Dyes and Pigments 96 (2013) 722-731

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments



journal homepage: www.elsevier.com/locate/dyepig

# Phenothiazine-based dyes with bilateral extension of $\pi$ -conjugation for efficient dye-sensitized solar cells

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## ARTICLE INFO

Article history: Received 2 August 2012 Received in revised form 2 November 2012 Accepted 6 November 2012 Available online 20 November 2012

Keywords: Dye-sensitized solar cells Phenothiazine Bilateral extension Recombination Photovoltaic performance Organic dye

#### 1. Introduction

## ABSTRACT

Four novel organic photo-sensitizers based on phenothiazine were designed, synthesized and characterized for efficient dye-sensitized solar cells. Anisole, octyloxybenzene and dodecyloxybenzene were incorporated into the phenothiazine by an Ullmann reaction. An additional octyloxybenzene was incorporated into one dye unit through a Suzuki coupling reaction. The modified phenothiazine moiety acts as an electron donor and cyanoacrylic acid acts as an electron acceptor and anchoring unit. The photophysical, electrochemical and sensitizing characteristics of the new dyes were evaluated. The bis(octyloxybenzene) substituted dye delivered the best performance with its sensitized solar cell displaying an overall power conversion efficiency of 5.73% under standard illumination. The results indicate that bilateral conjugate extension of the  $\pi$  conjugation can increase their light harvesting capacity and electron lifetime, leading to improvements in the efficiency of their dye-sensitized solar cells.

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Owing to the rapid and continuous depletion of fossil fuel resources, there are now serious concerns over alternative sources of energy sufficient to cater for the world's increasing energy requirements [1]. Solar energy, which is enormous and essentially inexhaustible, has the largest potential to satisfy the future global need for renewable energy without appreciable environmental issues [2].

During the past two decades dye-sensitized solar cells (DSSCs), a millennium technology [3] have already undergone intensive investigation as a promising inexpensive alternative to conventional p—n junction solar cells since O'Regan and Grätzel reported effective DSSCs in 1991 [4]. A significant and sustained effort has been made to make this technology commercially viable. Metals like ruthenium and zinc based organic dyes have already achieved efficiencies over 11% [5,6] and 12% [7] respectively, while metal free organic dyes have also delivered efficiency over 9% [8].

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Metal free organic dyes being inexpensive and easy to synthesize with high molar extinction coefficients are advantageous over metallic organic dyes which are rather expensive and hard to purify. However, organic dyes suffer from some drawbacks such as lower conversion efficiencies and stability as compared to metallic organic dyes [9–11]. One reason for the lower efficiency of the organic dyes is related to the fast recombination which is due to strong interaction between the organic dye and iodine. When dyes are adsorbed on the external surface of spherical TiO<sub>2</sub> nanoparticles, they facilitate the formation of a radial arrangement with the acceptor anchoring segment pointing toward the TiO<sub>2</sub> surface and the donor away from the surface. So, a rod like configuration of the dyes attached to TiO<sub>2</sub> pertains to which has interspaces that provide the path for redox couples [12]. Moreover, these rod shaped structures are susceptible to aggregation due to strong dipole-dipole interactions between the delocalized  $\pi$ -bonds, which creates hindrance in electron injection from the excited state of the dye to the conduction band of TiO<sub>2</sub>. Furthermore, lack of an electron donating moiety in the oxidized dye plays a vital role in recombination. Light harvesting capability of the dyes is another major factor for the conversion efficiency from solar light to electricity.



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It is believed that efficient electron injection from the dye to the conduction band of TiO<sub>2</sub>, reduction of recombination and dark current as well as effective regeneration of dye are the leading factors for the enhancement of power conversion efficiency [13-15]. The effectiveness of dyes can be increased by reduction of  $\pi - \pi$  stacking on the TiO<sub>2</sub> surface which always shortens the lifetime of excited states [16,17]. It has been reported that alkoxy groups besides electron donating also reduce aggregation of dyes in TiO<sub>2</sub> films [18]. Aromatic rings do not only increase the light harvesting capabilities but also reduce surface aggregation, leading to enhancement of the electron injection rates [19]. Recently, the effect of various alkoxy chains on triphenylamine (TPA) has been studied and high incident photon to electric current conversion efficiency and stability have been observed [20,21]. Various other studies conclude that alkyl chains linked to a donor increase Voc and suppress recombination processes [22,23]. Great progress has been made in this field and various electron donors like TPA [24], indoline [25], carbazole [26], merocyanine [27], polyene [28], hemicyanine [29], fluorene [30], tetrahydroquinoline [31], phenoxazine [32] and phenothiazine [33] have been investigated.

Phenothiazine (PTZ) is a non-planar heterocyclic compound which has electron rich sulfur and nitrogen atoms with a butterfly conformation at the ground state [34]. PTZ has been widely employed in thin film transistors, photovoltaic cells and light emitting diodes due to its impedance in molecular aggregation and potential hole transport characteristics [35]. Thermally and electrochemically stable phenothiazine is a strong electron donor, even better than triphenylamine, tetrahydroquinoline, carbazole and iminodibenzyles [36,37]. The additional electron rich sulfur atom renders PTZ a stronger donor than other amines. PTZ based dyes containing various  $\pi$  spacers have been thoroughly investigated [34,38,39]. Phenothiazine linked with other electron donating groups like triphenylamine were studied by Tian et al., but the efficiency remains low [35]. The dye with two PTZ units directly linked with the conjugated system was found to be less effective as compared to a single PTZ unit [40]. However, the dye with two PTZ units linked with an alkyl chain has greatly enhanced the efficiency [41,42]. Therefore, PTZ has great attraction due to its unique structure and it can be modified for efficient DSSCs.

In the current study, systematic modifications of PTZ were made for the enhancement of the light harvesting capabilities and reduction of aggregation, leading to increase in efficiency of DSSCs. Thus, a series of dyes **Z1–Z4** with lateral and bilateral conjugate extension of PTZ by incorporation of alkoxyphenyl moieties at the 7 and 10 positions were designed and synthesized (Scheme 1). Their photophysical, photochemical and photovoltaic characteristics were investigated in detail.

