Supplementary Material for Chemical Communications

Novel Organic Dyes for Efficient Dye-Sensitized Solar Cells

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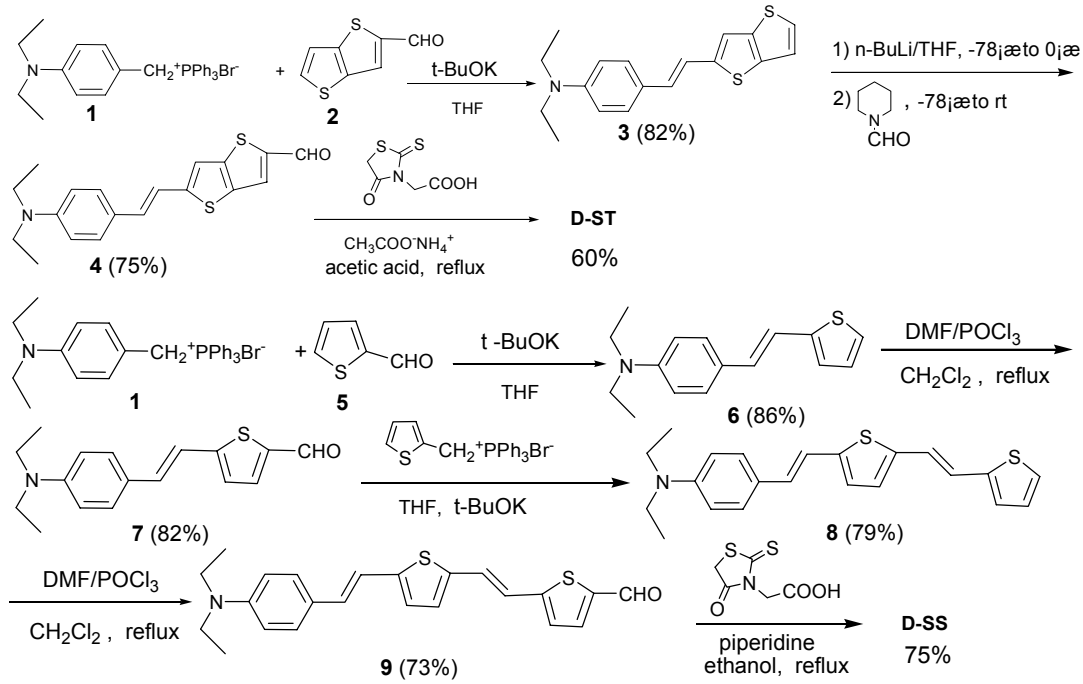
Supplementary data

Synthesis of Dyes

Scheme:



Procedures:

***N*,*N*-diethyl-4-((*E*)-2-(thieno[3,2-b]thien-2-yl)vinyl)aniline (3).** To a suspension of phosphonium salt **1** (0.9 g, 1.8 mmol) in THF (20 mL, dried) at room temperature under a N_2 atmosphere was added *t*-BuOK (0.23 g, 2.0 mmol), and the mixture turned red. After cooling to 0 ^{0}C, a solution of thieno[3,2-b]thiophene-2-carbaldehyde **2** (0.2 g, 1.2 mmol) was added dropwise. The mixture was stirred at 0 ^{0}C for 1 h and at room temperature for another 5 h. After being diluted with CH_2Cl_2, the mixture was washed twice with water, and dried over anhydrous Na_2SO_4. The solvent was evaporated by rota-vaporator, and the residue was purified by column chromatography on silica-gel with CH_2Cl_2/hexane (1:1, v/v) as eluent to give an yellow-orange crystal of the product **3** (0.31g, 82%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.18 (t, J = 6.96 Hz, 6H), 3.33 (q, J = 6.96 Hz, 4H), 6.66 (d, 2H, J = 8.35 Hz, 2H), 6.85 (d, J = 15.92 Hz, 1H), 7.01 (d, 1H, J = 15.97 Hz, 1H), 7.08 (s, 1H), 7.20 (d, J = 5.21 Hz, 1H), 7.28 (d, J = 5.21 Hz, 2H), 7.34 (d, J = 8.27 Hz, 1H); MALDI–TOF m/z: 313.2 (M^+).

