Efficient and stable dye-sensitized solar cells based on phenothiazine sensitizers with thiophene units[†]

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Three new phenothiazine organic dyes containing thiophene, 3-(5-(3-(4-(bis(4-methoxy phenyl)amino)phenyl)-10-octyl-10*H*-phenothiazin-7-yl)thiophen-2-yl)-2-cyanoacrylic acid (**P1**), 3-(5-(3-(4-(diphenylamino)phenyl)-10-octyl-10*H*-phenothiazin-7-yl)thiophen-2-yl)-2-cyanoacrylic acid (**P2**) and 2-cyano-3-(5-(10-octyl-3-(4-(2,2-diphenylvinyl)phenyl)-10*H*-phenothiazin-7-yl)thiophen-2-yl) acrylic acid (**P3**) were designed and synthesized as sensitizers for application in dye-sensitized solar cells (DSSCs). For these dyes, the phenothiazine derivative moiety and the cyanoacetic acid take the roles of electron donor and electron acceptor, respectively. The absorption spectra, electrochemical and photovoltaic properties of **P1–P3** and the cell long-term stability were extensively investigated. It was found that HOMO and LUMO energy level tuning can be conveniently accomplished by alternating the donor moiety. The DSSCs based on dye **P2** showed the best photovoltaic performance: a maximum monochromatic incident photon-to-current conversion efficiency (IPCE) of 84.9%, a short-circuit photocurrent density (J_{sc}) of 10.84 mA cm⁻², an open-circuit photovoltage (V_{oc}) of 592 mV, and a fill factor (*ff*) of 0.69, corresponding to an overall conversion efficiency of 4.41% under standard global AM 1.5 solar light conditions. These results demonstrated that the DSSCs based on phenothiazine dyes could achieve both high performance and good stability.

1. Introduction

Dye-sensitized solar cell (DSSC) systems based on highly porous nanocrystalline films of titanium dioxide are of considerable technological interest because of their demonstrated high-power conversion efficiency, potential low cost, and high semiconductor stability.¹⁻²⁶ As known to all, the sensitizer is a critical component in DSSCs. To overcome the prohibitive issues of ruthenium metal complexes, organic DSSCs have received more and more attention because of their ease of synthesis, high molar extinction coefficients and simple preparation process of low cost in comparison to Ru complexes. Coumarin,⁹⁻¹¹ merocyanine,¹² indoline,^{13,14} polyene,¹⁵ hemicyanine,^{16,17} triphenylamine,^{18–22} fluorene^{23–25} and tetrahydroquinoline²⁶ based-organic dyes have been developed and showed good performance. Recently, great progress has been made in this field and organic dyes would be a promising type of sensitizer for dye-sensitized solar cells.

Phenothiazine is a well-known heterocyclic compound with electron-rich sulfur and nitrogen heteroatoms, and the phenothiazine ring is nonplanar with a butterfly conformation in the ground state, which can impede the molecular aggregation and the formation of intermolecular excimers. Thus, phenothiazine is a potential hole transport semiconductor in organic devices,

presenting unique electronic and optical properties.²⁷ Therefore, phenothiazine-based polymers have been widely employed in thin film transistor, photovoltaic cell, and light-emitting diode applications. However, to the best of our knowledge, there was only one report on the application of a small molecular dye containing a phenothiazine moiety in DSSCs.²⁸ On the other hand. Haque and co-workers have reported a group of hole transport material (HTM) which can indeed slow the recombination between the photoinjected electrons and oxidized HTM through separating the holes spatially away from the electrons in the semiconductor, and thus improve the efficiency of DSSCs.²⁹ Triarylamine has been widely used in opto- and electro-active materials for its good electron donating and transporting capability, as well as its special propeller starburst molecular structure. Recently, organic photovoltaic functional materials with triarylamine as electron donor have aroused great interest and become the focus of intensive research in the field of solar cells. These materials have significantly reinforced the conversion efficiency of next-generation solar cells, especially dye sensitized solar cells.^{3a} The methoxy groups attached to the triphenylamine can enhance the extent of electron delocalization and the ability to donate the electron of the sensitizer. The 1,1,2-triphenylethene unit as a donor has been introduced in indoline dyes with high-performance dye-sensitized solar cells.^{29c} Also, the introduction of thiophene moieties was expected to allow a red-shift of the spectra, and broaden the spectral region of absorption. Based on these studies, three new organic dyes (P1-P3 shown in Scheme 1) have been designed and synthesized through the modification of simple phenoxazine-thiophene dyes (6-8 shown in Scheme 2) with hole transport group, corresponding molecular structures of the

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Scheme 1 Molecular structures of dyes (P1-P3).