#### 2. Experimental section

### 2.1. Instrumentation and materials

<sup>1</sup>H NMR spectra were conducted on Bruker 400 MHz spectrometer in  $CDCl_3$  or  $DMSO-d_6$  with tetramethylsilane as internal



Scheme 1. Syntheses of the dyes Z1–Z4. (i) Dichlorobenzene, Cu-powder, 18-crown-6-ether, K<sub>2</sub>CO<sub>3</sub>, 185 °C, 48 h; (ii) DMF, POCl<sub>3</sub>, 0 °C; then dichloroethane, 1b, 90 °C, overnight; (iii) cyanoacetic acid, piperidine, acetonitrile, reflux, 5 h; (iv) chloroform, NBS, 70 °C, 8 h; (v) hydroxyphenylboronic acid, THF, K<sub>2</sub>CO<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, 70 °C, 48 h; (vi) DMF, K<sub>2</sub>CO<sub>3</sub>, bromooctane, 130 °C, 24 h.

standard. MS data were recorded on an Esquire HCT PLUS mass spectrometer. Elementary analyses were performed by using Vario ELIII Analyzer while melting points were taken on Tektronix X4 microscopic MP apparatus. Infrared spectra (FT-IR) were recorded on KBr pellets with Bruker Tensor 27 spectrometer. The absorption and emission spectra of the dyes were conducted in THF and CH<sub>2</sub>Cl<sub>2</sub> solutions (1 × 10<sup>-4</sup> M) and measured at room temperature by Shimadzu UV-2450 UV–Vis spectrophotometer and Fluorolog III photoluminescence spectrometer, respectively.

Electrochemical redox potentials were measured by Cyclic Voltammetry (CV), using three electrode cells and an Ingsens 1030 electrochemical workstation (Ingsens Instrument Guangzhou, Co. Ltd., China) in a one compartment at a scan rate of 50 mV/s. The Ag/AgCl in KCl (3 M) solution and an auxiliary platinum wire were utilized as reference and counter electrodes while dye coated TiO<sub>2</sub> films were used as working electrode. Tetrabutylammonium perchlorate (n-Bu<sub>4</sub>NClO<sub>4</sub>) 0.1 M was used as supporting electrolyte in acetonitrile. All electrochemical measurements were calibrated by using ferrocene as standard (0.63 V vs NHE). The currentvoltage characteristics were recorded by using a Keithley 2400 source meter under simulated AM 1.5G (100 mW cm<sup>2</sup>) illumination with a solar light simulator (Oriel, Model: 91192). A 1000 W Xenon arc lamp (Oriel, Model: 6271) served as a light source and its incident light intensity was calibrated with an NREL standard Si solar cell. The incident monochromatic photon-to-current conversion efficiency (IPCE) spectra were measured as a function of wavelength from 350 to 800 nm on the basis of a Spectral Products DK240 monochromator. The electrochemical impedance spectra (EIS) measurements were conducted on the electrochemical workstation (Zahner Zennium) in dark condition, with an applied bias potential of -0.78 V. A 10 mV AC sinusoidal signal was employed over the constant bias with the frequency ranging between 1 MHz and 10 mHz. The impedance parameters were determined by fitting of the impedance spectra using Z-view software. The amount of dye load was measured by desorbing the dye from the films with 0.1 M NaOH in ethanol/H<sub>2</sub>O (1:1) and measuring UV–Vis spectrum [43].

1-lodo-4-octyloxybenzene (**1b**) and 1-iodo-4-dodecyloxybenzene (**1c**) were synthesized from iodophenol and respective alkyl halide reagent according to reported method [44] while iodoanisole (**1a**) and other reagents including phenothiazine, 18-crown-6-ether, Pd(PPh<sub>3</sub>)<sub>4</sub>, 4-hydroxyphenylboronic acid etc. and solvents like o-dichlorobenzene, petroleum ether (60–90 °C, PE), dichloromethane (DCM) were purchased as reagent grade and used without purification. All reactions were performed under nitrogen or argon and monitored by TLC (Merck 60 F254) and purified by column chromatography on silica gel (200–300 mesh).

### 2.2. Synthesis of dyes

### 2.2.1. 10-(4-Methoxyphenyl)-10H-phenothiazine (2a)

A mixture of iodoanisole (2.34 g, 10 mmol), phenothiazine (5.98 g, 30 mmol), potassium carbonate (12.43 g, 90 mmol) and electrolytic-copper powder (2.86 g, 45 mmol) in *o*-dichlorobenzene (40 mL) was stirred at 185 °C for 48 h. Inorganic salts were filtered while hot. The solvent was removed under reduced pressure. Purification of the crude product was carried out by column chromatography using silica gel and petroleum ether as mobile phase to yield **2a** (5.22 g, 57%) as colorless crystals, mp 174–176 °C <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  7.37–7.33 (m, 2H), 7.17–7.13 (m, 2H), 7.06–7.02 (m, 2H), 6.91–6.81 (m, 4H), 3.95–3.92 (s, 3H). FT-IR (KBr pellet, cm<sup>-1</sup>): 3061, 3005, 2947, 2827, 1605, 1567, 1510, 1299, 1248.

#### 2.2.2. 10-(4-Octyloxyphenyl)-10H-phenothiazine (2b)

Prepared by following the synthetic procedure of **1a**. 1-lodo-4-octyloxybenzene was reacted with phenothiazine instead of iodoanisole to give a colorless crystalline product **2b** in 54% yield, mp 63–64 °C <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  7.42–7.36 (m, 2H), 7.24–7.18 (m, 2H), 7.14–7.09(m, 2H), 6.95–6.87 (m, 4H), 6.38–6.32 (m, 2H), 4.16–4.10 (t, *J* = 6.4 Hz, 2H), 2.02–1.94 (m, 2H), 1.70–1.62 (m, 2H), 1.57–1.45 (m, 8 H), 1.12–1.06 (t, *J* = 6.8 Hz, 3H). FT-IR (KBr pellet, cm<sup>-1</sup>): 3061, 3005, 2949, 2848, 1605, 1570, 1510, 1295, 1248.

### 2.2.3. 10-(4-Dodecyloxyphenyl)-10H-phenothiazine (2c)

Prepared by following the synthetic method of **1a**. 1-lodo-4dodecyloxybenzene was reacted with phenothiazine instead of iodoanisole to give colorless crystals **2c** in 53% yield, mp 57–59 °C <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  7.41–7.36 (m, 2H), 7.23–7.18 (m, 2H), 7.12–7.08 (m, 2H) 6.95–6.86 (m, 4H), 6.36–6.31 (m, 2H), 4.16– 4.10 (t, *J* = 6.4 Hz, 2H), 2.01–1.93 (m, 2H), 1.69–1.62 (m, 2H), 1.54– 1.45 (m, 16H), 1.09–1.04 (t, *J* = 6.0 Hz, 3H). FT-IR (KBr pellet, cm<sup>-1</sup>): 3062, 3005, 2920, 2851, 1605, 1570, 1510, 1297, 1236.

