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Enhancement of photovoltaic performance in dye-sensitized solar cells fabricated with dendritic photosensitizer containing site-isolated chromophores

Myeong Seok Kim^{a,1}, Min Ju Cho^{b,1}, Young Cheol Choi^a, Kwang-Soon Ahn^a, Dong Hoon Choi^{b,*}, Kyungkon Kim^c, Jae Hong Kim^{a,**}

^a Department of Chemical Engineering, Yeungnam University, Gyungsan, Gyeongbuk 712-749, Republic of Korea

^b Department of Chemistry, Research Institute for Natural Sciences, Korea University, Sungbuk-gu, Seoul 136-701, Republic of Korea

^c Department of Chemistry, Ewha Womans University, Seodaemun-gu, Seoul 120-750, Republic of Korea

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ABSTRACT

We designed and synthesized a series of phenothiazine-based donor-acceptor type molecules which consist of different numbers of chromophores in a molecule for use as photosensitizers for dye-sensitized solar cells (DSSCs). Intriguingly, a dendritic molecule containing three chromophores not only gave a new possibility to modify the three dimensional structure, but also reduced aggregation between chromophores inducing dipole-dipole interaction. The DSSCs made of a dendritic photosensitizer system exhibited much higher cell efficiencies than those with the single- or double-chromophoric photosensitizers due to efficient electron extraction pathways in the dendritic molecule which lead to a significantly reduce recombination rate of electrons from the TiO₂ to the electrolyte when the same numbers of chromophores were loaded on the TiO₂ surface. In particular, the DSSC based on the dendritic molecule exhibited improved open-circuit voltage than that of the single- or double-chromophoric photosensitizers. This can be attributed to strong adsorption properties of the TiO₂ electrode and a screening effect to the electrolyte ions provided by the network structure of the dendritic photosensitizer. The different behavior of these DSSCs was explained by comparing the results of electrochemical impedance spectroscopy and measurement of open-circuit voltage decay.

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1. Introduction

After the historic paper on dye-sensitized solar cells (DSSCs) was published in 1991 by Grätzel et al., DSSCs have been widely investigated because of their special features such as low-cost fabrication with fairly high solar energy-to-conversion efficiencies relative to conventional p—n junction solar cells [1,2]. The improvement of solar energy-to-electricity conversion efficiency has continued to be an important research area for DSSCs.

The standard structure of the DSSC is an electrochemical cell composed of a Ru-complex photosensitizing dye-adsorbed wide band-gap electrode such as TiO₂ or ZnO, an electrolyte containing I^{-}/I_{3}^{-} redox couples, and a Pt-coated counter electrode [3–5]. The

photon-to-current conversion mechanism of DSSCs is based on the injection of electrons from the excited photosensitizers into the conduction band of nanocrystalline TiO₂ or ZnO. The oxidized photosensitizers are reduced by electron injection from the electrolyte. Thus, the photosensitizing dye plays an important role in capturing the photons and generating the electron/hole pair, transferring the charges to the interface of the semiconductor and the electrolyte. The sensitization of nanocrystalline TiO₂ by Rucomplex photosensitizers (e.g., N3, N719) have been investigated intensively and power conversion efficiencies (PCEs) higher than 11% under AM 1.5 irradiation have been achieved [4,6,7], whereas metal-free organic sensitizers have only showed PCEs between 6% and 9% [8-12]. Nevertheless, organic dyes have many advantages such as high molar extinction coefficients, ease of customized molecular design for showing desired photophysical and photochemical properties, low cost without the need for transition metals, and environment friendliness.

Conversely, it is known that the thickness, composition, and morphology of the dye layer at the interface on TiO_2 plays an





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^{*} Corresponding author. Tel.: +82 2 3290 3140; fax: +82 2 925 4284.

^{**} Corresponding author. Tel.: +82 53 810 2521; fax: +82 53 810 4631.

E-mail addresses: dhchoi8803@korea.ac.kr (D.H. Choi), jaehkim@ynu.ac.kr (J.H. Kim).

¹ These authors contributed equally to this work.

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important role in the performance of DSSCs [13]. If the electrolyte ions penetrate the dye layer easily, the recombination rate of electrons generated at the dye/TiO₂ interfaces with the electrolyte will increase in the DSSC, reducing open-circuit voltage (V_{oc}) significantly. If electrolyte ions do not penetrate into the dye layer, the potential drop will extend over a larger distance on the photoanode composed of TiO₂ semiconductors, thus inducing a longer electron lifetime in DSSCs [14]. Thus, it is obvious that the operation and efficiency of DSSCs will be strongly influenced by the morphology of the adsorbed dye molecules, layer thickness, and chemical structure of photosensitizers.

