

Electronic Supplementary Information for

The structure-property relationship of organic dyes in mesoscopic titania solar cells: only one double-bond difference†

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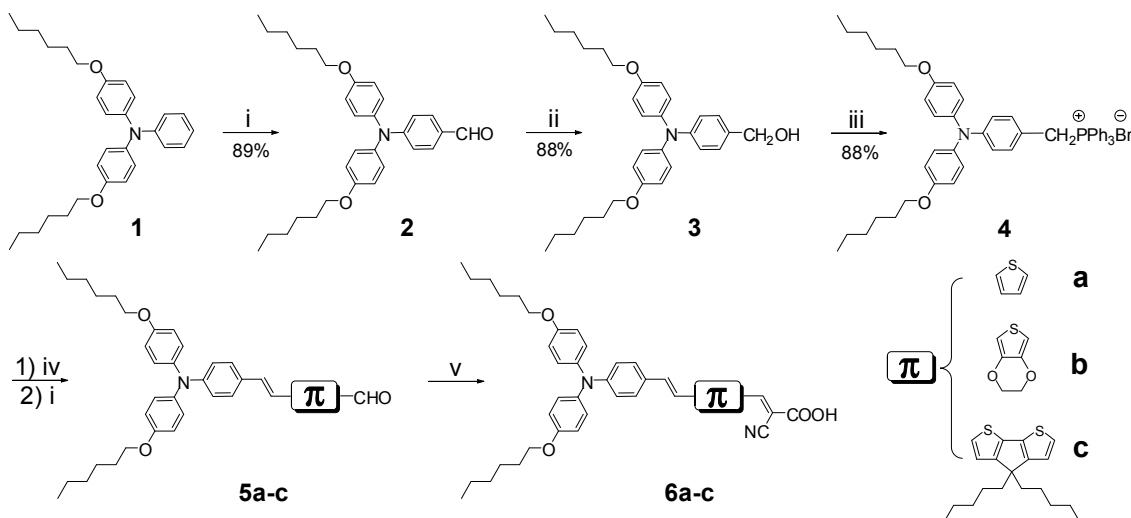
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1. Synthesis of intermediates

1.1. SCHEME S1: Synthetic Route of Dyes C236–C238 ^a



^a Reagents and conditions: (i) POCl₃, DMF, 1,2-dichloroethane, reflux, 10 h; (ii) NaBH₄, NaOH(0.1 M, aq.), ethanol, r.t., 4 h; (iii) PPh₃HBr, CHCl₃, reflux, 4 h; (iv) thiophene-2-carbaldehyde, 3,4-ethylenedioxy-2-formylthiophene or 4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde, *t*-BuOH, AN/THF(1/1, v/v), -60 °C, 1 h, r.t., 12 h; (v) cyanoacetic acid, piperidine, CHCl₃, reflux, 18 h.

1.2. Materials

Phosphorus chloride oxide (POCl₃), *N,N*-dimethylformide (DMF), acetonitrile and tetrahydrofuran (THF) were distilled before use. Triphenylphosphonium bromide (PPh₃HBr), thiophene-2-carbaldehyde were purchased from Sigma-Aldrich. *N,N*-Bis(4-hexyloxyphenyl)aniline (**1**),^{S1} 3,4-ethylenedioxy-2-formylthiophene^{S2} and 4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde^{S1} were synthesized according to the corresponding literature methods.

Synthesis of 4-formyl-*N,N*-bis(4-hexyloxyphenyl)aniline (2). To a cold solution of **1** (10.64 g, 23.88 mmol) and DMF (3.69 mL, 47.76 mmol) in 1,2-dichloroethane at 0 °C was added POCl₃ (4.45 mL, 47.76 mmol) under argon. The reaction solution was reflux for 10 h and then saturated sodium acetate aqueous solution (100 mL) added. The mixture was further stirred at room temperature for 1 h. The crude product was extracted into chloroform, and the organic layer was washed with brine and water, dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography (ethyl acetate/petroleum ether 60–90 °C, 1/10, v/v) on silica gel to yield a viscous yellow green oil (10.09 g, 89% yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ: 9.70 (s, 1H), 7.63 (d, *J*=8.4 Hz, 2H), 7.17 (d, *J*=8.8 Hz, 4H), 6.96 (d, *J*=8.8 Hz, 4H), 6.67 (d, *J*=8.4 Hz, 2H), 3.96 (t, *J*=6.4 Hz, 4H), 1.71 (m, 4H), 1.41 (m, 4H), 1.30 (m, 8H), 0.88 (t, *J*=6.8 Hz, 6H). MS (ESI) *m/z* calcd. for (C₃₁H₃₉NO₃): 473.3. Found: 474.2 ([M+H]⁺). Anal. Calcd. for C₃₁H₃₉NO₃: C, 78.61; H, 8.30; N, 2.96. Found: C, 78.50; H, 8.39; N, 2.83.