The starting materials phosphonium salt **1**[1] and thieno[3,2-b]thiophene-2-carbaldehyde **2**[2] were prepared according to literature procedures.

5-(4-(diethylamino)styryl)thieno[3,2-b]thiophene-2-carbaldehyde (4). A solution of N,N-diethyl-4-((E)-2-(thieno[3,2-b]thien-2-yl)vinyl)aniline **3** (0.30 g, 1 mmol) in THF (30 mL, dried) was cooled to −78 ^{0}C, and *n*-BuLi (0.9 mL, 2.7 M in hexane) was added via syringe with stirring. The reaction mixture was allowed to naturally rise to 0 ^{0}C and then again cooled down to −78 ^{0}C. Piperidine-1-carbaldehyde (0.12 g, 1.1 mmol) was added dropwise via syringe, and the reaction mixture was stirred at −78 ^{0}C for 0.5 h and allowed to warm to room temperature. The reaction was quenched with water (30 mL) and the mixture was neutralized with diluted hydrochloric acid (5%, w/w). The precipitate was filtered off and washed with water thoroughly. After drying in air, the solid was purified by column chromatography on silica-gel with CH_2Cl_2/hexane (2:1, v/v) as eluent to give a red powder of the product **4** (0.2 g, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.23 (t, *J* = 7.29 Hz, 6H), 3.42 (q, *J* = 6.55 Hz, 4H), 6.68 (d, *J* = 6.60 Hz, 2H), 6.98 (d, *J* = 15.78 Hz. 1H), 7.03 (d, *J* = 16.69 Hz, 1H), 7.14 (s, 1H), 7.37 (d, *J* = 5.95 Hz, 2H), 7.86 (s, 1H), 9.93 (s, 1H); MALDI–TOF m/z: 341.2 (M^+).

2-((5*E*)-5-((2-(4-(diethylamino)styryl)thieno[3,2-b]thien-5-yl)methylene)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid (D-ST). To acetic acid (30 mL) was added with stirring 5-(4-(diethylamino)styryl)thieno[3,2-b]thiophene-2-carbaldehyde **4** (0.20 g, 0.6 mmol), rhodanine-3-acetic acid (0.11 g, 0.6 mmol) and ammonium acetate (50 mg, 0.6 mmol). Then the mixture was heated to 120 ^{0}C. The reaction proceeded to completion after 30 min. Then the reaction mixture was allowed to cool down to room temperature. The solid was collected by filtration and washed with water thoroughly. After drying in air, the crude product was purified by column chromatography on silica-gel with $CHCl_3$/methnol (8:1, v/v) as eluent to give a black solid. The solid was recrystallized from methanol to give D-ST (0.19 g, 60%). Mp: > 250 ^{0}C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.10 (t, *J* = 6.98 Hz, 6H), 3.38 (q, *J* = 7.02 Hz, 4H), 4.49 (s, 2H), 6.67 (d, *J* = 8.02 Hz, 2H), 6.99 (d, *J* = 16.11 Hz, 1H), 7.26 (d, *J* = 15.98 Hz, 1H), 7.44 (d, *J* = 8.13 Hz, 2H), 7.52 (s, 1H), 8.08 (s, 1H), 8.20 (s, 1H); MALDI–TOF m/z: 514.4 (M^+). HRMS-SIMS (m/z): [M^-] calcd for $C_{24}H_{22}N_2O_3S_4$, 514.0513, found, 514.0525 (100%); [M-COOH]$^-$ calcd for $C_{23}H_{21}N_2O_1S_4$, 469.0537, found, 469.0549 (78%).

***N*,*N*-diethyl-4-((*E*)-2-(thiophen-2-yl)vinyl)aniline (6).** The product was synthesized according to the procedure as described above for synthesis of **3**, giving a yellow crystal of the product **6** in 86% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21 (t, *J* = 7.02 Hz, 6H), 3.41 (q, *J* = 7.08 Hz, 4H), 6.66 (d, *J* = 8.54 Hz, 2H), 6.92 (d, *J* = 16.02 Hz, 1H), 6.98 (d, *J* = 2.45 Hz, 1H), 7.03 (d, *J* = 16.05 Hz, 1H), 7.11 (dd, J_1 = 3.63 Hz, J_2 = 2.85 Hz, 1H), 7.35 (d, *J* = 8.51 Hz, 2H); TOF MS EI$^+$ m/z: 257 (M^+).