In this work, we demonstrate the synthesis of organic photosensitizing dyes with varying numbers of phenothiazine (PTZ)based chromophores in a molecule. The anchoring property of dye on the TiO₂ surface is critical in achieving high photovoltaic efficiency in DSSCs. The concept of multiple acceptors in a dye was already known in Ru-complexes and organic dyes which revealed that the multiple acceptors could enhance the J_{sc} , but reduce the $V_{\rm oc}$ in the DSSCs [15]. Thus, we designed and synthesized the new dyes bearing multiple PTZ-based chromophores which are connected through non-conjugated alkyl chains. PTZ-based chromophores have already provided potential advantages for nonlinear optical materials and photosensitizing dyes in DSSCs owing to high electron donability of the PTZ moiety [16]. The photovoltaic properties of the solar cells composed of new organic dyes were measured and compared with those of ruthenium dye (N3). Intriguingly, the tri-chromophoric dendritic dye-based cell showed much higher PCE values than the other two cells bearing mono- or di-chromophoric dyes, although the number of dye molecules anchored onto the TiO₂ was almost similar in the three devices. To investigate these solar cell performances, we measured decaying curve of V_{oc}, impedance spectrum, and electron life-time, respectively.

2. Experimental

2.1. Materials

All commercially available starting materials and solvents were purchased from Aldrich, TCI, and ACROS Co. and were used without further purification unless otherwise stated. HPLC grade toluene and tetrahydrofuran (THF) were purchased from Samchung Chemical and distilled from CaH₂ immediately before use.

2.2. Instrumental analysis

All ¹H NMR spectra were recorded on a Varian Mercury NMR 300 MHz spectrometer using CDCl₃ and DMSO-*d*₆ purchased from Cambridge Isotope Laboratories, Inc. The redox properties of three dyes were examined by using cyclic voltammetry (Model: CV-BAS-Epsilon). The electrolyte solution used was 0.10 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in freshly dried DMF. The Ag/AgCl and Pt wire (0.5 mm in diameter) electrodes were used as reference and counter electrodes, respectively. The scan rate was 100 mV/s. The mass spectrum was acquired using a JEOL HX-110 mass spectrometer. Elemental analysis was performed with Flash F. A1112 (Automatic Elemental Analyzer, CE. Instruments, Italy). Infrared spectra were obtained by the Perkin Elmer Fourier Transformed Infrared (FT-IR) spectrophotometer with a Miracle single bounce diamond ATR cell from PIKET Technologies. Dye desorption was conducted by detaching the dye from TiO₂ surface in ethanol/H₂O (1:1 v/v) with NaOH (50 mM). The solution bearing detached dyes was monitored with UV-Vis spectrophotometer.

2.3. Assembly and characterization of DSSCs

The fabrication method of the DSSCs is as follows. The conducting glass substrate (FTO; TEC8, Pilkington, 8 Ω/cm^2 , thickness of 2.3 mm) was cleaned in ethanol by ultrasonication. TiO₂ pastes (TiO₂ particle size approximately 20–30 nm) were prepared using ethyl cellulose (Aldrich), lauric acid (Fluka), and terpineol (Aldrich), The prepared TiO₂ paste was coated on the pre-cleaned glass substrate using a doctor blade and sintered at 450 °C for 30 min. The thickness of the sintered TiO₂ layer was measured with an Alphastep IQ surface profiler (KLA Tencor). The other TiO₂ paste was recoated over the sintered layer using TiO₂ particles (250 nm) as a scattering layer and sintered again at 450 °C for 30 min. The prepared TiO₂ film was dipped in a TiCl₄ aqueous solution (0.04 M) at 70 °C for 30 min. For dye adsorption, the annealed TiO₂ electrodes were immersed in a dye solution (0.3 mM of dye in DMF) at 30 °C for 8 - 12 h. Pt counter electrodes were prepared by thermal reduction of a thin film formed from 7 mM of H₂PtCl₆ in 2-propanol at 400 °C for 20 min. The dye-adsorbed TiO₂ electrode and Pt counter electrode were assembled using 60 µm-thick Surlyn® (Dupont 1702) as a bonding agent. A liquid electrolyte was introduced through a pre-punctured hole on the counter electrode. The electrolyte was composed of 3-propyl-1-methyl-imidazolium iodide (PMII, 0.7 M), lithium iodide (LiI, 0.2 M), iodine (I₂, 0.05 M), and t-butylpyridine (TBP, 0.5 M) in acetonitrile/valeronitrile (85:15). The active areas of the dye-adsorbed TiO₂ films were estimated using a digital microscope camera with image-analysis software (Moticam 1000). The photovoltaic I–V characteristics of the prepared DSSCs were measured under 1 sunlight intensity (100 mW/cm², AM 1.5), as verified with an AIST-calibrated Si-solar cell (PEC-L11, Peccell Technologies, Inc.). The incident monochromatic photon-to-current efficiencies (IPCEs) were plotted as a function of light wavelength using an IPCE measurement instrument (PEC-S20, Peccell Technologies, Inc.). The impedance spectra (EIS) and open-circuit photovoltage decay (OCVD) curves were acquired using an electrochemical impedance analyzer (Iviumstat Tec.).