Scheme 2 Synthesis route to dyes (P1–P3).

three dyes are shown in Scheme 1. Finally, three new sensitizers have been applied successfully to sensitization of nanocrystalline TiO₂-based solar cells and the corresponding photovoltaic properties, electronic and optical properties are also presented.

2. Experimental

2.1 Materials

FTO conducting glass (FTO glass, fluorine doped tin oxide overlayer, transmission > 90% in the visible, sheet resistance 15 Ω square⁻¹) was obtained from Geao Science and Educational Co. Ltd. of China. Methoxypropionitrile (MPN), 1-methylimidazole and n-iodobutane were purchased from Aldrich. Titania pastes of Ti-Nanoxide T/SP and Ti-Nanoxide 300 were from Solaronix. Lithium iodide was from Fluka and iodine, 99.999%, was from Alfa Aesar. 1-Propyl-3-methylimidazolium iodide (PMII) and 1-butyl-3-methylimidazolium iodide (BMII) were prepared according to published procedures.³⁰

THF was pre-dried over 4 A molecular sieves and distilled under argon atmosphere from sodium benzophenone ketyl immediately prior to use. Starting materials 10-octyl-phenothiazine, 4-(N,N-diphenylamino)-1-bromo-benzene, 4-(N,N-bis(4-methoxyphenyl)amino)-1-bromobenzene and 1,1-diphenyl-2-(4-bromophenyl)ethane were prepared according to published procedures.^{31–34} All other chemicals were purchased from Aldrich and used as received without further purification.

2.2 Preparation of photovoltaic devices

A screen-printed double layer of TiO₂ particles was used as photoelectrode. A 10 µm thick film of 13 nm sized TiO₂ particles (Ti-Nanoxide T/SP) was first printed on the FTO conducting glass and further coated with a 4 µm thick second layer of 400 nm light-scattering anatase particles (Ti-Nanoxide 300). Sintering was carried out at 450 °C for 30 min. Before immersion in the dye solution, these films were immersed into a 40 mM aqueous TiCl₄ solution at 70 °C for 30 min and washed with water and ethanol. Then the films were heated again at 450 °C for 30 min followed by cooling to 80 °C and dipping into a 3 \times 10 ⁻⁴ M solution of dye in acetonitrile for 12 h at room temperature. To prepare the counter electrode, the Pt catalyst was deposited on the cleaned FTO glass by coating with a drop of H₂PtCl₆ solution (0.02 M in 2-propanol solution) with the heat treatment at 400 °C for 15 min. A hole (0.8 mm diameter) was drilled on the counter electrode using a drill-press. The perforated sheet was cleaned with ultrasound in an ethanol bath for 10 min. For the assembly of DSSCs, the dye-covered TiO₂ electrode and Pt-counter electrode were assembled into a sandwich type cell and sealed with a hot-melt gasket of 25 µm thickness made of the ionomer Surlyn 1702 (DuPont). The size of the TiO₂ electrodes used was 0.25 cm² (*i.e.*, $5 \text{ mm} \times 5 \text{ mm}$). A drop of the electrolyte was put on the hole in the back of the counter electrode. It was introduced into the cell via vacuum backfilling. The hole in the counter electrode was sealed with a film of Surlyn 1702 and a cover glass (0.1 mm thickness) using a hot iron bar.

2.3 Electrolyte

The electrolyte employed was a solution of 0.6 M PMII (1-propyl-3-methylimidazolium iodide), 0.05 M I₂, 0.10 M LiI and 0.5 M 4-tert-butylpyridine in a mixture of acetonitrile and methoxypropionitrile (volume ratio, 7:3).