Synthesis of 4-hydroxymethyl-*N,N*-bis(4-hexyloxyphenyl)aniline (3). To a solution of compound **2** (9.53 g, 20.12 mmol) in ethanol (70 mL) was added dropwise NaBH₄ (0.40 g, 10.40 mmol) in NaOH aqueous (0.10 M, 20 mL), then

the resulting mixture was stirred for 4 h at room temperature. After dilution with water, the mixture was extracted into chloroform, and the organic layer was dried over anhydrous sodium sulfate. After Removing solvent under reduced pressure, the residue was purified by column chromatography (ethyl acetate/petroleum ether 60–90 °C, 1/3, *v/v*) on silica gel to yield a colorless oil (8.46 g, 88% yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ: 7.12 (d, *J*=8.8 Hz, 2H), 6.91 (d, *J*=8.8 Hz, 4H), 6.85 (d, *J*=8.8 Hz, 4H), 6.76 (d, *J*=8.8 Hz, 2H), 4.98 (br, 1H), 4.38 (d, *J*=5.2 Hz, 2H), 3.91 (t, *J*=6.6 Hz, 4H), 1.68 (m, 4H), 1.40 (m, 4H), 1.31 (m, 8H), 0.88 (t, *J*=6.8 Hz, 6H). MS (ESI) *m/z* calcd. for (C₃₁H₄₁NO₃): 475.3. Found: 476.4 ([M+H]⁺). Anal. Calcd. for C₃₁H₄₁NO₃: C, 78.28; H, 8.69; N, 2.94. Found: C, 78.20; H, 8.78; N, 2.89.

Synthesis of (4-(*N,N*-bis(4-hexyloxyphenyl)amino)benzyl)triphenyl-phosphonium bromide (4). The mixture of **3** (12.9 g, 27.20 mmol) and PPh₃HBr (9.32 g, 27.20 mmol) in 100 mL of dry chloroform was refluxed for 4 h under argon. Subsequently, the reaction mixture was concentrated under reduce pressure. The residue was wash with ether and filtered to give a white powder (19.2 g, 88% yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ: 7.90 (t, *J*=7.2 Hz, 3H), 7.74 (m, 6H), 7.67 (d, *J*=7.2 Hz, 3H), 7.64 (d, *J*=7.2 Hz, 3H), 6.94 (d, *J*=8.8 Hz, 4H), 6.87 (d, *J*=8.8 Hz, 4H), 6.71 (d, *J*=8.4 Hz, 2H), 6.53 (d, *J*=8.4 Hz, 2H), 5.02 (d, *J*=14.8 Hz, 2H), 3.92 (t, *J*=6.4 Hz, 4H), 1.69 (m, 4H), 1.41 (m, 4H), 1.31(m, 8H), 0.88 (t, *J*=6.8 Hz, 6H). MS (ESI) *m/z* calcd. for (C₄₉H₅₅BrNO₂P): 799.3. Found: 780.4 ([M+H]⁺). Anal. Calcd. for C₄₉H₅₅BrNO₂P: C, 73.49; H, 6.92; N, 1.75. Found: C, 73.61; H, 6.87; N, 1.69.

