pinacol ester, 4-methoxycarbonyl phenylboronic acid, chloroform (CHCl₃), tetrahydrofuran (THF), hexane, tetrakis(triphenylphosphine)palladium(0) [Pd(PPh₃)₄], 1,2-dimethoxyethane (DME), 2-dimethylaminoethanol (DMAE), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), zinc (II) acetate [Zn(OAc)₂] and sodium carbonate (Na₂CO₃) were purchased from Aldrich; Silica Gel 60 (0.04–0.063) was purchased from Merck. 4-Iodophthalonitrile (2) was synthesized as described in literature [19].

2.2. Synthesis of 4-(3-thienyl)phthalonitrile (4)

4-Iodophthalonitrile (127 mg, 0.5 mmol), 3-thienylboronic acid (70.05 mg, 0.55 mmol) and Pd(PPh₃)₄ (57.8 mg, 0.05 mmol) were dissolved in 20 mL of DME. To this mixture, aqueous solution of Na₂CO₃ (26.5 mg, 0.25 mmol) was added. The resultant reaction mixture was heated at 80 °C under argon atmosphere for 16 h and then the reaction mixture is allowed to cool to room temperature. The reaction mixture was filtered and solvent was evaporated and the solid obtained was subjected to silica gel column chromatography and eluted with chloroform:hexane (3:1) mixture. Yield: 75%. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 7.26 (m, 1H, Ar-H), 7.40 (m, 1H, Ar-H), 7.50 (m, 1H, Ar-H), 7.67 (m, 1H, Ar-H), 7.84 (m, 1H, Ar-H), 7.91–8.00 (m, 1H, Ar-H). ¹³C NMR (CDCl₃, 400 MHz): δ (ppm) = 113.57, 115.39, 115.50, 116.66, 124.26, 125.52, 128.14, 130.36, 131.07, 134.08, 138.18, 140.78. FTIR (KBr) ν (cm⁻¹): 3102, 2230 (CN), 1654, 1594 (Ar C=C), 1523, 1423, 1353, 1264, 1216, 1089, 891, 846, 794, 702, 651, 584, 521.

2.3. Synthesis of 4-(5'-hexyl-2,2'-bithiophene)phthalonitrile (6)

4-Iodophthalonitrile (254 mg, 1 mmol), 5'-hexyl-2,2'-bithiophene-5-boronic acid (414 mg, 1.1 mmol) and Pd(PPh₃)₄ (115.56 mg, 0.1 mmol) were dissolved in 20 mL of DME. To this mixture, aqueous solution of Na₂CO₃ (53 mg, 0.5 mmol) was added. The resultant reaction mixture was heated at 80 °C under argon atmosphere for 24 h and then the reaction mixture is allowed to

cool to room temperature. The reaction mixture was filtered and solvent was evaporated. The obtained solid was subjected to silica gel column chromatography and eluted with chloroform:hexane (3:1) mixture. Yield: 58%. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 0.94 (m, 3H, CH₃), 1.36 (m, 2H, CH₂), 1.42 (m, 2H, CH₂), 1.72 (m, 2H, CH₂), 2.84 (m, 2H, CH₂), 6.76 (m, 1H, Ar-H), 7.11 (m, 1H, Ar-H), 7.29 (m, 1H, Ar-H), 7.79 (m, 1H, Ar-H), 7.80 (m, 1H, Ar-H), 7.86 (m, 1H, Ar-H), 7.97 (m, 1H, Ar-H). ¹³C NMR (CDCl₃, 400 MHz): δ (ppm) = 14.07, 22.57, 28.74, 30.24, 31.54, 112.74, 115.24, 115.52, 116.73, 124.33, 124.76, 125.22, 127.38, 128.71, 129.48, 132.44, 134.04, 136.88, 139.29, 141.76, 147.38. FTIR (KBr) ν (cm⁻¹): 3106, 3067, 2954, 2920, 2841, 2229 (CN), 1719, 1593 (Ar C=C), 1554, 1495, 1446, 1439, 1411, 1369, 1314, 1280, 1219, 1202, 1175, 1104, 1065, 905, 879, 837, 796, 777, 723, 521, 486, 430.

