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Modifying organic phenoxazine dyes for efficient dye-sensitized solar cells[†]

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Four organic dyes bearing the phenoxazine chromophore have been synthesized and applied in dyesensitized solar cells (DSCs). The effect of different dye structures on the performance of the DSCs was investigated systematically with photophysical, photovoltaic as well as photoelectrochemical methods. Due to the slow recombination process between injected electrons and electrolyte, the IB3 dye with two 2,4-dibutoxyphenyl units showed the best efficiency of 7.0% under 100 mW cm⁻² light illumination in the liquid state-DSCs. Moreover, the phenoxazine dyes-based solid state-DSCs were fabricated for the first time. With the IB4 dye, a higher efficiency of 3.2% has been achieved under the same light intensity.

Introduction

Dye-sensitized solar cells (DSCs) provide a kind of more economical and effective method to carry out the energy conversion from solar light to electricity since O'Regan and Grätzel reported that in 1991.¹ As one of the crucial components in DSCs, the photosensitizers have always attracted everincreasing attention in the past decades. Due to the better costperformance compared to metal-complex sensitizers,²⁻⁷ the organic dyes exhibit the more brilliant future in commercial application. The traditional design concept of the organic dyes is the donor-linker-acceptor structure, also named the D- π -A configuration. The electron can be facile to transfer from the donor to the acceptor part via the linker unit, and then finish the electron injecting process from the dye to the conduction band (CB) of the semiconductor. Up to now, many kinds of organic dyes based on coumarin,8-11 perylene,12-15 triarylamine,16-25 carbazole,26-29 indoline30-32 and other chromophores33-40 as donating groups have been developed and have shown potential commercial application for DSCs. In addition, due to the strong electron donating ability and facile structure modification, tetrahydroquinoline^{41,42} and heteroanthracene (phenothiazine and

phenoxazine)43-48 have also been successfully utilized for the application of DSCs. In order to absorb the sun light as much as possible, a broad absorption spectrum of the dye is desirable. Usually, extension of the π -conjugated system (introducing more π units) is a feasible strategy to complete the mission. However, the passive effect is that the large π -conjugated system leads to poor photovoltaic properties due to dye aggregation as well as electron recombination issues. To diminish the dye aggregation and the electron recombination, the alkyl chain was often introduced into linker or donor subunits; consequently, the efficiency can be greatly improved. In this paper, we further develop this concept to design the phenoxazine (POZ) dyes (IB1~IB4, see Fig. 1) through simultaneously modifying both donor and linker units with the same aromatic groups and also investigate the effect of different substituents and linker positions on the photophysical, photochemical and photovoltaic properties.

Experiments

General synthetic procedure

NMR spectra were measured on a Bruker AVANCE 500 MHz spectrometer, using TMS as the internal standard. HR-MS was performed using a Q-Tof micro (micromass Inc., Manchester, England) mass spectrometer equipped with a Z-spray ionization source. Commercial reagents and solvents were used as received without further purification. 10-Octyl-10*H*-phenoxazine (2), 3-bromo-10-octyl-10*H*-phenoxazine (3), 10-octyl-10*H*-phenox-azine-3-carbaldehyde (8) and 7-bromo-10-octyl-10*H*-phenox-azine-3-carbaldehyde (9) were synthesized according to our previous publication.⁴⁸

5-(10-Octyl-10*H***-phenoxazin-3-yl)thiophene-2-carbaldehyde (4).** Compound (3) (mono- and di-brominated product mixture, 1.00 g, 2.5 mmol), (5-formylthiophen-2-yl)boronic acid (0.62 g,

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[†] Electronic supplementary information (ESI) available: NMR spectra of **IB** dyes; the NOESY spectrum of compound **11**; the absorption spectra of **IB4**-sensitized TiO_2 with different ratios of **IB4**/CDCA (mol/mol); the trend of photovoltaic properties of **IB4** with different amounts of CDCA. See DOI: 10.1039/c1jm12071a



Fig. 1 The structures of phenoxazine IB1~IB4 dyes.

4 mmol), potassium carbonate (1.80 g, 13 mmol) and [1,1'-bis (diphenylphosphino)ferrocene]-dichloropalladium(II) (0.20 g, 13 mmol) are dissolved in 12 ml of toluene/MeOH (1 : 1; v/v). The final solution was placed in two sealable tubes (6 ml per tube) and stirred at 80 °C for 3.5 h. After the reaction, 25 ml of water are added and the solution is extracted with dichloromethane (DCM) to give the crude product. Column purification with silica gel and DCM/MeOH (30 : 1; v/v) gives (4) as orange crystals (0.50 g). ¹H NMR (500 MHz, *d*₆-acetone): δ = 9.89 (s, 1H), 7.91 (d, *J* = 3.94 Hz, 1H), 7.51 (d, *J* = 3.92 Hz, 1H), 7.27 (dd, *J* = 8.41, 2.16 Hz, 1H), 7.03 (d, *J* = 2.13 Hz, 1H), 6.84–6.88 (m, 1H), 6.65–6.68 (m, 4H), 3.63–3.68 (m, 2H), 1.67–1.73 (m, 2H), 1.45–1.52 (m, 2H), 1.28–1.44 (m, 8H), 0.88 ppm (t, *J* = 6.87, 6.87 Hz, 3H).