# 2.2.4. 10-(4-Methoxyphenyl)-10H-phenothiazine-3-carbaldehyde (**3a**)

POCl<sub>3</sub> (3.84 g, 25 mmol) was added drop by drop into DMF (1.83 g, 25 mmol) at 0 °C under nitrogenous environment with continuous stirring. A solid glassy material formed which was dissolved in dichloroethane (30 mL) and stirred for additional 1 h. Then **1b** (1.53 g, 5 mmol) dissolved in ClC<sub>2</sub>H<sub>4</sub>Cl (20 mL) was injected into the flask and maintained at 90 °C for overnight. After cooling, the reaction mixture was poured into water (200 mL) and pH was neutralized by slow addition of the dilute solution of NaOH. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (200 mL). Organic layer was separated and washed three times with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporator. The concentrated mixture was subjected to column chromatography using silica gel and petroleum ether/dichloromethane (PE/DCM) (1:1) as mobile phase. Bright yellow color cystals of **3a** were obtained in 68% (1.14 g) yield, mp 163-165 °C <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  9.71–9.67 (s, 1H), 7.47–7.43 (m, 1H), 7.31-7.27 (m, 3H), 7.18-7.13 (m, 2H), 6.98-6.94 (m, 1H), 6.86-6.82 (m, 2H), 6.23-6.16 (m, 2H), 3.94-3.91 (s, 3H). FT-IR (KBr pellet, cm<sup>-1</sup>): 3068, 3004, 2926, 2835, 1684, 1595, 1574, 1510, 1285, 1247.

# 2.2.5. 10-(4-Octyloxyphenyl)-10H-phenothiazine-3-carbaldehyde (**3b**)

Prepared by the synthetic procedure of **3a**. **2b** was used instead of **2a** to give yellow crystals in 71.2% yield, mp 113–115 °C <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  9.72–9.68 (s, 1H), 7.48–7.44 (m, 1H), 7.30–7.25 (m, 3H), 7.16–7.12 (m, 2H), 6.99–6.94 (m, 1H), 6.87–6.82 (m, 2H), 6.24–6.17 (m, 2H), 4.08–4.03 (t, *J* = 6.4 Hz, 2H), 1.91–1.83 (m, 2H), 1.57–1.50 (m, 2H), 1.43–1.31 (m, 8H), 0.96–0.91 (t, *J* = 6.4 Hz, 3H). FT-IR (KBr pellet, cm<sup>-1</sup>): 3061, 3001, 2919, 2849, 1681, 1593, 1571, 1505, 1284, 1244.

### 2.2.6. 10-(4-Dodecyloxyphenyl)-10H-phenothiazine-3-

#### carbaldehyde (**3c**)

Prepared by the synthetic method of **3a**. **2c** was used instead of **2a** to give **3c** as yellow crystals in 69.3% yield, mp 123–125 °C <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  9.72–9.68 (s, 1H), 7.46–7.42 (m, 1H), 7.31–7.28 (m, 1H), 7.27–7.22 (m, 2H), 7.16–7.11 (m, 2H), 7.09–7.05 (m, 1H), 6.94–6.89 (m, 1H), 6.24–6.19 (m, 1H), 6.05–6.00 (m, 1H), 4.08–4.03 (t, *J* = 6.4 Hz, 2H), 1.90–1.83 (m, 2H), 1.55–1.49 (m, 2H), 1.39–1.29 (m, 16H), 0.93–0.88 (t, *J* = 6.4 Hz, 3H). FT-IR (KBr pellet, cm<sup>-1</sup>): 3059, 3001, 2922, 2851, 1682, 1594, 1571, 1510, 1288, 1250.

# *2.2.7.* 7-Bromo-10-(4-octyloxyphenyl)-10H-phenothiazine-3-carbaldehyde (**4**)

10-(4-Octyloxyphenyl)-10H-phenothiazine-3-carbaldehyde **3b** (0.86 g, 2.0 mmol) was dissolved in CHCl<sub>3</sub> (20 mL) and maintained at 0 °C. Then N-bromosuccinimide (NBS) (0.44 g, 2.5 mmol) dissolved in chloroform (5 mL) was injected slowly under nitrogen. The temperature was raised to 70 °C and reaction was monitored by TLC. After 8 h the reaction mixture was cooled down to room temperature and poured into the water. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (150 mL) and organic layer was washed three times with brine solution. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and solvent was evaporated on rotary evaporator. Purification of the desired product was carried out by column chromatography using silica gel and PE/DCM (1:1) as mobile phase to give required product **4** as dark yellow solid (0.767 g) in 76.7% yield, mp 109–111 °C <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  9.71–9.87 (s, 1H), 7.45-7.41 (m, 1H), 7.31-7.28 (m, 1H), 7.26-7.21 (m, 2H), 7.16-7.11 (m, 2H), 7.09–7,04 (m, 2H), 6.93–6.88 (m, 1H), 6,23–6.19 (m, 1H), 6.04–5.98 (d, 1H), 4.08–4.02 (t, J = 6.4 Hz, 2H), 1.90–1.83 (m, 2H), 1.56–1.49 (m, 2H), 1.41–1.30 (m, 8H), 0.96–0.88 (t, J = 6.4 Hz, 3H). FT-IR (KBr pellet, cm<sup>-1</sup>): 3069, 3008, 2924, 2853, 1682, 1594, 1571, 1509, 1285, 1249.