2.4. Synthesis of 4-(4-methoxycarbonylphenyl)phthalonitrile (8)

4-Methoxycarbonylphenylboronic acid (300 mg, 1.67 mmol), 4-iodophthalonitrile (381 mg, 1.50 mmol) and Pd(PPh₃)₄ (173.34 mg, 0.15 mmol) were dissolved in 20 mL of DME and stirred under argon for 10 min. Then, aqueous Na₂CO₃ (318 mg, 3 mmol) was added slowly in a few portions, and the mixture was heated at 80 °C for 12 h. After cooling to room temperature, the solvent was removed under vacuum and the residue was dissolved in 100 mL CHCl₃, washed three times with distilled water and dried over Na₂SO₄. The drying agent was removed by filtration and CHCl₃ evaporated in vacuum. The resulting solid was purified by column chromatography on silica gel by using CH₂Cl₂ as an eluent. Compound **8** was obtained as a white solid (250 mg, 65.4%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 8.23–8.21 (1H, Ar-H), 8.08 (1H, Ar-H), 8.01 (1H, Ar-H), 7.99 (1H, Ar-H), 7.96–7.94 (1H, Ar-H), 7.71 (1H, Ar-H), 7.69 (1H, Ar-H), 4.00 (m, 3H, CH₃). FTIR (KBr): ν (cm⁻¹) = 3422, 3104, 3071 (H-Ar), 2956, 2849, 2389, 2291, 2230 (CN), 1714 (C=O), 1600 (Ar C=C), 1484 (Ar C=C), 1426, 1384, 1295 (C-O), 1186, 1109, 1015, 956, 918, 841, 765, 695, 519.

2.5. Synthesis of 2-(4-carboxyphenyl)-9(10), 16(17), 23(24)-tris(3-thienyl)phthalocyaninato zinc(II) (ZnPc-1)

4-(3-Thienyl)phthalonitrile (1.05 mmol, 220.76 mg), 4-(4-methoxycarbonylphenyl)phthalonitrile (0.35 mmol, 91.79 mg) and Zn(OAc)₂ (10 mmol, 183 mg) were dissolved in 10 mL DMAE. The mixture was added by three drops of DBU and heated at 130 °C under argon atmosphere for 12 h. The reaction mixture was then allowed to cool to room temperature and the solvent was removed under vacuum. The residue was washed with a MeOH:H₂O (5:1) mixture. The solid obtained was purified by column chromatography on silica gel. A THF eluent removed most of the symmetric tetrakis(3-thienyl)phthalocyanine and a THF:DMF (10:1) eluent to separate the **ZnPc-1 methyl ester**. This fraction was dissolved in 20 mL of THF:MeOH (3:1) mixture and was hydrolyzed at 60–70 °C for 1 h. The reaction mixture was then allowed to cool to room temperature and the organic solvent was removed under vacuum. The pH of the reaction mixture was set to pH 3–4 by adding 1 M HCl solution, and the precipitate was formed. The precipitate was collected and washed several times with MeOH:H₂O mixture and dried to give **ZnPc-1** as a green solid (11% overall yield for two steps). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 9.42–9.11 (broad, m, 12H, Ar-H), 8.41–7.97 (4H Ar-H), 6.89–6.53 (12H, thienyl, Ar-H). FTIR (KBr): ν (cm⁻¹) = 3630, 3059 (Ar-H), 2953, 2912, 2866 (aliphatic C-H), 1691 (C=O), 1653, 1607, 1526, 1486, 1435, 1411, 1390, 1363, 1320, 1276, 1229, 1168, 1081, 1059, 888, 859, 832, 778, 759, 742, 688, 667, 623, 520, 461, 430. UV–Vis (THF): λ_{max} , nm (log ϵ , M⁻¹.cm⁻¹) = 358 (4.92), 618 (4.62) and 684 (5.30). MALDI TOF MS: calcd for C₅₁H₂₆N₈O₂S₃Zn ([M+H]⁺) 944.41; found 944.07.

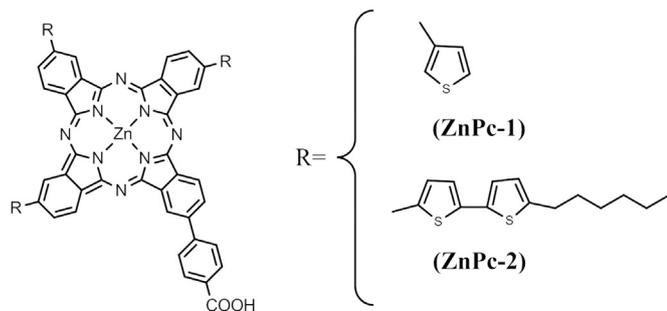


Fig. 1. Molecular structures of ZnPc-1 and ZnPc-2.

2.6. Synthesis of 2-(4-carboxyphenyl)-9(10), 16(17), 23(24)-tris(5'-hexyl-2,2'-bithiophene)phthalocyaninato zinc(II) (ZnPc-2)

4-(5'-hexyl-2,2'-bithiophene)phthalonitrile (0.54 mmol, 203 mg), 4-(4-methoxycarbonylphenyl)phthalonitrile (0.18 mmol, 47.2 mg) and Zn(OAc)₂ (10 mmol, 183 mg) were dissolved in 10 mL DMAE. The mixture was added by three drops of DBU and heated at 130 °C under argon atmosphere for 12 h. The reaction mixture was then allowed to cool to room temperature and the solvent was removed under vacuum. The residue was washed with a MeOH:H₂O (5:1) mixture. The solid obtained was purified by column chromatography on silica gel. A THF eluent removed most of the symmetric tetrakis(5'-hexyl-2,2'-bithiophen)phthalocyanine and a THF:DMF (10:1) eluent to separate the **ZnPc-2 methyl ester**. This fraction was dissolved in 20 mL of THF:MeOH (3:1) mixture and hydrolyzed at 60–70 °C for 1 h. The reaction mixture was then allowed to cool to room temperature and the organic solvent was removed under vacuum. The pH of the reaction mixture was set to pH 3–4 by adding 1 M HCl solution, and the precipitate was formed. The precipitate was collected and washed several times with MeOH:H₂O mixture and dried to give **ZnPc-2** as a green solid. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 9.25–6.80 (several m, 28H, Ar-H), 2.11–0.85 (several m, 39H, alkyl). FTIR (KBr): 3063 (aromatic C-H), 2923–2850 (aliphatic C-H), 1686, 1607, 1489, 1433, 1398, 1329, 1283, 1253, 1172, 1091, 1052, 946, 894, 824, 791, 761, 740, 693, 653, 583, 486, 430. UV–Vis (THF): λ_{max}, nm (log ε, M⁻¹·cm⁻¹) = 359 (4.93), 632 (4.54) and 700 (5.23). MALDI TOF MS: calcd for C₈₁H₆₈N₈O₂S₆Zn ([M+H]⁺): 1443.26; found 1441.26.

2.7. DSSC preparation

TiO₂ electrodes consist of an adsorbent mesoporous layer with 20 nm anatase TiO₂ particle size in 7 mm thicknesses and a second light scattering layer with 400 nm anatase TiO₂ particle size of 5 mm thicknesses. Preparation and characterization of double-layer TiO₂ electrode were previously described by Wang et al. [20].

TiO₂ coated FTO substrates were sintered at 450 °C and immersed in a 0.5 mM solution of the dye solutions in THF:t-butanol (1:1) at room temperature overnight, and dried under a flow of nitrogen. The active solar cell area was 0.16 cm². Pt catalyst was deposited on the FTO glasses by coating with a drop of platinum acid solution with the heat treatment at 450 °C for 15 min. The cell was sealed using a Surlyn (60 μm, Solaronix) and the 0.6 M *N*-methyl-*N*-butyl-imidazolium iodide (BMII) + 0.1 M LiI + 0.05 M I₂ + 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile as redox electrolyte solution was introduced through pre-drilled holes in the counter electrode. The filling holes were sealed using Surlyn and a microscope cover glass. Current–voltage (*J*–*V*) curves were obtained using Keithley measurement unit and the light source consisted of an Oriel Xe-lamp.

2.8. Characterization

FTIR spectra were measured between 400 and 4000 cm⁻¹ from KBr pellets on a Perkin Elmer Spectrum BX FTIR system (Beaconsfield, Buckinghamshire, HP91QA, England). The NMR (400 MHz) spectra were recorded using a Bruker Ultrashield Plus Biospin GmbH spectrometer in CDCl₃. The absorption spectra were recorded using Perkin Elmer Lambda 20 UV–Vis spectrometer. The fluorescence spectra were measured on Varian Cary Eclipse fluorescence spectrophotometer. Mass spectra were measured using Bruker Microflex LT MALDI-TOF mass spectrometer. The electrochemical measurement was recorded using a Gamry PCI4/300 model the potentiostat.

3. Results and discussion

Asymmetrically substituted phthalocyanines show interesting properties due to the presence of different groups in the same macrocycle. In the literature, three methods have been commonly used for the synthesis of unsymmetrical phthalocyanines: a statistical condensation [21], a polymer support [22] or using sub-phthalocyanines [23]. Among these methods, the statistical cyclotetramerization was used to prepare the phthalocyanines in this study. According to this method, two phthalonitriles (A and B) mixture was used, for which one used in excess (A) to obtain in good of the desired A₃B structure. Scheme 1 shows the synthetic route of the phthalocyanines.

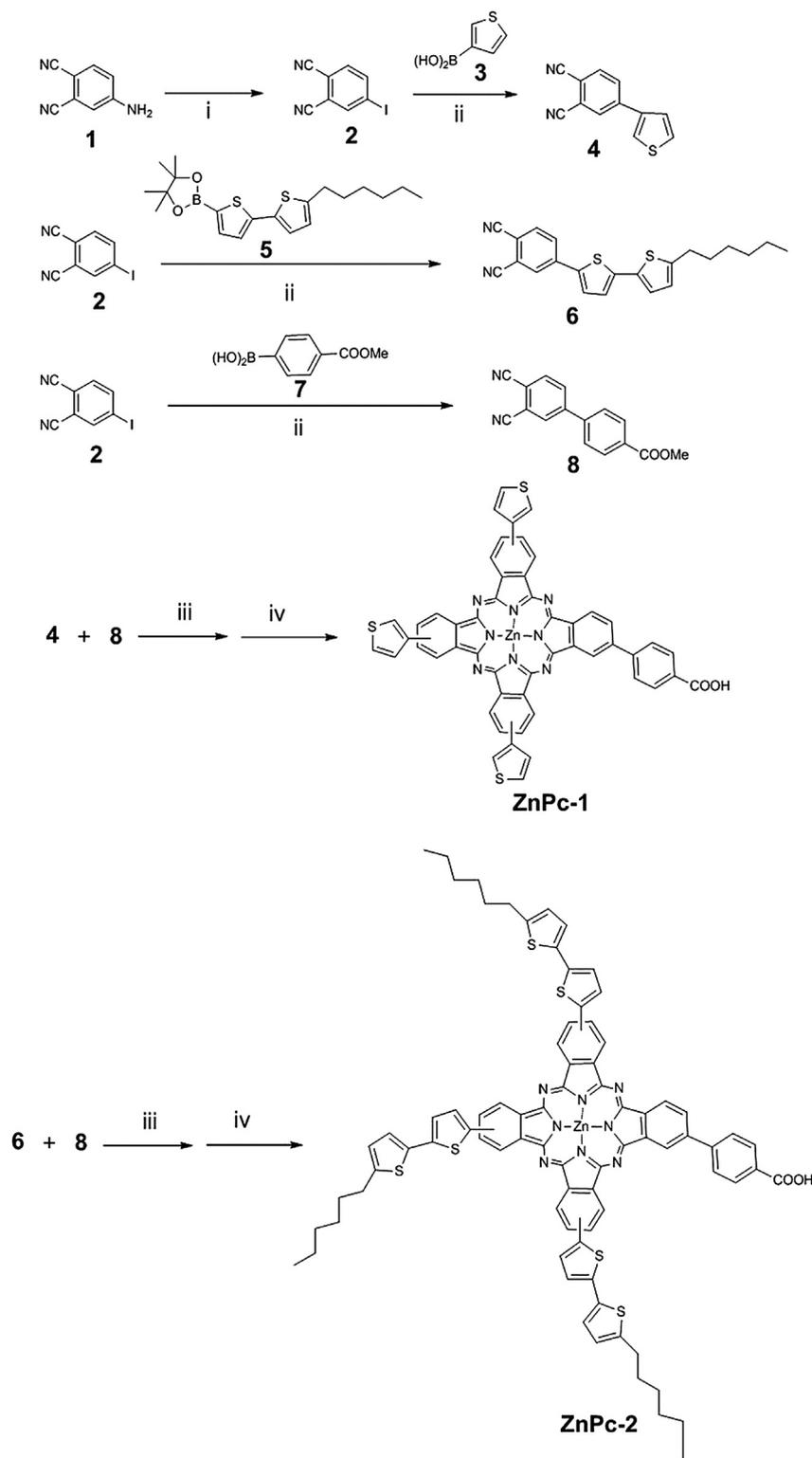
Fig. 2 shows absorption spectra of phthalocyanines recorded in THF solution. The spectrum of ZnPc-1 shows the Q-band at 684 nm, whereas ZnPc-2 shows a maximum absorbance at 700 nm. The Q-band observed in phthalocyanines was attributed to π–π* transitions from the highest occupied molecular orbital (HOMO) and to lowest unoccupied molecular orbital (LUMO) of the conjugated macrocycle. Both compounds, ZnPc-2 and ZnPc-3, present a Soret band absorption around at 358 and 359 nm, respectively. The Soret band was observed due to the transitions from the deeper π levels to the LUMO. ZnPc-2 additionally presents an absorption band between 400 and 550 nm, which is related to the peripheral, π-conjugated, bithiophene substituent [24]. The fluorescence spectra of phthalocyanines were presented in Fig. 3. The fluorescence maxima of ZnPc-1 and ZnPc-2 were observed at 690 and 710 nm, respectively.

Zero–zero excitation energy (*E*_{0–0}) was obtained from the intersection of absorption and emission spectra (λ_{int}):

$$E_{0-0} = \frac{1240}{\lambda_{\text{int}}}$$

The *E*_{0–0} energies of ZnPcs were given in Table 1.

The electrochemical behavior of the phthalocyanines was investigated using cyclic voltammetry (CV). The experiments were carried out in a typical three-electrode cell in which a glass sheet with deposited indium–tin-oxide (ITO) was used as the working electrode, a platinum wire was used as the counter electrode, an Ag/AgCl electrode was used as the reference electrode and THF containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) was used as electrolyte. Fig. 4 shows the cyclic voltammograms of ZnPc-1 and ZnPc-2. The oxidation and reduction behaviors of metallophthalocyanine derivatives are due to the interaction between the phthalocyanine ring and the central metal [25]. The LUMO of phthalocyanines should have a higher energy than the conduction band edge of TiO₂ and the HOMO energy level of phthalocyanines should have a lower energy than the redox potential of the electrolyte for dye regeneration. The HOMO energy level can be calculated from the onset oxidation potential. The electrochemically HOMO energy levels of ZnPc-1 and ZnPc-2 were calculated as –4.81 and –4.61 eV, respectively. The lowest unoccupied molecular orbital (LUMO) levels were estimated from the differences between the HOMO energy levels and *E*_{0–0} [26]. The LUMO levels of the phthalocyanines were estimated to be –3.01 and –2.87 eV, respectively. The LUMO levels are lower than the conduction band energy of TiO₂, suggesting that there should be enough thermodynamic driving force for electron injection from the excited state of the dyes into the conduction band of TiO₂. Furthermore, the HOMO energy levels of the dyes were also lower than the energy level of the redox couple I⁻/I₃⁻ in the electrolyte, indicating more efficient dye regeneration by electron transfer from I⁻ [27]. The HOMO–LUMO gap decreased upon increasing the conjugation length [28]. Muto et al. reported the similar



Scheme 1. i) H_2SO_4 , NaNO_2 , KI; ii) $\text{Pd}(\text{PPh}_3)_4$, Na_2CO_3 , DME, 80°C , reflux; iii) $\text{Zn}(\text{OAc})_2$, DBU, DMAE, 130°C , reflux; iv) THF:MeOH (3:1), NaOH, 70°C , reflux.

observation for 2-thienyl and [2-2'-bithiophene]-5-yl substituted 1,4,8,11,15,18,22,25-octabutoxyphthalocyanines ((OBu)₈Pcs) [17]. The results of CV experiments of ZnPc-1 and ZnPc-2 were summarized in Table 1. Both the 3-thienyl substituted ZnPc-1 and 5'-hexyl-2,2'-bithiophene substituted ZnPc-2 showed reversible oxidation peaks at 0.61 and 0.43 V, respectively. In addition, both of

phthalocyanines showed the second oxidation peak at 1.10 and 0.88 V, respectively.

The photovoltaic characterizations of solar cells based on the ZnPc-1 and ZnPc-2 sensitizers using TiO_2 layers obtained with a sandwich cell using electrolyte of 0.6 M N-methyl-N-butyl-imidazolium iodide (BMII) + 0.1 M LiI + 0.05 M I_2 + 0.5 M 4-tert-

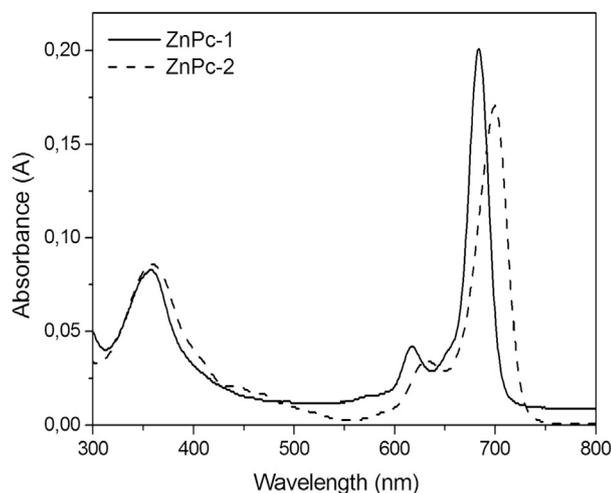


Fig. 2. UV–Vis absorption spectra of ZnPc-3 and ZnPc-4 in THF (1.0×10^{-6} M).

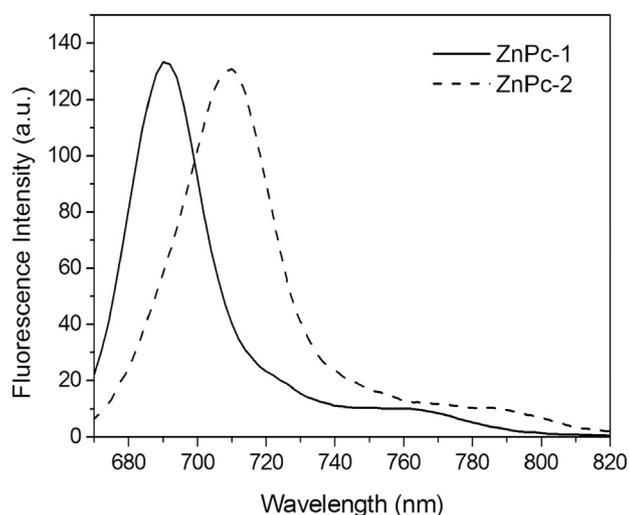


Fig. 3. Fluorescence spectra of ZnPc-3 and ZnPc-4 in THF (1.0×10^{-6} M).

butylpyridine (TBP) in acetonitrile as redox electrolyte were presented in Fig. 5. And all photovoltaic data were summarized in Table 2. ZnPc-1 and ZnPc-2 sensitized DSSCs were fabricated using substrates with $7 \mu\text{m}$ of standard 20 nm particle titania paste, along with a $5 \mu\text{m}$ thick scattering layer. Under standard global AM 1.5 solar conditions, the ZnPc-2 sensitized cell devices gave a short-circuit photocurrent density (J_{sc}) of 3.81 mA/cm^2 , an open-circuit voltage (V_{oc}) of 500, and a fill factor (ff) of 0.59, corresponding to

Table 1
Electrochemical and optical properties of ZnPc-1 and ZnPc-2.

	E_{ox}^{on} (V) ^a	λ_{int} (nm) ^b	E_{0-0} (eV) ^c	HOMO (eV) ^d	LUMO (eV) ^e
ZnPc-1	0.61	1.10	687	1.80	-4.81
ZnPc-2	0.43	0.88	705	1.76	-4.63

^a Oxidation onset potential vs. Ag/AgCl reference electrode.

^b Measured from the intersection of the normalized absorption and emission spectra.

^c Estimated from the λ_{int} .

^d HOMO = $-[(E_{ox}^{on} - E_{ferrocene}) + 4.8] \text{ eV}$, where 0.6 V is the value for ferrocene vs. Ag/AgCl and 4.8 eV is the energy level of ferrocene below the vacuum.