For the quasi-solid state electrolyte, fumed silica nanoparticles (5 wt%) with 12 nm primary particle size, kindly provided by Degussa, were mixed with BMII (1-butyl-3-methylimidazolium iodide) based liquid electrolyte containing 0.5 M iodine and 0.45 M BI (benzimidazole) in an agate mortar.

2.4 Measurements

Photovoltaic measurements employed an AM 1.5 solar simulator equipped with a 300 W xenon lamp (Model No. 91160, Oriel). The power of the simulated light was calibrated to 100 MW cm⁻² using a Newport Oriel PV reference cell system (Model 91150V). I-V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter. The voltage step and delay time of photocurrent were 10 mV and 40 ms, respectively. Cell active area was tested with a mask of 0.158 cm². The photocurrent action spectra were measured with a IPCE test system consisting of a Model SR830 DSP Lock-In Amplifier and a Model SR540 Optical Chopper (Stanford Research Corporation, USA), a 7IL/PX150 xenon lamp and power supply, and a 7ISW301 Spectrometer. Impedance spectra were recorded using a CHI-660c electrochemical station.

3. Synthesis

Full synthesis procedures for all important intermediate compounds are available in the ESI.†

3-(5-(3-(4-(Bis(4-methoxyphenyl)amino)phenyl)-10-octyl-10*H*-phenothiazin-7-yl)thiophen-2-yl)-2-cyanoacrylic acid (P1)

Compound 6 (139 mg, 0.19 mmol), 2-cyanoacetic acid (48 mg, 0.57 mmol), ammonium acetate (3 mg) and acetic acid (11 mL) at 120 °C for 12 h. After cooling the solution, water was added to quench the reaction. The precipitate was filtered and washed with water. The residue was purified by column chromatography on silica (CH₂Cl₂-ethanol = 10/1, v/v) to yield 133 mg of red solid (yield 88.5%). ¹H NMR (DMSO- d_6 , 500 MHz), δ : 0.84 (t, J = 6.7Hz, 3H), 1.25 (m, 8H), 1.46 (m, 2H), 1.78 (m, 2H), 3.75 (s, 6H), 4.32 (m, 2H), 6.85 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 8.7 Hz, 4H), 7.06 (d, J = 8.7 Hz, 4H), 7.62 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 9.0Hz, 2H), 7.76 (s, 2H), 7.97 (m, 2H), 8.12 (s, 1H), 8.17 (m, 1H), 8.33 (m, 1H). ¹³C NMR (DMSO-d₆, 125 MHz), δ: 165.5, 158.0, 150.1, 149.0, 142.7, 142.0, 139.7, 138.6, 138.1, 135.8, 132.6, 132.3, 131.6, 130.3, 129.9, 129.1, 129.0, 128.4, 126.7, 126.5, 121.6, 121.3, 119.4, 119.3, 117.2, 111.1, 110.5, 57.4, 34.5, 33.3, 31.1, 30.9, 30.8, 28.2, 28.0, 24.2, 16.1. HRMS (m/z): $[M]^+$ calcd for C₄₈H₄₅N₃O₄S₂, 791.2851; found, 791.2834.

3-(5-(3-(4-(Diphenylamino)phenyl)-10-octyl-10*H*-phenothiazin-7yl)thiophen-2-yl)-2-cyanoacrylic acid (P2)

The synthesis method resembles that of compound **P1**, and the compound was purified by column chromatography on silica (CH₂Cl₂–ethanol = 10/1, v/v) to yield 55 mg of orange solid (yield 86.5%). ¹H NMR (DMSO-*d*₆, 500 MHz), δ : 0.86 (t, *J* = 6.9 Hz, 3H), 1.28 (m, 8H), 1.48 (m, 2H), 1.82 (m, 2H), 4.38 (m, 2H), 7.08 (m, 8H), 7.34 (t, *J* = 7.8 Hz, 4H), 7.75 (m, 6H), 8.01 (m, 2H), 8.11 (s, 1H), 8.25 (d, *J* = 1.6 Hz, 1H), 8.37 (s, 1H). ¹³C NMR (DMSO-*d*₆, 125 MHz), δ : 165.8, 158.1, 150.2, 149.3, 142.5, 142.1, 139.6, 138.5, 138.3, 135.4, 132.3, 132.1, 131.2, 130.4, 129.7, 129.3, 129.3, 128.2, 126.5, 126.3, 121.2, 121.1, 119.2, 119.5, 117.1, 111.3, 110.6, 34.2, 33.1, 31.2, 30.7, 30.6, 28.1, 28.0, 24.1, 16.3. HRMS (*m*/*z*): [M]⁺ calcd for C₄₆H₄₁N₃O₂S₂, 731.2640; found, 731.2625.

