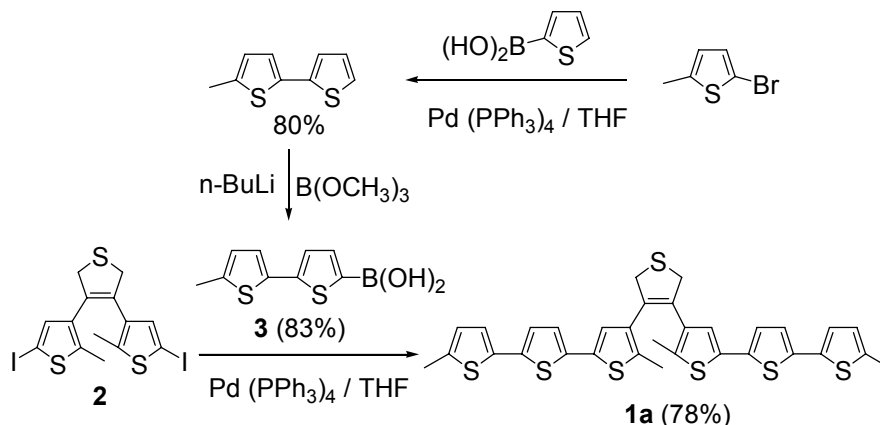


Electronic Supplementary Information



Scheme 1S Synthetic route of diarylethene **1a**

Diarylethene **1a** was synthesized according to the synthetic route presented in Scheme 1, and the detailed procedure is as follows:

1) **5-methyl-2,2'-bithiophene**: To a solution of 2-methyl-5-bromothiophene ¹ (3.54 g, 20 mmol) in THF (100 ml), Pd(PPh₃)₄ (500 mg, 3 mol%) and a solution of K₂CO₃ solution (2.5 M, 30 ml) were added. The resulting solution was stirred for 10 min under nitrogen gas at ambient temperature. To the mixture was added the thiophene-2-boronic acid (2.56 g, 20 mmol) in THF (100 ml). The resulting solution was refluxed under nitrogen and the reaction was monitored by TLC. After the starting material disappeared, the solution was cooled down to ambient temperature and ice water (100 ml) was added to the residue, and the product was extracted with Et₂O (3 × 50 ml). The combined organic phase was washed with H₂O (50 ml) and a saturated solution of NaCl (50 ml), respectively, and dried over MgSO₄. After evaporation of the solvent, the crude product was purified by flash column chromatography with petroleum as eluent to afford 5-methyl-2,2'-bithiophene in 80% yield. ¹H NMR (300 MHz, CDCl₃): 7.21 (d, 1H, J = 5.0), 7.15 (d, 1H, J = 2.7), 7.05 – 7.02 (m, 2H), 6.71 (d, 1H, J = 2.4), 2.53 (s, 3H). [M⁺] calcd. for C₉H₈S₂ : 180.2942. Found: 180.2938.

2) **5-methyl-2,2'-bithiophene-5'-boronic acid (3)**: To a solution of 5-methyl-2,2'-bithiophene (360 mg, 2 mmol) in THF (30 ml), n-BuLi (1.6 M in hexane, 3 ml) was added slowly at –50°C. The resulting solution was stirred for 30 min at –50°C, followed by slow addition of B(OCH₃)₃ (1 ml) in THF (5 ml) at –78°C. The mixture was stirred for 4 h, during this time the temperature was increased slowly to 0°C. After no 5-methyl-2,2'-bithiophene was detected by TLC, the mixture was poured into HCl solution (5 M, 20 ml), the product was extracted with Et₂O (3 × 50 ml). The combined organic phase was a saturated solution of NaCl (30 ml) and dried over MgSO₄. After evaporation of the solvent, the crude product was purified by flash column chromatography with petroleum and ethyl acetate (2:1) as eluent to afford 5-methyl-2,2'-bithiophene-5'-boronic acid **3** in 83% yield. ¹H NMR (300 MHz, CDCl₃): 7.17 (d, 1H, J = 4.9), 7.09 (d, 1H, J = 3.1), 7.05 – 6.96

(m, 2H), 6.66 (d, 1H, $J = 2.6$), 2.52 (s, 3H), 1.55 (s, 2H). HRMS (m/z) [M^+] calcd. for $C_9H_9BO_2S_2$: 224.1111. Found: 224.1118.