2.4. Synthesis

2.4.1. 10-Hexyl-10H-phenothiazine (1)

An oven dried, 250 mL round bottom flask (RBF) was charged with dimethylformamide (100 mL), 1-bromohexane (10.7 g, 0.065 mol) and sodium hydride (1.8 g, 0.075 mol). Then, a DMF solution of phenothiazine (10 g, 0.05 mol) was added to the mother solution, and the reaction mixture was maintained for 10 h at room temperature. After completion of the reaction, the solution was neutralized with a dilute HCl aqueous solution. The mixture was extracted with chloroform/water. The dried solution was concentrated. The resulting crude, oily product was purified by column chromatography on silica gel with hexane. The product was obtained as a colorless liquid. Yield: 11.2 g (79%). ¹H NMR (300 MHz, DMSO-*d*₆): δ (ppm) 7.20 (d, *J* = 5.7 Hz, 2H), 7.14 (d, *J* = 6.9 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.91 (t, *J* = 7.2 Hz, 2H), 3.84 (t, *J* = 6.9 Hz, 2H), 1.67–1.60 (m, 2H), 1.41–1.27 (m, 2H), 1.23–1.19 (m, 4H), 0.86–0.80 (m, 3H).

2.4.2. 10-Hexyl-10H- phenothiazine-3-carbaldehyde (2)

An oven dried, 250 mL RBF was charged with a solution of DMF (13.2 g, 0.18 mol) and 1,2-dichloroethane (20 mL). Then, 10-hexyl-10*H*-phenothiazine, **1**(5.0 g, 0.017 mol) in 1,2-dichloroethane (20 mL) was slowly added to the mixture for 30 min. Next, POCl₃ (10.7 g, 0.07 mol) was added dropwise over 30 min. The mixture was stirred for 10 h at 90 °C. It was poured into ice water (300 mL) and neutralized with an aqueous solution of NaOH. The solution

was extracted with chloroform. The resulting product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:5 v/v). The product was obtained as a yellow solid. Yield: 2.7 g (51%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 9.79 (s, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.58 (s, 1H), 7.17 (d, J = 7.5 Hz, 1H), 7.11 (d, J = 7.2 Hz, 1H), 6.97 (d, J = 7.2 Hz, 1H), 6.92 (d, J = 8.1 Hz, 1H), 6.88 (d, J = 7.5 Hz, 1H), 3.88 (t, J = 7.2 Hz, 2H), 1.85–1.76 (m, 2H), 1.43–1.30 (m, 6H), 0.87 (m, 3H).

2.4.3. 2-Cyano-3-(10-hexyl-10H-phenothiazine-3-yl)acrylic acid (1(PTZCA)) (3)

In a dried, 100 mL RBF, 10-hexyl-10H-phenothiazine-3carbaldehyde, 2(2.0 g, 6.4 mmol), cyano acetic acid (0.71 g, 8.3 mmol), and ammonium acetate (0.64 g, 8.3 mmol) were dissolved in acetic acid (10 mL) under argon. After heating the solution at 110 °C, a trace amount of piperidine was added dropwise. After 12 h of reaction, the solvent was evaporated to obtain a dark solid. The resulting product was purified by recrystallization in acetonitrile. The product was obtained as a black solid. Yield: 1.9 g (42%). Melting point (M_p): 155–156 °C. FT-IR (KBr, cm⁻¹): 3425 (O–H); 2221 (-CN); 1685 (carboxylic C=O). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.09 (s, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.68 (s, 1H), 7.17 (d, J = 6.9 Hz, 1H), 7.09 (d, J = 7.5 Hz, 1H), 6.96 (d, J = 7.5 Hz, 1H), 6.87 (d, J = 7.8 Hz, 2H), 3.88 (t, J = 6.9 Hz, 2H), 1.80 (d, J = 6.9 Hz, 2H), 1.44-1.31 (m, 6H), 0.88 (m, 3H). HRFAB (*m*/*z*): Calculated for C₂₂H₂₂N₂O₂S, 378.14; Found: 378.33. Anal.: C₂₂H₂₂N₂O₂S (378.14); Calcd: C 69.81, H 5.86, N 7.40, S 8.47; Found: C 69.64, H 5.90, N 7.57, S 8.46.

2.4.4. 1,6-Di(10H-phenothiazine-10-yl)hexane (4)

An oven dried, 250 mL RBF was charged with DMF (150 mL), 1,6dibromohexane (5.0 g, 20.5 mmol) and sodium hydride (1.48 g, 61.5 mmol). Then, a DMF solution of phenothiazine (8.99 g, 45.1 mmol) was added to the mother solution, and the reaction mixture was maintained for 12 h at room temperature. After completion of the reaction, the solution was neutralized with a dilute HCl aqueous solution. The mixture was extracted with chloroform/water. The dried solution was concentrated. The resulting crude, oily product was purified by recrystallization using methanol. The product was obtained as a white powder. Yield: 8.3 g (84.3%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.15 (d, *J* = 8.4 Hz, 4H), 7.09 (d, *J* = 7.5 Hz, 4H), 6.90 (d, *J* = 8.4 Hz, 4H), 6.81 (d, *J* = 8.4 Hz, 4H), 3.81 (t, *J* = 8.4 Hz, 4H), 1.79–1.75 (m, 4H), 1.44 (m, 4H).