General Synthesis of 5. To a cold solution of **4** (1.30 mmol) in 10 mL of dry THF/acetonitrile (1/1, *v/v*) at 0 °C was added *t*-BuOK (1.30 mmol) under argon. The reaction solution was stirred at the same temperature for 20 min. Then the mixture was cooled to –60 °C, and a solution of thiophene-2-carbaldehyde or 3,4-ethylenedioxy-2-formylthiophene or 4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*] dithiophene-2-carbaldehyde (1.08 mmol) in dry THF (5 mL) was added. The mixture was slowly warmed to room temperature and stirred for another 3 h. The reaction was quenched with water, extracted into dichloromethane, and the organic layer was washed with brine and water, dried over anhydrous sodium sulfate, after evaporating the solvent in vacuum, the residue was roughly separated by column chromatography (ethyl acetate/petroleum ether 60–90 °C, 1/50, *v/v*) on a silica gel column and used directly in the next step without further purification. To a cold solution of *N,N*-dimethylformide (0.11 g, 1.49 mmol) and the crude product obtained above (0.75 mmol) in 1,2-dichloroethane (30 mL) at 0 °C was added POCl₃ (0.23 g, 1.49 mmol) under argon. The reaction solution was refluxed for 10 h. After cooling down to room temperature, saturated sodium acetate aqueous solution (50 mL) added. The mixture was further stirred at room temperature for 1 h. The crude product was extracted into dichloromethane, the organic layer was washed with brine and water, dried over anhydrous sodium sulfate. After evaporating the solvent in vacuum, the residue was purified by column chromatography on a silica gel column.

5-(4-(*N,N*-Bis(4-hexyloxyphenyl)amino)styryl)-thiophene-2-carbaldehyde (5a). Ethyl acetate/petroleum ether 60–90 °C (1/50, *v/v*) was used as eluent to obtain a viscous yellow oil (88% yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ: 7.38 (d, *J*=5.2 Hz, 1H), 7.35 (d, *J*=8.8 Hz, 2H), 7.19 (d, *J*=16 Hz, 1H), 7.12 (d, *J*=3.6 Hz, 1H), 7.03 (m, 1H), 6.99 (d, *J*=8.8 Hz, 4H), 6.89 (d, *J*=9.2 Hz, 4H), 6.70 (d, *J*=8.8 Hz, 2H), 3.93 (t, *J*=6.4 Hz, 4H), 1.68 (m, 4H), 1.41 (m, 4H), 1.31 (m, 8H), 0.88 (t, *J*=6.8 Hz, 6H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 155.29, 147.92, 142.83, 139.62, 128.27, 127.81, 127.52, 127.13, 126.72, 125.60, 124.26, 118.98, 117.75, 115.40, 67.58, 30.97, 28.68, 25.18, 22.04, 13.86. ESI-MS *m/z*

calcd. for (C₃₇H₄₃NO₃S): 581.3. Found: 582.3 ([M+H]⁺). Anal. Calcd. for C₃₇H₄₃NO₃S: C, 76.38; H, 7.45; N, 2.41. Found: C, 76.29; H, 7.57; N, 2.28.

5-(4-(*N,N*-Bis(4-hexyloxyphenyl)amino)styryl)-(3,4-ethylenedioxythiophene)-2-carbaldehyde (5b). Ethyl acetate/petroleum ether 60–90 °C (1/2, *v/v*) was used as eluent to obtain a viscous orange oil (81% yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ: 9.80 (s, 1H), 7.41 (d, *J*=8.8 Hz, 2H), 7.09 (d, *J*=16 Hz, 1H), 7.04 (d, *J*=8.8 Hz, 4H), 7.02 (d, *J*=16 Hz, 1H), 6.92 (d, *J*=8.8 Hz, 4H), 6.68 (d, *J*=8.8 Hz, 2H), 4.45 (m, 2H), 4.40 (m, 2H), 3.94 (t, *J*=6.4 Hz, 4H), 1.70 (m, 4H), 1.40 (m, 4H), 1.31 (m, 8H), 0.88 (t, *J*=6.8 Hz, 6H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 178.52, 155.62, 149.28, 148.88, 139.19, 138.22, 131.30, 127.93, 127.49, 127.18, 127.01, 118.12, 115.46, 113.84, 113.63, 67.59, 65.51, 64.54, 30.95, 28.65, 25.15, 22.02, 13.84. ESI-MS *m/z* calcd. for (C₃₉H₄₅NO₅S): 639.3. Found: 640.3 ([M+H]⁺). Anal. Calcd. for C₃₉H₄₅NO₅S: C, 73.21; H, 7.09; N, 2.19. Found: C, 73.31; H, 7.16; N, 2.11.