4-Bromo-5-(7-bromo-10-octyl-10*H***-phenoxazin-3-yl)thiophene-2-carbaldehyde (5).** Compound (4) (450 mg, 1.1 mmol) is dissolved in 10 ml DCM in an ice bath and bromine (360 mg, 2.2 mmol), dissolved in 4 ml of DCM, is added to the solution dropwise over 30 min. Stirring of the reaction mixture at room temperature (RT) is continued for 2.5 h. The reaction is quenched by adding 25 ml of dilute sodium hydroxide solution and extracted with DCM. Column purification with silica gel and DCM gives (5) (185 mg, 30%). ¹H NMR (500 MHz, *d*₆-acetone): $\delta = 9.91$ (s, 1H), 7.98 (s, 1H), 7.27 (dd, J = 8.42, 2.14 Hz, 1H), 7.06 (d, J = 2.16 Hz, 1H), 7.01 (dd, J = 8.64, 2.30 Hz, 1H), 6.85 (d, J = 8.54 Hz, 1H), 6.83 (d, J = 2.26 Hz, 1H), 6.71 (d, J = 8.64Hz, 1H), 3.64–3.69 (m, 2H), 1.67–1.74 (m, 2H), 1.45–1.52 (m, 2H), 1.30–1.44 (m, 8H), 0.88 ppm (t, J = 6.91, 6.91 Hz, 3H).

4-(4-(Diphenylamino)phenyl)-5-(7-(4-(diphenylamino)phenyl)-10-octyl-10*H***-phenoxazin-3-yl)thiophene-2-carbaldehyde (6). A mixture of compound (5) (115 mg, 0.2 mmol), (4-(diphenylamino)phenyl)boronic acid (236 mg, 0.8 mmol), potassium carbonate (280 mg, 2.0 mmol) and [1,1'-bis(diphenylphosphino) ferrocene]-dichloropalladium(II) (23 g, 0.03 mmol) are placed in** a sealable flask and dissolved in 6 ml of toluene/MeOH (1 : 1; v/v) and stirred at 75 °C for 3 h. Then 25 ml of water are added and the solution extracted with DCM. Column purification with silica gel and DCM as eluent gives (6) (160 mg, 89%) as dark orange crystals. ¹H NMR (500 MHz, d_6 -acetone): $\delta = 9.94$ (s, 1H), 7.98 (s, 1H), 7.54 (d, J = 8.65 Hz, 2H), 7.27–7.32 (m, 10H), 7.17 (dd, J = 8.36, 2.07 Hz, 1H), 7.02–7.17 (m, 17H), 6.96 (d, J = 2.09 Hz, 1H), 6.79 (d, J = 8.42 Hz, 1H), 6.72 (d, J = 8.39 Hz, 1H), 6.54 (d, J = 2.05 Hz, 1H), 3.63–3.69 (m, 2H), 1.68–1.75 (m, 2H), 1.46–1.53 (m, 2H), 1.30–1.45 (m, 8H), 0.88 ppm (t, J = 6.91, 6.91 Hz, 3H).

4-(2,4-Dibutoxyphenyl)-5-(7-(2,4-dibutoxyphenyl)-10-octyl-10Hphenoxazin-3-yl)thiophene-2-carbaldehyde (7). A mixture of compound (5) (185 mg, 3.3 mmol), (2,4-dibutoxyphenyl)boronic acid (350 mg, 1.3 mmol), potassium carbonate (230 mg, 1.6 mmol) and [1,1'-bis(diphenylphosphino)ferrocene]-dichloropalladium(II) (60 mg, 0.07 mmol) are placed in a sealable flask and dissolved in 6 ml of toluene/MeOH (1 : 1; v/v) and stirred at 75 °C for 3 h. Then 25 ml of water are added and the solution extracted with DCM. Column purification with silica gel and pentane/DCM (1 : 20; v/v) as eluent gave (7) (233 mg, 83.6%) as dark orange crystals. ¹H NMR (500 MHz, d_6 -acetone): $\delta = 9.87$ (s, 1H), 7.77 (s, 1H), 7.14 (d, J = 8.40 Hz, 1H), 7.07 (d, J = 8.35 Hz, 1H), 6.97 (dd, J = 8.30, 1.89 Hz, 1H), 6.84 (dd, J = 8.40, 1.96 Hz, 1H), 6.80 (d, J = 1.90 Hz, 1H), 6.63 (d, J = 8.40 Hz, 1H), 6.49–6.59 (m, 6H), 3.96–4.00 (m, 6H), 3.88 (t, J = 6.49, 6.49 Hz, 2H), 3.54-3.57 (m, 2H), 1.63-1.76 (m, 8H), 1.43-1.53 (m, 10H), 1.26–1.37 (m, 10H), 0.83–0.98 ppm (m, 15H).

10-Octyl-7-(thiophen-2-yl)-10H-phenoxazine-3-carbaldehyde (10). Compound (9) (1.30 g, 3.2 mmol), thiophen-2-ylboronic acid (0.87 g, 6.5 mmol), potassium carbonate (2.23 g, 5.0 mmol) and [1,1'-bis(diphenylphosphino)ferrocene]-dichloropalladium(II) (400 mg, 0.5 mmol) are placed in two sealable flasks and dissolved in 6 ml of toluene/DCM (1 : 1; v/v) each flask. The mixtures are then stirred at 80 °C for 3.5 h. After the reaction 30 ml of water are added and the solution extracted with DCM. Column purification with silica gel and petroleum ether/DCM (v/v) 1 : 1 and later 1 : 2 as eluent gives (**10**) (0.97 g, 74%) as dark oil. ¹H NMR (500 MHz, d_6 -acetone): $\delta = 9.68$ (s, 1H), 7.40 (dd, J = 8.29, 1.78 Hz, 1H), 7.37 (d, J = 5.08 Hz, 1H), 7.34 (d, J = 3.58 Hz, 1H), 7.13 (dd, J = 8.35, 2.07 Hz, 1H), 7.07 (dd, J = 5.02, 3.66 Hz, 1H), 7.04 (d, J = 1.79 Hz, 1H), 6.95 (d, J = 2.08 Hz, 1H), 6.82 (d, J = 8.30Hz, 1H), 6.78 (d, J = 8.39 Hz, 1H), 3.65–3.74 (m, 2H), 1.66–1.75 (m, 2H), 1.44–1.51 (m, 2H), 1.27–1.43 (m, 7H), 0.88 ppm (t, J =6.80, 6.80 Hz, 3H).