2.4.5. 10,10'-(Hexane-1,6-diyl)bis(10H-phenothiazine-3-carbaldehyde) (**5**)

An oven dried, 250 mL RBF was charged with a solution of DMF (13.7 g, 0.187 mol) and 1,2-dichloroethane (20 mL). Then, 1,6-di(10*H*-phenothiazine-10-yl)hexane, **4** (10.0 g, 0.024 mol) in 1,2-dichloroethane (20 mL) was slowly added to the mixture for 30 min. Next, POCl₃ (9.56 g, 62.4 mmol) was added dropwise over 30 min. The mixture was stirred for 10 h at 90 °C. It was poured into ice water (300 mL) and neutralized with an aqueous solution of NaOH. The solution was extracted with chloroform. The resulting product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:3 v/v). The product was obtained as a yellow solid. Yield: 2.4 g (43%). ¹H NMR (300 MHz, DMSO-*d*₆): δ (ppm) 9.77 (s, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.55 (s, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 6.9 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 2H), 1.65 (m, 4H), 1.38 (m, 4H).

2.4.6. 3,3'-(10,10'-(Hexane-1,6-diyl)bis(10H-phenothiazine-10,3diyl))bis(2-cyanoacrylic acid) (**2**(**PTZCA**)) (**6**)

In a dried 100 mL RBF, 10,10'-(hexane-1,6-diyl)bis(10*H*-pheno-thiazine-3-carbaldehyde), **5** (2.0 g, 3.7 mmol), cyano acetic acid

(0.94 g, 11.1 mmol), and ammonium acetate (0.86 g, 11.1 mmol) were dissolved in acetic acid (20 mL) under argon. After heating the solution at 110 °C, a trace amount of acetic acid was added dropwise. After 12 h of reaction, the solvent was evaporated to obtain a dark solid. The resulting product was purified by recrystallization using methanol. The product was obtained as a black solid. Yield: 1.9 g (42%). M_p: 165–167 °C. FT-IR (KBr, cm⁻¹): 3446 (O–H); 2223 (-CN); 1695 (carboxylic C=O). ¹H NMR (300 MHz, DMSO-*d*₆): δ (ppm) 8.14 (s, 2H), 7.89 (d, *J* = 6.6 Hz, 2H), 7.78 (s, 2H), 7.21 (d, *J* = 7.2 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 6.3 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 7.8 Hz, 2H), 3.88 (t, *J* = 7.8 Hz, 4H), 1.66 (m, 4H), 1.41 (m, 4H). HRFAB(*m*/*z*): Calculated C₃₈H₃₀N₄O₄S₂, 670.17; Found: 670.41. Anal.: C₃₈H₃₀N₄O₄S₂ (670.17); Calcd: C 68.04, H 4.51, N 8.35, S 9.56; Found: C 67.68, H 4.51, N 8.12, S 9.87.

2.4.7. 10-(6-Bromohexyl)-10H-phenothiazine (7)

An oven dried, 250 mL RBF was charged with DMF (100 mL), 1,6dibromohexane (10 g, 0.041 mol) and sodium hydride (0.98 g, 0.041 mol) under argon at 0 °C. Then, a DMF solution of phenothiazine (5.0 g, 0.025 mol) was added to the mother solution, and the reaction mixture was maintained for 10 h at room temperature. After completion of the reaction, the solution was neutralized with a dilute HCl aqueous solution. The mixture was extracted with chloroform/water, and the organic layer was dried under MgSO₄. After the organic layer was concentrated, the resulting crude, oily product was purified by column chromatography on silica gel with chloroform/hexane (1:5 v/v). The product was obtained as a colorless oil. Yield: 4.5 g (49.7%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.13 (d, J = 5.1 Hz, 2H), 7.09 (d, J = 7.5 Hz, 2H), 6.98 (d, J = 7.2 Hz, 2H), 6.82 (d, J = 8.1 Hz, 2H), 3.84 (t, J = 6.9 Hz, 2H), 3.33 (t, J = 6.6 Hz, 2H), 1.87–1.76 (m, 4H), 1.47–1.40 (m, 4H).

2.4.8. 10-(6-Chlorohexyl)-10H-phenothiazine-3-carbaldehyde (8)

An oven dried, 250 mL RBF was charged with a solution of DMF (10.88 g, 0.15 mol) and 1,2-dichloroethane (20 mL). Then, 10-(6-bromohexyl)-10*H*-phenothiazine, **7** (4.5 g, 12.4 mmol) in 1,2-dichloroethane (20 mL) was slowly added to the mixture for 30 min. Next, POCl₃ (7.6 g, 50 mmol) was added dropwise over 30 min. The mixture was stirred for 10 h at 90 °C. It was poured into ice water (300 mL) and neutralized with an aqueous solution of NaOH. The solution was extracted with chloroform. The resulting product was purified by column chromatography on silica gel with chloroform/hexane (1:3 v/v). The product was obtained as a yellow solid. Yield: 2.5 g (51.6%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 9.78(s, 1H), 7.63 (d, *J* = 8.7 Hz, 1H), 7.59 (s, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 9.9 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 3.90 (t, *J* = 7.2 Hz, 2H), 3.49 (t, *J* = 6.3 Hz, 2H), 1.82–1.79 (m, 4H), 1.45 (m, 4H).

