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Tuning of spacer groups in organic dyes for efficient inhibition of charge recombination in dye-sensitized solar cells

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ABSTRACT

Most of the studied organic dyes for dye-sensitized solar cell have exhibited low photovoltage due to fast charge recombination. Here, we report on synthetic strategy of organic dye to get high photovoltage. Phenothiazine (**PTZ**) moieties are incorporated between electron donating triphenylamine (**D**) and electron accepting cyanoacrylic acid (**A**) to enhance non-planarity. Compared to one **PTZ** incorporation (**D-PTZ-A**), hypsochromic shift in absorption is observed by incorporation of two **PTZs** (**D-PTZ1–PTZ2-A**) due to transition from HOMO-1 to LUMO as confirmed by density functional theory (DFT) calculation. **D-PTZ1–PTZ2-A** shows higher photovoltage (0.804 V) than **D-PTZ-A** (0.781 V), those which are even higher than that of the ruthenium-based **N719**-snesitized one (0.775 V). Little difference in electron transport rate is observed for **PTZ** derivatives and **N719**, while electron life time is increased in the order of **D-PTZ1–PTZ2-A** > **D-PTZ-A** > **N719**. Retardation of electron recombination is responsible for the high photovoltage, which is associated with bent conformation induced by **PTZ** spacer group.

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1. Introduction

Dve-sensitized solar cell (DSSC) has been considered as a promising next generation solar cell because of cost-effective technology and fascinating appearance thanks to colorful dyes and semi-transparency [1]. Nanocrystalline TiO₂ film, redox electrolyte and dye are inevitable constituent in preparing DSSC. Among these constituents, dye is key component since it absorbs light and generates electrons. Band gap energy and molar extinction coefficient of dye molecule are most important physical quantities because photocurrent density is mostly affected by such optoelectronic parameters. It is obvious that photocurrent will increase as band gap energy decreases and molar extinction coefficient increases. However, when considering DSSC as a photoelectrochemical solar cell, that is, solid-liquid junction structure, modification of dye can also have influence on photovoltage. Photovoltage is determined by the difference between conductionband edge (more precisely, Fermi energy) of TiO₂ and redox

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potential. The conduction-band energy can be modified by interfacial environment. Thus, photovoltage can be tuned by different dve attached on TiO₂ surface because of the interfacial modification. Dye is generally classified into organometallic dye and organic dye. Ruthenium is commonly used as a central metal in organometallic dyes and N719-coded dye is a typical example [2]. In case of organic dye, the molecular structure is constructed based on electron donor, electron acceptor and bridging unit to connect them. Electron donor plays a role in pushing electrons in order for the photo-excited electrons to be injected into TiO₂. Various electron donors have been investigated to get high photovoltaic performance, including an electron-hole transporting triphenylamine unit [3], a coumarin unit with improved electron injection rate [4], a synthetically facile carbazole unit [5], a cost-effective indoline unit [6] and a fluorene unit less degradable than arylamine unit [7]. Although organic dyes have advantages over Ru complex dyes because of relatively low cost and high molar extinction coefficient, most of the studied organic dyes showed lower photovoltage than N719. For instance, compared with the open-circuit voltage (V_{OC}) of more than 0.8 V for N719 dye, organic dyes showed relatively lower V_{OC} ranging from 0.55 V to 0.75 V for triphenylamine dyes [8–10] coumarin dyes [11,12] carbazole dyes [5] indoline dyes [13,14] and fluorene dyes [7,15]. It has been argued



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that the low voltages observed generally from organic dyes might be due to fast recombination kinetics [16,17]. A strong interaction between organic dye and iodine in electrolyte was proposed to be responsible for accelerating recombination [18,19] and the lack of electron donating moiety in the oxidized organic dye was also proposed to have influence on fast recombination, compared to **N719** with electron donating NCS ligand [12,20]. In addition, dye aggregation due to planar or sterically less-hindered structure was also proposed as one of major factors for lowering voltage [21,22]. It is therefore required to design molecular structure of organic dye to reduce recombination and/or prevent dye aggregation.

