3D Structural Optimization of Zinc Phthalocyanine-Based Sensitizers for Enhancement of Open-Circuit Voltage of Dye-Sensitized Solar Cells

Takuro Ikeuchi 1, Ryota Kudo 1, Yu Kitazawa 2, Shogo Mori 1 and Mutsumi Kimura 1,2,*

1 Department of Chemistry and Materials, Faculty of Textile Science and Technology, Shinshu University, Ueda 386-8567, Japan; 15st101d@shinshu-u.ac.jp (T.I.); 18fs410j@shinshu-u.ac.jp (R.K.); shogmori@shinshu-u.ac.jp (S.M.)
2 Research Initiative for Supra-Materials (RISM), Interdisciplinary Cluster for Cutting Edge Research (ICCER), Shinshu University, Ueda 386-8567, Japan; yu_kitazawa0311@shinshu-u.ac.jp

* Correspondence: mkimura@shinshu-u.ac.jp; Tel.: +81-268-21-5499

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Abstract: We designed and synthesized two zinc phthalocyanine sensitizers (PcS27 and PcS28), substituted with branched or cyclic alkoxy chains, to investigate the structural effect of peripheral alkyl chains on the performance of dye-sensitized TiO2 solar cells. The bulky cyclic alkyl chains of PcS28 decreased the adsorption density of PcS28 on the TiO2 electrode, while the terminal branches of alkoxy chains of PcS27 did not influence the adsorption density in comparison to the previously published PcS20 with linear alkoxy chains. Under one sun conditions, PcS27 cells exhibited higher open-circuit voltage but a slightly lower energy conversion efficiency, 6.0% less than PcS20. These results suggest that the small alternation of alkoxy chains resulted in decreasing electron pushing ability of peripheral phenoxy units, giving lower short-circuit current.

Keywords: dye-sensitized solar cell; phthalocyanine; open-circuit voltage; branched alkyl chain

1. Introduction

Dye-sensitized solar cells (DSSCs) have drawn special attention as a promising alternative to conventional silicon-based solar cells [1,2]. The solar-to-electronic power conversion efficiency (PCE) of DSSCs has been enhanced by several approaches such as the systematic structural exploration of light-harvesting dyes, the reduction of mismatch between the oxidation potential of the dye and the redox potential of redox couples in electrolyte solutions, and the optimization of the device structures [3]. The light-harvesting dyes, which consist of chromophore units and adsorption sites, play the following three roles: the absorption of light energy, the injection of electrons from the excited dye to the semiconductor electrodes such as TiO2 and ZnO, and as a barrier to unfavorable contact of redox shuttles with the surface of nanoparticles [4]. Whereas several chromophores with absorption bands in red and near-IR light regions have been applied as light-harvesting dyes for DSSCs, these chromophores have not shown high PCE values. This is partially because of the difficulty of matching HOMO and LUMO energy levels of dyes with two potentials in the DSSC system (the conduction band of the semiconductor electrode and the redox potential of the redox shuttle) [3,5].

Phthalocyanines (Pcs), and especially their metal complexes (MPcs), have been widely used as blue and green dyes and pigments for various applications [6]. The Pcs exhibit intense Q bands in red and near-IR light regions, whose positions can be tuned by the introduction of substituents on the aromatic core and/or modification of central metal species [6]. Thus, the MPcs are good candidates to be the light-harvesting chromophore in DSSCs to harvest red and near-IR light regions. The PCEs of DSSCs sensitized by Pc-based dyes have been improved by several approaches [7–13]. In 2013, we achieved a
PCE of 6.4% from a DSSC employing PcS20 under one sun conditions [13]. The decoration of short propoxy chains around the Pc core resulted in the formation of a dense adsorption layer of dyes on the surface of TiO2 without the formation of aggregates. While the incident photon-to-current conversion efficiency (IPCE) at the Q bands for DSSCs based on PcS20 dye reached 85%, the open-circuit voltage ($V_{oc}$) (0.60 V) was lower than the reported $V_{oc}$ values for the other dyes because of short electron lifetime in the electrodes of the DSSCs [3]. The attachment of alkyl chains around chromophores has been reported as an effective approach to enhance $V_{oc}$ values in DSSCs [14]. The alkyl chains of sensitizers form a dense barrier layer at the interface of dye-adsorbed TiO2 surfaces and electrolytes, and the formation of this barrier leads to an increase in electron lifetime. Therefore, further exploration of interfacial engineering for Pc-based dyes is required to achieve high PCE values. In this paper, we examined the structural effect of alkyl chains around the Pc core on the photovoltaic properties.