5-(4-(diethylamino)styryl)thiophene-2-carbaldehyde (7). A mixture of DMF (10 mL, dried) and CH_2Cl_2 (50 mL, dried) was cooled to 0 ^{0}C under a N_2 atmosphere and then $POCl_3$ (3 mL) was added dropwise, with stirring for 10 min. To the mixture was added a solution of *N*,*N*-diethyl-4-((*E*)-2-(thien-2-yl)vinyl)aniline **6** (4.0 g, 15.56 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was allowed to warm to room temperature, and then heated to reflux until the reaction was completed (monitored by TLC). After cooling to room temperature, 50 mL of iced water was poured into the reaction mixture, followed by neutralizing with aqueous NaOH (10%, w/w). The mixture was extracted with CH_2Cl_2, and the organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was removed by rotary-evaporator, and the residue was purified by column chromatography on silica-gel with CH_2Cl_2/hexane (2:1, v/v) as eluent to give an orange powder of the product **7** (3.64 g, 82%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21 (t, *J*

= 7.04 Hz, 6H), 3.41 (q, *J* = 7.03 Hz, 4H), 6.66 (d, *J* = 8.69 Hz, 2H), 6.98 (d, *J* = 15.93 Hz, 1H), 7.05 (d, *J* = 3.85 Hz, 1H), 7.10 (d, *J* = 15.99 Hz, 1H), 7.38 (d, *J* = 8.73 Hz, 2H), 7.64 (d, *J* = 3.90 Hz, 1H), 9.82 (s, 1H); TOF MS EI^+ m/z: 284 (M^+-H).

***N*,*N*-diethyl-4-((1*E*)-2-(5-((*E*)-2-(thien-2-yl)vinyl)thien-2-yl)vinyl)aniline (8).** According to the procedure as described above for the synthesis of **3**, the product **8** was obtained in 79% yield as a waxy solid which can directly be used in the next reaction.

The starting material (2-thienylmethyl)triphenylphosphonium bromide was synthesized according to the method described in reference 1.

5-((1*E*)-2-(5-(4-(diethylamino)styryl)thien-2-yl)vinyl)thiophene-2-carbaldehyde (9). According to the procedure as described above for the synthesis of **7**, the product **9** was obtained in 73% yield as a red-purple powder. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21 (t, *J* = 7.04 Hz, 6H), 3.40 (q, *J* = 7.05 Hz, 4H), 6.66 (d, *J* = 8.78 Hz, 2H), 6.88 (d, *J* = 15.89 Hz, 1H), 6.89 (d, *J* = 3.75 Hz, 1H), 6.93 (d, *J* = 15.68 Hz, 1H), 6.98 (d, *J* = 15.94 Hz, 1H), 7.01 (d, *J* = 3.71 Hz, 1H), 7.10 (d, *J* = 3.92 Hz, 1H), 7.22 (d, *J* = 15.71 Hz, 1H), 7.35 (d, *J* = 8.76 Hz, 2H), 7.65 (d, *J* = 3.90Hz, 1H), 9.85 (s, 1H); TOF MS EI^+ m/z: 392(M^+-H).

2-((5*E*)-5-((5-((1*E*)-2-(5-(4-(diethylamino)styryl)thien-2-yl)vinyl)thien-2-yl)methylene)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid (D-SS). To 40 mL of ethanol was added 5-((1E)-2-(5-(4-(diethylamino)styryl)thiophen-2-yl)vinyl)thiophene-2-carbaldehyde 12 (0.5 g, 1.3 mmol), rhodanine-3-acetic acid (0.25 g, 1.3 mmol) and piperidine (0.11 g, 1.3 mmol). The reaction mixture was refluxed with stirring until the reaction was completed (monitored by TLC). The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica-gel with $CHCl_3$/methonal (8:1, v/v) as eluent to give a black solid. The solid was recrystallized from methanol to give D-SS (0.55 g, 75%). Mp: > 250 ^{0}C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.10 (t, *J* = 6.98 Hz, 6H), 3.34 (q, *J* = 6.96 Hz, 4H), 4.46 (s, 2H), 6.64 (d, *J* = 8.76 Hz, 2H), 6.82 (d, *J* = 15.77 Hz, 1H), 7.03 (d, *J* = 3.49 Hz, 1H), 7.11 (d, *J* = 16.15 Hz, 1H), 7.13 (d, *J* = 15.82 Hz, 1H), 7.22 (d, *J* = 3.77 Hz, 1H), 7.36–7.39 (m, 3H), 7.43 (d, *J* = 15.89 Hz, 1H), 7.71 (d, *J* = 3.86 Hz, 1H), 8.04 (s, 1H); MALDI–TOF m/z: 566.1(M^+). HRMS-SIMS (m/z): [M^-] calcd for $C_{28}H_{26}N_2O_3S_4$, 566.0826, found, 566.0837 (100%); [M-COOH]$^-$ calcd for $C_{27}H_{25}N_2O_1S_4$, 521.0850, found, 521.0851 (100%).