Recently, heterocyclic phenothiazine (PTZ), originally used in drug application [23,24], has been adopted as a novel electron donor in organic dye because PTZ contains electron-rich sulfurnitrogen heteroatoms and its ring has sterically hindered nonplanar butterfly conformation, incorporation of PTZ derivatives in organic dye backbone is expected to inhibit molecular aggregation [25–28]. Yang and co-workers synthesized **PTZ** based organic dye series and compared their solar energy-to-electricity conversion efficiency [25]. Among them, 3-(10-butyl-10H-phenothiazin-3-yl)-2-cyanoacrylic acid (T2-1) based DSSC showed an efficiency of 5.5% with short-circuit current density (I_{SC}) of 10.9 mA/cm², V_{OC} of 0.712 V and fill factor (FF) of 0.71. Another attempt to modify PTZ units for DSSCs was made by Hua and co-workers, where PTZthiophene dyes with hole transporting group such as triphenylamine and 1,1,2-triphenylethene were synthesized [27]. But these dyes showed only 2.48–4.41% conversion efficiency due to low V_{OC} ranging 0.505–0.592 V. Despite a variety of molecular engineering of the PTZ species, V_{OC} of PTZ-contained dye has not been dramatically improved as expected over those of other organic dyes. For overcoming these limitations, we design and synthesize new organic dyes for high voltage DSSC based on PTZ moiety, where two different structural modifications are attempted to induce bent conformation and steric hindrance as well. Fig. 1 shows the synthesized organic dyes, where one PTZ is placed as a spacer group between electron donating triphenylamine (**D**) and electron accepting carboxylic acid (A) (D-PTZ-A) and two PTZs are introduced between electron donor and electron acceptor (D-PTZ1–PTZ2-A). Photocurrent-voltage characteristics, electron transport and electron life time of D-PTZ-A and D-PTZ1-PTZ2-A dyes are compared. Photovoltaic properties of D-PTZ-A and



D-PTZ1-PTZ2-A

Fig. 1. Molecular structures of 10-hexyl-10*H*-phenothiazine incorporated **D-PTZ-A** and D-**PTZ1-PTZ2**-A dyes.

D-PTZ1–PTZ2-A are also compared to that of the conventional ruthenium-based **N719** dye.

2. Experimental

2.1. Materials and reagents

3-Bromo-10-hexyl-10H-3-phenothiazine-carboxaldehyde (1) [29], N-(4-vinylphenyl)-N',N'-diphenylamine (2) [30] and 10-hexyl-3-vinyl-10H-phenothiazine (3) [31] were synthesized according to the reported methods. Reagents and solvents were purchased as reagent grade and used without further purification. All reactions were performed using dry glassware under nitrogen atmosphere. Analytical thin layer chromatography (TLC) was carried out on Merck 60 F254 silica gel plate and column chromatography was performed on Merck 60 silica gel (230–400 mesh).

2.2. Analytical instruments and measurements

Melting points were determined on an Electrothemal IA 9000 series melting point apparatus. NMR spectra were recorded on a Varian Mercury-400 (400 MHz) spectrometer with TMS peak as reference. MALDI-TOF MS spectra were recorded with an Applied Biosystems Voyager-DE-STR. Elemental analyses were performed with a Perkin-Elmer 2400 analyzer.

2.3. Synthesis of dyes

7-[{4-(N.N-Diphenvlamino)phenvl}ethen-3-vl]-10-hexvl-10H-phenothiazine-3-carboxaldehyde (4). To a solution of compound 2 (398 mg, 1.46 mmol) and compound 1 (569 mg, 1.46 mmol) in DMF (20 ml) were added Pd(OAc)₂ (65 mg 0.29 mmol), Bu₄NBr (941 mg, 2.91 mmol), K₂CO₃ (703 mg, 5.83 mmol) and the mixture was stirred at 105 °C for 16 h. After cooling, the solution was poured into water (50 ml) and the crude product was extracted with dichloromethane $(3 \times 50 \text{ ml})$. The combined organic layer was dried over Na₂SO₄ and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel with dichloromethane/n-hexane (1:2 v/v) to give compound 4 (452 mg, 53.1%) in a yellowish solid. Melting point was 54 °C. ¹H NMR (400 MHz, CDCl₃): $\delta = 9.78$ (s, 1H), 7.61 (dd, J = 2 Hz, 2 Hz, 1H), 7.48 (s, 1H), 7.35–7.21 (m, 8H), 7.13–7.00 (m, 8H), 6.92-6.81 (m, 4H), 3.88 (t, 2H), 1.80 (m, 2H), 1.43 (m, 2H), 1.31 (m, 4H), 0.88 (t, 3H). Anal. calcd (%) for C₃₉H₃₆N₂OS: C 80.65, H 6.25, N 4.82. Found: C 80.38, H 6.61, N 4.61.

3-[7-[{4-(N,N-diphenylamino)phenyl}ethen-3-yl]-10-hexyl-10H-phenothiazinyl]-2-cyanoacrylic acid (D-PTZ-A). A mixture of compound 4 (290 mg, 0.5 mmol) and cyanoacetic acid (425 mg, 5 mmol) in dry chloroform (30 ml) was refluxed in the presence of piperidine (1 ml) for 16 h. After cooling, the solution was poured into water (50 ml) and the crude product was extracted with chloroform $(3 \times 50 \text{ ml})$. The combined organic layer was dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography with dichloromethane/ MeOH (10:1 v/v) to give compound **D-PTZ-A** (226 mg, 69.7%) in a red solid. Melting point was 123 °C. ¹H NMR (400 MHz, DMSO-d₆): $\delta = 7.97$ (s, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.73 (s, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.37 (m, 2H), 7.30 (m, 4H), 7.12-7.01 (m, 11H), 6.92 (m, 2H), 3.91 (t, 2H), 1.68(m, 2H), 1.38 (m, 2H), 1.24 (m, 4H), 0.81 (t, 3H). MS (MALDI-TOF): *m*/*z* 647.8 [M⁺]. Anal. Calcd (%) for C₄₂H₃₇N₃O₂S: C 77.87, H 5.76, N 6.49. Found: C 77.53, H 5.99, N 6.37.