2-Cyano-3-(5-(10-octyl-3-(4-(2,2-diphenylvinyl)phenyl)-10*H*-phenothiazin-7-yl)thiophen-2-yl) acrylic acid (P3)

The synthesis method resembles that of compound **P1**, and the compound was purified by column chromatography on silica (CH₂Cl₂–ethanol = 10/1, v/v) to yield 69 mg of orange solid (yield 69.8%). ¹H NMR (DMSO- d_6 , 500 MHz), δ : 0.84 (m, 3H), 1.25 (m, 8H), 1.46 (m, 2H), 1.77 (m, 2H), 4.34 (m, 2H), 7.12 (d, J = 8.3 Hz, 2H), 7.15 (s, 1H), 7.22 (d, J = 7.0 Hz, 2H), 7.35 (m, 5H), 7.47 (m, 3H), 7.62 (d, J = 8.1 Hz, 2H), 7.72 (m, 2H), 7.77 (s, 2H), 8.01 (m, 2H), 8.19 (s, 1H), 8.26 (d, J = 1.6 Hz, 1H), 8.35 (d, J = 1.7 Hz, 1H). ¹³C NMR (DMSO- d_6 , 125 MHz), δ : 163.9, 147.2, 142.4, 141.8, 140.0, 136.6, 136.2, 136.1, 130.0, 129.7, 129.1, 128.6, 128.3, 128.2, 127.7, 127.6, 127.1, 127.0, 125.6, 124.6, 124.4, 117.4, 117.1, 115.2, 79.2, 78.9, 54.9, 46.8, 40.0, 39.9, 39.8, 39.7,

39.5, 39.3, 39.2, 39.0, 31.1, 30.4, 28.7, 28.6, 26.1, 25.8, 22.0, 13.9. HRMS (*m*/*z*): $[M]^+$ calcd for C₄₈H₄₂N₂O₂S₂, 742.2687; found, 742.2653.

4. Results and discussion

4.1 Synthesis

The synthesis route to phenothiazine dyes containing thiophene (P1-P3) is depicted in Scheme 2. The octyl chain on the phenothiazine nucleus can improve the solubility and form a tightly packed insulating monolayer blocking the I_3^- or cations approaching the TiO_2 . The thiophenyl unit is attached to the core phenothiazine by a Suzuki coupling reaction. The reaction produced the di-substituted side products as well, fortunately monocapped compounds can be easily separated by column chromatography. In the next step, this bromo-exposed intermediate was reacted with arylphenylboronic acids (3-5) by Suzuki coupling reaction, respectively. Finally, the target products (P1-P3) were synthesized via Knoevenagel condensation reaction of the respective carbaldehydes with cyanoacetic acid in the presence of acetic acid and ammonium acetate. All the key intermediates and three new organic phenothiazine sensitizers (P1-P3) were confirmed by ¹H NMR, ¹³C NMR and HRMS.

4.2 Absorption properties in solution and on TiO₂ film

UV-Vis absorption spectra of dyes P1-P3 in a diluted solution of CH₂Cl₂ are shown in Fig. 1 and their absorption data are listed in Table 1. In the UV-Vis spectra, P1-P3 exhibit two major prominent bands, appearing at 300-400 nm and at 400-600 nm, respectively. The former is ascribed to a localized aromatic π - π^* transition and the later is of charge-transfer character. The absorption maxima for P1–P3 in CH₂Cl₂ are at $\lambda = 460$ nm, 450 nm and 449 nm, respectively. Compared with P2 and P3, P1 has two methoxy groups attached to the triphenylamine on the electron donor side, which enhanced the extent of electron delocalization over the whole molecule, so its maximum absorption peak was red shifted a little. In comparison with conventional ruthenium complexes (for example, 1.39×10^{4} M⁻¹ cm⁻¹ at 541 nm for N3)³⁵ the present dye molecules show about absorption coefficients. twice as high The greater maximum absorption coefficients of the organic dyes allow



Fig. 1 UV-Vis absorption spectra of P1–P3 in CH_2Cl_2 (3 × 10⁻⁵ M).