6-(4-(*N,N*-Bis(4-hexyloxyphenyl)amino)styryl)-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (5c). Ethyl acetate/petroleum ether 60–90 °C (1/5, *v/v*) was used as eluent to obtain a viscous carmine oil (76% yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ: 9.81 (s, 1H), 7.96 (s, 1H), 7.38 (d, *J*=8.8 Hz, 2H), 7.24 (d, *J*=16 Hz, 1H), 7.23 (s, 1H), 7.03 (d, *J*=8.8 Hz, 4H), 6.94 (d, *J*=16 Hz, 1H), 6.91 (d, *J*=8.8 Hz, 4H), 6.72 (d, *J*=8.8 Hz, 2H), 3.94 (t, *J*=6.4 Hz, 4H), 1.82 (m, 4H), 1.71 (m, 4H), 1.42 (m, 4H), 1.32 (m, 8H), 1.12 (m, 12H), 0.88 (m, 10H), 0.77 (t, *J*=6.8 Hz, 6H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 182.62, 162.76, 157.47, 155.30, 148.40, 148.13, 146.42, 142.61, 139.42, 132.71, 130.92, 127.98, 127.83, 127.11, 126.64, 119.77, 119.19, 118.80, 115.17, 67.52, 53.33, 36.75, 30.91, 28.89, 28.64, 25.12, 23.91, 21.98, 21.92, 13.73, 13.67. ESI-MS *m/z* calcd. for (C₅₄H₆₉NO₃S₂): 843.5. Found: 844.6 ([M+H]⁺). Anal. Calcd. for C₅₄H₆₉NO₃S₂: C, 76.82; H, 8.24; N, 1.66. Found: C, 76.72; H, 8.32; N, 1.53.

1.3. References

- S1. R. Li, J. Liu, N. Cai, M. Zhang and P. Wang, *J. Phys. Chem. B*, 2010, **114**, 4461.
- S2. J.-M. Raimundo, P. Blanchard, N. Gallego-Planas, N. Mercier, I. Ledoux-Rak, R. Hierle and J. Roncali, *J. Org. Chem.*, 2002, **67**, 205.

2. Additional experimental data

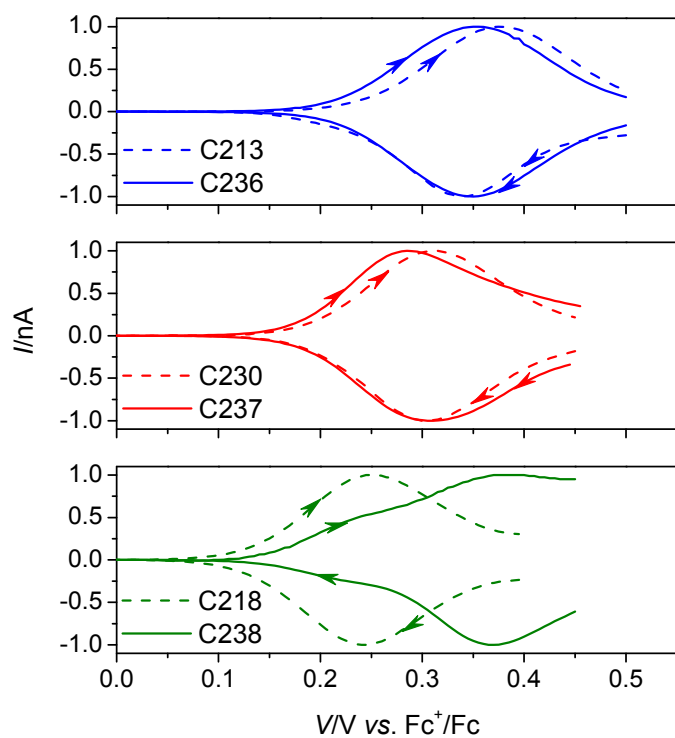


Fig. S1 Square-wave voltammograms of dye-coated titania films. The arrows indicate scan directions. Supporting electrolyte: 0.3 M 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide.