

Effect of Five-Membered Heteroaromatic Linkers to the Performance of Phenothiazine-Based Dye-Sensitized Solar Cells

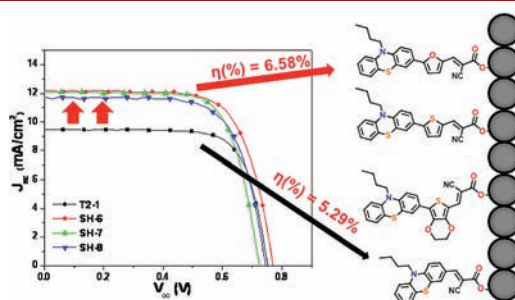
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ABSTRACT



Phenothiazine derivatives with various conjugated linkers (furan, thiophene, and 3,4-ethylenedioxythiophene) were synthesized and used in dye-sensitized solar cells to study the effect of conjugated linkers on device performance. Among them, one with furan as a conjugated linker showed a solar energy-to-electricity conversion efficiency (η) of 6.58%, an improvement of over 24% compared with the T2-1 reference cells' 5.29% under AM 1.5 G irradiation.

Dye-sensitized solar cells (DSSCs) have been recently considered promising solar devices since Grätzel et al. reported Ru sensitizers in 1991.¹ Although Ru sensitizers (N3, N719, and black dye) have been reported to give high photoelectric conversion efficiencies of over 11% at AM 1.5 conditions,² the use of rare and expensive metals in dye synthesis limits their commercial applicability.

On the other hand, non-Ru sensitizers (organic dyes, porphyrins, and analogues) are relatively inexpensive and easy to synthesize, and their structures can be easily modified. They also have high molar extinction coefficients. For these reasons, non-Ru sensitizers have been

extensively studied. Recently, the high efficiencies up to 11% by porphyrin dyes have been reported.³

Phenothiazine contains electron-rich nitrogen and sulfur heteroatoms in a heterocyclic structure with high electron-donating ability. Its nonplanar butterfly conformation can inhibit molecular aggregation⁴ (Supporting Information (SI) Figure S4A). These advantages, along with their unique electro-optical properties, make phenothiazine and its derivatives suitable hole transport materials (HTMs) for organic devices.⁵ Haque et al. reported a group of HTMs with incorporated phenothiazines. The materials retarded the recombination of photoinjected electrons and holes through their spatial separation in the semiconductor.⁶ Therefore, DSSCs' efficiency could be increased through the use of phenothiazine as sensitizer.

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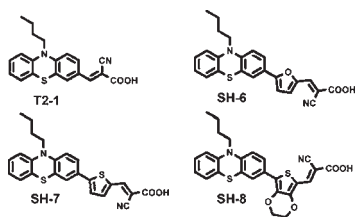


Figure 1. Structure of the dyes.

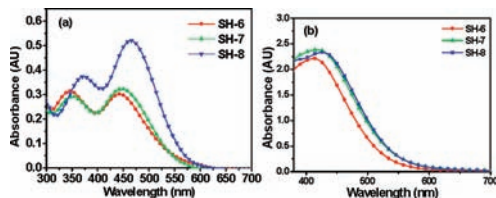


Figure 2. UV-vis absorption spectra of SH-6–8 dyes: (a) in CH_2Cl_2 solutions and (b) on TiO_2 films.

However, despite its potential, there is little work reporting phenothiazine-based sensitizers in DSSCs.

Electrons should be easily transferred from donor (D) to acceptor (A) for improved efficiency of DSSCs with D- π -A structure. For this, a suitable π -conjugated linker is required between the donor and the acceptor. Although various conjugated linkers (e.g., furan,⁷ thiophene, and 3,4-ethylenedioxythiophene (EDOT)) have been tested with several donor moieties,⁸ their use with phenothiazine moieties has not been greatly studied.

Therefore, this work evaluates the use of various conjugated linkers with different resonance energies with phenothiazine for improved efficiency. To study the effects of chenodeoxylic acid (CDCA) as a coadsorbent on the performance of DSSCs, conversion efficiency was compared between DSSCs with (10 mM and saturated) and without CDCA.

The evaluation aided the design and synthesis of D- π -A structure for use as DSSCs. Phenothiazine with high electron-donating ability was used as the electron donor. Five-membered heteroaromatic rings with low resonance energy (furan, 16; thiophene, 29 kcal/mol)⁹ and electron-rich EDOT, which has been applied in polymer-based photovoltaic devices,¹⁰ were used as π -conjugated linkers. The electron acceptor was cyanoacrylic acid.

To the best of the authors' knowledge, this is the first report of tuning photovoltaic performance through structural modification of various π -conjugated linkers with phenothiazine donor moieties. The synthesized organic dyes (T2-1¹¹ and SH-6–8) are shown in Figure 1, and their synthetic routes are depicted in SI Scheme 1.