Dye	$\lambda_{ m max}{}^a/ m nm~(arepsilon imes 10$ $^{-4}$ $ m M^{-1}~ m cm^{-1})$	λ_{\max}^{b}/nm	HOMO ^c /V (vs.NHE)	$E_{0-0}{}^d/\mathrm{eV}$	LUMO ^e /V (vs. NHE)
P1	460 (2.4)	476	0.68	2.17	-1.49
P2	450 (3.1)	475	0.90	2.26	-1.36
P3	449 (2.3)	480	1.23	2.34	-1.11

Table 1 Absorption and electrochemical properties of P1-P3





Fig. 2 Absorption spectra of P1-P3 adsorbed on TiO₂ film.

a correspondingly thinner nanocrystalline film so as to avoid the decrease of the film mechanical strength. This also benefits the electrolyte diffusion in the film and reduces the recombination possibility of the light-induced charges during transportation.^{12,36}

Fig. 2 shows the absorption spectra of **P1–P3** on TiO₂ films after 12 h adsorption. As shown in Fig.2, the maxima absorption peaks for **P1–P3** on the TiO₂ film are at $\lambda = 476$ nm, 475 nm and 480 nm and their absorption bands are red-shifted by 16 nm, 25 nm, 31 nm compared with the solution spectrum, respectively. The red shifts of the absorption spectra on TiO₂ of **P1–P3** could be ascribed to the aggregation of the dyes on the TiO₂ surface, which can occur readily because of the presence of carboxyl groups in the molecules. The interaction between the carboxylate group and the surface Ti⁴⁺ ions may lead to increased delocalization of the π^* orbital of the conjugated framework. The energy of the π^* level is decreased by this delocalization, which explains the red shift for the absorption spectra.

4.3 Electrochemical properties

Suitable highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the sensitizer are required to match the conduction band (CB) edge level of the TiO₂ electrode. To evaluate the possibility of electron transfer from the excited dye molecule to the conduction band (E_{cb}) of TiO₂, cyclic voltammograms (Fig. 3) were recorded in acetonitrile solvent using 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, TiO₂ films stained with sensitizer as the working electrode, Pt as the counter



Fig. 3 Cyclic voltammetry plots of **P1–P3** attached to a nanocrystalline TiO₂ film deposited on conducting FTO glass.

electrode and saturated calomel electrode (SCE) as the reference electrode. The SCE reference electrode was calibrated using a ferrocene/ferrocenium (Fc/Fc⁺) redox couple as an external standard, and the $E_{1/2}$ of the Fc/Fc⁺ redox couple was found to be 0.37 V versus the SCE reference electrode. It can be speculated from Fig. 3 that the first half-wave potentials of P1-P3 are 0.28, 0.50 and 0.83 V (vs. Fc/Fc⁺). Therefore, the ground state oxidation potential corresponding to the HOMO levels are 0.68, 0.90 and 1.23 V (vs. NHE), respectively. From Fig. 2, we know that the absorption thresholds for dyes P1-P3 are 572, 550 and 529 nm on TiO₂ film, which correspond to the band gap energy (E_{0-0}) of 2.17, 2.26 and 2.34 eV, respectively. The estimated excited state potential corresponding to the LUMO levels, calculated from $E_{\text{HOMO}} - E_{0-0}$, are -1.48, -1.36 and -1.11 V, respectively. The examined HOMO levels and the LUMO levels are listed in Table 1. From these data, we found the HOMO levels of P1-P3 to be sufficiently more positive than the iodine/ iodide redox potential value (0.4 V), indicating that the oxidized dyes formed after electron injection into the CB of TiO₂ could thermodynamically accept electrons from I⁻ ions. The LUMO levels of these dyes (see Table 1) were sufficiently more negative than the conduction-band-edge energy level (E_{cb}) of the TiO₂ electrode (-0.5 V vs. NHE), which implies that electron injection from the excited dye into the CB of TiO₂ is feasible.