7-{(10-Hexyl-10H-phenothiazin-3-yl)ethen-3-yl}-10-hexyl-10H-phenothiazine-3-carboxaldehyde (5). To a solution of compound **3** (7.92 g, 25.6 mmol) and compound **2** (10 g, 25.6 mmol) in DMF (100 ml) were added Pd(OAc)₂ (1.14 g, 5 mmol), Bu₄NBr (16.5 g, 51.1 mmol), K₂CO₃ (12.3 g, 102 mmol) and the mixture was stirred at 105 °C for 16 h. After cooling, the solution was poured into water (150 ml) and the crude product was extracted with dichloromethane (3 × 150 ml). The combined organic layer was dried over Na₂SO₄ and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel with dichloromethane/n-hexane (1:4 v/v) to give compound **5** (11.3 g, 71.5%) in red oil. ¹H NMR (400 MHz, CDCl₃): δ = 9.80 (s, 1H), 7.62 (dd, J = 2 Hz, 2 Hz, 1H), 7.57 (d, J = 2 Hz, 1H), 7.26–7.19 (m, 4H), 7.14–7.11 (m, 2H), 6.92–6.78 (m, 7H), 3.85 (m, 4H), 1.81(m, 4H), 1.43 (m, 4H), 1.30 (m, 8H), 0.78 (m, 6H). Anal. Calcd (%) for C₃₉H₄₂N₂OS: C 75.69, H 6.84, N 4.53. Found: C 75.35, H 7.09, N 4.69.

7-{(7-Bromo-10-hexyl-10H-phenothiazin-3-yl)ethen-3-yl}-10-hexyl-10H-phenothiazine-3-carboxaldehyde (6). To a solution of compound **5** (11.3 g, 18.2 mmol) in DMF (50 ml), was added *N*-bromosuccinimide (3.41 g, 19.1 mmol). The reaction mixture was stirred at room temperature for 5 h, and then water (150 ml) was added to the solution. The reaction solution was extracted with dichloromethane (3 × 150 ml). The combined organic layer dried over MgSO₄ and evaporated under reduced pressure. The crude product was purified by column chromatography dichloromethane/ n-hexane (1:3 v/v) to give compound **6** (8.62 g, 67.8%) in red oil. ¹H NMR (400 MHz, CDCl₃): δ = 9.78 (s, 1H), 7.64–7.56 (m, 2H), 7.25–7.11 (m, 5H), 6.91–6.78 (m, 7H), 3.85 (m, 4H), 1.80(m, 4H), 1.41 (m, 4H), 1.29 (m, 8H), 0.89 (m, 6H). Anal. Calcd. (%) for C₃₉H₄₁N₂OS₂Br: C 67.13, H 5.92, N 4.01. Found: C 67.26, H 6.27, N 3.88.

7-[[7-[{4-(N,N-Diphenylamino)phenyl}ethen-3-yl]-10-hexyl-10H-phenothiazinyl]-ethen-3-yl]-10-hexyl-10H-phenothiazine-**3-carboxaldehvde (7).** To a solution of compound **2** (94 mg. 0.35 mmol) and compound 6 (244 mg, 0.35 mmol) in DMF (10 ml) were added Pd(OAc)₂ (15 mg, 0.067 mmol), Bu₄NBr (225 mg, 0.69 mmol), K₂CO₃ (168 mg, 1.39 mmol) and the mixture was stirred at 105 °C for 16 h. After cooling, the solution was poured into water (50 ml) and the crude product was extracted with dichloromethane $(3 \times 50 \text{ ml})$. The combined organic layer was dried over Na₂SO₄ and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel with dichloromethane/n-hexane (1:2 v/v) to give compound 7 (198 mg, 63.8%) in red oil. ¹H NMR (400 MHz, CDCl₃): $\delta = 9.78$ (s, 1H), 7.64-7.57 (m, 3H), 7.33-7.05 (m, 17H), 6.91-6.79 (m, 10H), 3.85 (m, 4H), 1.81(m, 4H), 1.43 (m, 4H), 1.31 (m, 8H), 0.87 (m, 6H). Anal. Calcd. (%) for C₅₉H₅₇N₃OS₂: C 79.78, H 6.47, N 4.73. Found: C 79.46, H 6.78, N 4.51.