7-(3,5-Dibromothiophen-2-yl)-10-octyl-10*H***-phenoxazine-3-carbaldehyde (11). Compound (10) (0.49 g, 1.2 mmol) is dissolved in 5 ml DCM in an ice bath and bromine (0.38 g, 2.4 mmol) dissolved in 4 ml DCM is added to the solution over 20 min. The mixture is stirred at 0 °C for additional 30 min and then removed from the ice bath to continue stirring for 2.5 h. When the reaction is finished, 20 ml of dilute sodium hydroxide solution is added and the solution extracted with DCM. Column purification with silica gel and DCM as eluent gives (11) (0.52 g, 77.5%) as brown solid. ¹H NMR (500 MHz,** *d***₆-acetone): \delta = 9.60 (s, 1H), 7.28 (dd, J = 8.27, 1.71 Hz, 1H), 7.03 (s, 1H), 6.98 (dd, J = 8.37, 2.09 Hz, 1H), 6.92 (d, J = 1.73 Hz, 1H), 6.79 (d, J = 2.13 Hz, 1H), 6.66 (d, J = 8.33 Hz, 1H), 6.61 (d, J = 8.45 Hz, 1H), 3.48–3.53 (m, 2H), 1.55–1.62 (m, 2H), 1.25–1.43 (m, 8H), 0.86 ppm (t, J = 6.85, 6.85 Hz, 3H).**

7-(3,5-Bis(4-(diphenylamino)phenyl)thiophen-2-yl)-10-octyl-10Hphenoxazine-3-carbaldehyde (12). The compound (11) (250 mg, 0.4 mmol), (4-(diphenylamino)phenyl)boronic acid (500 mg, 1.8 mmol), potassium carbonate (300 mg, 2.2 mmol) and [1,1'-bis (diphenylphosphino)ferrocene]-dichloropalladium(II) (80 mg, 0.1 mmol) are placed in two sealable flasks and dissolved in 6 ml of toluene/DCM (1:1; v/v) each flask. The mixtures are then stirred at 80 °C for 3 h. After the reaction 30 ml of water are added and the solution is extracted with DCM. Column purification with silica gel and petroleum ether/DCM (v/v) 1:1 and later 1 : 2 as eluent gives (12) (290 mg, 73%) as a yellow solid. 1 H NMR (500 MHz, d_6 -acetone): $\delta = 9.70$ (s, 1H), 7.62 (d, J = 8.63Hz, 2H), 7.40-7.43 (m, 2H), 7.27-7.35 (m, 10H), 7.08-7.12 (m, 10H), 7.00–7.06 (m, 7H), 6.91 (dd, J = 8.33, 2.04 Hz, 1H), 6.84 (d, J = 8.33 Hz, 1H), 6.75 (d, J = 8.42 Hz, 1H), 6.55 (d, J = 2.03 Hz, 1H), 3.66-3.70 (m, 2H), 1.67-1.74 (m, 2H), 1.45-1.52 (m, 2H), 1.29–1.44 (m, 8H), 0.87 ppm (t, J = 6.84, 6.84 Hz, 3H).

(*E*)-2-Cyano-3-(5-(10-octyl-10*H*-phenoxazin-3-yl)thiophen-2-yl) acrylic acid (IB1). Compound (6) (62 mg, 0.15 mmol) and 2-cyanoacetic acid (50 mg, 0.6 mmol) are dissolved in 10 ml acetonitrile. 4 drops of piperidine are added and the mixture is then refluxed for 2 h. After evaporation of the solvent the crude product is purified by column chromatography with silica gel and DCM as eluent at first, then change to DCM/ethyl acetate (v/v) 5 : 1 and finally 10 : 1. To get rid of remained impurities the dye is recrystallized with 5 ml acetone and 5 ml pentane to finally give **IB1** (40 mg, 56%) as a deep red powder. ¹H NMR (500 MHz, *d*₆-DMSO): $\delta = 8.44$ (s, 1H), 7.96 (d, J = 4.03 Hz, 1H), 7.63 (d, J = 4.06 Hz, 1H), 7.25 (dd, J = 8.38, 2.13 Hz, 1H), 7.09 (d, J = 2.14 Hz, 1H), 6.85–6.88 (m, 1H), 6.76–6.97 (m, 4H), 3.58–3.61 (m,

2H), 1.53–1.59 (m, 2H), 1.37–1.41 (m, 2H), 1.26–1.33 (m, 8H), 0.87 ppm (t, J = 6.89 Hz, 3H); ¹³C NMR (126 MHz, d_6 -DMSO): $\delta = 163.8$, 152.5, 146.4, 144.4, 143.7, 141.6, 134.4, 133.1, 131.7, 124.8, 124.3, 123.8, 122.6, 121.6, 116.7, 115.2, 112.4, 112.3, 112.2, 31.2, 28.8, 28.7, 26.0, 24.5, 22.1, 13.9 ppm; ESI-HRMS calcd. for C₂₈H₂₈N₂O₃S [M⁺] 472.1815, found 472.1831.

