



# Highly conjugated electron rich thiophene antennas on phenothiazine and phenoxazine-based sensitizers for dye sensitized solar cells



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## ABSTRACT

Four new organic dyes, coded as **CSORG6**, **CSORG7**, **CSORG8** and **CSORG9**, comprising electron rich thiophene derivatives as antennas and cyanoacrylic acid as acceptor, bridged by phenothiazine or phenoxazine were designed and synthesized for dye-sensitized solar cells applications. They were fully characterized with their photophysical, electrochemical properties, density functional theory (DFT), time dependent density DFT (TDDFT) and the light-harvesting properties of the new sensitizers were evaluated with nanocrystalline TiO<sub>2</sub>-based devices. Among the four diheteroanthracene based dyes, phenoxazine (**CSORG7** and **CSORG9**) based devices afforded the best photovoltaic performance ( $\eta$ ) of 6% under standard AM 1.5G solar irradiation, whereas, **N719** showed ( $\eta$ ) 6.4% under the similar fabrication and evolution conditions.

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## 1. Introduction

Dye sensitized solar cells (DSSCs) [1–3] are cheaper and attractive alternate renewable energy sources compared to currently used conventional silicon based solar cells. To date, power conversion efficiencies greater than 11% have been achieved with ruthenium sensitizers using liquid electrolyte under AM 1.5 irradiation [4–9]. However, the large scale production of these ruthenium dyes are difficult because of high cost and environmental issues [10]. Recently, more attention has been paid to metal-free organic dyes due to their high molar-extinction coefficients and easy synthesis procedures, as well as lesser environmental concerns compared to the heavy-metal-based complexes [4,6]. The remarkable structural diversity of this class of sensitizers offers infinite possibilities to tune the photophysical and electrochemical properties for the optimization of solar cell performance. In particular, encouraging efficiency up to 10.3% has been reported by using metal free organic dyes [11]. The metal free organic sensitizers not

only perform as efficient single dyes but also improve the performance as co-adsorbents along with a base-dye [12,13]. Recently, we achieved a record efficiency of 11.4% using a simple organic sensitizer as a co-adsorbent in a black dye based test cell [14]. In addition, the highest solar to power conversion efficiency, exceeding 13% was reported based on Zn-porphyrin complex with cobalt redox electrolyte [15]. More recently, organometallic perovskites attracted intense interest as light-harvesting materials for mesoscopic solar cells, which can be processed with solution-based techniques at low-temperatures [16–19]. Graetzel et al. [20] reported a high efficiency 14.14%, certified cell of this class, which put the perovskite solar cells ahead of several traditional technologies.

Regardless of photophysical nature of the dyes, electron recombination with the electrolyte is reflected to be more detrimental to the power conversion efficiency in DSSC devices. In order to prevent this, introduction of long pendant groups on the sensitizer is one of the strategies that separates the electrolyte from direct contact with electrode material. Additionally, this phenomenon increases the long-term stability of the device. The presence of alkyl chains can inhibit the recombination losses in DSSCs [21–25] and the introduction of thiophene moieties as stable diene equivalents improve the molar extinction coefficient associated with broadening of absorption towards red. Moreover, a strategy of tethering

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alkyl thiophene moiety on the sensitizer reduced the aggregation effect leading to higher PCE in DSSCs [21].

Recently, triphenylamine (TPA) [26–29], phenothiazine (PTZ) [30–35] and phenoxazine (POZ) [36,37]-based chromophores have received great attention due to their potential as electron donors. Especially diheteroanthracene like PTZ and POZ moieties are containing electron rich nitrogen, oxygen or sulphur atoms, and these rings have unique butterfly conformations which can impede the molecular aggregation and the formation of intermolecular excimers [38]. Further, Tian et al. [39] have studied the effect of different electron donors in DSSCs and showed that sensitizers with a PTZ electron-donating unit gave promising efficiencies, with even better performance than the TPA based dyes. Sun et al. [31,36] described that a POZ (tricyclic isoster of PTZ) based dye exhibited improved performance over PTZ as the PTZ and POZ units displayed a stronger electron-donating ability than the TPA unit [40]. To the best of our knowledge only a few reports available in the literature on the application of small molecular dyes containing PTZ and especially POZ moieties in DSSCs [30–37].

Based on the above consideration, and our experience on ruthenium [41–52] and metal free [34,53–55] organic sensitizers engineered with PTZ [34] and thiophene units [54,55], we have designed and synthesized four new efficient organic diheteroanthracene-based dyes (CSORG6–CSORG9 shown in Fig. 1) with cyanoacrylic acid anchoring group and variation of  $\pi$ -conjugated donor antennas. The new sensitizers have been successfully applied to the sensitization of nanocrystalline TiO<sub>2</sub>-based solar cells. The optical, electrochemical and photovoltaic properties of the four new sensitizers were investigated.