2. Materials and Methods

**General.** NMR spectra were recorded on a Bruker AVANCE 400 FT NMR spectrometer at 399.65 MHz and 100.62 MHz for $^1$H and $^{13}$C in CDCl3 solution. Chemical shifts are reported relative to internal tetramethylsilane. Absorption and fluorescence spectra were measured on a SHIMAZU UV-2600 and a JASCO spectrophotometer FP-8600, respectively. MALDI-TOF mass spectra were obtained on a Bruker Microflex spectrometer with dithranol as the matrix. Mass spectra with electrospray ionization were obtained on a Bruker Daltonics microOTOF II. Differencail pulse voltammetry (DPV) data were recorded with an ALS 720C potentiostat, and electrochemical experiments were performed under purified nitrogen gas. Nanoporous TiO2 electrodes with 6 μm thickness as the working electrodes of DPV measurements were prepared by applying pastes of TiO2 nanoparticles with 15–20 nm diameter onto fluoride-doped tin oxide (FTO) glass substrates (Asahi Glass) following sintering at 550 °C for 30 min in air. The TiO2 electrodes were immersed into 50 μM PcS27 or PcS28 solutions in dry toluene for 3 h, and the dye-stained electrodes were used as working electrodes. The reference electrode was Ag/AgCl, which we corrected for junction potentials by referencing it with the ferrocenium/ferrocene (Fc+/Fc) couple.

All chemicals were purchased from commercial suppliers and used without further purification. Column chromatography was performed with activated alumina (Wako, 200 mesh) or silica gel (Wakogel C-200). Recycling preparative gel permeation chromatography was carried out by a Japan Analytical Industry recycling preparative HPLC using CHCl3 as an eluent. Analytical thin layer chromatography was performed with commercial Merck plates coated with silica gel 60 F254 or aluminum oxide 60 F254.

**Synthesis of Phthalocyanine Precursors 1 and 2 (Figure 1)**

![Figure 1. Structure of phthalocyanine precursors 1 and 2.](image)

1: 2,6-(3'-methylbutoxy)phenol [13,15] (0.78 g, 2.9 mmol) and 4,5-dichlorophthalonitriile (0.23 g, 1.2 mmol) were dissolved in 2.0 mL of DMSO. Powder of dried K2CO3 (1.23 g, 8.93 mmol) was added to the mixture and stirred at 105 °C for 8 h [12]. After cooling down to room temperature, the reaction mixture was poured into 30 mL of water, and the reaction mixture was extracted with CH2Cl2. The combined organic phases were dried over MgSO4, and the solvent was evaporated. The crude product was purified by silica column chromatography (CH2Cl2) and recycling preparative HPLC (CHCl3) to obtain 1. Yield 0.42 g (55%). $^1$H NMR(CDCl3, 400.13 MHz): δ/ppm = 7.17 (2H, t, J = 8.4 Hz,
ArH), 6.86 (2H, s, ArH), 6.66 (4H, d, J = 8.4 Hz, ArH), 4.01 (8H, t, J = 6.6 Hz, -OCH₃), 1.56 (12H, m, -CH₂), 0.84 (24H, m, -CH₃). ¹³C NMR (CDCl₃, 100.61 MHz): δ/ppm = 22.5, 25.1, 37.7, 67.6, 106.5, 108.3, 115.8, 118.1, 126.5, 131.1, 151.3, 152.3. FT-IR (ATR): ν = 2230 (-CN) cm⁻¹. ESI-TOF HRMS (APCI): m/z 657.4023 [M + H⁺], calcd. for C₄₀H₅₂N₂O₆: m/z 657.3898.