3-[7-[[7-[{4-(N,N-Diphenylamino)phenyl}ethen-3-yl]-10hexyl-10H-phenothiazinyl]-ethen-3-yl]-10-hexyl-10H-phenothiazin-3-yl]-2-cyanoacrylic acid (D-PTZ1-PTZ2-A). A mixture of compound 7 (198 mg, 0.22 mmol) and cyanoacetic acid (187 mg, 2.2 mmol) in dry chloroform (30 ml) was refluxed in the presence of piperidine (1 ml) for 16 h. After cooling, the solution was poured into water (50 ml) and the crude product was extracted with chloroform $(3 \times 50 \text{ ml})$. The combined organic layer was dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography dichloromethane/MeOH (10:1 v/v) to give compound D-PTZ1-PTZ2-A (122 mg, 58.3%) in a red solid. Melting point was 114 °C. ¹H NMR (400 MHz, DMSO-d₆): δ = 7.89 (s, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.68 (s, 1H), 7.57 (m, 2H), 7.34–7.28 (m, 6H), 7.20–6.90 (m, 17H), 6.81-6.73 (m, 4H), 3.89 (m, 4H), 1.67(m, 4H), 1.38 (m, 4H), 1.24 (m, 8H), 0.82 (m, 6H). MS: *m*/*z* 955.0 [M⁺]. Anal. Calcd. (%) for C₆₂H₅₈N₄O₂S₂: C 77.95, H 6.12, N 5.86. Found: C 77.62, H 6.46, N 5.61.

2.4. Fabrication of dye-sensitized solar cells

Anatase TiO_2 nanoparticle and its non-aqueous paste were prepared according to the method reported elsewhere [32]. For depositing TiO₂ layer on fluorine-doped tin oxide (FTO) substrate, FTO glasses (Pilkington, TEC-8, $8 \Omega/sq$) were washed in ethanol using an ultrasonic bath for 10 min. The FTO layer was first covered with 0.1 M Ti(IV) bis(ethyl acetoacetato)-diisopropoxide (Aldrich) in 1-butanol (Aldrich) solution by spin-coating method, on which the nanocrystalline TiO₂ paste was deposited using a doctor-blade technique. After the TiO₂ films were heated at 550 °C for 1 h, the sides of TiO₂ films was trimmed to 9 mm wide and 5 mm long. The thickness of TiO₂ films was measured by Alpha step profiler (KLA Tencor). The annealed TiO₂ electrodes were immersed in ethanol (E)-2-cyano-3-(7-((E)-4-(diphenylamino))containing 0.5 mM styryl)-10-hexyl-10H-phenothiazin-3-yl)acrylic acid (D-PTZ-A) and 0.5 mM (*E*)-2-cyano-3-(7-((*E*)-2-(7-((*E*)-4-(diphenylamino) styryl)-10-hexyl-10H-phenothiazin-3-yl)vinyl)-10-hexyl-10H-phenothiazin-3-yl)acrylic acid (D-PTZ1-PTZ2-A) for 5 h at 40 °C. For comparison, ethanolic solution of 0.5 mM N719 dye (Esolar, TBA₂[RuL₂(NCS)₂], where L and TBA represent 4-carboxylic acid-4'carboxylate-2,2'-bipyridine and tetrabutylammonium, respectively) was used for N719 sensitization. Pt counter electrode was prepared by spreading a droplet of 7.0 mM H₂PtCl₆ in 2-propanol on top of a FTO substrate and heated at 400 °C for 20 min. The two electrodes were sealed with 25-µm thick Surlyn (Meltonix 1170-25, Solaronix). Redox electrolyte was introduced through a small hole drilled in the counter electrode. The electrolyte was composed of 0.7 M 1-methyl-3-propylimidazolium iodide (MPII), 0.05 M I₂ (Aldrich, 99.8%), 0.2 M LiI, 0.5 M 4-tert-butylpyridine (TBP) (Aldrich, 96%) in acetonitrile (Fluka, 99.9%) and valeronitrile (Aldrich, 99.5%) (85:15 v/v).