4.4 Performances of liquid electrolyte dye-sensitized solar cells

Fig. 4 shows the incident monochromatic photon-to-current conversion efficiencies (IPCEs) obtained with a sandwich-type

Dye	$J_{\rm sc}/{ m mA~cm^{-2}}$	$V_{\rm oc}/{\rm mV}$	ff	η (%)	Amount ^a /mol cm ⁻²	$J_{\rm sc}^{\ \ b}/{\rm mA~mol^{-1}}$
P1	9.43	584	0.69	3.78	1.12×10^{-7}	8.39×10^{7}
P2	10.84	592	0.69	4.41	1.41×10^{-7}	7.70×10^{7}
P3	7.39	505	0.66	2.48	9.76×10^{-8}	7.57×10^7

Table 2 Photovoltaic performance of DSSCs based on P1-P3 dye with liquid electrolyte

^a Amount of dye adsorbed on TiO₂ film. ^b The short-circuit photocurrent generated per mole of dye molecules.



Fig. 4 Photocurrent action spectra of the TiO₂ electrodes sensitized by P1 (\blacksquare), P2 (\bullet) and P3 (\blacktriangle) with liquid electrolyte.

two electrode cell. The dye-coated TiO₂ film was used as the working electrode, platinized FTO glass as the counter electrode and 0.6 M MPII, 0.05 M I2, 0.10 M LiI and 0.5 M 4-tertbutylpyridine in acetonitrile and methoxypropionitrile (volume ratio, 7:3) mixture solution as the redox electrolyte. The losses of light reflection and absorption by the conducting glass were not corrected. As shown in Fig. 4, all three dyes can efficiently convert visible light to photocurrent in the region from 350 nm to 700 nm. The IPCE exceeds 70% in the spectral range 380-520 nm for P1, which reaches its maximum of 85.3% at 450 nm. The IPCE of P2 reached a maximum (84.9%) at 510 nm. And the maximum IPCE of P3 reaches 83.4% at 460 nm. The P2 sensitized TiO₂ electrode generates the highest conversion yield among three dyes (Table 2), which may be due to its broader photocurrent action spectra. We have noted that the IPCE spectrum of P1-P3 is red-shifted compared with the absorption spectrum of the dye adsorbed on TiO_2 (Fig. 4). This important red shift in the photocurrent response is attributed to lateral interaction in the adsorbed layer of the sensitizer and the detailed reason for this needs further studies.

Fig. 5 shows the current–voltage characteristics of dye-sensitized solar cells employing three phenothiazine dyes **P1–P3** as sensitizers under standard global AM 1.5 solar light conditions. The photovoltaic characteristic parameters of short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (*ff*), and photovoltaic conversion efficiency (η) are listed in Table 2. As shown in Fig. 5 and Table 2, we obtained a solar energy to electricity conversion efficiency of 3.78% ($J_{sc} = 9.43$ mA cm⁻², $V_{oc} = 584$ mV, ff = 0.69), 4.41% ($J_{sc} = 10.84$ mA cm⁻², $V_{oc} = 592$ mV, ff = 0.69) and 2.48% ($J_{sc} = 7.39$ mA cm⁻², $V_{oc} = 505$ mV, ff= 0.66) with DSSCs based on **P1–P3**, respectively. At the same time we also tested the apparent Fermi levels of **P1–P3** dyes by



Fig. 5 Photocurrent density *vs.* voltage curves for DSSCs based on **P1** (\blacksquare), **P2** (\bullet) and **P3** (\blacktriangle) under irradiation of AM 1.5G simulated solar light (100 mW cm⁻²) with liquid electrolyte.

