Electronic Supplementary Information

Efficient and stable dye-sensitized solar cells based on phenothiazine sensitizers with thiophene unit

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General

^{1}H NMR and ^{13}C NMR spectra were recorded on a spectrometer operating at 500 and 125 MHz. The UV–Vis spectra were measured with model CARY 100 spectrophotometer. MS were recorded on ESI mass spectroscopy. The cyclic voltammograms of dyes were estimated with a Versastat II electrochemical workstation using a normal three- electrodes cell with a Pt working electrode, a Pt wire auxiliary electrode, and a regular calomel reference electrode in saturated KCl solution.

Full synthetic procedures for the important intermediate compounds are as follows:

3, 7-dibromo-10-octyl-phenothiazine (1)

A modified version of a previously reported method was used. 10-octyl-pheno-thiazine (3.11 g, 0.01 mol) was added in 20 mL CH_2Cl_2. Liquid bromine (6.40 g, 0.04 mol) was added to the mixture slowly, and reacted under stirring at room temperature for 4 h. Then NaOH aqueous solution was added to neutralize the mixture holding a half-hour and extracted with CH_2Cl_2 and saltwater. The organic portion was combined and dried with anhydrous $MgSO_4$ and removed by rotary evaporation. The residue was purified by column chromatography with silica gel using petroleum ether and methylene chloride (1/2, V/V) as eluent to yield 3.0 g of a white powder (yield 64.0 %). ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.91 (t, J = 6.6 Hz, 3H), 1.37 (m, 8H), 1.50 (m, 2H), 1.90 (m, 2H), 4.12 (t, J = 8.0 Hz, 2H), 7.27 (ss, 2H), 7.68 (dd, $J1$ = 2.3 Hz, $J2$ = 2.3 Hz, 2H), 8.01 (d, J = 2.3 Hz, 2H). EI-MS

(M): m/z 469.

3-(5-formyl-2-thiophene)-7-bromo-10-octyl-phenothiazine (2)

Compound 1 (1.18 g, 2.5 mmol), 2.0 M K_2CO_3 aqueous solution (12.5 mL), little $Pd(PPh_3)_4$ in 20 mL of THF were heated to 50 °C and stirred under argon atmosphere for 0.5 h. 20 mL of THF containing 5-formylthienyl-2-boronic acid (0.47 g, 3.0 mmol) was added to the mixture, then heated to about 80 °C at reflux for 24 h. When the reaction was completed, water was added to quench the reaction. The product was extracted with dichloromethane. The organic layer was collected, dried over anhydrous $MgSO_4$. The precipitate was purified by column chromatography on silica (CH_2Cl_2) to yield 0.62 g as orange solid (yield 50.0 %). ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.91 (t, J = 6.5 Hz, 3H), 1.37 (m, 8H), 1.50 (m, 2H), 1.94 (m, 2H), 4.20 (m, 2H), 7.31 (d, J = 9.1 Hz, 1H), 7.45 (m, 2H), 7.73 (dd, $J1$ = 2.2 Hz, $J2$ = 2.2 Hz, 1H), 7.77 (d, J = 3.9 Hz, 1H), 7.90 (dd, $J1$ = 2.1 Hz, $J2$ = 2.1 Hz, 1H), 8.07 (d, J = 2.2 Hz, 1H), 8.22 (d, J = 2.1 Hz, 1H), 9.89 (s, 1H).

4-(bis(4-methoxyphenyl)amino)phenylboronic acid (3)