The UV-vis absorption spectra of the dyes in CH_2Cl_2 solutions are shown in Figure 2a. Their absorption,

Table 1. Optical and Electrochemical Properties of SH-6–8 Dyes

dye	absorption ^a		emission ^a		oxidation potential data ^f		
	$\lambda_{\text{max}}/\text{nm}$	$\epsilon/\text{M}^{-1}\text{cm}^{-1}$	$\lambda_{\text{max}}/\text{nm}$	$\lambda_{\text{max}}/\text{nm}$	E_{ox}/V	E_{0-0}^d/V	$E_{\text{ox}}-E_{0-0}^d/\text{V}$
SH-6	442	15 100	412	641	0.78	2.26	-1.48
SH-7	448	16 200	416	634	0.89	2.24	-1.35
SH-8	466	26 000	426	546	0.87	2.20	-1.33

^a Measured in 2×10^{-5} M of CH_2Cl_2 solutions at room temperature.

^b Measured on TiO_2 film. ^c Measured in DMF containing 0.1 M of tetrabutylammonium tetrafluoroborate (TBABF₄) electrolyte (working electrode: glassy carbon; counter electrode: Pt; reference electrode: Ag/Ag⁺; calibrated with ferrocene/ferrocenium (Fc/Fc⁺) as an internal reference and converted to NHE by addition of 630 mV).¹² ^d Estimated from onset wavelength in absorption spectra.

emission, and electrochemical properties are listed in Table 1. The absorption spectra show two major bands at ca. 300–400 nm and at ca. 400–600 nm. UV absorption was attributed to localized aromatic π - π^* transitions. Visible absorption was ascribed to intramolecular charge-transfer (ICT) transitions. The absorption maxima (λ_{max}) of SH-6–8 were at 442, 448, and 466 nm, respectively. The λ_{max} of SH-7 with thiophene linker was red-shifted 6 nm compared with that of SH-6 with furan linker.

This was due to better delocalization of electrons over the whole molecule when thiophene was used rather than furan. The λ_{max} of SH-8 with EDOT linker was red-shifted 18 nm compared with that of SH-7. This was also due to better delocalization of electrons over the π -conjugated molecules by the electron-rich EDOT. The molar extinction coefficients at λ_{max} of SH-6–8 were 15 100, 16 200, and 26 000 $\text{M}^{-1}\text{cm}^{-1}$, respectively. These are higher than those of standard ruthenium dyes N3 and N719 (13 900 and 14 000 $\text{M}^{-1}\text{cm}^{-1}$, respectively).¹³ In solution, these dyes' molar

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extinction coefficients and absorption spectra were enhanced and red-shifted as the electronegativity of the heteroatoms decreased and the electron density in the conjugation linkers increased. Higher molar extinction coefficients in organic dyes afford the use of thinner TiO₂ film for a given efficiency, which in turn increases the rate of electron diffusion in the film due to lower resistance and reduces the charge recombination rate during electron transport.⁴ The absorption maxima of **SH-6–8** on TiO₂ films are shown in Figure 2b. They were blue-shifted by 30, 32, and 40 nm, respectively, from those in CH₂Cl₂ solutions, likely because of H-aggregation^{11,14} of the dyes or deprotonation¹⁵ of carboxylic acid upon its adsorption to the TiO₂.

Cyclic voltammetry (CV) of the dyes was performed in CH₂Cl₂ solutions to measure first oxidation potentials (E_{ox}) corresponding to the dyes' HOMO levels (SI Figure S1). The HOMO and LUMO levels of the dyes are listed in Table 1 (SI Figure S1). All the dyes' HOMO levels were more positive than that of iodine–iodide (0.4 V vs NHE)¹⁶ and were sufficiently positive to regenerate oxidized dyes from the redox electrolyte (I⁻/I₃⁻). The LUMO level of a dye can be obtained by subtracting the zeroth–zeroth energy (E_{0-0}), estimated from the onset wavelength of the absorption spectrum, from $E - E_{ox}$. The LUMO levels of these dyes were sufficiently more negative than the conduction band energy level (E_{cb}) of TiO₂ (–0.5 V vs NHE)¹⁶ to allow excited electrons to be efficiently injected into the TiO₂ electrode (Table 1).