References

1. Shang–Shing P. Chou and Yu–Hsin Yeh, *Tetrahedron Letters* **2001**, 42, 1309.
2. Lance S. Fuller, Brian Iddon and Kevin A. Smith, *J. Chem. Soc. Perkin Trans.1*. **1997**, 3465.

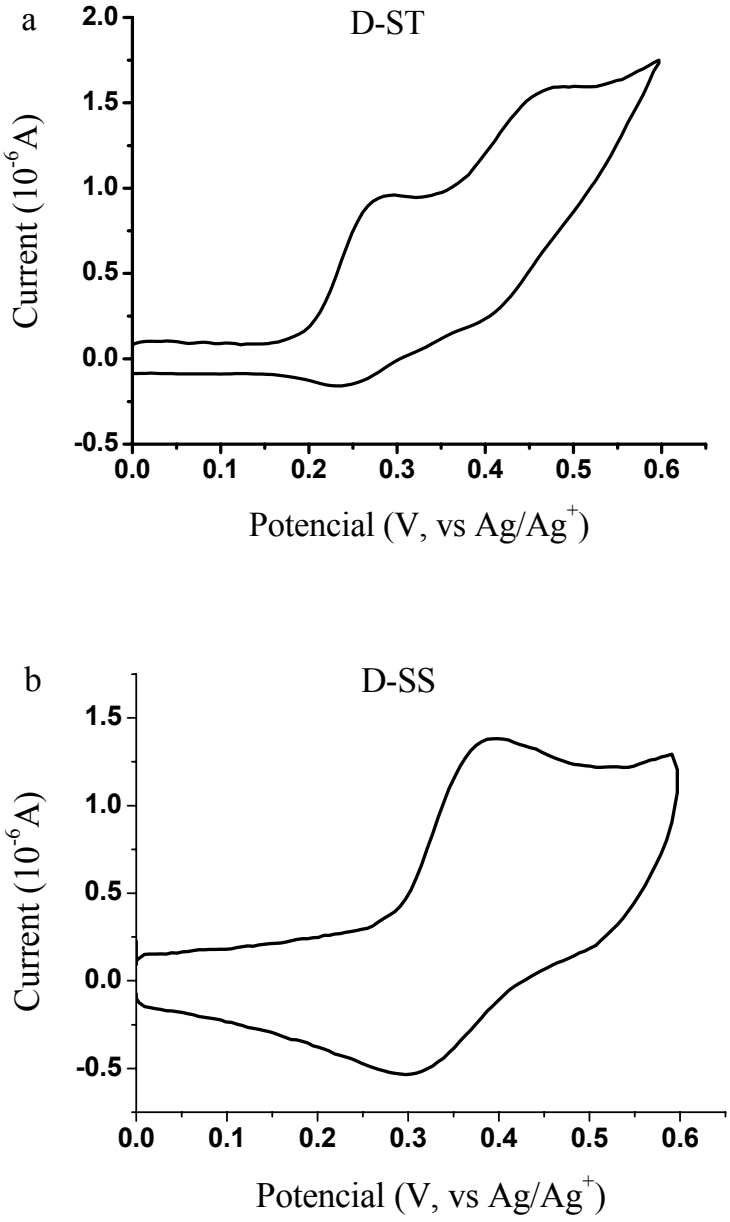


Fig 1. Cyclic voltammograms of (a) D-ST and (b) D-SS. Redox potential were measured in 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. Scanning rate: 20 mVs^{-1}.