Mott–Schottky plot method (see ESI^{\dagger} Fig.S1), which are -0.31V, -0.35 V, -0.27 V, respectively. It was found that the $V_{\rm oc}$ of P1-P3 corresponded to the apparent Fermi level and the different dyes have different apparent Fermi levels. From the adsorption amounts and the short-circuit photocurrents in Table 2, the contribution of one mole of dye molecules to the shortcircuit photocurrent could be calculated and the values are also listed in Table 2. About the molecular structure of three dyes, one can find that they have the same acceptor and conjugation chain but different donors. The results show that P1 containing the methoxy group has a broader absorption spectrum than P2 and P3 in dichloromethane solution because of the larger electron delocalization, and consequently leads to better photoelectric conversion properties to some extent. For example, one mole of **P1** produced 8.39×10^7 mA short-circuit photocurrent, while the short-circuit photocurrents generated by one mole of P2 and P3 are 7.70×10^7 and 7.57×10^7 mA, respectively. However, the photovoltaic conversion efficiency of P2 is higher than that of P1 due to the lower molar absorption coefficient, adsorption amount and short-circuit current density of P1. Therefore, it was found that the increase of electron donating ability is not always beneficial to improve the photoelectric conversion efficiency of DSSCs. These results agree well with the corresponding IPCE spectra.

Electrochemical impedance spectroscopy (EIS) analysis was performed to elucidate the photovoltaic findings further. Fig. 6 compares the impedance spectra for **P1–P3**-sensitized cells measured in the dark under a forward bias of -0.40 V with a frequency range of 0.1 Hz to 100 kHz. The important differences for the these organic dye-sensitized solar cells were found



Fig. 6 Impedance spectra of DSSCs based on P1 (\blacksquare), P2 (\bullet), P3 (\blacktriangle) and N3 (\bigcirc) dye measured at -0.40 V bias in the dark. (a) Nyquist plots; (b) Bode phase plots.

for the conductivity. The Nyquist plots (Fig. 6a) show the radius of the middle semicircle to increase in the order P3 < P1 < P2, indicating that the electron recombination resistance augments from P3, P1 to P2.37 Under similar conditions black dye N3 was tested, which is in good accordance with the data previously reported by Fabregat-Santiago et al.38 The electron lifetime values derived from curve fitting are 6.07, 6.52 and 5.99 ms for P1, P2, P3-sensitized solar cells, respectively. The longer electron lifetime observed with P2- relative to P1- or P3-sensitized cells indicates more effective suppression of the back reaction of the injected electron with the I₃⁻ in the electrolyte and is reflected in the improvements seen in the photocurrent, yielding substantially enhanced device efficiency. The Bode phase plots shown in Fig. 6b likewise support the differences in the electron lifetime for TiO₂ films derivatized with the three dyes. The middle-frequency peak of the DSSCs based on P2 shifts to lower frequency relative to P1 and P3, indicating a longer electron lifetime for P2. This result is in agreement with the observed shift in the V_{oc} value under standard global AM 1.5 illumination.

Since long-term stability is a vital parameter for sustained cell operation, we substituted the liquid electrolyte with a quasi-solid-state one. **P1–P3** organic dyes were evaluated as sensitizers for the quasi-solid-state dye-sensitized solar cell using 0.5 M iodine and 0.45 M benzimidazole (**BI**) in pure 1-butyl-3-meth-ylimidazolium iodide (**BMII**) as redox electrolyte which was solidified with fumed silica nanoparticles (5 wt%).³⁹ Fig. 7 shows



Fig. 7 Photocurrent action spectra of the TiO₂ electrodes sensitized by P1 (\blacksquare), P2 (\bullet) and P3 (\blacktriangle) with quasi-solid state electrolyte.

the IPCE of TiO₂ electrodes obtained with quasi-solid-state solar cells sensitized by dyes **P1–P3**. From Fig. 7 we can see that **P1–P3** can also efficiently convert visible light to photocurrent in the region from 400 to 650 nm with a quasi-solid state electrolyte. The IPCE data exceed 40% for **P1**, 50% for **P2** and 35% for **P3** in the spectral range 400–500 nm, respectively, which reaches its maximum of 49.4% for **P1** at 450 nm, 55.4% for **P2** at 450 nm and 47.8% for **P3** at 440 nm. The IPCE performance of the quasi-solid-state DSSC based on **P2** is higher than those of **P1** and **P3**, though the action spectrum for **P2** is similar to those for **P1** and **P3**. Therefore, phenothiazine sensitizer with triphenylamine hole

Table 3 Performance parameters of quasi-solid-state solar cells sensi-
tized by $dyes^a$

Dye	$J_{\rm sc}/{ m mA~cm^{-2}}$	$V_{\rm oc}/{ m mV}$	ff	η (%)
P1	5.95	544	0.66	2.13
P2	6.36	551	0.70	2.47
P3	5.45	536	0.70	2.04

^{*a*} The listed data are results from the measurement which has the closest values to the average of 6 measurements.