2.4.9. 10,10',10"-(6,6',6"-(4,4',4"-(Ethane-1,1,1-triyl)tris(benzene-4,1-diyl))tris(oxy)tris (hexane- 6,1-diyl))tris(10H-phenothiazine-3carbaldehyde) (**9**)

10-(6-Chlorohexyl)-10*H*-phenothiazine-3-carbaldehyde, **8** (2.5 g, 6.4 mmol), 1,1,1-tris(4-hydroxyphenyl)ethane (0.64 g, 2.1 mmol), K₂CO₃ (4.15 g, 12.8 mmol), and a catalytic amount of 18-crown-6 were dissolved in DMF (20 mL) under argon. The reaction mixture was stirred at 110 °C for 24 h. The resulting mixture was filtered, and the organic layer was diluted with 100 mL of chloroform and washed with water (200 mL) several times. The organic layer was dried over MgSO₄, and the solvent was removed in vacuo after filtration. The resulting product was purified by column chromatography on silica gel with ethylacetate/chloroform (1:10 v/v). The product was obtained as a yellow solid. Yield: 1.3 g (50.1%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 9.77 (s, 3H), 7.62 (d, *J* = 8.4 Hz, 3H), 7.56 (s, 3H), 7.16 (d, *J* = 7.8 Hz, 3H), 7.10 (d, *J* = 7.8 Hz, 3H), 6.96 (d,

J = 8.1 Hz, 9H), 6.88 (d, *J* = 8.1 Hz, 6H), 6.73 (d, *J* = 7.2 Hz, 6H), 3.89 (m, 12H), 2.09 (s, 3H), 1.84–1.75 (m, 12H), 1.49 (m, 12H).

2.4.10. (2E,2'E,2"E)-3,3',3"-(10,10',10"-(6,6',6"-(4,4',4"-(Ethane-1,11-triyl)tris(benzene-4,1-diyl))tris(oxy)tris(hexane-6,1-diyl)) tris(10H-Phenothiazine-10,3-diyl))tris(2-cyanoacrylic acid) (**3(PTZCA**)) (**10**)

In a dried, 100 mL RBF, 9 (1.3 g, 1.05 mmol), cvano acetic acid (0.45 g, 5.25 mmol) and ammonium acetate (0.40 g, 5.25 mmol) were mixture under argon. After heating the solution at 110 °C, a trace amount of acetic acid was added dropwise. After 12 h of reaction, the solvent was evaporated to obtain a red solid. The resulting product was purified by recrystallization in acetonitrile. The product was obtained as a red solid. Yield: 0.8 g (53.3%). M_n: 182–185 °C. FT-IR (KBr, cm⁻¹): 3448 (O–H); 2220 (-CN); 1685 (carboxylic C=O). ¹H NMR (300 MHz, DMSO- d_6): δ (ppm) 8.09 (s, 3H), 7.87 (d, J = 8.1 Hz, 3H), 7.77 (s, 3H), 7.22 (d, J = 7.8 Hz, 3H), 7.17 (d, J = 5.7 Hz, 3H), 7.13 (d, J = 6.0 Hz, 3H), 7.07 (d, J = 8.1 Hz, 3H),6.98 (d, J = 7.5 Hz, 3H), 6.88 (d, J = 8.7 Hz, 6H), 6.76 (d, J = 8.7 Hz, 6H), 3.94-3.88 (m, 12H), 2.00 (s, 3H), 1.69-1.66 (m, 12H), 1.44 (m, 12H). HRFAB (*m*/*z*): Calculated for C₈₆H₇₈N₆O₉S₃ (1434.50); Found: 1434.80. Anal.: C86H78N6O9S3 (1434.50); Calcd.: C 71.94, H 5.48, N 5.85, S 6.70; Found: C 71.25, H 5.23, N 6.12, S 6.93.

3. Results and discussion

3.1. Synthesis and characterization

Three different organic photosensitizers containing cyanoacrylic acid as an electron acceptor and PTZ as an electron donor were prepared (Scheme 1). The synthetic procedures used to access **1(PTZCA)**, **2(PTZCA)**, and **3(PTZCA)** photosensitizers are illustrated in Schemes 2 and 3. The compounds **1**, **4**, and **7** were synthesized from phenothiazine and bromoalkane in the presence of sodium hydride. The formylation of each compound was conducted to yield **2**, **5**, and **8** through Vilsmeier–Haack reaction. Knoevenagel condensation with cyanoacetic acid in the presence of piperidine provided the final desired products. In particular, **2(PTZCA)** was synthesized by using dimerized PTZ with a hexylene bridge and

3(PTZCA) was synthesized by using aldehyde-functionalized PTZs, which were attached to 1,1,1-tris(4-hydroxyphenyl)ethane as a core unit. Each chromophore in **2(PTZCA)** and **3(PTZCA)** was connected through a nonconjugated alkylene spacer which acted as a blocking moiety to prevent the recombination of electrons on the TiO₂ surface into electrolytes.

3.2. Optical and electrochemical properties

Fig. 1A and B display the UV–Vis absorption spectra of the dyes in DMF solution and on the TiO₂ layer, respectively. The detailed optical properties of the dyes are summarized in Table 1. The maximum absorption wavelength (λ_{max}) corresponding to the π – π^* transition of each of the three dyes appeared at around 420 nm; however, the molar extinction coefficients (ε_{max}) of **1(PTZCA)**, **2(PTZCA)**, and **3(PTZCA)** were determined to be 1.2 × 10⁴, 2.1 × 10⁴, and 3.0 × 10⁴ M⁻¹ cm⁻¹, respectively. For a larger number of chromophores induced in a molecule, a higher molar extinction coefficient was observed, following a linear proportionality. The formation of aggregates of dyes on the TiO₂ surface induced the bathochromic shift of absorption spectra, in comparison with that of the solution state (Table 1) [17].