DSSCs were fabricated using these dyes as sensitizers, and their photovoltaic properties were measured under AM 1.5 G irradiation (100 mW cm⁻²). Details of the devices' manufacture and testing are described in SI

The effect of various conjugated linkers on the DSSCs' performance was assessed by measuring cells' conversion efficiencies relative to a **T2-1** reference (Table 2). Figure 3a and b show cells' photocurrent–voltage ($J-V$) curves and incident photocurrent conversion efficiency (IPCE) spectra in 10 mM of CDCA, where the best efficiency was obtained. $J-V$ curves under other conditions are shown in SI Figure S3. In 10 mM of CDCA, the efficiencies of **SH-6–8** increased 24.3, 19.4, and 15.1% ($\eta = 6.58, 6.32,$ and 6.09%), respectively, compared with that of **T2-1** ($\eta = 5.29\%$, Table 2). The dyes' J_{sc} values increased in the order: **T2-1** (reference; $J_{sc} = 9.47$ mA cm⁻²) < **SH-8** (23.3% improvement; $J_{sc} = 11.68$ mA cm⁻²) < **SH-7** (27.2% improvement; $J_{sc} = 12.05$ mA cm⁻²) < **SH-6** (28.6% improvement; $J_{sc} = 12.18$ mA cm⁻²). The IPCE spectra of **SH-6–8** showed higher and broader spectral ranges than that of **T2-1** (Figure 3b). The dyes' IPCE maxima increased in the order: **T2-1** (74.92% at 450 nm) < **SH-8** (75.09% at 500 nm) < **SH-7** (75.16% at 460 nm) < **SH-6** (78.22% at 510 nm). The IPCE maxima increased in order with J_{sc} values and the cells' efficiencies. The results indicate that **SH-6–8** with bridge group to phenothiazine moiety afford higher and broader IPCE spectra than **T2-1**. These, in turn,

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Table 2. Photovoltaic Performance Data of the Dyes^a

dye	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	η (%)	λ_{max}/nm (IPCE, %)
T2-1	9.47	751.5	74.31	5.29	450/74.92
SH-6	12.18	771.7	70.02	6.58	510/78.22
SH-7	12.05	724.5	72.33	6.32	460/75.16
SH-8	11.68	745.7	69.95	6.09	500/75.09

^a Measured under AM 1.5 G irradiation (100 mW cm⁻¹) with 0.24 cm² working area. Dyes were maintained at 0.5 mM in CH₂Cl₂ solutions, with 10 mM of CDCA coadsorbent. Electrolyte was 0.7 M 1-propyl-3-methyl-imidazolium iodide (PMII), 0.2 M of LiI, 0.05 M of I₂, and 0.5 M of TBP in acetonitrile–valeronitrile (v/v, 85/18).

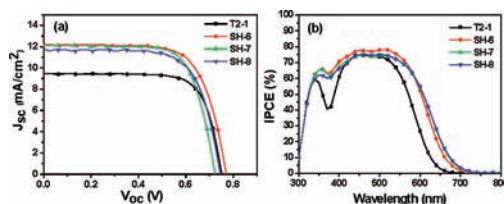


Figure 3. (a) $J-V$ curves for DSSCs based on the dyes (with 10 mM of CDCA) under illumination of AM 1.5 G simulated sunlight (100 mW cm⁻²). (b) IPCE spectra of the same DSSCs.

increase J_{sc} values which led to improved photovoltaic performances of the DSSCs. **SH-6**, with furan moiety, had the highest J_{sc} value and best photovoltaic performance.

To gain further insight on the above results, density functional theory (DFT) calculations were carried out at the B3LYP/6-31G(d,p) level. The optimized structures and electron distributions of the dyes' HOMOs and LUMOs are depicted in SI Figure S4. The torsion angle of **SH-6**, measured between the PTZ donor and the conjugated linker in the dyes, was smaller than those of **SH-7** and **SH-8**; it had a flatter structure. The electron distributions of the dyes' HOMOs were mainly delocalized over the PTZ moiety and the conjugation linkers. The LUMOs showed localized electron distributions though the cyanoacrylic acid and its adjacent conjugation linkers. Therefore, HOMO–LUMO excitation induced by light irradiation could shift the electron distribution from the PTZ-donor moiety to the anchoring moiety. This separation of electrons will ensure efficient electron injection from the dye to the TiO₂ film.

SH-6 with furan showed higher J_{sc} than **SH-7** with thiophene and **SH-8** with EDOT because electrons could be more easily transferred from the PTZ-donor moiety into the TiO₂ due to the flatter structure and low resonance energy of the furan compared with those of the thiophene or EDOT. Nonbonded S–S and S–O interactions¹⁷ of thiophene and EDOT may also have had deleterious effects on the injection of the excited electrons into the TiO₂. These interactions can occur between adjacent bridge groups when dyes are aggregated and slightly increase the tendency of thiophene to trap charges from the donor.^{7b}

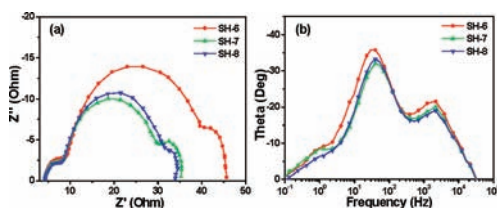


Figure 4. EIS spectra of DSSCs based on **SH-6–8** dyes measured at -0.6 V forward bias in the dark: (a) Nyquist and (b) Bode phase plots.