# 2.2.8. 7-(4-Hydroxyphenyl)-10-(4-(octyloxy)phenyl)-10H-phenothiazine-3-carbaldehyde (5)

A mixture of compound 4 (0.51 g, 1 mmol), THF (35 mL), aqueous solution of K<sub>2</sub>CO<sub>3</sub> (2 M, 6 mL) and Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mol%) was heated to 45 °C for half an hour under argon. Then 4hydroxyphenylboronic acid (0.17 g, 1.2 mmol) dissolved in THF (5 mL) was injected slowly into the reaction mixture. The reaction mixture was heated to 70 °C and maintained for 48 h. After cooling, it was dropped into water (500 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (150 mL). The organic layer was washed three times with water (200 mL each), then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under reduced pressure and purification was carried out by column chromatography using silica gel and DCM as mobile phase to give **5** as orange color solid (0.21 g) in 41% yield, mp 132– 134 °C <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 9.70–9.63 (s, 1H), 7.49– 7.41 (m, 1H), 7.35-7.30 (m, 2H), 7.27-7.24 (m, 2H), 7.15-7.10 (m, 2H) 7.00-6.94 (m, 1H), 6.89-6.81 (m, 2H), 6.24-6.13 (m, 2H), 5.76-5.55 (s, 1H), 4.09–3.98 (t, J = 6.4 Hz, 2H), 1.89–1.80 (m, 2H), 1.55– 1.46 (m, 2H), 1.39–1.25 (m, 8H), 0.93–0.86 (t, J = 6.0 Hz, 3H). FT-IR (KBr pellet, cm<sup>-1</sup>): 3400, 3055, 2926, 2854, 1667, 1580, 1568, 1507, 1289, 1248. APCI-MS: m/z 523.22 Found 522.31 [M-H]<sup>-</sup>. Anal. calcd. for C33H33NO3S: C, 75.69; H, 6.35; N, 2.67; S, 6.12. Found: C, 76.07; H, 6.34; N, 2.60; S, 5.98.

# 2.2.9. 7,10-Bis(4-(octyloxy)phenyl)-10H-phenothiazine-3-carbaldehyde (**6**)

A mixture of **5** (0.183 g, 0.35 mmol), K<sub>2</sub>CO<sub>3</sub> (0.073 g, 0.53 mmol) and DMF (35 mL) was stirred for half an hour at room temperature and then bromooctane (0.135 g, 0.7 mmol) was injected under nitrogen. It was then heated to 130 °C and maintained for 24 h. After cooling, the reaction mixture was poured into water (500 mL) and stirred for half an hour. Then CH<sub>2</sub>Cl<sub>2</sub> (200 mL) was added and water layer was separated. The organic layer was washed several times with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then solvent was removed by rotary evaporator. Column chromatography was carried out by using silica and PE/DCM (1:1) as mobile phase to yield **6** (0.170 g, 91%) as yellow solid, mp 82–84  $^{\circ}$ C <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): § 9.75–9.69 (s, 1H), 7.52–7.46 (d, 1H), 7.43–7.38 (d, 2H), 7.32-7.27 (m. 3H), 7.20-7.13 (d, 3H), 7.06-6.99 (m, 1H), 6.97-6.90 (d, 2H), 6.29–6.19 (m, 2H), 4.11–4.04 (t, J = 6.4 Hz, 2H), 4.03– 3.96 (t, *J* = 6.4 Hz, 2H), 1.91–1.78 (m, 4H), 1.57–1.47 (m, 4H), 1.41– 1.30 (m, 16H), 0.95–0.90 (t, J = 7.2 Hz 6H). FT-IR (KBr pellet, cm<sup>-1</sup>): 3062, 2925, 2854, 1678, 1607, 1580, 1505, 1296, 1245. APCI-MS: m/z635.34. Found 636.5  $[M\ +\ H]^-.$  Anal. Calcd. for  $C_{41}H_{49}NO_3S$ : C, 77.44; H, 7.77; N, 2.20; S, 5.04. Found: C, 78.12; H, 7.67; N, 2.17; S, 4.95.

# 2.2.10. 2-Cyano-3-(10-(4-methoxyphenyl)-10H-phenothiazin-3-yl) acrylic acid (**Z1**)

A mixture of **3a** (0.25 g, 0.75 mmol), dissolved in acetonitrile (30 mL), was reacted with cyanoacrylic acid (0.64 g, 7.5 mmol) in the presence of piperidine (0.3 mL, 3 mmol) was refluxed for 5 h under nitrogen. After cooling the mixture was poured into 2 M aqueous solution of HCl. It was stirred for 15 min and CH<sub>2</sub>Cl<sub>2</sub> (200 mL) was added. The organic layer was separated and washed again two times with water. Then organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the crude product was subjected to column chromatography using silica gel. First it was eluted with DCM and then by DCM/CH<sub>3</sub>OH (20:1) to yield Z1 (0.189 g, 63.1%) as reddish black solid, mp 193–195 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz, ppm): δ 7.79– 7.70 (s, 1H), 7.63-7.55 (s, 1H), 7.28-7.18 (m, 2H), 7.09-7.00 (m, 1H), 6.97-6.81 (m, 2H), 6.20-6.20 (m, 2H), 3.92-3.80 (s, 3H). FT-IR (KBr pellet, cm<sup>-1</sup>): 3445, 3067, 2925, 2853, 2215, 1620, 1589, 1510, 1284, 1248. APCI-MS: *m*/*z* 400.09. Found 399.5 [M–H]<sup>-</sup>. Anal. calcd. for C<sub>23</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>S: C, 68.98; H, 4.03; N, 7.00; S, 8.01. Found: C, 68.89; H, 4.13; N, 6.95; S, 7.93.

# 2.2.11. 2-Cyano-3-(10-(4-(octyloxy)phenyl)-10H-phenothiazin-3-yl)acrylic acid (**Z2**)

Prepared by the synthetic procedure of **Z1**. **3b** was used instead to **3a** to give **Z2** as dark black solid in 71.1% yield, mp 225–227 °C <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz, ppm):  $\delta$  7.90–7.82 (s, 1H), 7.67–7.63 (s, 1H), 7.47–7.42 (m, 1H), 7.34–7.30 (m, 2H), 7.22–7.17 (m, 2H), 7.06–7.02 (m, 1H), 6.93–6.85 (m, 2H), 6.15–6.09 (t, 2H), 4.08–4.00 (t, *J* = 6.4 Hz, 2H), 1.78–1.72 (m, 2H), 1.47–1.41 (m, 2H), 1.32–1.24 (m, 8H), 0.88–0.84 (t, *J* = 6.8 Hz, 3H). FT-IR (KBr pellet, cm<sup>-1</sup>): 3444, 3061, 2926, 2854, 2216, 1618, 1589, 1510, 1291, 1247. APCI-MS: *m/z*, 498.20, Found: 497.1 [M–H]<sup>-</sup>. Anal. calcd. for C<sub>30</sub>H<sub>30</sub>N<sub>2</sub>O<sub>3</sub>S : C, 72.26; H, 6.06; N, 5.62; S, 6.43. Found: C, 72.68; H, 5.90; N, 5.52; S, 6.44.

## 2.2.12. 2-Cyano-3-(10-(4-(dodecyloxy)phenyl)-10H-phenothiazin-3-yl)acrylic acid (Z3)

Prepared by the synthetic procedure of **Z1**. Compound **3c** was condensed with cyanoacrylic acid instead of **3a** to give **Z3** as black solid in 66.7% yield, mp 213–215 °C <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz, ppm):  $\delta$  7.95–7.79 (s, 1H), 7.71–7.58 (s, 1H), 7.50–7.41 (m, 1H), 7.39–7.26 (m, 2H), 7.25–7.13 (m, 2H), 7.09–7.00 (m, 1H), 6.97–6.79 (m, 2H), 6.29–5.97 (m, 2H), 4.12–3.99 (t, *J* = 6.4 Hz, 2H), 1.83–1.65 (m, 2H), 1.48–1.40 (m, 2H), 1.39–1.12 (m, 16H), 0.91–0.79 (t, *J* = 6.8 Hz, 3H). FT-IR (KBr pellet, cm<sup>-1</sup>): 3444, 3066, 2924, 2853, 2218, 1610, 1568, 1510, 1290, 1248. APCI-MS: *m*/*z* 554.2. Found: 553.0 [M–H]<sup>-</sup>. Anal. calcd. for C<sub>34</sub>H<sub>38</sub>N<sub>2</sub>O<sub>3</sub>S: C, 73.61; H, 6.91; N, 5.05; S, 5.78. Found: C, 73.65, H, 6.82; N, 5.06; S, 5.88.

### 2.2.13. 2-Cyano-3-(7,10-Bis(4-(octyloxy)phenyl)-10Hphenothiazin-3-yl)acrylic acid (**Z4**)

Prepared by the synthetic procedure of **Z1**. Compound **6** was condensed with cyanoacrylic acid instead of **3a** to give **Z4** as dark red solid in 61.6% yield, mp 144–146 °C <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz, ppm):  $\delta$  7.93–7.89 (s, 1H), 7.70–7.69 (m, 1H), 7.50–7.46 (m, 3H), 7.36–7.32 (m, 2H),7.31–7.29 (m, 1H), 7.22–7.19 (m, 1H), 7.17–7.14 (m, 1H), 6.96–6.92 (m, 2H), 4.07–4.03 (t, *J* = 6.4 Hz, 2H), 3.98–3.94 (t, *J* = 6.4 Hz, 2H), 1.78–1.73 (m, 2H), 1.72–1.67 (m, 2H), 1.46–1.38 (m, 4H), 1.32–1.24 (m, 16H), 0.89–0.84 (t, *J* = 7.2 Hz, 6H). FT-IR (KBr pellet, cm<sup>-1</sup>): 3446, 3060, 2926, 2855, 2218, 1608, 1576,

1509, 1286, 1245. APCI-MS: m/z 702.35, Found: 701.7 [M–H]<sup>–</sup>, Anal. Calcd. for C<sub>40</sub>H<sub>50</sub>N<sub>2</sub>O<sub>4</sub>S: C, 75.18; H, 7.17; N, 3.99; S, 4.56. Found: C, 74.76; H, 6.97; N, 3.99; S, 4.48.

### 2.3. Fabrication of the dye-sensitized solar cells

Fluorine-doped tin oxide (FTO) glasses were washed with detergent, water, ethanol and acetone in an ultrasonic bath for removing dirt and debris anatase TiO<sub>2</sub> nano-particles (20 nm) were prepared through a hydrothermal treatment with a precursor solution containing Ti(OBu)<sub>4</sub> (10 mL), ethanol (20 mL), acetic acid (18 mL) and deionized water (50 mL) according to the previously reported paper [20,45]. The synthesized TiO<sub>2</sub> powder (1.0 g) was ground for 40 min in the mixture of ethanol (8.0 mL), acetic acid (0.2 mL), terpineol (3.0 g) and ethyl cellulose (0.5 g) to form homogeneous slurry. Finally, the slurry was sonicated for 15 min in an ultrasonic bath to form a viscous white TiO<sub>2</sub> paste. Then the TiO<sub>2</sub> photoanodes (about 18 µm in thickness) were prepared via screen-printing process onto FTO glass. The prepared films were annealed through a procedure (325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min, and 500 °C for 15 min) to remove the organic substances. Then TiO<sub>2</sub> films were soaked in 0.04 M TiCl<sub>4</sub> aqueous solution for 30 min at 70 °C to improve the photocurrent and photovoltaic performance. Treated films were rinsed with deionized water and ethanol and then sintered again at 520 °C for 30 min. After cooling to 80 °C the films were immersed in a 5.0  $\times$  10<sup>-4</sup> M solution of **Z1–Z4** dyes for 16 h (0.5 mM dye in a mixture of tetrahydrofuran and dichloromethane, 1:1 volume ratio). Afterward these films were rinsed with CH<sub>2</sub>Cl<sub>2</sub> in order to remove physical adsorbed organic dye molecules. To evaluate their photovoltaic performance, the dve-sensitized TiO<sub>2</sub>/FTO glass films were assembled into a sandwiched type together with Pt/FTO counter electrode. Platinized counter electrodes were fabricated by thermal depositing H<sub>2</sub>PtCl<sub>6</sub> solution (5 mM in isopropanol) onto FTO glass at 400 °C for 15 min. The electrolyte (0.6 M 1-methyl-3-propylimidazolium iodide (PMII), 0.10 M guanidinium thiocyanate, 0.03 M I<sub>2</sub> and 0.5 M tert-butylpyridine) in acetonitrile/valeronitrile (85:15) was injected from a hole made on the counter electrode into the space between the sandwiched cells. The active area of the dye coated TiO<sub>2</sub> film was 0.16 cm<sup>2</sup>.

## 3. Results and discussion

### 3.1. Synthesis and structural characterization

The synthetic route of the dyes is shown in Scheme 1. Iodoanisole (**1a**) was purchased while 1-iodo-4-octyloxybenzene (**1b**) and 1-iodo-4-dodecyloxybenzene (**1c**) were prepared from iodophenol via alkylation reaction with bromooctane and bromododecane respectively. Compounds **2a**–**c** were prepared by the Ullmann reaction using electrolytic copper and 18-crown-6-ether as catalyst in *o*-dichlorobenzene at 185 °C. The aldehydes **3a**–**c** were then synthesized by the Vilsmeier–Haack reaction in the presence of DMF and POCl<sub>3</sub>. These reagents were condensed with cyanoacrylic acid via Knoevenagel condensation reactions in the presence of piperidine resulting in the dyes **Z1**, **Z2** and **Z3**. Reagent **3b** was brominated with NBS in chloroform to give compound **4**. Suzuki coupling reaction of compound **4** was carried out with 4-hydroxyphenylboronic acid to give compound **5**, which was alkylated in the presence of DMF and potassium carbonate to give compound **6**. Finally **6** was converted by Knoevenagel condensation to the dye **Z4**. All the intermediates and target dyes were confirmed by standard spectroscopic methods.

# 3.2. Photophysical properties

UV-Vis absorption and emission spectra of the dyes Z1-Z4 in THF/DCM (1:1) solution (1  $\times$  10<sup>-4</sup> M) and adsorbed on a thin TiO<sub>2</sub> film are presented in Table 1, Figs. 1 and 2. The UV spectra of the dves exhibit two distinct bands, one at 306–324 nm and the other at 420–459 nm. The first band corresponds to the  $\pi$ – $\pi$ \* transition of the localized conjugated skeleton while the other band can be assigned to an intramolecular charge transfer (ICT) between the central phenothiazine (electron donor) and the cyanoacetic acid (electron acceptor and anchoring moiety). UV absorption  $\lambda_{max}$ increases by 39 nm from **Z1** with methoxy group to **Z2** with octyloxy chain due to the increase in chain length which imparts a strong electron donating capability or may effect J-type aggregation. The dye Z3 with a dodecyloxy chain in comparison to Z2 was 31 nm blue shifted due to its flexible structure since the interchain distances increased linearly with increasing length of alkyl chain. Similar studies with dramatic results from increasing alkyl chain length have been reported [46-50]. The dye Z4 gave a maximum absorption similar to the dye Z2 but its molar extinction coefficient ( $\varepsilon = 34,350 \text{ M}^{-1} \text{ cm}^{-1}$ ) was higher than the dye **Z2** ( $\varepsilon = 20,640 \text{ M}^{-1} \text{ cm}^{-1}$ ), which indicates that the absorption capacity of the dye Z4 was enhanced by the bilateral extension. Molar extinction coefficients of the dyes were in the order of Z4 > Z2 > Z3 > Z1 (Table 1). Red shift and enhanced epsilon favor the light harvesting and hence photocurrent generation in DSSCs. Furthermore, the octyloxy chain gives a more compact and balanced structure and better absorbance of light [51]. After being adsorbed on the surface of TiO<sub>2</sub> films, all dyes showed broadening of UV–vis absorption and a red shift of  $\lambda_{max}$  as compared to those in solution (Table 1), which favors the light harvesting potential of solar cells leading to increase of J<sub>sc</sub>. Red shifts of 30 nm, 7 nm, 37 nm and 11 nm in absorption maxima were observed in the dyes Z1, Z2, Z3 and Z4 respectively The variations in absorption spectra of Z1 and Z3 were more pronounced which may be ascribed to a change in the format of aggregation on TiO<sub>2</sub> surface as compared to solution. Hypsochromic shifts on the TiO<sub>2</sub> surface were assigned to the interaction of the anchoring group with surface anions which directly reduces the energy of the  $\pi^*$ level and the formation of J-aggregates on the TiO<sub>2</sub> surface [16,52,53].

Table 🛛	1
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Absor	ption	and	emission	characteristics	of	the	dyes	Z1	-Z	4
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Dye	Absorption $\lambda_{max} (nm)^a$	$\varepsilon (M^{-1} cm^{-1})^b$	Emission $\lambda_{max} (nm)^{c}$	Absorption $\lambda_{max} (nm)^d$	Red shift of absorption $\lambda_{max}$ (nm)	Amount of dye load $(Mol^{-1} cm^{-2})$
Z1	313, 420	18,500, 7750	550	450	30	$2.10  imes 10^{-7}$
Z2	324,459	20,640, 11,920	566	463	7	$1.12 \times 10^{-7}$
Z3	315, 428	18,820, 8260	552	465	37	$1.03 \times 10^{-7}$
Z4	306, 459	34,350, 14,680	570	470	11	$1.26  imes 10^{-7}$

<sup>a</sup> Absorption maximum of dyes measured in THF/DCM (1:1) with concentration  $1 \times 10^{-4}$  mol/L.

<sup>b</sup> The molar extinction coefficient at  $\lambda_{max}$  in solution.

<sup>c</sup> Emission maximum of dyes in THF/DCM (1:1) with concentration  $1 \times 10^{-4}$  mol/L.

<sup>d</sup> Absorption maximum of dyes adsorbed on the surface of TiO<sub>2</sub>.



Fig. 1. (a) Normalized absorption spectra and (b) normalized emission spectra of the dyes in THF/CH<sub>2</sub>Cl<sub>2</sub>.

#### 3.3. Electrochemical properties

In order to investigate the ability of electron transfer from the excited dye molecule to the conductive band of TiO2 the redox behavior of dyes Z1-Z4 was studied by cyclic voltammetry (CV) (Figs. 3 and 4, Table 2). CV was carried out in tetrabutylammonium perchlorate (0.1 M) in acetonitrile as supporting electrolyte, Ag/ AgCl in KCl (3 M) solution as reference electrode, Platinum wire as counter electrode and TiO<sub>2</sub> films as working electrode. Each measurement was calibrated with Fc/Fc<sup>+</sup> (ferrocene/ferrocenium ion) and converted to NHE by the addition of 0.63 eV. Onset oxidation potentials of the dyes figured out the highest occupied molecular orbitals (HOMO) of 1.54 eV, 1.35 eV, 1.47 eV and 1.44 eV (Fc/Fc<sup>+</sup> vs NHE) for **Z1**, **Z2**, **Z3** and **Z4** respectively. The lowest unoccupied molecular orbitals (LUMO) were estimated by oxidation potential and the energy at the intersection of absorption and emission spectra, which are -0.97 eV, -1.09 eV, -1.03 eV and -0.93 eV for Z1, Z2, Z3 and Z4 respectively. The band gap of Z4 was reduced considerably by the introduction of bilateral substituents as compared to those of Z1-Z3 with the lateral substitution alone. Maximum absorption and higher extinction coefficient dyes have shorter energy gaps. These findings are quite similar to the



Fig. 2. Absorption spectra of the dyes adsorbed on TiO<sub>2</sub> films.

previous studies [19]. All LUMO levels of dyes are reasonably suitable for providing sufficient thermodynamic driving force for electron injection from the excited state to the conduction band of TiO<sub>2</sub> (0.5 eV vs NHE) [54]. The requirement for appropriate electron injection from the excited state to the conduction band of titanium dioxide is 0.2 eV [55]. The HOMO energies of all dyes are also well in accordance, lower than  $I^-/I_3^-$  potential (0.4 eV vs NHE) [56], suggesting that there should be enough driving force for the regeneration of the dyes.