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels are typically used to estimate the efficiency of electron injection from the dye in the excited state to the TiO₂, as well as the efficiency of dye regeneration in DSSCs [18]. The HOMO energy levels of the dyes were determined by measuring the oxidation potentials in cyclic voltammograms (Table 1). The optical band gaps (E_g^{opt}) were employed to determine the LUMO energy levels. The results showed that all the dyes had more positive HOMO levels than the redox potential (0.4 V) of I^-/I_3^- in the electrolyte: +0.827, +0.836, and +0.822 V for **1(PTZCA)**, **2(PTZCA)**, and **3(PTZCA)**, respectively. This implies that the oxidized dyes could be regenerated easily by the I^-/I_3^- redox couple.

The dyes containing different numbers of chromophores were used to fabricate DSSCs in order to study their photovoltaic performance. To measure the dye adsorption, the TiO₂ electrodes were



Scheme 1. Structure of photosensitizers containing a PTZ-based chromophore, and Ru-complex dyes (N3 and N719).



Scheme 2. Synthesis of organic photosensitizers (3) 1(PTZCA) and (6) 2(PTZCA): i) POCl₃, DMF, 1,2-dichloroethane; ii) cyanoacetic acid, ammonium acetate, acetic acid.



Scheme 3. Synthesis of organic photosensitizer **3(PTZCA)**: i) POCl₃, DMF, 1,2-dichloroethane; ii) 1,1,1-tris(4-hydroxyphenyl)ethane, K₂CO₃, 18-crown-6, DMF; iii) cyanoacetic acid, ammonium acetate, acetic acid.

immersed in each dye solution in DMF (0.3 mM) at 30 °C for about 8–12 h. It is known that the interaction and adsorption mechanism of anchoring groups in dyes on the TiO₂ surface directly affects the electron transfer and performance in DSSCs [19a]. Thus, we observed the attenuated total reflection Fourier transform infrared (ATR-FT-IR) spectra to investigate the adsorption mechanism of dyes on the TiO₂ surface, and the results are shown in Fig. 2. The wave number assigned to $-C \equiv N$ stretching in organic dyes (~2220 cm⁻¹) did not change in the spectra before or after the dye adsorbed on the TiO₂ surface, which indicates that no interaction occurred between the cyano moieties and the TiO₂ during the

adsorption process. The carbonyl stretching band in -COOH observed at ~1690 cm⁻¹ in the neat sample disappeared in dyes adsorbed on the TiO₂ surface and shifted to a higher wave number region at 1735 cm⁻¹, which suggests the presence of a monodentate binding mode of dye molecules on the TiO₂ surface during the dye adsorption [19b,19c].

3.3. Photovoltaic performance of DSSCs

The synthesized PTZ-based photosensitizers were used for fabricating DSSCs in order to study their current density–voltage characteristics under almost identical numbers of chromophores adsorbed on the TiO₂ electrode. The photovoltaic performances of the DSSCs including three different dyes (i.e., **1(PTZCA)**, **2(PTZCA)**, and **3(PTZCA)**) were compared using the variation of flow current with the bias voltage, incident photon-to-current (IPCE) efficiencies, impedance, and electron life-time analysis.

The photovoltaic properties of the DSSCs were measured and compared with those of a DSSC containing N3 dye, as shown in Fig. 3A, and the measured parameters are summarized in Table 2. Fig. 3B shows the IPCE spectra of the DSSCs containing different organic dyes under simulated solar light (AM 1.5G, 100 mW/cm²). More importantly, we loaded the number of dye molecules in order to provide nearly the same number of chromophores on the TiO₂ surface, which made it possible to compare the photovoltaic performance of three devices with different dye structures. To calculate the amount of dye adsorbed on the TiO₂ film, we obtained molar desorptivities for **1(PTZCA)**, **2(PTZCA)**, and **3(PTZCA)** of 9.48, 5.50, and 3.80 (×10⁻⁸) mol cm⁻², respectively, as listed in Table 2. The molar desorptivity was measured at the maximum absorbance wavelength of all dyes in 50 mM NaOH [20]. Thus, it is interesting that the numbers of chromophores on the TiO₂ surfaces containing



Fig. 1. Absorption spectra of synthesized dyes in the DMF solution (A) and adsorbed dyes on TiO₂ films (B).

Dyes	$\lambda_{max}^{a}/nm~(\epsilon imes 10^{-4}~M^{-1}~cm^{-1})$	λ_{max}^{b}/nm	E_{0-0}^{c}/eV	$E_{\rm ox}/V$	$E_{\rm ox}-E_{0-0}/{\rm eV}$	HOMO/eV	LUMO/eV
1(PTZCA) 2(PTZCA)	424 (1.2) 417 (2.1)	426 423	2.505 2.535	0.827 0.836	-1.678 -1.699	-5.153 -5.148	-2.648 -2.613
3(PTZCA)	413 (3.0)	427	2.574	0.822	-1.752	-5.141	-2.567

 Table 1

 Absorption and electrochemical parameters of the organic dyes.