3) **3,4-bis[5-(5'-methyl-2,2'-bithiophene)-2-methylthien-3-yl]-2,5-dihydrothiophene (1a)**: To a solution of 3,4-bis(5-iodo-2-methylthien-3-yl)-2,5-dihydrothiophene **2**² (106 mg, 0.2 mmol) in THF (10 ml), $Pd(PPh_3)_4$ (25 mg, 10 mol%) and a solution of K_2CO_3 solution (2.5 M, 1 ml) were added. The resulting solution was stirred for 10 min under nitrogen gas at ambient temperature. To the mixture was added the 5-methyl-2,2'-bithiophene-5'-boronic acid **3** (112 mg, 0.5 mmol) in THF (10 ml). The resulting solution was refluxed under nitrogen and the reaction was monitored by TLC. After the starting material disappeared, the solution was cooled down to ambient temperature and ice water (20 ml) was added to the residue, and the product was extracted with Et_2O (3×20 ml). The combined organic phase was washed with H_2O (20 ml) and a saturated solution of NaCl (20 ml), respectively, and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by flash column chromatography with petroleum and ethyl acetate (10:1) as eluent to afford target compound 3,4-bis[5-(5'-methyl-2,2'-bithiophene)-2-methylthien-3-yl]-2,5-dihydrothiophene **1a** in 78% yield. 1H NMR ($CDCl_3$): 6.95 – 6.93 (m, 6H), 6.87 (s, 2H), 6.66 (s, 2H), 4.17 (s, 4H), 2.49 (s, 6H), 1.99 (s, 6H). ^{13}C NMR ($CDCl_3$): 139.3, 136.5, 135.4, 135.3, 134.8, 134.1, 133.6, 133.1, 126.1, 123.8, 123.6, 123.2, 122.9, 42.9, 15.4, 14.4. HRMS (m/z) [M^+] calcd. for $C_{32}H_{26}S_7$: 635.0194. Found: 635.0197. Anal. Calcd. for $C_{32}H_{26}S_7$: C, 60.53; H, 4.13; S, 35.35. Found: C, 60.58; H, 4.11; S, 35.38.

References

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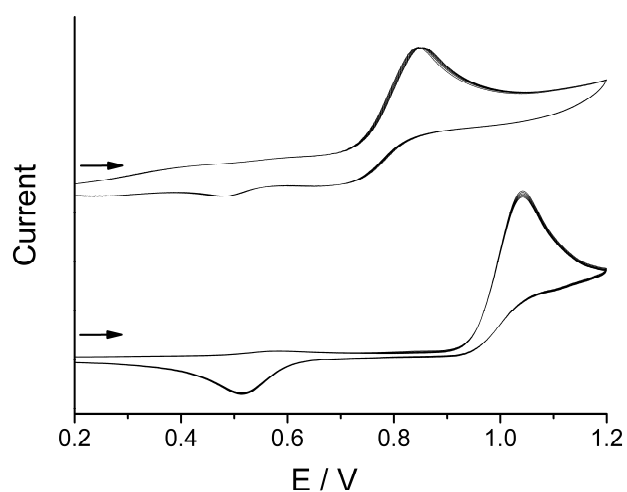


Fig. 1S Cyclic voltammograms of **1a** (bottom) and **1b** (top) in CH₃CN solution (1×10^{-3} M) at 50 mV s⁻¹ after 10 cycles with UV/Vis irradiation.