^e LUMO = HOMO + E_{0-0} .

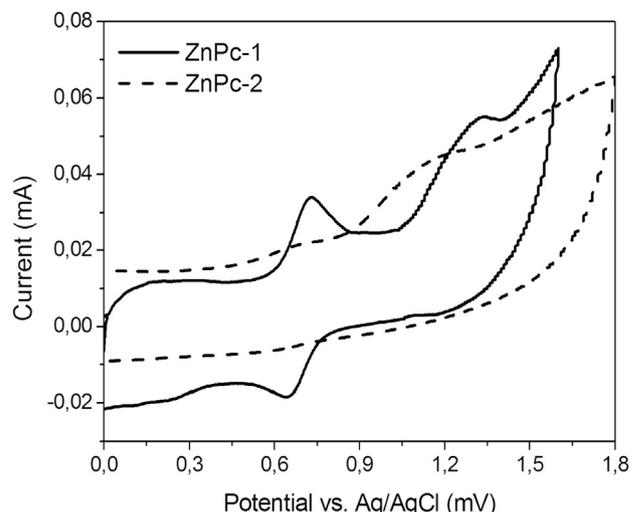


Fig. 4. Cyclic voltammograms of ZnPc-1 and ZnPc-2 recorded in 0.1 M TBAPF6/DMF at a scan rate of 25 mV/s.

an overall conversion efficiency η , derived from the equation (η) $J_{sc} V_{oc} ff / \text{light intensity}$, of 1.12% (see Table 2).

ZnPc-2 was modified over ZnPc-1 with the thiophene bridged bulky alkyl chains. Introduction of soluble thiophene alkyl chain moieties to phthalocyanine allowed for an efficient sensitizer for dye sensitized solar cells. In dye sensitized solar cell devices, it was found that ZnPc-1 exhibited low photovoltaic performance that could be rationalized by lack of thiophene bridged alkyl chains that prevents back electron reactions as a spacer. The ZnPc-2 dye, however, exhibited high photocurrent and high photoresponse than ZnPc-1 for efficient dye sensitized solar cell. The introduction of thiophene bridged alkyl chain groups in ZnPc-2 dye reduced molecular aggregation as well as increased solubility. ZnPc-1 showed higher photocurrent than ZnPc-2 because of a little bit large amount of absorbed photons in absorption spectra.

The incident photon to current conversion efficiency (IPCE) of ZnPc-1 and ZnPc-2 was displayed in Fig. 6. The ZnPc-2 based DSSC device exhibited a broad IPCE between 550 and 800 nm, but was limited to low efficiency. The absorption of ZnPc-2 was red shifted compared to ZnPc-1 sensitizers while maintaining the energy

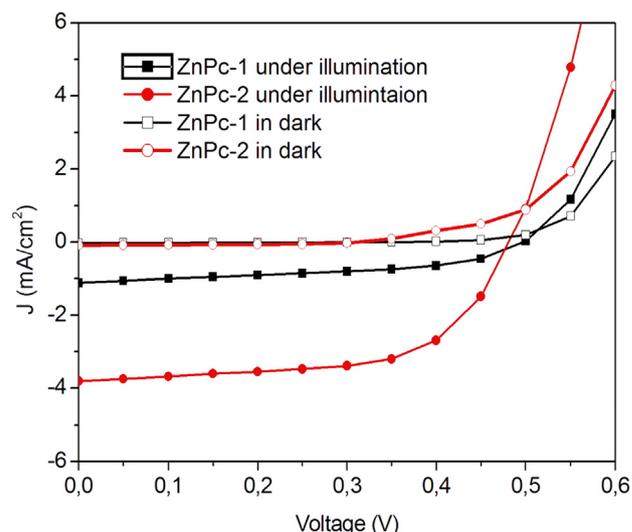


Fig. 5. J - V curves of dye sensitized solar cells.

Table 2
Photovoltaic performance of TiO₂ based dye sensitized solar cells.

	J_{sc} (mAcm ⁻²)	V_{oc} (mV)	FF	η (%)
ZnPc-1	1.08	500	0.47	0.25
ZnPc-2	3.81	500	0.59	1.12

levels necessary for efficient electron injection and hole regeneration in dye sensitized solar cells. In addition, the selection of thio-phene bridged bulky alkyl chains supplied for additional functionality such as minimizing recombination, increasing solubility, and preventing dye aggregation. The molecular engineering approach demonstrated herein was an example of the possibility to prepare new types of phthalocyanines. Further structural optimization reducing the chances of aggregation and enhancing the directionality of charge redistribution in the excited state is very likely to yield more efficient sensitizers. Our work will continue in fine-tuning phthalocyanine sensitizer for more efficient dye for dye sensitized solar cells.

In line with these statements, we reported the efficiency under standard conditions obtained for ZnPc-2 sensitizer using 7 (transparent) + 5 (scattering) μm TiO₂ layers that showed 500 mV open circuit voltage, 3.81 mA/cm² short-circuit current, 0.59 fill factor and 1.12% overall conversion efficiency.

The new dyes including ZnPc-1 and ZnPc-2 show an extended π -conjugation system, which produces a redshift in the maximum absorption, in comparison with three *tert*-butyl groups substituted TT1 dye [29]. TT1 dye shows a Q-band absorption at 679 nm, whereas ZnPc-1 and ZnPc-2 dyes show a maximum absorption at 684 and 700 nm, respectively. The use of *tert*-butyl groups enhances the solubility, minimizes the aggregation, and tunes the LUMO level of the phthalocyanine [29,30]. In ZnPc-2 dye, three 5'-hexyl-2,2'-bithiophene groups decrease the aggregation and increase the conversion efficiency. However, this efficiency is generally lower than those of TT1 and other *tert*-butyl substituted phthalocyanine dyes [29–31]. Similar results were reported by Ince et al. for ZnPc dye 2 with 5'-hexyl-2,2'-bithiophene groups [24]. It was indicated that the efficiency was increased to 2.70% by changing the electrolyte and by using coadsorbent chenodeoxycholic acid (CDCA). As a result, the aggregation phenomena play an important role on the overall efficiency and explain the low efficiency obtained by ZnPc-2 dye.

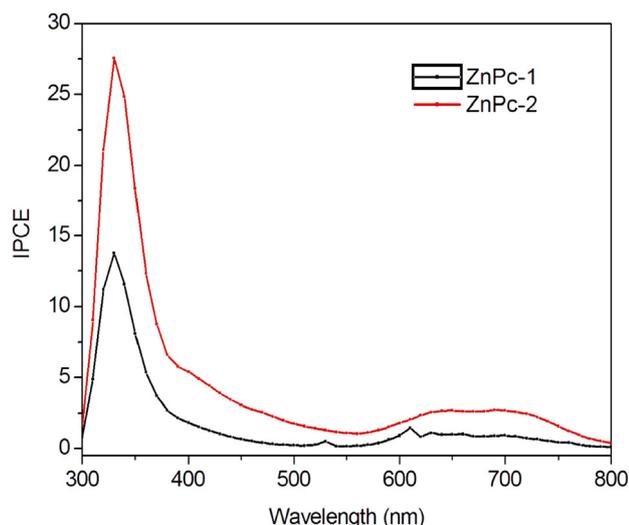


Fig. 6. Incident photon to charge carrier efficiency of dye sensitized solar cells.

4. Conclusions

In conclusion, we have successfully synthesized two unsymmetrical phthalocyanine dyes containing 3-thienyl and 5'-hexyl-2,2'-bithiophene groups at peripheral position of the macrocycle. Photophysical properties (absorption, emission and electrochemical) of phthalocyanines were investigated. It was found that 5'-hexyl-2,2'-bithiophene substituent shifted the absorption maxima to red region and decreased the HOMO-LUMO gap upon increasing conjugation length. We have also demonstrated phthalocyanine sensitizers in the visible and near-IR region of the solar spectrum. We have successfully fabricated dye-sensitized solar cells using Zinc phthalocyanines. We reported the efficiency obtained with 7 (transparent) + 5 (scattering) μm TiO₂ transparent layers under standard conditions for ZnPc-2 dye that achieved a short circuit current (J_{sc}) of 3.81 mA/cm², an open circuit voltage (V_{oc}) of 500 mV, and a fill factor (ff) of 0.59 for a total efficiency of 1.12%.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.dyepig.2014.09.018>.

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