^a Measured in the DMF solution.

^b Absorption maximum on TiO₂ film.

^c Determined from the intersection of the absorption and emission spectra in the DMF solution.

different organic dyes were similar, although the performance of the DSSCs was observed to be significantly different.

The molar extinction coefficient of **3(PTZCA)** was three times higher than that of **1(PTZCA)** (Fig. 1B) but the amount of the adsorbed **3(PTZCA)** on the TiO_2 was 2/5-fold of that of the adsorbed

1(PTZCA), indicating that the similar light harvesting efficiency (LHE) values should be expected for all the dyes in the DSSCs. However, a higher photon-to-current efficiency was achieved in the DSSC based on the **3(PTZCA)** photosensitizer compared to either **1(PTZCA)** or **2(PTZCA)**, primarily because of the higher J_{sc} and V_{oc}



Fig. 2. ATR-FT-IR spectra of 1(PTZCA) (a), 2(PTZCA) (b), and 3(PTZCA) (c). A: neat dye samples, B: dyes adsorbed on the TiO₂.



Fig. 3. (A) Current density–voltage characteristics for DSSCs containing organic dyes under simulated solar light (AM 1.5, 100 mW/cm²). (B) IPCE curves for DSSCs based on organic dyes: (a) N3, (b) **1(PTZCA**), (c) **2(PTZCA**), and (d) **3(PTZCA**). *Sample conditions: Blocking layer, TiO₂ paste:B32, organic dye 0.5 mM – PMII (0.7 M) + LiI (0.2 M) + I₂ (0.05 M) + TBP (0.5 M) in ACN/VN = 85:15 with a Pt electrode solution (7 mM), 60 μ m Surlyn[®], and a doctor blade (2T). (C) Measured impedance spectra of DSSC at the light illumination. (D) The Bode-phase plots for the DSSC cells. Square: **1(PTZCA**), Circle: 2(PTZCA), Triangle: **3(PTZCA**).

-		-	5						
Dyes	$J_{\rm sc}/{ m mA~cm^{-1}}$	$V_{\rm oc}/V$	FF/%	η /%	Amount of dye/mol cm ⁻²	$R1^a/\Omega$	$R2^{b}/\Omega$	$R3^{c}/\Omega$	τ ^d /ms
N3	17.02	0.678	60.07	6.93	_	_	_	_	-
1(PTZCA)	9.03	0.631	62.79	3.57	$9.48 imes 10^{-8}$	16.38	22.88	34.77	11.2
2(PTZCA)	10.32	0.628	60.22	3.91	$5.50 imes 10^{-8}$	14.58	15.82	24.93	15.9
3(PTZCA)	11.96	0.681	60.15	4.90	3.80×10^{-8}	13.61	14.30	22.84	17.4

Photovoltaic performance and results of impedance analysis of DSSCs. (Scattering layer: 250 nm, 4 µm + TiCl₄, cell areas: 0.24 cm²).

^a R1 is FTO interface resistance.

^b R2 is due to the resistance between the counter electrode and the electrolyte.

^c R3 is possibly originated from the backward charge transfer from TiO₂ to the electrolyte and the electron conduction porous TiO₂ film.

 $^{\rm d}$ τ is life-time of an electron in DSSC.

values (Table 2). The DSSC based on **3(PTZCA)** produced a maximum IPCE of approximately 70% at 460 nm, while DSSCs based on the other dyes produced a maximum IPCE of approximately 60% for both **1(PTZCA)** and **2(PTZCA)**.

Table 1 shows that the LUMO level slightly increased as the number of chromophores in the dye molecule increased. This led to a higher driving force for the electron injection from the dyes to the conduction band of the TiO₂, indicating that the **3(PTZCA)** dye could provide more efficient electron extraction pathways and superior electron injection efficiency (η_{inj}). The charge collection efficiency (η_{cc}) was also influenced by the number of chromophores in the dye molecular structure, which will be discussed later.

It is noteworthy that the V_{oc} for the DSSC based on the **3(PTZCA)** photosensitizer, which contains three isolated chromophores in a molecule, was higher than that of either **1(PTZCA)** or **2(PTZCA)**.

3.4. Electrochemical impedance spectroscopy

Electrochemical impedance spectra (EIS) analysis was performed to study the electrode kinetics and interfacial charge transfer process in the DSSCs. The precise analysis of the impedance



Fig. 4. (A) V_{oc} decay curves of DSSCs with an anchoring process of PTZ-based organic photosensitizers, depending on the number of chromophores recorded during relaxation from an illuminated quasi-equilibrium state to the dark equilibrium. (B) The electron life-time derived from Equation (1) as a function of V_{oc} . (a) **1(PTZCA)**, (b) **2(PTZCA)**. (c) **3(PTZCA)**.

variations in DSSCs composed of various organic photosensitizers allowed us to compare the electron life-times in three different DSSCs [21].

We observed and analyzed the EIS under light illumination conditions, as shown in Fig. 3C, and the results are summarized in Table 2. There are two well-defined semicircles in the high frequency (f ~ 1000 Hz) and medium frequency (f ~ 10 Hz) regions. The ohmic serial resistance (R1) corresponds to the resistance between the electrolyte and the fluorine doped-tin-oxide (FTO) substrate, and R2 and R3 are the resistances retarding the charge transfer process occurring at the Pt counter electrode and at the interfaces of the TiO₂/dye/electrolyte, respectively. Thus, the R3 value possibly originates from the charge transfer process from the TiO₂ to the electrolyte and from the electron conduction in porous TiO₂ films. The R3 values significantly decreased for the 3(PTZCA) dye, indicating much faster electron transport. It also implies that the alkyl chains present in 3(PTZCA) retarded the backward electron transfer from the TiO₂ to the electrolyte and facilitated forward electron transport from the TiO₂ to the FTO substrate. The recombination rate caused by the backward electron transfer was estimated by the Bode-phase spectra for the DSSCs, as shown in Fig. 3D. The electron life-times were calculated and are illustrated in Table 2. The peak shift from high frequency to low frequency reveals longer electron life-time because the frequency (f_{med}) can be related to the inverse of electron life-time (τ_e) in TiO₂ films as ($\tau_e = 1/2\pi f_{med}$) [22,23]. A much longer electron life-time (17.4 ms) was obtained for the 3(PTZCA)based device, compared with 11.2 ms and 15.9 ms for the 1(PTZCA)and 2(PTZCA)-based devices, respectively.

The observed electron life-time of the **3(PTZCA)**-based device showed a significant difference compared with that of either **1(PTZCA)**- or **2(PTZCA)**-based devices, as shown in Table 2. The



Fig. 5. Schematic representation of the anchoring process of newly synthesized photosensitizers as a function of the number of chromophores: (a) **1(PTZCA)**, (b) **2(PTZCA)**, and (c) **3(PTZCA)**.

Table 2

results suggest that the **3(PTZCA)** photosensitizer containing three "site-isolated" chromophores in a molecule hampered the contact of electrolyte ions with charges generated from the photosensitizers.

Thus, the recombination rate of electrons on the TiO_2 surface decreases significantly, which extends the electron life-time on the TiO_2 surface, thus supporting the higher V_{oc} value in **3(PTZCA)**-based DSSCs compared to that of either of the other two photosensitizers [24]. To confirm the electron life-times in the DSSCs, we also measured open-circuit photovoltage decay (OCVD) curves [25,26]. The OCVD technique is a method of monitoring the subsequent decay of photovoltage V_{oc} after turning off the illumination in a steady state. Fig. 4A shows that V_{oc} decay curves of DSSCs with organic PTZ-based photosensitizers were recorded during relaxation from an illuminated quasi-equilibrium state to the dark state. Fig. 4B shows electron life-times calculated from the OCVD curves, according to the following equation:

$$\tau_{\rm e} = -\frac{\kappa_{\rm B}T}{e} \left\{ \frac{\mathrm{d}V_{oc}}{\mathrm{d}t} \right\}^{-1} \tag{1}$$

where $k_{\rm B}T$ is the thermal energy, *e* is the positive elementary charge, and dV_{oc}/dt is the first derivative of the open-circuit voltage. The photovoltaic decay rate is directly related to electron life-time (τ_e) because as the illumination of the DSSC at the open circuit is interrupted, excess electrons are diminished through recombination [27]. The 3(PTZCA) dye exhibited much longer electron life-times $(\tau_e s)$ compared to either **1(PTZCA)** or **2(PTZCA)**, which is in good agreement with the results obtained from Fig. 4B. These results can suggest that the alkyl chains connecting the three PTZ-based chromophores in one dye molecule significantly suppressed the recombination rate, resulting in the much longer electron life-time. Therefore, 3(PTZCA) provided much faster electron transport and significantly prolonged electron life-time, giving rise to the significantly improved electron collection efficiency (η_{cc}) because the value of η_{cc} is determined by using two factors such as electron transport and recombination rates. Consequently, the improved *I*_{sc} and V_{oc} of the DSSC with the **3(PTZCA)** can be mainly attributed to the improved η_{ini} and η_{cc} values.

Fig. 5 is a schematic representation of the possible anchoring process of the three photosensitizers on the TiO_2 surface, manifesting the dependence of "site-isolation" of the chromophore on the adsorbed geometry of the TiO_2 surface. The dye **3(PTZCA)** covered the TiO_2 surface effectively, thereby possibly acting as a blocking layer for the recombination of electrons into the electrolyte.

4. Conclusion

We demonstrate a series of phenothiazine based dyes containing different numbers of chromophores in a molecule were employed as photosensitizers for a DSSC. Although these dyes showed similar optical and electrochemical properties, the DSSC device based on **3(PTZCA)** exhibited much higher PCE value than the other two devices bearing either **1(PTZCA)** or **2(PTZCA)** dyes. These DSSC results were supported by studying the decay curve of V_{oc} , impedance spectrum, and electron life-time.

It is noteworthy that the performance of DSSCs can be improved only by sheaving the ends of the dye molecules together to form the dendritic photosensitizer, even though the number of adsorbed dye molecules is almost identical on the semiconductor electrode.

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