(E)-2-Cyano-3-(4-(4-(diphenylamino)phenyl)-5-(7-(4-(diphenylamino)phenyl)-10-octyl-10H-phenoxazin-3-yl)thiophen-2-yl)acrylic acid (IB2). Compound (10) (160 mg, 0.2 mmol) and 2-cyanoacetic acid (60 mg, 0.7 mmol) are dissolved in 20 ml acetonitrile. 4 drops of piperidine are added and the mixture is then refluxed for 1 h. After evaporation of the solvent the crude product is purified by column chromatography with silica gel and DCM/MeOH (20:1; v/v) as eluent to give **IB2** (126 mg, 73%) as a deep red powder. ¹H NMR (500 MHz, d_6 -DMSO): $\delta = 8.42$ (s, 1H), 7.97 (s, 1H), 7.49 (d, J = 8.5 Hz, 2H), 7.25-7.31 (m, 8H), 7.28 (d, J = 8.5 Hz, 2H),7.12 (d, 3.26 Hz, 1H), 6.89–7.09 (m, 18 H), 6.79 (d, J = 8.46 Hz, 1H), 6.74 (d, J = 8.31 Hz, 1H), 6.56 (d, J = 1.86 Hz, 1H), 3.52– 3.55 (m, 2H), 1.53–1.46 (m, 2H), 1.45–1.38 (m, 2H), 1.35–1.29 (m, 8H), 0.88 ppm (t, J = 6.88, 6.88 Hz, 3H); ¹³C NMR (126 MHz, d_6 -DMSO): $\delta = 163.5$, 147.0, 146.9, 146.2, 144.0, 143.7, 138.0, 133.5, 132.8, 132.6, 130.8, 130.0, 129.5, 128.5, 126.5, 124.8, 124.6, 124.0, 123.4, 123.3, 123.1, 122.8, 121.6, 116.6, 114.7, 112.7, 112.6, 112.1, 31.2, 28.8, 28.7, 26.0, 24.5, 22.1, 13.4 ppm; ESI-HRMS calcd. for C₆₄H₅₄N₄O₃S [M⁺] 958.3911, found 958.3909.

(E)-2-Cyano-3-(4-(2,4-dibutoxyphenyl)-5-(7-(2,4-dibutoxyphenyl)-10-octyl-10*H*-phenoxazin-3-yl)thiophen-2-yl)acrylic acid (**IB3**). Compound (9) (230 mg, 0.28 mmol) and 2-cyanoacetic acid (90 mg, 1.1 mmol) are dissolved in 12 ml acetonitrile. 10 drops of piperidine are added and the mixture is then refluxed for 2.5 h. After evaporation of the solvent the crude product is purified by column chromatography with silica gel and DCM/MeOH (20:1; v/v) as eluent to give **IB3** (190 mg, 75%) as a deep red powder. 1 H NMR (500 MHz, d_6 -acetone): $\delta = 8.35$ (s, 1H), 7.81 (s, 1H), 7.14 (d, J = 8.40 Hz, 1H), 7.09 (d, J = 8.35 Hz, 1H), 6.96 (dd, J = 8.30),1.89 Hz, 1H), 6.87 (dd, J = 8.40, 1.96 Hz, 1H), 6.80 (d, J = 1.90 Hz, 1H), 6.49–6.63 (m, 7H), 3.99–3.95 (m, 6H), 3.86 (t, J = 6.49, 6.49 Hz, 2H), 3.57-3.53 (m, 2H), 1.60-1.77 (m, 8H), 1.54-1.39 (m, 10H), 1.24–1.39 (m, 10H), 0.84–0.98 ppm (m, 15H); ¹³C NMR (126 MHz, d_6 -acetone): $\delta = 164.4$, 161.6, 160.6, 158.2, 157.8, 149.4, 147.1, 145.5, 144.6, 144.5, 136.2, 134.9, 133.0, 132.7, 132.4, 131.3, 131.1, 127.2, 125.4, 124.8, 122.7, 117.6, 117.2, 117.1, 115.0, 112.3, 112.3, 106.6, 106.5, 101.1, 100.9, 98.7, 68.6, 68.4, 68.3, 44.3, 32.6, 32.2, 32.1, 31.8, 27.4, 23.4, 20.0, 19.9, 19.8, 14.4, 14.2 ppm; ESI-HRMS calcd. for $C_{56}H_{68}N_2NaO_7S$ [M + Na⁺] 935.4639, found 935.4597.

(*E*)-3-(7-(3,5-Bis(4-(diphenylamino)phenyl)thiophen-2-yl)-10octyl-10*H*-phenoxazin-3-yl)-2-cyanoacrylic acid (IB4). The compound (13) (220 g, 2.4 mmol) and 2-cyanoacetic acid (80 mg, 1.0 mmol) are dissolved in 15 ml acetonitrile. 10 Drops of piperidine are added and the mixture is then refluxed for 2.5 h. After evaporation of the solvent the crude product is purified by column chromatography with silica gel and DCM/MeOH (10 : 1; v/v) as eluent to give **IB4** (113 mg, 49%) as a dark powder. ¹H NMR (500 MHz, *d*₆-acetone): $\delta = 7.99$ (s, 1H), 7.58 (d, *J* = 8.65 Hz, 2H), 7.53 (dd, *J* = 8.57, 2.01 Hz, 1H), 7.46 (s, 1H), 7.37 (d, $J = 2.05 \text{ Hz}, 1\text{H}), 7.33-7.24 \text{ (m, 10H)}, 7.07-7.10 \text{ (m, 12H)}, 7.06-7.00 \text{ (m, 4H)}, 6.87 \text{ (dd, } J = 8.34, 2.03 \text{ Hz}, 1\text{H}), 6.80 \text{ (d, } J = 8.62 \text{ Hz}, 1\text{H}), 6.70 \text{ (d, } J = 8.48 \text{ Hz}, 1\text{H}), 6.54 \text{ (d, } J = 2.04 \text{ Hz}, 1\text{H}), 3.63-3.63 \text{ (m, 2H)}, 1.64-1.71 \text{ (m, 2H)}, 1.43-1.50 \text{ (m, 2H)}, 1.28-1.42 \text{ (m, 8H)}, 0.86 \text{ ppm (t, } J = 6.80, 6.80 \text{ Hz}, 3\text{H}); ^{13}\text{C NMR} (126 \text{ MHz}, d_6\text{-DMSO}): \delta = 165.6, 146.9, 146.8, 143.5, 129.6, 129.5, 124.3, 124.1, 123.5, 123.2, 122.9, 122.9, 115.6, 31.2, 28.7, 28.3, 24.6, 22.4, 22.0, 13.9 \text{ ppm; ESI-HRMS calcd. for C}_{64}\text{H}_{54}\text{N}_4\text{O}_3\text{S} \text{ [M}^+] 958.3911, found 958.3920.$