## 2. Experimental

### 2.1. Materials and instruments

The starting materials phenothiazine, phenoxazine, bromohexane, hexylthiophene boronic acid, hexylbithiophene boronic acid, *N*-bromosuccinimide and cyanoacetic acid were purchased from Sigma–Aldrich. The solvents were purified by standard procedures and purged with nitrogen before use. All other chemicals used in this work were of analytical grade and were used without further purification, and all reactions were performed under argon atmosphere. Chromatographic separations were carried out on silica gel (60–120 mesh). <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra were recorded on Avance 300 and 500 MHz spectrometer using TMS as internal standard. Mass spectra were recorded on Shimadzu LCMS-2010EV model with ESI probe. Absorption spectra were recorded on a shimadzu UV-Vis to near IR 3600 spectrophotometer. Emission spectra were recorded on a Fluorolog 3, J.Y. Horiba fluorescence spectrometer. Electrochemical data were recorded using Autolab potentiostat/Galvanostat PGSTAT30. The cyclic voltammogram curves were obtained from a three electrode cell in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> *N,N*-tetrahydrofuran solution at a scan rate of 100 mV s<sup>-1</sup>, Pt wire as a counter electrode and an Ag/AgCl reference electrode and calibrated with ferrocene.

### 2.2. Preparation of TiO<sub>2</sub> electrode

Nanocrystalline TiO<sub>2</sub> photoelectrodes of about 20  $\mu$ m thickness (area: 0.23 cm<sup>2</sup>) were prepared using a variation of a method reported by Graetzel and co-workers [56]. Fluorine-doped tin oxide coated (FTO) glass electrodes (Nippon Sheet Glass Co., Japan) with a sheet resistance of 8–10  $\Omega$  m<sup>-2</sup> and an optical transmission of >80% in the visible range were used. Anatase TiO<sub>2</sub> colloids (particle size  $\sim$ 13 nm) were obtained from commercial sources (Ti-Nanoxide D/SP, Solaronix). The nanocrystalline TiO<sub>2</sub> thin films of

approximately 20  $\mu$ m thickness were deposited onto the conducting glass by screen-printing. The film was then sintered at 500 °C for 1 h. The film thickness was measured with a Surfcom 1400A surface profiler (Tokyo Seimitsu Co. Ltd.). The electrodes were impregnated with a 50 mM titanium tetrachloride solution and sintered at 500 °C. The dye solutions ( $2 \times 10^{-4}$  M) were prepared in 1:1 acetonitrile and *tert*-butyl alcohol solvents. The electrodes were immersed in the dye solutions and then kept at 25 °C for 20 h to adsorb the dye onto the TiO<sub>2</sub> surface.

### 2.3. Fabrication of dye-sensitized solar cell

Photovoltaic measurements were performed in a two-electrode sandwich cell configuration. The dye-deposited TiO<sub>2</sub> film was used as the working electrode and a platinum-coated conducting glass as the counter electrode. The two electrodes were separated by a Surlyn spacer (40  $\mu$ m thick) and sealed up by heating the polymer frame. The electrolyte was composed of 0.6 M dimethylpropylimidazolium iodide (DMPII), 0.05 M I<sub>2</sub>, 0.5 M TBP and 0.1 M LiI in acetonitrile and is introduced into the device by vacuum filling method through the predrilled hole on the counter electrode followed by ceiling of the hole.

### 2.4. Photovoltaic characterization

The working electrode was illuminated through a conducting glass. The current–voltage characteristics were measured using the previously reported method [57] with a solar simulator (AM-1.5, 100 mW/cm<sup>2</sup>, WXS-155S-10: Wacom Denso Co., Japan). Monochromatic incident photon-to-current conversion efficiency (IPCE) for the solar cell, plotted as a function of excitation wavelength, was recorded on a CEP-2000 system (Bunkoh-Keiki Co. Ltd.). Incident photon-to-current conversion efficiency (IPCE) at each incident wavelength was calculated from Eq. (1), where  $J_{SC}$  is the photocurrent density at short circuit in mA cm<sup>-2</sup> under monochromatic irradiation,  $q$  is the elementary charge,  $\lambda$  is the wavelength of incident radiation in nm, and  $P_0$  is the incident radiative flux in W m<sup>-2</sup>.

$$\text{IPCE}(\lambda) = 1240 \left( \frac{J_{SC}}{q\lambda P_0} \right) \quad (1)$$

### 2.5. Synthesis

**10-Hexyl-10H-phenothiazine (1a):** A 100 mL 3-neck flask was charged with phenothiazine (2.00 g, 10.036 mmol), NaH (0.29 g, 12.043 mmol), and DMF (30 mL). The resulting mixture was stirred for 30 min, bromohexane (1.806 mL, 12.043 mmol) was then added and the mixture was stirred overnight at room temperature. The reaction mixture was quenched with ice water (400 mL) and extracted three times with ethylacetate. The combined organic fractions were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using *n*-hexane/ethylacetate (9/1, v/v) as the eluent to give viscous liquid **1** (82%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.05–7.10 (m, 4H), 6.78–6.87 (m, 4H), 3.81 (t, 2H), 1.74–1.83 (m, 2H), 1.25–1.44 (m, 6H), 0.86 (t, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 145.27, 127.34, 127.09, 124.84, 122.23, 115.32, 47.38, 31.43, 26.85, 26.62, 22.55, 13.95. ESI-HRMS calcd for C<sub>18</sub>H<sub>22</sub>NS (M+H)<sup>+</sup>: 284.14675, found: 284.14709.

**10-Hexyl-10H-phenithiazine-3-carbaldehyde (2a):** To a solution of 10-hexyl-10H-phenothiazine (**1a**) (0.800 g, 2.836 mmol) and dry DMF (0.240 mL, 3.120 mmol) in 1,2-dichloroethane (DCE) (10 mL), POCl<sub>3</sub> (0.294 mL, 3.120 mmol) was added slowly at 0 °C in an ice water bath. The mixture was heated at reflux overnight. The reaction mixture was quenched with water and extracted three times

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