## 3.4. Molecular orbital calculations

To gain further insight into the above mentioned results density function theory (DFT) calculations were carried out by using Gaussian 09 software at the B3LYP/6-31G (d, p) levels [57]. Optimized structures and the electronic distribution in HOMO and LUMO levels are presented in Fig. 4, Table 2. The electron distributions of the Z1-Z4 in the HOMOs levels were mainly localized on phenothiazine moiety while the LUMOs showed localized electron distribution through the cyanoacrylic acid upon light illumination. Therefore, HOMO-LUMO excitation by light induced shift of the electron from the PTZ donor moiety to the acceptor moiety. This separation of electrons ensures the efficient electron injection from the dye to the TiO<sub>2</sub> film. The geometry of phenothiazine was butterfly shaped due to the  $sp^3$  hybridization of the N and S heteroatoms. The side chain (alkoxybenzene) attached to the 7 and 10 positions of phenothiazine increases the bulkiness of the molecules, therefore preventing the formation of excimers and aggregates [58].

### 3.5. Photovoltaic performance of the DSSCs

A set of dye-sensitized solar cells was fabricated as described in the experimental section and tested under standard conditions (AM 1.5G, 100 mW cm<sup>-2</sup>) in order to investigate the photovoltaic performance of the dyes. The incident monochromatic photon-tocurrent conversion efficiency (IPCE) and photocurrent density– voltage (*J*–*V*) curves of the four dyes **Z1–Z4** were obtained with a sandwich cell comprising of 18 µm TiO<sub>2</sub> photoanode and  $I^-/I_3^$ redox electrolyte.

The J-V curves based on dyes **Z1–Z4** are shown in Fig. 5. The detailed parameters of short-circuit photocurrent density ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), fill factor (FF) and overall conversion



Fig. 3. Cyclic voltammetry (a) and HOMO/LUMO levels (b) of the dyes Z1-Z4.

efficiency  $(\eta)$  are summarized in Table 3. Among these dyes, the cell based on Z4 exhibits a maximum efficiency of 5.73%  $(J_{sc} = 10.35 \text{ mA cm}^{-2}, V_{oc} = 802 \text{ mV}, FF = 0.69)$  under standard global AG 1.5G solar light illumination (100 mW cm<sup>-2</sup>). Under similar measuring conditions, other cells sensitized with the dyes **Z1, Z2** and **Z3** showed J<sub>sc</sub> of 8.56, 8.65 and 8.47 mA cm<sup>-2</sup>, V<sub>oc</sub> of 773, 785 and 768 mV and FF of 0.69, 0.71 and 0.70, corresponding to  $\eta$  of 4.53, 4.79 and 4.54%, respectively. As seen in the results, the  $V_{\rm oc}$ increases from 773 mV to 785 mV by increasing chain length from methoxy (Z1) to octyloxy (Z2). This was assigned to reduced recombination ability at TiO<sub>2</sub>/dye/electrolyte interface by insulating alkoxy chains on the dyes. The dye Z3 has a smaller open circuit-voltage as compared to the dye **Z2** though the chain length increases from octyloxy to dodecyloxy, which can be ascribed to its loose structure and less resistance in recombination as well as hindrance in dye regeneration. The dye **Z4** has maximum  $V_{\rm oc}$ 802 mV, which is due to its bilateral resistance by alkoxy chains.



**Fig. 4.** Optimized structures and frontier molecular orbitals of the HOMO and LUMO calculated by DFT on a B3LYP/6-31 + G (d, p) level.

A similar trend was observed in  $J_{sc}$ , i.e. Z4 > Z2 > Z1 > Z3, corresponding to 10.35, 8.65, 8.56 and 8.47 mA cm<sup>-2</sup>, respectively. This behavior of the dyes can be attributed to alkoxy chains selfassembling into layers which are apt to extend between TiO<sub>2</sub> film and  $I^{-}/I_{3}^{-}$  electrolyte, thus blocking the recapture of the photoinjected electrons by triiodide ions. In addition, lengthening of the alkoxy chains of the dyes could result in a longer distance between the TiO<sub>2</sub> laver and the electrolyte. The efficiency of the dve **Z3** is lower as the alkoxy chain is soft and twisted and may be too long for this structure, so that Z3 cannot effectively improve the photovoltaic performance. This long chain may create hindrance for the hole transportation leading to a more pronounced effect of recombination. Furthermore, it also masks the TiO<sub>2</sub> surface and render less effective attachment of the anchoring unit. This phenomenon was confirmed by measuring the dye load (Table 1), which indicates that **Z3** has the minimum dye load as compared to other dyes. **Z3** also has a lowest  $J_{sc}$  value which is associated with the weak adsorption onto the TiO<sub>2</sub> surface, low charge separation and low transportation efficiency. The highest efficiency of the cell based on **Z4** is due to its relatively higher J<sub>sc</sub>, which is ascribed to its higher light harvesting capacity in the visible region. It was reported that variations in open-circuit voltage and short-circuit current density are related to electron lifetime in the conduction band of TiO<sub>2</sub> [59].

IPCE spectra of Z1-Z4 for DSSCs are plotted in Fig. 6. The IPCE values of DSSCs based on Z4 exceed 70% from 450 nm to 550 nm with a maximum value of 84.39% at 470 nm and tail-off toward 670 nm. While maximum IPCE of the dyes Z1, Z2 and Z3 exceeds 71, 79 and 69% at 460, 460 and 450 nm with tail off toward 640, 630 and 640 nm, respectively. This trend of IPCE spectra (Z4 > Z2 > Z1 > Z3) is in good accordance with the order of shortcircuit photocurrent density indicating that higher wavelength absorption dyes have higher  $J_{sc}$ . It is worth noting that the IPCE spectrum of a Z4 based cell shows an obvious shift to a longer wavelength. The highest IPCE value of Z4 was attributed to its broader absorption and enhanced molar extinction coefficient in the visible region, which is in good agreement with the absorbance spectra of the dyes in solution and on the TiO<sub>2</sub> films. Therefore, the higher and broader IPCE of the cell based on Z4 leads to a higher short-circuit photocurrent density, which is conducive to improve the photovoltaic performance of DSSCs.