Interfacial charge transfer in DSSCs can be investigated by electrochemical impedance spectroscopy (EIS).¹⁸

Nyquist and Bode phase (Figure 4a and b, respectively) plots typically have three semicircles and frequency peaks. The middle semicircle in the Nyquist plots indicates charge-transfer resistance at the TiO_2 /dye/electrolyte interface. The radius of the middle semicircles indicates charge recombination resistance, radii were ranked: **SH-7** < **SH-8** < **SH-6** and represented electron lifetimes (τ) of 6.99, 9.31, and 16.81 ms, respectively. Longer electron lifetime indicates improved suppression of back reactions between the injected electrons and the electrolyte; they lead to improvement of V_{oc} due to reduced charge recombination rate.¹⁹ The middle-frequency peak in the Bode phase plots also corresponds to charge transfer at the TiO_2 /dye/electrolyte interface. The DSSC based on **SH-6** showed a lower frequency peak than those based on **SH-7** or **SH-8**, indicating a longer electron lifetime.¹⁸ The ranking of electron lifetimes observed by EIS coincided with that of V_{oc} values: **SH-6**, with the highest V_{oc} , had a longer electron recombination lifetime than **SH-7** or **SH-8**.

This may be due to its reduced molecular aggregation, which facilitates charge recombination between molecules. The PTZ donors of the dyes had nonplanar structures with butterfly conformations that inhibit molecular aggregation.⁴ The PTZ-torsion angles of the dyes were ranked: **SH-7** < **SH-8** < **T2-1** < **SH-6** (Figure S4A). The ranking of torsion angles correlated with that of V_{oc} values. Increased torsion angle could reduce molecular aggregation through steric hindrance and improve V_{oc} .

The effects of CDCA were assessed by testing DSSCs with (10 mM and saturated) and without CDCA in the dye solutions (SI Table S1). Cells fabricated with CDCA generally showed improved performance parameters (J_{sc} , V_{oc} , and FF). Each cell's efficiency was also increased by

CDCA. J_{sc} and V_{oc} were higher in cells fabricated with 10 mM of CDCA than in those fabricated with saturated CDCA. Accordingly, η was higher when 10 mM of CDCA was used. This could be due to increased competition for adsorption on the TiO_2 surface between the dye and the CDCA molecules when saturated CDCA was used. This implies that CDCA needs to be used at an appropriate concentration depending on the structure of the dye to obtain high V_{oc} and efficiency.

Improvements of V_{oc} are generally related to negative shifts of the conduction band edge or suppression of charge recombination.¹⁵ CDCA molecules were adsorbed on the TiO_2 surface as chenodeoxycholate anions, hence the TiO_2 surface was negatively charged. Therefore, the conduction band edge of the TiO_2 should be negatively shifted by the coadsorption of CDCA, increasing V_{oc} .²⁰ The coadsorption of CDCA can also suppress charge recombination between injected electrons and I_3^- ions in the electrolyte, improving V_{oc} .¹⁵ These results show that the appropriate addition of CDCA was effective in improving V_{oc} and DSSC efficiency.

In summary, novel phenothiazine-based organic dyes (**T2-1**¹¹ and **SH-6–8**) were designed and synthesized to study the effects of various conjugated linkers and CDCA on the performance of DSSCs in D- π -A systems. Cells' η values increased both by the introduction of π -conjugated linkers (furan, thiophene, and EDOT) and by the addition of CDCA coabsorbent. The introduction of π -conjugated linkers and CDCA mainly contributed to improving the dyes' J_{sc} and V_{oc} , respectively. The most efficient π -conjugated linker was furan (16 kcal/mol), which had a lower resonance energy and longer electron recombination lifetime than thiophene (29 kcal/mol) or EDOT. Incorporating CDCA into cells increased their efficiency. Cells' η values were highest when CDCA was used at 10 mM. The highest solar energy-to-electricity conversion efficiency was achieved by a cell fabricated with **SH-6** ($\eta = 6.58\%$, $J_{sc} = 12.18$ mA/cm², $V_{oc} = 771.7$ mV, $FF = 70.02\%$, $\text{IPCE}_{\text{max}} = 78.22\%$ at $\lambda_{\text{max}} = 510$ nm). Its efficiency was 24% higher than the 5.29% achieved by **T2-1** under similar conditions (AM 1.5 G sunlight). These results suggest that phenothiazine moieties are promising donor groups for high-performance DSSCs. Performance and stability could be improved by appropriate control of the energy levels of π -conjugated linkers through further structure modification of the D- π -A system.

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Supporting Information Available. DSSCs fabrication, synthesis, and characterization details for new compounds. The material is available free of charge via the Internet at <http://pubs.acs.org>.

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