Fig. 8 Photocurrent–voltage curves of **P1** (\blacksquare), **P2** (\bullet) and **P3** (\blacktriangle) sensitized TiO₂ electrodes under standard global AM 1.5 illumination (100 mW cm⁻²) with quasi-solid-state electrolyte.

transport could become very attractive, because the introduction of the triphenylamine moiety was indeed to locate the cationic charge from the TiO₂ surface and efficiently restrict recombination between the conduction band electron and oxidized sensitizer.3,7

4.5 Performances of quasi-solid-state electrolyte dye-sensitized solar cells

Photovoltaic performances of the P1-P3 sensitized TiO₂ film electrodes with a quasi-solid-state electrolyte are listed in Table 3

800

Fig. 9 Stability test photovoltaic parameters (J_{sc} , V_{oc} , ff, and η) variations with aging time for the devices based on P1 (a), P2 (b) and P3 (c) sensitized TiO2 films with quasi-solid-state electrolyte during successive 1 sun visible-light soaking at 55 °C.

under standard global AM 1.5 solar light conditions (100 mW cm⁻²), and the corresponding photocurrent-voltage curves are shown in Fig. 8. The P2-sensitized cell gave a short circuit photocurrent density (J_{sc}) of 6.36 mA cm⁻², an open circuit voltage (V_{oc}) of 551 mV and a fill factor (ff) of 0.70, corresponding to an overall conversion efficiency (η) of 2.47%. Under the same conditions, the P1-sensitized cell gave a J_{sc} value of 5.95 mA cm⁻², a $V_{\rm oc}$ of 544 mV and an *ff* of 0.66, corresponding to the η value of 2.13% and P3 gave a $J_{\rm sc}$ of 5.45 mA cm⁻², a $V_{\rm oc}$ of 536 mV, an ff of 0.70 and η of 2.04%.

Fig. 9 shows the photovoltaic performance during long term accelerated aging of P1-P3-sensitized solar cells using a quasisolid-state electrolyte in a solar simulator at full intensity and 55 °C. Values for the short-circuit current (J_{sc}) , open-circuit potential (V_{oc}), fill factor (*ff*), and overall efficiency (η) were recorded over a period of 1000 h. All the solar cells were subjected to accelerated testing in a solar simulator at 100 mW cm^{-2} intensity at 55 °C. J_{sc} increased gradually for the first 400 h and then remained almost constant for 1000 h. The increases in photocurrent for P1-P3 from the initial value are calculated to be 26.4%, 42.4% and 32.7%, respectively. Contrasting to the J_{sc} increase under illumination, Voc dropped by 48, 50 and 48 mV for P1-P3 respectively. The decrease in V_{oc} may be due to an enhancement of the dark current. The J_{sc} gain compensates the loss of $V_{\rm oc}$, resulting in almost constant efficiency during light soaking. As a consequence, η first increased before 500 h and then remained almost constant for 1000 h for three dyes.

Conclusions 5.

In summary, three new phenothiazine organic dyes (P1-P3) containing thiophene have been synthesized for dve-sensitized solar cells. These dyes are successfully adsorbed on nanocrystalline anatase TiO₂ particles, and subsequently efficient dyesensitized solar cells have been fabricated. The absorption spectra, electrochemical and photovoltaic properties of the three dyes were extensively studied. It was found that the introduction of the triphenylamine group as the electron-donor brought about improved photovoltaic performance compared with methoxytriphenylamine and 1,1,2-triphenylethene for phenothiazine dyes. A maximum solar energy to electricity conversion efficiency of 4.41% ($J_{sc} = 10.84 \text{ mA cm}^{-2}$, $V_{oc} = 592 \text{ mV}$, ff = 0.69) under simulated AM 1.5 solar light irradiation (100 mW cm⁻²) with a DSSC based on P2 was obtained. Most importantly, long-term stability of the phenothiazine DSSCs under 1000 h light-soaking was demonstrated. Our findings demonstrate that phenothiazine organic sensitizers are promising for the further improvement of the conversion efficiency of DSSCs owing to the original and versatile molecular design.

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