2: 2 was synthesized from 2,6-bis(cyclohexylmethoxy)phenol (0.74 g, 2.3 mmol) and 4,5-dichlorophthalonitrile (0.18 g, 0.9 mmol) according to the same method as 1. Yield: 34%. ¹H NMR (CDCl₃, 400.13 MHz): δ/ppm = 7.13 (2H, t, J = 8.8 Hz, ArH), 6.92 (2H, s, ArH), 6.64 (4H, d, J = 12.4 Hz ArH), 3.76 (8H, d, J = 6.0 Hz, -CH₂), 1.5–1.69 (24H, m, -CH₂), 0.87–0.90 (8H, m, -CH₃); ¹³C NMR (CDCl₃, 100.61 MHz): δ/ppm = 25.6, 26.4, 29.6, 37.4, 74.5, 106.5, 108.2, 119.2, 126.3, 131.5, 151.6, 152.3. FT-IR (ATR): ν = 2231 (-CN) cm⁻¹. ESI-TOF HRMS (APCI): m/z 761.4724 [M + H⁺], calcd. for C₄₈H₄₀N₂O₆: m/z 761.4524.

Synthesis of Sensitizers PcS27 and PcS28

PcS27: PcS27 was synthesized from 1 (0.42 g, 0.6 mmol), methyl 3,4-dicyanobenzoate (40 mg, 0.2 mmol), and Zn(CH₃COO)₂ (59 mg, 0.3 mmol) according to the reported method [12,13]. Yield: 50 mg (10%). UV-Vis in toluene λ_max/nm (log ε): 693 (4.99) and 678 (4.89). ¹H NMR (CDCl₃, 400.13 MHz): δ/ppm = 10.1 (br, 1H, COOH), 8.4–8.8 (9H, br, Pc-H), 6.5–7.4 (18H, m, ArH), 4.0–4.1 (24H, m, -OCH₂), 1.2–1.6 (36H, m, -CH₂), 0.6 (72H, m, -CH₃). IR (ATR): ν = 1681 (-COOH) cm⁻¹. MALDI-TOF Ms (dithranol): m/z 2206.32 (M + H⁺), Calcd for C₉₂H₁₀₀N₆O₂₀Zn: m/z 2205.12.

PcS28 was synthesized from 2 and methyl 3,4-dicyanobenzoate. Yield: 14%. UV-Vis in toluene λ_max/nm (log ε): 695 (4.94) and 679 (4.89). ¹H NMR (CDCl₃, 400.13 MHz): δ/ppm = 10.5 (1H, br, COOH), 8.4–8.7 (9H, br, Pc-H), 6.5–7.4 (18H, m, ArH), 3.7–4.0 (24H, m, -OCH₂), 1.5–1.7 (72H, m, -CH₂), 1.1–1.3 (36H, m, -CH₂), 0.75–0.90 (24H, m, -CH₂). IR (ATR): ν = 1681 (-COOH) cm⁻¹. MALDI-TOF Ms (dithranol): m/z 2521.38 (M + H⁺), Calcd for C₁₅₃H₁₈₄N₆O₂₀Zn: m/z 2520.57.

Fabrication of PcS27 and PcS28 DSSC Cells [13]

TiO₂ electrodes (apparent surface area: 0.25 cm² (0.5 × 0.5 cm)) were printed onto FTO glass substrates by a screen printing technique using two TiO₂ nanoparticle pastes with different diameters of 15–20 and 400 nm. After sintering at 550 °C for 30 min in air, the TiO₂ electrodes were treated with TiCl₄. The PcS27 or PcS28 sensitizers were adsorbed onto TiO₂ films by immersion of electrodes in 50 µM toluene solutions of the dyes for 24 h at 25 °C. The dye-adsorbed TiO₂ electrode and Pt counter electrode were sealed by heating of a 50 µm thick hot melt ring (Surlyn, DuPont). Redox electrolytes (ELA-1: 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, 0.1 M LiI, 0.05 M I₂, 0.5 M tert-butyl pyridine in acetonitrile) were injected into the space between two electrodes, and then the photovoltaic performance was measured by applying black mask (0.16 cm²) under a standard AM 1.5 solar condition (100 mW cm⁻²) with a solar simulator (Otenso-Sun 3SD, Bunko Keiki).

Adsorption Densities of PcS27 and PcS28 on the TiO₂ Surface [12,13]

The adsorption densities of PcS27 and PcS28 were determined by measuring the absorbance of dyes released from the TiO₂ electrodes (thickness: 6 µm) by immersing into THF containing tetrabutylammonium hydroxide methanoic solution. The absorbance at the Q band of the released dye was converted into the concentration of dye in the TiO₂ electrode. The adsorption density of dye was calculated from the concentration in the TiO₂ electrode, the surface area of mesoporous TiO₂ (61 m²/g determined by Brunauer-Emmett-Teller surface area analyzer), and the weight of the TiO₂ electrode on the FTO substrate.
3. Results and Discussion

Two ZnPc-based dyes, PcS27 and PcS28, bearing branched 3-methylbutoxy and cyclic cyclohexylmethoxy chains at the 2 and 6 positions of three peripheral phenoxy units, were designed (Figure 2). We expected the branched and cyclic alkoxy chains to improve the barrier property of the dye monolayer on the TiO2 surface. Phthalocyanine precursors 1 and 2 were synthesized from resorcinol and 1-bromo-3-methylbutane or (bromomethyl)cyclohexane according to the same procedures as PcS20 [12,13]. Target ZnPcs PcS27 and PcS28 were prepared by a mixed cyclotetramerization between phthalocyanine precursor and methyl 3,4-dicyanobenzoate in the presence of Zn(OAc)2, and a following hydrolysis [13]. Two ZnPcs and their corresponding intermediates were characterized by using standard spectroscopic techniques.

Figure 2. Structure of phthalocyanine sensitizers PcS20, PcS27, and PcS28. Red: structural differences with PcS20.

Figure 3a,b shows absorption spectra of PcS27 and PcS28 in toluene. The spectrum of PcS28 exhibited split Q bands at 675 and 695 nm, which were in fair agreement with the previously reported peak positions of PcS20 [13]. The appearance of split Q bands implies that the degeneracy of LUMO and LUMO+1 energy levels is broken by the asymmetrical substitution of electron-withdrawing carboxylic acid and electron-donating 2,6-dialkoxyphenoxy groups in PcS28. The split width between two Q band positions for PcS27 was narrower than that of PcS28. Both ZnPcs emitted a fluorescence at 698 nm upon exciting at the Soret band, indicating that the zero-zero excitation energy ($E_{0-0}$) obtained by the intersection of the normalized absorption and fluorescence spectra for PcS27 and PcS28 was almost the same.

Figure 3. Absorption spectra of PcS27 (a) and PcS28 (b) in toluene (solid line) and adsorbed onto TiO2 film (dotted line).
The TiO$_2$ electrodes were immersed in toluene solutions of PcS27 and PcS28 (50 µM) for 24 hr to give dye-stained TiO$_2$ electrodes. FT-IR spectra of TiO$_2$ films stained with PcS27 or PcS28 did not show absorption peaks corresponding to carboxylic acid, implying the formation of bidentate binding between carboxylic acid in the dyes and the TiO$_2$ surface. The absorption spectra of PcS27 and PcS28 adsorbed onto TiO$_2$ films exhibited a single Q band at 692 and 697 nm (Figure 3a,b). The fluorescence emissions from PcS27 and PcS28 were quenched on the surface of TiO$_2$. The absorption spectral changes and fluorescence quenching suggest a good electronic communication between ZnPc and TiO$_2$ by anchoring carboxylic acid in dyes on the TiO$_2$. Moreover, the sharp Q bands for both dyes indicate the prevention of molecular aggregation among the ZnPc sensitizers on the TiO$_2$ surface. The first oxidation potentials ($E_{ox}$) of PcS27 and PcS28 were determined by differential pulse voltammetry measurements using dye-stained TiO$_2$ electrodes in acetonitrile containing 0.1 M Bu$_4$NClO$_4$ as a supporting electrolyte [12]. The $E_{ox}$ values of PcS27 and PcS28 were 0.92 and 0.90 V vs. normal standard electrode (NHE), which were attributed to the phthalocyanine ring-based oxidation process. The $E_{ox}$ value of PcS27 was slightly higher than that of PcS28 because of the difference in electron-donating properties between 3-methylbutoxy and cyclic cyclohexylmethoxy chains on the peripheral phenoxy units. The $E_{ox}$ values of PcS27 and PcS28 are more positive than the potential of the I$_3$\textsuperscript{-}/I$_3$\textsuperscript{3-} redox couple (+0.4 V vs. NHE) [2,16]. Excited oxidation potentials ($E_{ox}^*$) of PcS27 and PcS28 are $-0.82$ and $-0.84$ V vs. NHE calculated from $E_{ox}$ and $E_{D,0}$. The $E_{ox}^*$ values of PcS27 and PcS28 are lower than the conduction-band-edge potential of TiO$_2$ (ca. $-0.5$ V vs. NHE) [2]. These results suggest that both PcS27 and PcS28 dyes possess sufficient potential differences for electron injection from the excited dyes to TiO$_2$ and the regeneration of the dyes [2].

The DSSC performances of PcS27 and PcS28 were conducted using double-layered TiO$_2$ electrodes with an I$_3$\textsuperscript{-}/I$_3$\textsuperscript{3-} redox electrolyte, ELA-1, under a standard AM 1.5 solar condition (100 mW cm$^{-2}$). Photocurrent density vs. voltage ($J$–$V$) curves are shown in Figure 4a,b. The short-circuit photocurrent density ($J_{sc}$), $V_{oc}$, fill factor ($FF$), and PCE values for the cells sensitized with PcS27 or PcS28 are listed in Table 1. The PcS27 cell exhibited a $J_{sc}$ of 14.1 mA cm$^{-2}$, a $V_{oc}$ of 610 mV, and an $FF$ of 0.70, yielding a PCE of 6.0%. In contrast, the PcS28 cell displayed a low PCE value in comparison to the PcS27 cell. Figure 4c shows the IPCE spectra of PcS27 and PcS28 cells. The maximum IPCE values for PcS27 and PcS28 cells were 82% and 71% at 600–750 nm corresponding to the Q band of ZnPc sensitizers, and the IPCE spectrum of the PcS28 cell was narrower than that of the PcS27 cell. In order to examine the performance difference in the PcS27 and PcS28 cells, the adsorption densities of dyes on the TiO$_2$ surface were determined. The adsorption densities were determined to be $8.2 \times 10^{-11}$ and $4.9 \times 10^{-11}$ mol cm$^{-2}$ for PcS27 and PcS28, respectively [17]. The projected molecular area of PcS27 on the TiO$_2$ surface calculated from the adsorption density was 2.0 nm$^2$, and this value agreed with the area (2.1 nm$^2$) estimated from density functional theory (DFT) and the Corey–Pauling–Kolton (CPK) space-filling model (Figure 5), implying that PcS27 formed a dense packing layer on the TiO$_2$ surface. Despite the projected molecular area of PcS28 (2.1 nm$^2$) being the same as that of PcS27, the steric crowding among rigid cyclic cyclohexane side chains in PcS28 may result in poor packing among dyes on the TiO$_2$ surface. Therefore, the lower PCE of the PcS28 cell was due to the lower adsorption density on the TiO$_2$ surface.

Table 1. Photovoltaic performance of DSSCs sensitized with PcS27 and PcS28.

| Dye   | Adsorption Density $\times 10^{-11}$/mol cm$^{-2}$ | $V_{oc}$/mV | $J_{sc}$/mA cm$^{-2}$ | $FF$  | PCE/% |
|-------|-----------------------------------------------|-------------|----------------------|-------|-------|
| PcS27 | 8.2                                           | 610         | 14.1                 | 0.70  | 6.0   |
| PcS28 | 4.9                                           | 590         | 9.3                  | 0.74  | 4.1   |
We found that the terminal branches of alkoxy chains did not influence the adsorption density on the TiO₂ surface. The peripheral phenoxy units were examined. The PcS₂⁰ unit as compared to the Q band and the higher interfacial charge recombination from the conduction band of TiO₂. The adsorption densities were determined to be 8.2 × 10⁻⁶.0% efficiency when used as a light-harvesting sensitizer on a TiO₂ electrode under one sun conditions.

Since there is no difference in adsorption density between PcS₂⁷ and our previously reported PcS₂⁰ decorated with linear propoxy chains [13], the branching terminal units do not influence the packing density on the surface of TiO₂. The Voc value of the PcS₂⁷ cell was 10 mV higher than that of the PcS₂⁰, and the offset potential of dark current of the PcS₂⁷ cell was higher than that of the PcS₂⁰ cell. This suggests that covering the ZnPc core with branched alkyl chains in PcS₂⁷ may retard the interfacial charge recombination from the conduction band of TiO₂ to I₃⁻. The narrower split width of the Q band and the higher Eox for PcS₂⁷ revealed the poor electron-pushing ability of peripheral units as compared to PcS₂⁰. This poor electron-pushing ability of PcS₂⁷ relative to PcS₂⁰ leads to the inferior Jsc and IPCE values in DSSCs.

4. Conclusions

The performances of DSSCs based on ZnPcs decorated with branched or cyclic alkoxy chains at the peripheral phenoxy units were examined. The PcS₂⁷ cell with 3-methylbutoxy chains showed 6.0% efficiency when used as a light-harvesting sensitizer on a TiO₂ electrode under one sun conditions. We found that the terminal branches of alkoxy chains did not influence the adsorption density on the TiO₂ surface, and the PcS₂⁷ cell exhibited a higher Voc value than the PcS₂⁰ with linear alkoxy chains on the peripheral phenoxy units. The obtained adsorption density on the TiO₂ surface was calculated from the adsorption density was 2.0 nm², and this value agreed well with the projected molecular area of 2.1 nm² estimated from density functional theory (DFT) and the Corey–Pauling–Koltun (CPK) model of PcS₂⁷. 

![Figure 4](image_url) **Figure 4.** Photocurrent–voltage curves obtained with dye-sensitized solar cells (DSSCs) based on PcS₂⁷ (a) and PcS₂⁰ (b) under a standard global AM 1.5 solar condition (solid line) and darkness (dashed line); (c) incident photon-to-current conversion efficiency spectra for DSSCs based on PcS₂⁷ (solid line) and PcS₂⁰ (dashed line).

![Figure 5](image_url) **Figure 5.** Corey–Pauling–Koltun (CPK) model of PcS₂⁷ ((a) top view; (b) side view) calculated by Gaussian 16.

The performances of DSSCs based on ZnPcs decorated with branched or cyclic alkoxy chains at the peripheral phenoxy units were examined.
chains. The obtained $V_{oc}$ value of the PcS27 cell was still lower than the potential difference (0.9 V) between the conduction-band-edge potential of TiO₂ and the redox potential of the I⁻/I₃⁻ redox shuttle. The covering of the ZnPc core with alkyl chains should be effective to prevent unfavorable charge recombination. However, the excess decoration of the ZnPc core with alkyl chains leads to a decrease in the adsorption density of sensitizers on the TiO₂ surface. The achievement of high $V_{oc}$ values for ZnPc-based DSSCs requires further substituent design of a large π-surface of the ZnPc core to enhance the blacking function to the approach of I₃⁻ in electrolytes, while keeping high adsorption density on the TiO₂ surface.

Author Contributions: All authors contributed equally. M.K. and S.M. conceived the original idea and guided the project. M.K. designed sensing materials and wrote the manuscript. T.I., R.K., and Y.K. carried out dye synthesis, characterization, and fabrication of DSSCs. All authors assisted with the manuscript preparation and discussed the results. All authors have read and agreed to the published version of the manuscript.

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