To further illustrate the difference in  $V_{oc}$  among the DSSCs based on different dyes and investigate the interfacial charge transfer process within DSSCs, the electrochemical impedance spectra (EIS) was performed in the dark under a forward bias

Table 2					
Electrochemical	characteristics	of the	dves	Z1-	-Z4.

Dyes	$\lambda (nm)^a$	HOMO (eV) vs NHE <sup>b</sup>	$E_{0-0}$ (eV) vs NHE <sup>c</sup>	LUMO (eV) vs NHE <sup>d</sup>	HOMO (eV) vs vacuum <sup>e</sup>	LUMO (eV) vs vacuum <sup>e</sup>	E-gap (eV)
Z1	494.4	1.54	2.51	-0.97	-5.22	-2.57	-2.65
Z2	508.2	1.35	2.44	-1.09	-5.19	-2.56	-2.63
Z3	496.8	1.46	2.50	-1.04	-5.20	-2.56	-2.64
Z4	522.2	1.44	2.37	-0.93	-5.09	-2.50	-2.59

<sup>a</sup>  $\lambda$  intersection obtained from the cross point of absorption and emission spectra in THF/DCM (1:1) solution.

<sup>b</sup> HOMO of dyes measured by cyclic voltametery in 0.1 M tetrabutylammonium perchlorate in acetonitrile solution as supporting electrolyte, Ag/AgCl as reference electrode and Pt as counter electrode.

<sup>c</sup>  $E_{0-0} = 1240/\lambda$  intersection.

<sup>d</sup> LUMO was estimated by  $E_{0-0}$  – HOMO.

<sup>e</sup> HOMO and LUMO were calculated at B3LYP-3 G(d, p) level in vacuum.



Fig. 5. J-V curves of DSSCs sensitized by the dyes Z1-Z4.

of -0.78 V to investigate the interfacial charge transfer process within DSSCs. As shown in Fig. 7, two semicircles were observed in the Nyquist plots. The smaller (higher frequency from  $10^3$  to  $10^5$  Hz) and larger semicircles (lower frequency from 1 to  $10^2$  Hz) in the Nyquist plots were attributed to the charge transfer at the counter electrode/electrolyte interface and the TiO<sub>2</sub>/dye/electrolyte interface respectively. Small circles were almost similar in all the dves due to the use of same counter electrode and electrolyte. On the other hand, there is an obvious difference in the large semicircles, which indicates that charge transfer behavior between TiO<sub>2</sub> and electrolyte was significantly altered, which was likely due to the surface modifications with different dyes. As shown in Fig. 7, the recombination resistance of the dye Z4 based cell was larger than those of other cells according to the value derived from curve fitting in Z-view software. Electron lifetime calculated by fitting the equation  $\tau_r = R_{rec} \times CPE2$  (CPE2, chemical capacitance) [60-62] decreased gradually in the order of **Z4** > **Z2** > **Z1** > **Z3** (210, 184, 161 and 130 ms, respectively), these results are in good agreement with the variation tendency of  $V_{\rm oc}$  $(\mathbf{Z4} > \mathbf{Z2} > \mathbf{Z1} > \mathbf{Z3})$  measured by the *J*–*V* curves. The longer electron lifetime within different dye based cells leads to less possibility of electron recombination within the DSSCs and thus

Table 3					
Photovoltaic	parameters of	DSSCs	based	on <b>Z1–Z4</b> .	

Dyes	$J_{\rm sc}$ (mA cm <sup>-2</sup> )	$V_{\rm oc}({ m mV})$	FF	η (%)	Electron lifetime ( $\tau_r$ , ms)
Z1	8.56	773	0.69	4.53	0.161
Z2	8.65	785	0.71	4.79	0.184
Z3	8.47	768	0.70	4.54	0.130
Z4	10.35	802	0.69	5.73	0.210



Fig. 6. IPCE spectra of DSSCs based on the dyes Z1-Z4.

results in a larger value of  $V_{oc}$ . The dye **Z3** with a dodecyloxy chain has least electron lifetime and resistance of recombination as compared to the dye **Z2** with an octyloxy chain. It has been reported that an alkoxy chain can act as charge suppression function of the charge recombination [63]. We have found that the dodecyloxy chain was less effective than octyloxy chain, which may be due to inefficient hole mobility which results in recombination and lowers the values. Similar results were found in regioregular poly (3-alkylthiophene)s, where charge mobility was influenced by increasing alkyl chain from C4 to C12 [60]. The dye **Z4** performs the best in respect of all photovoltaic parameters because the bilateral conjugation of octyloxybenzene plausibly



Fig. 7. Electrochemical impedance spectra of the dyes Z1–Z4 measured in the dark.

increases light harvesting capacity, electron lifetime and resistance to recombination of electrons.

### 4. Conclusions

Four novel dyes (Z1-Z4) based on modifications of phenothiazine with different alkoxy chain lengths and increased conjugation were designed and synthesized. The dye **Z2** with octyloxy chain was found superior to the dye **Z3** with dodecyloxy chain in respect to effective suppression of the charge recombination, increased  $V_{0c}$  and electron lifetime. Furthermore, the dye **Z4** with bilateral extension of PTZ with an octyloxybenzene unit prominently displayed the best results in all parameters with Jsc of 10.35 mÅ cm<sup>-2</sup>,  $V_{oc}$  of 802 mV, FF of 0.69 and  $\eta$  of 5.73%. This work provides beneficial and crucial information for developing and designing new organic dyes for highly efficient DSSCs. Further structural modifications of the dye Z4 to acquire even better power conversion efficiency of DSSCs performance is in progress.

### Acknowledgments

We are grateful to the National Natural Science Foundation of China (20872038, 20873183, 21072064), the Natural Science Foundation of Guangdong Province, China (10351064101000000, S2012010010634) and the Fund from Guangzhou Science and Technology Project, China (2012]4100003) for the financial support.

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