Preparation of liquid-solar cells

Fluorine-doped tin oxide (FTO) glass plates (Pilkington-TEC15) were cleaned in subsequent order of detergent solution, water and EtOH using an ultrasonic bath overnight. The conducting glass substrates were immersed into a 40 mM aqueous TiCl₄ solution at 70 °C for 30 min and washed with water and ethanol. The screen-printing procedure was repeated (layer of 2 µm) with TiO₂ paste (Dyesol, 18 NR-T) to obtain a transparent nanocrystalline film of a thickness around 10 µm and an area of 0.25 cm². Two scattering layers ($\sim 4 \mu m$, solaronix R/SP) were deposited on the top of a 10 µm transparent layer to form the $10 + 4 \mu m TiO_2$ film. The TiO₂ electrodes were gradually heated in an oven (Nabertherm Controller P330) in an ambient air atmosphere. The temperature gradient program used included two stationary plateaus at 325 °C (10 min), and 450 °C (30 min). After sintering the electrodes once again underwent, as described above, a post-TiCl₄ treatment. A second and final sintering, at 450 °C for 30 min, was performed. When the temperature decreased to 30~40 °C after the sintering the electrodes were immersed into 0.2 mM dye solutions with 2 mM chenodeoxycholic acid (CDCA) and kept for 16~17 h in dark at room temperature. The mixture of EtOH (99.5%)/DCM (4:1; v/v) was used as solvent for all dyes. After the adsorption of the dyes, the electrode was further rinsed with the EtOH. The electrodes were assembled with a platinized counter electrode (\sim 8.6 µg cm⁻²)⁴⁹ using a 25 µm thick hot-melt film (Surlyn, Solaronix). The redox electrolyte containing 0.04 M I₂ (99.9%), 0.06 M LiI (99.9%), 0.4 M 4-tert-butylpyridine (4-TBP, 99%), 0.6 M 3-hexyl-1,2dimethylimidazolium iodide (DMHII, 98%), in MeCN/valeronitrile (VN) (85 : 15; v/v) was introduced through a hole drilled in the back of the counter electrode. Finally, the hole was also sealed with the Surlyn film.

Preparation of solid state-solar cells

A compact TiO₂ layer (TiO₂ underlayer) was firstly deposited onto the FTO substrate by spray pyrolysis, and then TiO₂ particles (Dyesol, 18 NR-T) were deposited by doctor-blading method to obtain a ~2.2 µm thick mesoporous film including the TiO₂ underlayer. The TiO₂ electrodes were gradually heated in an oven at air atmosphere to two levels, at 250 °C (20 min) and 500 °C (30 min). After sintering, the electrodes were immersed into 40 mM aqueous TiCl₄ solution at 70 °C for 30 min and washed with water and ethanol. A second and final sintering, at 500 °C for 30 min, was performed. When the temperature decreased to 30~40 °C after the sintering, the electrodes were immersed into 0.2 mM dye solutions with the addition of 2 mM co-adsorbent chenodeoxycholic acid (CDCA) in EtOH/DCM (4 : 1; v/v) and kept for 16~17 h in dark at room temperature. After the adsorption of the dyes, the electrodes were rinsed with the same solvent. The hole transporting material (HTM) solution containing 120 mM Spiro-OMeTAD, 60 mM 4-TBP, and 15 mM LiN(CF₃SO₂)₂ (Li-TFSI) in chlorobenzene was deposited onto the dye-coated TiO₂ film and left stationary for 1 min in order to penetrate the HTM solution into TiO₂ pores prior to spin coating. Then, the substrate was spun up to 1400 rpm for 30 s. Finally, a 50 nm of Ag was thermally evaporated on top of the HTM as counter electrode to form our test cells.

Photocurrent density-voltage (J-V) measurements

Prepared solar cells were characterized by current–voltage characteristics and incident photon-to-current conversion efficiency (IPCE). Current–voltage characteristics were carried out with an AM 1.5G solar simulator, 300 W xenon (ozone free). The incident light intensity was 1000 W m⁻² calibrated with a standard Si solar cell. For the J-V curves of liquid DSCs, the active area is 0.25 cm² and a black mask 0.64 cm² (8 mm × 8 mm) was used in the subsequent photovoltaic studies. For solid state DSCs, the active area is determined to 0.16 cm² (4 mm × 4 mm) with a back mask. IPCE measurements were carried out with a computerized set-up consisting of a xenon arc lamp (300 W Cermax, ILC Technology), followed by a 1/8 m monochromator (CVI Digikrom CM 110). The data collection was done with a Keithley 2400 source/meter, and a Newport 1830-C power meter with 818-UV detector head.

Photophysical measurements

The UV-Vis absorption spectra of the dye-loaded transparent film (2 μ m, sensitized 30 min in dye bath) and the dye solution (0.02 mM, in EtOH/DCM (4 : 1, v/v) in a normal quartz sample cell (1 cm path length) were recorded on a Lambda 750 spectrophotometer. The fluorescence spectra of dye solution were recorded on Cary Eclipse fluorescence spectrophotometer using the same concentration as the UV-Vis measurement.

Adsorption amount of dyes on TiO₂

The dye-loading on TiO₂ film was estimated from the dye desorption in 0.1 M tetrabutylammonium hydroxide (TBAOH) MeOH solution by means of UV-Vis absorption spectroscopy, two pieces TiO₂ film with total 0.5 cm² (0.25 cm² per piece) were used for all dyes.

Electrochemical measurements

Electrochemical experiments were performed with a CH Instruments electrochemical workstation (model 660A) using a conventional three-electrode electrochemical cell. Measurements were obtained with 1 mM solution of dyes in DCM by using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte. A glass carbon disk was used as the working electrode, a platinum wire served as a counter electrode, a Ag/Ag⁺ electrode was utilized as a reference electrode, and the scan rate used was 50 mV s⁻¹. All redox potentials were calibrated *versus* a normal hydrogen electrode (NHE) by the addition of ferrocene as an internal standard taking $E(Fc/Fc^{+}) = 630 \text{ mV } vs. \text{ NHE.}^{16}$

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) tests were carried out using an Autolab PGstat12 potentiostat with an impedance module in the frequency range 10 kHz to 0.1 Hz, using 20 mV AC amplitude, under dark conditions with an applied bias voltage -0.68 V potential.

Photoelectrochemical measurements

Electron lifetimes for the solar cells were measured using a redlight-emitting diode (Luxeon, 1 W) as the light source. Voltage and current traces were recorded by a 16-bit resolution data acquisition board (DAQ National Instruments) in combination with a current amplifier (Stanford Research SR570). The relation between potential and charge was studied using a combined voltage decay/charge extraction method. Charge extraction measurements were carried out as follows: the solar cell was illuminated for 5 s under open-circuit conditions, and then the light was switched off and the voltage was let to decay to a voltage V. At a certain voltage V, the cell was short-circuited, and the current was measured under 10 s and then integrated to obtain $Q_{\rm oc}$ (V). Electron lifetime was tested by monitoring transient photovoltage response after a small perturbation of light intensity.

Molecular orbital calculation

The structural and electronic properties of the dyes were calculated with the B3LYP hybrid functional at the 6-31G



Fig. 2 Synthetic routes of **IB1**~**IB4** dyes: (a) C_8H_{17} Br, NaOH, $C_{16}H_{33}$ NMe₃Br, acetone, 12 h, reflux; (b) 1 equiv. Br₂, DCM, 2 h; (c) (5-formylthiophen-2-yl)boronic acid, K₂CO₃, Pd(dppf)Cl₂, toluene/MeOH, 3.5 h, 80 °C; (d) 2 equiv. Br₂, DCM, 0° to RT, 2 h; (e) (2,4-dibutoxyphenyl)boronic or (4-(diphenylamino)phenyl)boronic acid, K₂CO₃, Pd(dppf)Cl₂, toluene/MeOH, 3h, 75 °C; (f) POCl₃, DMF, CHCl₃, 75 °C, 15 h; (g) 2-cyanoacetic acid, piperidine, MeCN, 2 h.

(d) level in gas phase using the Gaussian 03 program package.⁵⁰ Long alkyl substituents, which have no significant impact on the frontier orbitals of the chromophores, were truncated to methyl groups to hasten the convergence of optimizations.

Results and discussion

Synthesis

The detailed synthetic routes of IB1~IB4 dyes are depicted in Fig. 2. All of the dyes were synthesized according to the traditional methods: alkylation, bromination, Vilsmeyer-Haack formylation, Suzuki-coupling and Knoevenagel condensation. The N-alkylation was performed in acetone with 1-bromooctane, NaOH as the base and palmityl trimethylammonium bromide as the phase transfer catalyst. Formylation was accomplished by the Vilsmeyer-Haack reaction. Monobromination and dibromination were controlled by the amount of bromine added in the reaction. The dibromination products (compounds 5 and 11) are very easy to be purified compared with the mono-brominated product due to much lower polarity. The position of the Br atom in the dibrominated compounds was further proved by NOESY spectra. The final reaction for all dyes was the condensation of corresponding aldehyde with 2-cyanoacetic acid by the Knoevenagel reaction in the presence of piperidine. All the compounds were characterized by ¹H- and ¹³C-NMR spectroscopy. The final dyes were also characterized by HR-MS.

Calculation study

In order to explain the experimental spectra and gain insights into the structural properties of the chromophores, density functional theory (DFT) calculations were performed. The optimized geometries and isodensity plots of the frontier orbitals of the chromophores are shown in Table 1. The isodensity plots were generated in Avogadro⁵¹ using an isovalue of 0.02.

A first insight gained from the calculations is that introducing a substituent on the thiophene in a position adjacent to the phenoxazine will disrupt the dihedral angle between the POZ and thiophene. As the dihedral angle between these two aromatic units in the chromophore grows from 20° in **IB1** to $36-39^{\circ}$ in **IB2** and **IB4**, conjugation over the π -system is disrupted. This disruption of the conjugation is reflected in the experimental optical spectra of the chromophores in that **IB1** has the strongest absorption.

Photophysical properties

The absorption spectra of **IB1~IB4** dyes in EtOH/DCM (4:1; v/v) solution and on TiO₂ films are illustrated in Fig. 3. The corresponding photophysical data are collected in Table 2. **IB2** and **IB3** dyes show slightly blue-shifted absorption peaks (λ_{max}) and lower extinction coefficient comparing with **IB1** due to the weak π -conjugated system caused by the increased twist angle between the POZ unit and the thiophene group, which has been proved with the DFT calculation. Interestingly, when the thiophene unit in **IB2** was changed from right to left of the POZ unit

Table 1 The optimized structures and electron distribution in HOMO and LUMO levels of the IB dyes





Fig. 3 The absorption spectra of IB1~IB4 dyes in EtOH/DCM (4 : 1; v/v) solution (a) and on TiO₂ films (b).

to construct the **IB4** dye, the absorption peak is red-shifted from 483 nm to 492 nm, but the absorption region was narrowed due to the change of the π -conjugated system of the structure. Compared with the absorption spectra of the dyes in solution, the absorption spectra of **IB2** and **IB3** on TiO₂ films show almost no obvious change, probably due to the suppression of dye aggregation on TiO₂ ascribed to the extra units in both the POZ and thiophene units. However, the **IB1** and **IB4** dyes have the obvious blue-shifted absorption spectra on the TiO₂ surface. The effect of different ratios of **IB4**/CDCA on the absorption spectra (see Fig. S1[†]) was performed to study if the aggregation causes the blue-shift phenomenon. However, no obvious red-shift of absorption spectrum was observed when the concentration of CDCA in the dye bath was increased. Therefore, we consider

Table 3 The adsorption amount of IB1 \sim IB4 dyes on TiO₂ films^{*a*}

Dye	Dye-load/mol cm ⁻³ $(\times 10^{-8})$		
IB1	2.0		
IB2	1.8		
IB3	1.8		
IB4	2.5		

^{*a*} The dye load on the TiO_2 film was estimated from the dye desorption in 0.1 M tetrabutylammonium hydroxide methanol solution by means of UV-Vis absorption spectroscopy.



Fig. 4 The J-V curves (a) and IPCE spectra (b) of DSCs based on **IB** dyes.

 Table 2
 Photophysical and electrochemical properties of IB1~IB4 dyes

Dye	Absorption				Potentials		
	$\lambda_{\rm max}/{\rm nm}$	$\varepsilon/M^{-1} \mathrm{~cm}^{-1}$	λ_{max} on TiO ₂ /nm	Emission λ_{emi}/nm	E_{0-0} /V (vs. NHE)	HOMO/V (vs. NHE)	LUMO/V (vs. NHE)
IB1	486	21 000	466	638	2.19	0.91	-1.28
IB2	483	15 000	483	650	2.17	0.81	-1.36
IB3	482	17 000	480	650	2.17	0.79	-1.38
IB4	492	19 000	475	605	2.28	0.93	-1.35

that the blue-shift of the **IB4** dye on TiO₂ could be caused by different configurations of **IB4** on the TiO₂ surface from that in solution, not the aggregation. Noticeably, with the same thickness of the TiO₂ film (2 µm) and the sensitized time (30 min) in the same concentration of dye-bath, the **IB4** dye shows a stronger absorbance even than the **IB1** dyes (Fig. 3b). According to dye adsorption amount measurements (Table 3), one finds that **IB4** dyes show a much greater adsorption amount on TiO₂ film, 2.5×10^{-8} mol cm⁻³ than **IB1**, 2.0×10^{-8} mol cm⁻³, although the CDCA has been added into the dye-bath to diminish the dye aggregation. Coincidentally, **IB2** and **IB3** dyes display the same adsorption amount on TiO₂, 1.8×10^{-8} mol cm⁻³, which is lower than that of the **IB1** dye on TiO₂ due to the special molecular configuration. This result could imply that the **IB4** dye has the fast sensitization rate as compared to other dyes.

Electrochemical properties

The electrochemical properties of IB1~IB4 are shown in Table 2. The oxidation potentials (E_{ox}) of these dyes were measured by cyclic voltammetry. The first oxidation potential versus normal hydrogen electrode (vs. NHE) calibrated by Fc/Fc⁺ (with 630 mV vs. NHE) corresponds to the HOMO level of the dye. The HOMO levels of all the dyes are more positive than the redox potential of I⁻/I₃⁻ (0.3~0.4 V vs. NHE),⁵² which means that the oxidized dyes can be regenerated effectively. For IB2 and IB3 dyes, the introduction of an extra electron donor in both POZ and thiophene makes the HOMO level more negative compared with IB1 due to the increase of electron donating ability. However, when the substituted thiophene was moved from the right side of the POZ (IB2) to the left side of the POZ (IB4), the HOMO level was significantly changed. IB4 shows more positive HOMO potential than IB2 due to the weaker π -conjugated system in molecular structure. The LUMO levels of these dyes were calculated by $E_{\rm ox} - E_{0-0}$, where E_{0-0} is the zeroth-zeroth energy of the dyes estimated from the intersection between the absorption and emission spectra. As shown in Table 2, the LUMO potentials of these dyes are much more negative than the conduction band (CB) of the TiO₂ level (-0.5 V vs. NHE), which means that the electrons could be efficiently injected into the CB of TiO₂ from the excited dyes. Furthermore, the large difference between the TiO₂ CB and the LUMO levels of the dyes suggests that 4-tert-butylpyridine can be used in the electrolyte to move the CB negatively, yielding higher photovoltage (V) values.

Photovoltaic and photoelectrochemical properties

The photocurrent density-photovoltage (J-V) curves of DSCs based on **IB1~IB4** dyes performed under standard AM 1.5G illumination (100 mW cm⁻²) are shown in Fig. 4. The corresponding photovoltaic data are collected in Table 4. The basic dye structure **IB1** dye gave an efficiency of 6.2% with a shortcircuit photocurrent density (J_{sc}) of 13.2 mA cm⁻², open-circuit photovoltage (V_{oc}) of 0.7 V and fill factor (*ff*) of 0.68. Featuring the TPA groups in the POZ and thiophene units, the **IB2** dye rendered a higher V_{oc} value, 0.76 V. However, replacing the TPA groups with 2,4-dibutoxyphenyl units to construct the **IB3** dye, the V_{oc} value was further improved to 0.8 V without decrease of photocurrent, hence yielding an ideal efficiency of 7.0% under

Table 4 Photovoltaic performance of DSCs based on the different $IB1 \sim IB4$ dyes^{*a*}

Dye ^b	$J_{\rm sc}/{ m mA~cm^{-2}}$	$V_{\rm oc}/{ m V}$	ff	η (%)
IB1	13.2	0.70	0.68	6.2
IB2	12.8	0.76	0.65	6.3
IB3	13.7	0.80	0.63	7.0
IB4	13.4	0.74	0.66	6.5

^{*a*} Light intensity: under standard AM 1.5G illumination (100 mW cm⁻²); active area: 0.25 cm²; thickness of TiO₂ film: 10 μ m transparent layer + 4 μ m scattering layer. ^{*b*} Dye bath: 0.2 mM in EtOH/DCM (4 : 1; v/v); sensitized time: 16~17 h; electrolytes: 0.6 M DMPII, 0.06 M LiI, 0.04 M I₂, 0.4 M TBP in MeCN/VN (85 : 15; v/v).

same light illumination. The position of thiophene also significantly affects the photovoltaic properties. The **IB4** dye shows a lower photovoltage value, 0.74 V, and higher IPCE values, between 400 and 600 nm, than the **IB2** dye.