A modified version of a previously reported method was used. 4-(N,N-bis(4-methoxyphenyl)amino)-1-bromobenzene(384 mg, 1 mmol) was dissolved in dry THF (8 mL), and the reaction was cooled to -78 °C, followed by the addition of *n*-butyl lithium (1.6 M in hexane, 1 mL, 1.6 mmol) by a syringe. After stirring for 1.5 h at -78 °C, trimethyl borate (1.0 mL, 8.7 mmol) was added by a syringe, and the reaction was stirred for 0.5 h at -78 °C, warmed to ambient temperature, and stirred for an additional 1.5 h. Water was first added to the reaction mixture and then HCl (6 M) was added in a dropwise fashion until an acidic mixture was obtained. The reaction mixture was poured into water and extracted with dichloromethane. The organic layers were combined, and the solution was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. Washing the white solid with EtOAc/hexane (10 mL/10 mL) and drying under vacuum afforded the desired 4-(bis(4-methoxyphenyl)amino) phenyl- boronic acid (195 mg, 55.9 %).^{1}H NMR (DMSO-d_6, 500 MHz), δ: 3.79 (s, 6H), 6.77 (d, 2H), 7.02-7.08 (m, 6H), 7.12

(t, 4H), 7.58 (d, 2H).

4-(N,N-diphenylamino)phenylboronic acid (4)

The synthetic procedure for compound 4 was followed using 4-(N,N-diphenyl-amino)-1-bromobenzene (324 mg, 1 mmol), 1.6 M *n*-butyl lithium (1 mL, 1.6 mmol) and trimethyl borate (1.0 mL, 8.7 mmol). The pure product was separated by a silica gel column chromatography using CH_2Cl_2: EtOAc as a gradient eluent affording 200 mg (69.2 %). ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 6.88 (d, J = 8.1 Hz, 2H), 7.04 (m, 6H), 7.30 (t, J = 8.1 Hz, 4H), 7.68 (d, J = 8.1 Hz, 2H).

4-(2,2-diphenylvinyl)phenylboronic acid (5)

The synthetic procedure for compound 5 was followed using 1,1-diphenyl-2-(4-bromophenyl)ethane (335 mg, 1 mmol), 1.6 M *n*-butyl lithium (1 mL, 1.6 mmol) and trimethyl borate (1.0 mL, 8.7 mmol). The pure product was separated by a silica gel column chromatography using ether/ethyl acetate (10/1, V/V) as a gradient eluent affording 144 mg (48.0 %) of a white solid. ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 6.98 (m, 3H), 7.13 (br, 2H), 7.28 (m, 8H), 7.47 (d, J = 7.6 Hz, 2H).

5-(3-(4-(bis(4-methoxyphenyl)amino)phenyl)-10-octyl-10*H*-phenothiazin-7-yl)thiophene-2-carbaldehyde (6)

Compound 2 (200 mg, 0.40 mmol), 2.0 M K_2CO_3 aqueous solution (2 mL) and a catalytic amount $Pd(PPh_3)_4$ (5 mole %) in 3 mL of THF were heated to reflux for 0.5 h and then injected 5 mL THF containing compound 3 (195 mg, 0.56 mmol) , and the mixture was reacted at reflux for 15 h. When the reaction was completed, water was added to quench the reaction. The product was extracted with dichloromethane. The organic layer was collected, dried over anhydrous $MgSO_4$ and removed by rotary evaporation. The precipitate was purified by column chromatography on silica (CH_2Cl_2/Ethyl acetate = 10/1, V/V) to yield 6 as orange solid (yield 48.0 %). ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.87 (m, 3H), 1.31 (m, 8H), 1.46 (m, 2H), 1.99 (m, 2H), 3.81 (s, 6H), 4.26 (m, 2H), 6.87 (ss, 4H), 7.00 (ss, 2H), 7.12 (ss, 4H), 7.44 (m, 5H), 7.76 (d, J = 3.9 Hz, 1H), 7.85 (dd, $J1$ = 1.9 Hz, $J2$ = 1.9 Hz, 1H), 7.91 (dd, $J1$ = 2.1 Hz, $J2$ = 2.1 Hz, 1H), 8.13 (d, J = 2.0 Hz, 1H), 8.25 (d, J = 2.1 Hz, 1H), 9.89 (s,

1H).

5-(3-(4-(diphenylamino)phenyl)-10-octyl-10*H*-phenothiazin-7-yl)thiophene-2-carbaldehyde (7)

The synthetic procedure for compound 7 was followed using 2 (175 mg, 0.35 mmol), 2.0 M K_2CO_3 aqueous solution (2 mL) and a catalytic amount $Pd(PPh_3)_4$ (5 mole %) in 3 mL of THF were heated to reflux for 0.5 h and then injected 5 mL THF containing compound 4 (180 mg, 0.62 mmol). The pure product was separated by a silica gel column chromato- graphy using CH_2Cl_2/Ethyl acetate (10/1, V/V) to yield 7 as orange solid (yield 25.0 %). ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.91 (t, J = 6.9 Hz, 3H), 1.37 (m, 8H), 1.50 (m, 2H), 1.94 (m, 2H), 4.25 (m, 2H), 7.06 (t, J = 7.4 Hz, 2H), 7.16 (m, 6H), 7.29 (m, 4H), 7.47 (m, 5H), 7.75 (d, J = 3.9 Hz, 1H), 7.88 (m, 2H), 8.14 (d, J = 2.1 Hz, 1H), 8.25 (d, J = 2.2 Hz, 1H), 9.87 (s, 1H).

5-(10-octyl-3-(4-(2,2-diphenylvinyl)phenyl)-10*H*-phenothiazin -7-yl)thiopenene-2-carbaldehyde (8)

The synthetic procedure for compound 8 was followed using 2 (175 mg, 0.35 mmol), 2.0 M K_2CO_3 aqueous solution (2 mL) and a catalytic amount $Pd(PPh_3)_4$ (5 mole %) in 3 mL of THF were heated to reflux for 0.5 h and then injected 5 mL THF containing compound 5 (144 mg, 0.48 mmol). The pure product was separated by a silica gel column chromatography using CH_2Cl_2/Ethyl acetate (10/1, V/V) as a gradient eluent affording 90 mg (38.1 %) of as orange solid. ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.90 (m, 3H), 1.33 (m, 8H), 1.56 (m, 2H), 1.99 (m, 2H), 4.26 (m, 2H), 7.02 (s, 1H), 7.13 (ss, 2H), 7.26 (s, 2H), 7.35 (m, 8H), 7.46 (m, 5H), 7.76 (d, J = 3.9 Hz, 1H), 7.86 (dd, J1 = 2.0 Hz, J2 = 2.0 Hz, 1H), 7.92 (dd, J1 = 2.1 Hz, J2 = 2.1 Hz, 1H), 8.13 (d, J = 2.0 Hz, 1H), 8.24 (d, J = 2.1 Hz, 1H), 9.89 (s, 1H).

The Mott-Schottky plots of P1~ P3 sensitized TiO_2 electrodes

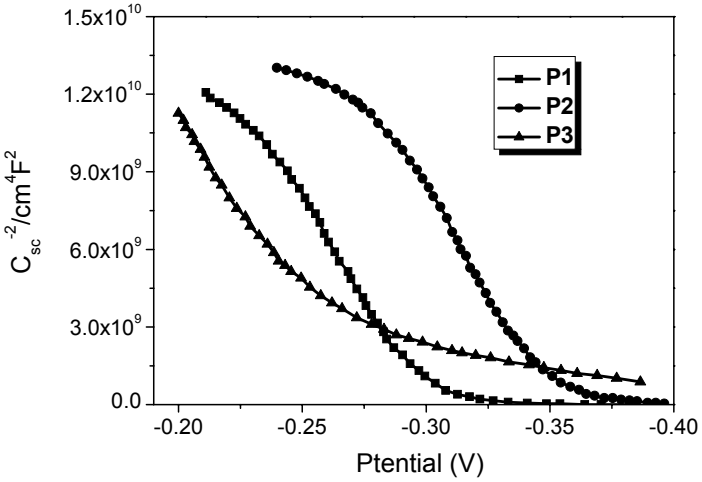

Figure S1. The Mott-Schottky plots of P1(■), P2(●) and P3 (▲) sensitized TiO_2 electrodes, Frequency: 10 Hz, AC disturbance signal: 10 mV.