2.5. Characterization of photoelectrochemical and photovoltaic properties

Photocurrent and voltage were measured from a solar simulator (Oriel Sol 3A class AAA) equipped with 450 W Xenon lamp (Newport 6279NS) and a Keithley 2400 source meter. Light intensity was adjusted with the NREL-calibrated Si solar cell having KG-2 filter for approximating one sun illumination (100 mW/cm²). The cell was covered with an aperture mask to measure photocurrent and voltage accurately. The incident photon-to-current efficiency (IPCE) spectra were measured under DC mode using an IPCE system (PV Measurements, Inc.), where 75 W Xe light source was used for monochromatic light. The electrochemical impedance spectra were obtained at open-circuit voltage under aperture mask and one sun illumination with a potentiostat (Metrohm Autolab B.V.). Cyclic voltammetry was carried out with a potentiostat (Metrohm Autolab B.V.) using a three electrode cell in 0.1 M tetrabutylammonium perchlorate $((C_4H_9)_4NClO_4)$ in methylene chloride and scan rate was 100 mV/s. Pt sheet, Au electrode and Ag/AgCl electrode were used as a counter electrode, a working electrode and a reference electrode, respectively. The redox potentials are reported with a ferrocenium/ferrocene (Fc⁺/Fc) redox couple as an internal reference [33]. The absorbance was recorded by a UV-Vis spectrophotometer (Agilent 8453). The emission spectra were recorded using a photoemission yield spectrometer (RIKEN KEIKI). The concentration of dyes solution for absorbance and emission was 0.01 mM in methylene chloride. The time constants for photoinjected electron transport and recombination were measured according to published procedures [32].

3. Results and discussion

3.1. Synthesis

Synthesis of the organic dyes **D-PTZ-A** and **D-PTZ1–PTZ2-A** is performed by following the steps as depicted in Scheme 1. Each

step of the reaction sequence proceeds smoothly and efficiently to give a good or moderate yield of the product (see Section 2 for the synthetic details). The Heck reaction [34] of brominated phenothiazine aldehyde **1** with vinyl group of compound **2** produces triphenylamine substituted phenothiazine aldehyde **4** in 53.1% yield. The aldehyde **4** is reacted with cyanoacetic acid in the presence of piperidine to produce the dye **D-PTZ-A** in 69.7% yield. The dye **D-PTZ1–PTZ2-A** is synthesized starting from compound **1**, which is reacted with the vinylphenothiazine **3** under Heck reaction condition to give compound **5** in 71.5% yield. Subsequent bromination with NBS (*N*-bromosuccinimide) produces compound **6** in 67.8% yield. The aldehyde **7** is synthesized by the Heck type cross coupling reaction of compound **6** with compound **2** in 63.8% yield. Finally, Knoevenagel condensation of aldehyde **7** and cyanoacetic acid give the dye **D-PTZ1–PTZ2-A** in 58.3% yield.

The sensitizers **D-PTZ-A** and **D-PTZ1–PTZ2-A** and their precursor compounds **4–7** are highly soluble in aromatic solvents (i.e., toluene, *o*-dichlorobenzene and benzonitrile) and other common organic solvents (i.e., acetone, ethanol, CH₂Cl₂, CHCl₃, DMF, DMSO and THF). The structure and purity of the new compounds are confirmed by ¹H NMR and elemental analysis. ¹H NMR spectra of these compounds are consistent with the proposed structures, showing the expected features with the correct integration ratios. The MALDI-TOF mass spectra provide a direct evidence for the structures of **D-PTZ-A** and **D-PTZ1–PTZ2-A** showing a singly charged molecular ion peak at m/z = 647.8 and 955.0, respectively, that matches the calculated value for the molecular weight of each compound.

3.2. Optical and electrochemical properties

Fig. 2 shows absorption and emission spectra of **D-PTZ-A** and **D-PTZ1–PTZ2-A**. Absorption peaks at 317 nm (molar extinction coefficient $\varepsilon = 40,360 \text{ M}^{-1} \text{ cm}^{-1}$), 384 nm ($\varepsilon = 31,180 \text{ M}^{-1} \text{ cm}^{-1}$) and 476 nm ($\varepsilon = 18,680 \text{ M}^{-1} \text{ cm}^{-1}$) appear from **D-PTZ-A** dye solution and **D-PTZ1–PTZ2-A** shows three peaks at 260 nm ($\varepsilon = 38,500 \text{ M}^{-1} \text{ cm}^{-1}$), 319 nm ($\varepsilon = 25,350 \text{ M}^{-1} \text{ cm}^{-1}$) and 468 nm

 $(\varepsilon = 15,930 \text{ M}^{-1} \text{ cm}^{-1})$. Compared to **D-PTZ-A**, **D-PTZ1–PTZ2-A** shows hypsochromic shift and decreases its extinction coefficient, which is related to structure, associated with electron delocalization [35,36], and photo-excitation (see details from time dependent-density functional theory (TD-DFT) calculation below). It can be seen from the emission spectra that there is relatively large Stocks shift for the dve **D-PTZ1-PTZ2-A** as compared to that of **D-PTZ-A**, which underlines that the emitted photon has much less energy than the absorbed photon for the case of **D-PTZ1–PTZ2-A**. Such a large shift in the absorption and emission bands for the D-PTZ1-PTZ2-A dye may be attributed to large change in the geometrical distortion of the molecule in the excited state [37], associated with double PTZ spacer molecules. From both absorption and emission spectra, band gap of D-PTZ-A is determined to be 2.55 eV from intersection wavelength of 487 nm and that of D-PTZ1-PTZ2-A is 2.48 eV from 500 nm.

To determine highest occupied molecular orbital (HOMO) energy levels, cyclic voltammetric measurements are performed. Fig. 3 shows cyclic voltammogram for D-PTZ-A and D-PTZ1-PTZ2-A, where 1.0 mM of each dye is prepared in methylene chloride and 0.1 M tetrabutylammonium perchlorate is used as supporting electrolyte. The HOMO energy levels of **D-PTZ-A** and **D-PTZ1–PTZ2-A** are figured out from the onset oxidation potential of cyclic voltammogram. The HOMO energy level of D-PTZ-A is determined to be 1.02 V versus saturated calomel electrode (SCE) (-5.76 eV versus vacuum), and that of D-PTZ1-PTZ2-A lies at 0.84 V versus SCE (-5.58 eV versus vacuum). Based on the band gap data observed from absorption-emission spectra and HOMO energies, lowest unoccupied molecular orbital (LUMO) energy levels are determined to be -1.53 V and -1.62 V (versus SCE) for D-PTZ-A and D-PTZ1-PTZ2-A, respectively. Energetic data for D-PTZ-A and D-PTZ1-PTZ2-A are listed in Table 1.

3.3. Photovoltaic performance

Fig. 4 shows photocurrent-voltage curves and IPCE spectra for the (**D-PTZ-A**)-sensitized and (**D-PTZ1–PTZ2-A**)-sensitized DSSCs,



Scheme 1. Synthesis of D-PTZ-A and D-PTZ1–PTZ2-A; (a) compound 2, Pd(OAc)₂, Bu₄NBr, K₂CO₃, DMF, 105 °C, 16 h, 53.1% for 3, 63.8% for 7. (b) Cyanoacetic acid, piperidine, chloroform, reflux, 16 h, 69.7% for D-PTZ-A, for 53.8% for D-PTZ1–PTZ2-A. (c) compound 3, Pd(OAc)₂, Bu₄NBr, K₂CO₃, DMF, 105 °C, 16 h, 71.5%. (d) NBS, DMF, rt, 5 h, 67.8%.



Fig. 2. Absorption (black line) and emission (blue line) spectra of **D-PTZ-A** and D-**PTZ1–PTZ2-A** dyes (0.01 mM solution in methylene chloride). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

along with those of **N719**-sensitized one. Photovoltaic parameters are summarized in Table 2. Photocurrent of (**D-PTZ-A**)-sensitized DSSC is higher than that of (**D-PTZ1–PTZ2-A**)-sensitized one, which is due to higher molar extinction coefficient and more delocalized electron distribution in HOMO state as well (see iso-density surface plot in Fig. 6). V_{OC} is 23 mV higher for the (**D-PTZ1–PTZ2-A**)-sensitized DSSC than for the (**D-PTZ-A**)-sensitized DSSC than f

Table 1

Electrochemical properties of D-PTZ-A and D-PTZ1-PTZ2-A dyes.

Dye	$E_{\rm pa}\left(V\right)$	$E_{\rm pc}\left(V\right)$	E _{HOMO} ^a (V) versus SCE	$E_{0-0}(\mathrm{eV})^\mathrm{b}$	<i>E</i> _{LUMO} ^c (V) versus SCE
D-PTZ-A	1.30	0.75	1.02	2.55	-1.53
D-PTZ1-PTZ2-A	0.94	0.75	0.84	2.46	-1.62

The conduction-band level of the TiO₂ electrode and the redox potential of I^-/I_3^- were estimated to be -0.7 V versus SCE and 0.2 V versus SCE, respectively [38,39]. ^a HOMO level was measured by $E_{\text{HOMO}} = (E_{\text{pa}} - E_{\text{pc}})/2$.

^b E_{0-0} was estimated from intersection between absorbance and emission.

^c LUMO level was estimated by subtracting E_{0-0} from HOMO.

sensitized one. It is noticed that V_{OC} of 0.781 V for the (**D-PTZ-A**)sensitized DSSC and 0.804 V for the (**D-PTZ1–PTZ2-A**)-sensitized DSSC are higher than that for the **N719**-sensitized one (0.775 V) at the given 4.8-µm thick TiO₂ film. Such the tendency is preserved even at the increased film thickness of about 14 µm (nanocrystalline under layer: 10 µm, light scattering overlayer: 4 µm), where **D-PTZ-A** and **D-PTZ1–PTZ2-A** show V_{OC} of 0.746 V and 0.759 V, respectively, whereas V_{OC} of **N719** is 0.713 V (Table 2). The higher V_{OC} s for the organic dyes with **PTZ** spacer group are probably related to the recombination kinetics at TiO₂/electrolyte interface, which will be discussed in detail with transient photovoltage and impedance spectra.

To gain a further insight into the effect of the introduction of **PTZ** on photovoltaic performance, DFT is used to calculate the electronic structures and TD-DFT is adopted to investigate electronic transition from the ground state to the excited state, where the computational calculations are performed using Gaussian09 software package [40]. B3LYP exchange-correlation functional [41] and 6–31G(*d*) basis set [42] in DFT calculation are applied for the geometry optimization. The optimized geometries of both **D-PTZ-A** and **D-PTZ1–PTZ2-A** are shown in Fig. 5. The optimized geometrical parameters are quite reasonable for the X-ray structure of **PTZ** species [43], indicating that the geometry is bent along the



Fig. 3. Cyclic voltammogram of D-PTZ-A and D-PTZ1-PTZ2-A (1 mM solution in methylene chloride).



Fig. 4. (a) Photocurrent density–voltage curves and (b) incident photon-to-current conversion efficiency (IPCE) spectra for (**D-PTZ-A**)-, (**D-PTZ1–PTZ2-A**)- and N719-sensitized DSSCs. TiO₂ film thickness was 4.8 μ m.

Table 2

Comparison of short-circuit photocurrent density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF) and conversion efficiency (η) for (**D-PTZ-A**)-, (**D-PTZ1–PTZ2-A**)- and **N719**-sensitized solar cells.^a

Dye	J _{sc} (mA/cm ²)	$V_{\rm OC}\left({\rm V} ight)$	FF	η (%)	Area (cm ²)	Film thickness (µm)
D-PTZ-A	10.7	0.781	0.55	4.6	0.442	4.8
D-PTZ1-PTZ2-A	9.1	0.804	0.56	4.1	0.461	
N719	9.8	0.775	0.73	5.5	0.401	
D-PTZ-A	14.1	0.746	0.58	6.1	0.457	14.5
D-PTZ1-PTZ2-A	12.2	0.759	0.58	5.3	0.400	
N719	16.1	0.713	0.69	7.9	0.455	

^a An aperture black mask was used during measurement at AM 1.5 G 1 sun light illumination (100 mA/cm²). Electrolyte used was composed of 0.7 M 1-methyl-3-propylimidazolium iodide (MPII), 0.05 M I₂ (Aldrich, 99.8 %), 0.2 M Lil, 0.5 M 4-*tert*-butylpyridine (TBP) (Aldrich, 96 %) in acetonitrile (Fluka, 99.9 %) and valeronitrile (Aldrich, 99.5 %) (85:15 v/v).

nitrogen–sulfur (*N*–*S*) axis for **PTZ** species. The dihedral angle between the two planes of the phenyl group is about 161°, leading to a crooked geometry. At these results, we can expect that the sterically more hindered **D-PTZ1–PTZ2-A** dye will be favorable for counteracting the dye aggregation, which can be effective for higher V_{OC} than **D-PTZ-A** [44–46].

The calculated frontier molecular orbitals and electronic structures of **D-PTZ-A** and **D-PTZ1–PTZ2-A** are shown in Fig. 6. The first three single excited transition parameters of the dyes are summarized in Table 3. The electron density distribution in HOMO level of **D-PTZ-A** is spread over triphenylamine through **PTZ**. The HOMO-1 (the first lower orbital than HOMO) and HOMO-2 (the second lower orbital than HOMO) states are delocalized from **PTZ** to ethylene linker. At LUMO level, the electron density distribution is concentrated on the cyanoacrylic acid unit. For the **D-PTZ-A** dye, the



Fig. 5. Optimized molecular structures of **D-PTZ-A** and **D-PTZ1–PTZ2-A** at the B3LYP/ 6-31G(*d*) level theory.

TD-DFT calculation leads to a lowest transition at 2.21 eV, which corresponds to an excitation from HOMO to LUMO. As compared to experimental absorption maximum in Fig. 2, the absorption peak at 476 nm (2.61 eV) is attributed to the π - π * transition from HOMO to LUMO. The calculated transition is red-shifted by about 0.4 eV because it is not properly captured by TD-DFT calculation employing current exchange-correlation functional [7]. The reason



Fig. 6. Isodensity surface plot (isodensity contour = 0.02) of D-PTZ-A and D-PTZ1-PTZ2-A.

Table 3

TD-DFT calculated electronic transition configurations, excitation energy and oscillator strengths (>0.01) for the single \rightarrow single transitions of **D-PTZ-A** and **D-PTZ1–PTZ2-A**.

Dye	Transition configurations	Excitation energy (nm, eV)	Oscillator strength
D-PTZ-A	HOMO \rightarrow LUMO (97%)	559.8 (2.21)	0.4700
	HOMO-1 \rightarrow LUMO (2%)		
	HOMO-1 \rightarrow LUMO (92%)	$IOMO-1 \rightarrow LUMO (92\%)$ 472.0 (2.63)	
	$HOMO \rightarrow LUMO(3\%)$		
	$HOMO \rightarrow LUMO + 1 (2\%)$		
	$HOMO \rightarrow LUMO + 2 (93\%)$	402.1 (3.08)	1.0433
	HOMO-1 \rightarrow LUMO (2%)		
	Homo-3 \rightarrow LUMO (3%)		
D-PTZ1-PTZ2-A	HOMO \rightarrow LUMO (97%)	603.9 (2.05)	0.2742
	HOMO-1 \rightarrow LUMO (3%)		
	HOMO-1 \rightarrow LUMO (85%)	518.0 (2.39)	0.3894
	HOMO-2 \rightarrow LUMO (9%)		
	HOMO \rightarrow LUMO (3%)		
	Homo-2 \rightarrow LUMO (79%)	472.6 (2.62)	0.3266
	HOMO-1 \rightarrow LUMO (12%)		
	$HOMO \rightarrow LUMO + 1 (6\%)$		

for the difference between calculation ob observation results is that experimental results are for the dye molecules in the solution where intermolecular interactions between the dye molecules themselves and solvent-dye molecular interactions exist while TD-DFT calculation is generally performed on single molecule in gas phase. For the case of **D-PTZ1–PTZ2-A**, the LUMO state is quite similar to that of **D-PTZ-A** but electrons in the HOMO level are merely delocalized from triphenylamine to the first **PTZ** moiety (**PTZ1**).

As shown in Table 3, these disconnection between HOMO and LUMO causes to decrease the intensity for the lowest transition at 2.05 eV. Compared to lowest transition, the second transition occurs from HOMO-1 to LUMO at 2.39 eV and the intensity is much higher. This is related to the electron distribution in HOMO-1 level, where electrons spread over from triphenylamine to the second **PTZ** moiety (**PTZ2**). Such the differences in electron distribution and excited transition property can explain well the hypsochromic shift in absorption spectra for **D-PTZ1–PTZ2-A** in Fig. 2 and the larger photocurrent for **D-PTZ-A**.

In order to discuss in detail about high V_{OCS} observed in **D-PTZ-A** and **D-PTZ1–PTZ2-A** dyes, time constants for electron transport and recombination are compared. No significant difference is seen in the electron transport rate (Fig. 7a), indicating that bent conformation of organic dye has little influence on electron transport, while substantial change is observed in time constant for electron recombination as can be seen in Fig. 7b. Time constant for electron recombination increases in the following order



Fig. 7. Time constants for (a) electron transport and (b) recombination as a function of light intensity, represented by photocurrent density. TiO_2 film thickness was 4.8 μ m.



Fig. 8. (a) Nyquist plots from the impedance measurement. ω_{max} represents the frequency at the maximum imaginary resistance of the Nyquist plot. (b) V_{OC} as a function of the logarithm of the inverse of ω_{max} .

N719 < D-PTZ-A < D-PTZ1–PTZ2-A, which indicates that electron life time increases as going from N719 to D-PTZ1–PTZ2-A. Electron life time is an order of magnitude higher for D-PTZ1–PTZ2-A than for N719. Thus, compared to N719, higher V_{OC}s for the organic dyes with PTZ space group are due to slow charge recombination.

Electrochemical impedance measurements are performed to confirm the relation between V_{OC} and the charge recombination rate. The frequency at the maximum imaginary resistance of the second semicircle (ω_{max}) in the Nyquist plot (Fig. 8a) is related to back reaction constant and V_{OC} was reported to br proportional to $\ln(1/\omega_{max})$ [47]. As can be seen in Fig. 8b, the observed V_{OC} s are linearly proportional to $\ln(1/\omega_{max})$, which indicates that the opencircuit voltages for **D-PTZ-A**, **D-PTZ1–PTZ2-A** and **N719** are related to the interfacial charge transfer rate, associated with electron recombination rate. The synthesized **D-PTZ1–PTZ2-A** dye retards back reaction more effectively than **D-PTZ-A** and **N719**, which is well consistent with the result observed from transient photovoltage measurement.

4. Conclusions

We introduced one or two phenothiazine (**PTZ**) spacer group between electron donor and electron acceptor to induce bent conformation of organic dye. As a result, compared to the reported organic dyes, high voltages were obtained and those were even higher than that of the ruthenium-based **N719** dye. Incorporation of two **PTZ**s led to slower recombination than one **PTZ**, which might be related to enhancement of non-planarity and thereby enhancement of steric hindrance against electron back reaction. Non-planar geometry in organic dye was proved to be one of important factors affecting photovoltage.

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