In order to gain further insight into the reasons for the increased photovoltage, the lifetime and charge extraction of these dyes based DSCs were measured. As shown in Fig. 5, all of the dyes show the same effect on charge extraction experiments, which means that the DSCs based on these dyes using the same electrolyte show the same effect on the CB of TiO_2 . However, the



Fig. 5 The electron lifetime (a) and charge extraction (b) of DSCs based on **IB** dyes.

measurement of the injected electron lifetime (τ_e) of DSCs based on different **IB** dyes presents an interesting result. The τ_e values of DSCs based on **IB** dyes are in order of **IB1 < IB4 < IB2 < IB3**. The result implies that the introduction of 2,4-dibutoxyphenyl units can greatly suppress the electron recombination between the injected electron and the electrolyte or oxidized dye. Comparing **IB2** and **IB4** dyes, when the TPA substituted thiophene unit is close to the anchor group, in other words, near to the TiO₂ surface, the injected electron will be further protected to avoid the recombination process mentioned above, rendering the higher V_{oc} .

In addition, electrochemical impedance spectroscopy (EIS) also was employed to study the electron recombination and electrolyte reduction process in DSCs based on these **IB1~IB4** dyes under -0.68 V bias applied voltage in the dark. The Nyquist and Bode plots are shown in Fig. 6. Some important parameters can be obtained by fitting the EIS spectra to an electrochemical model.⁵³ R_S , R_{rec} and R_{CE} represent the series resistances, charge-transfer resistances at the dye/TiO₂/electrolyte interface and counter electrode (CE), respectively. We can find the series resistance (R_S) and electrolyte reduction resistance (R_{CE}) corresponding to the first semicircle show almost same value in all dyes-based DSCs due to the same electrode material and same electrolyte. From the EIS measurements, the electron lifetime (τ_e) expressing the electron recombination between the electrolyte and TiO₂ may be extracted from the angular frequency (ω_{rec}) at



Fig. 6 The Nyquist (a) and Bode plots (b) of DSCs based on IB dyes.



Fig. 7 The J-V curve and IPCE (inset) of solid state DSCs based on **IB4** dyes.

the mid frequency peak in the Bode phase plots using the relation $\tau_e = 1/\omega_{rec}$. The **IB1** dye gives the lowest R_{rec} value, 60 Ω , and the shortest τ_e , 26 ms in TiO₂, among these dyes. However, τ_e and R_{rec} of the **IB3** dye are 455 ms and 1560 Ω , respectively, which are much higher than that of the other dyes. The lifetime obtained by EIS is in order of **IB1** < **IB4** < **IB2** < **IB3**. This trend is in accordance with the τ_e vs. V_{oc} results above. This result suggests that the electron recombination rate between the TiO₂ film and the electrolyte is indeed suppressed by introduction of the extra electron donor groups on the POZ and thiophene units efficiently.

We also adopted **IB3** and **IB4** to fabricate the solid state DSCs using the Spiro-OMeTAD⁵⁴ as the hole conductor. The J-V curve and IPCE spectrum of **IB4** based solid state DSCs are shown in Fig. 7. The **IB4** dye showed an efficiency of 3.2% with a $J_{\rm sc}$ of 6.4 mA cm⁻², $V_{\rm oc}$ of 0.81 V and *ff* of 0.62 under standard light illumination. The maximum IPCE value obtained by the **IB4** dye is 63% at 480 nm. However, under the same condition, the **IB3** dye in solid state DSCs gave an efficiency of just 1.6%



Fig. 8 The electron lifetime of solid state DSCs based on IB3 and IB4 dyes.

with much lower V_{oc} and ff values of 0.59 V and 0.34, respectively. According to the lifetime measurement (Fig. 8), interestingly, the IB3 dve shows a much shorter lifetime than IB4. The trend is totally different from that in liquid DSCs. The serious electron recombination between the injected electrons and oxidized dyes or Spiro-OMeTAD will result in the lower V_{oc} value, probably as well as a low ff value, yielding a disappointing efficiency of DSCs based on the IB3 dve. The potential of Spiro-OMeTAD is 0.8 V vs. NHE,55 which means that the regeneration of oxidized IB3 dye could be difficult by this material. However, from experiment, the solid state DSCs based on the IB3 dye also produced a high current of about 8.0 mA cm⁻², which proved that the IB3 dyes also can be regenerated by Spiro-OMeTAD in solid state DSCs. This result suggests that the redox potentials of **IB3** and/or Spiro-OMeTAD in solid state DSCs are not exactly same as those in organic solvent.

Conclusion

Through modification of the basic dye structure (**IB1**) from both the linker and donor units, a series of phenoxazine dyes were designed and developed for dye-sensitized solar cells (DSCs). An efficiency of 7.0% has been achieved under the standard light illumination (AM 1.5G, 100 mW cm⁻²) by the **IB3** dye with 2,4-dibutoxyphenyl units. The detailed photoelectrochemical study discovers that the introduction of triphenylamine or 2,4-dibutoxyphenyl can decrease the recombination process between the injected electrons and electrolytes, yielding the high photovoltage in liquid state DSCs. Furthermore, the solid state DSCs based on phenoxazine dyes were reported for the first time. The **IB4** dye rendered an efficiency of 3.2% under the standard light illumination. This strategy of structural modification will pave a road to develop more efficient organic dyes in the future.

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