Supporting Information

All ^{1}H-NMR spectra were obtained from a Varian Germina-300 spectrometer. MS was measured with a Trio-2000 GC-MS spectrometer.

The procedures of preparation and characterization data for **1a – 8a**

5-cholor-2-methylthiophene: A mixture of 2-methylthiophene (9.8g, 100 ml), N-chlorosuccimimide (14.6g, 110 mmol), benzene (60 ml) and acetic acid (60 ml) was refluxed at 80 C for 7h. The ice-water (100 ml) was added to the mixture. The product was extracted with CH_2Cl_2 (50 ml 3). The combined organic phases were dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by distillation (oil, 21.8g, 82% yield). ^{1}H-NMR ($CDCl_3$, ppm) 6.73-6.12 (d, 1H), 6.56-6.55(d, 1H), 2.44(s, 3H).

5-chloro-2-methyl-3-acetylthiophene: The mixture of acetyl chloride (3.2g, 40 mmol), $AlCl_3$ (6.7g, 50 mmol) and CH_2Cl_2 (100 ml) was stirred for half hour at 0 C. 5-cholor-2-methylthiophene (5.4g, 40 mmol) in CH_2Cl_2 (50 ml) was added slowly to the mixture above at 0 C for 4h. The product was stirred for 5h and the reaction temperature was allowed to rise to room temperature. Ice-water (100 ml) was then added to the product, the organic layer was washed with 10% $NaHCO_3$ (50 ml), followed by brine (50 ml), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatograph using 10:1 petroleum/ethyl acetate as eluent. (yellow oil, 6.4g, 78% yield). ^{1}H-NMR($CDCl_3$, ppm) 7.14(s, 1H), 2.64(s, 3H), 2.44(s, 3H).

5-chloro-2-methyl-3-(1'-bromine)-acetyl thiophene: To the solution of 5-chloro-2-methyl-3-acetylthiophene (8.8g, 50 ml) in $CHCl_3$ (100 ml) was added slowly Br_2 (2.5ml, 50 mmol) in $CHCl_3$ (30 ml) for 4h. The mixture was stirred for 8h and poured into water (100 ml). The organic layer was washed by water (30 eml 2), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography using 10:1 petroleum / ethyl acetate as eluent. (colorless solid, 8.1g, 53% yield). ^{1}H-NMR($CDCl_3$, ppm) 7.19(s, 1H), 4.21(s, 2H), 2.68 (s, 3H).

Bis-5-chloro-2-methyl-3-acetylthiophene sulfide: To solution of 5-chloro-2-methyl-3-(1'-bromine)-acetyl thiophene (2.55g, 10 mmol) in EtOH (50 ml) was added Na_2S (0.39g, 5 mmol). The mixture was stirred for 1h at room temperature. After the solvent was evaporated off, the product was washed by water (30 ml 2). The crude product was purified by recrystallization from EtOH. (colorless crystal, 1.98g, 65% yield). ^{1}H-NMR($CDCl_3$, ppm) 7.16 (s, 2H), 3.72(s, 4H), 2.66 (s, 6H).

Diarylethene 1a: To a suspension of Zinc powder (10g, 0.3 mol) in THF (350 ml) under nitrogen flux was added $TiCl_4$ (10 ml) at 0 C by syringe. The mixture was then refluxed for 1h. To the mixture bis-5-chloro-2-methyl-3-acetylthiophene sulfide (5.7g, 15 mmol) in THF (250 ml) was added very slowly at room temperature for 24h. The reaction mixture was stirred for another 24h in darkness, followed by quenching with 40% K_2CO_3 solution (80 ml). The solid was filtered and washed with diethyl ether (50 ml). The combined organic phases were concentrated to 50 ml under reduced pressure. Water (50 ml) was then added to the residue. The product was extracted with diethyl ether (50 ml 3), and dried over Mg_2SO_4. After evaporation of the solvent, the crude product was purified by flash column chromatograph with 6:1 petroleum / ethyl acetate as eluent. (yellow solid, 3.6g, 70% yield). M.p.= 135 – 136 C, ^{1}H-NMR ($CDCl_3$)(ppm): 6.58 (s, 2H, thiophene-H), 4.05 (s, 4H, CH_2-S), 1.91 (s, 6H, CH_3). MS (m/z): 348 (M+2 80), 346 (M$^+$ 100).

Diarylethenes 2a or 3a and 4a: To a cooled (-78 C) solution of diarylethene 1a (0.7g, 2 mmol) in 40 ml of THF was added dropwise 3.2 ml (for 2a) and 6.5 ml (for 3a and 4a) of n-butyllithium (1.6 M in hexane) under nitrogen. The reaction mixture was stirred for 15min, allowing the temperature to rise to –50 C, and then was cooled again to –78 C. After addition of DMF (0.36ml), the reaction mixture was stirred for another 4h, allowing the temperature to rise to 0 C, and then was poured into 50 ml of ice-water. The product was extracted with CH_2Cl_2 (50 ml 2), and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by flash column chromatograph with 6:1 petroleum / ethyl acetate as eluent. (2a: 60% yield, 3a: 53% yield, 4a: 8% yield). **2a** M.p.= 125 – 126 C, ^{1}H-NMR ($CDCl_3$)(ppm): 9.76 (s, 1H, CHO), 7.46 (s, 1H, thiophene-H), 6.59 (s, 1H, thiophene-H), 4.11 (m, 4H, CH_2-S), 2.11 (s, 3H, CH_3), 1.87 (s, 3H, CH_3). MS: (m/z) 342 (M+2 54), 340 (M$^+$ 100). $C_{15}H_{13}ClOS_3$, Found: C. 52.56, H. 3.78, Cl. 10.41, S. 28.29; requires: C. 52.86, H. 3.82, Cl. 10.42, S. 28.19. **3a** M.p.= 200 – 201 C, ^{1}H-NMR ($CDCl_3$)(ppm): 9.75 (s, 2H, CHO), 7.46 (s, 2H, thiophene-H), 4.10 (s, 4H, CH_2-S), 2.10 (s, 6H, CH_3). MS (m/z): 334 (M$^+$ 100). **4a** M.p.= 112-113 C, ^{1}H-NMR ($CDCl_3$)(ppm): 10.04 (s, 1H, CHO), 9.71 (s, 1H, CHO), 7.35 (s, 1H, thiophene-H), 4.10-4.23 (m, 4H, CH_2-S), 2.18 (s, 3H, CH_3), 2.00 (s, 3H, CH_3). MS (m/z): 368 (M$^+$ 100).

Diarylethenes 5a or 6a: To a solution of 2a (100mg, 0.3 mmol) or 3a (100mg, 0.3 mmol) in 15 ml of EtOH was added $NaBH_4$ (15mg, 0.3 mmol for 2a; 30mg, 0.3 mmol for 3a). The mixture was stirred at room temperature for 8h, and then was poured into ice-water (30 ml). The product was extracted with $CHCl_3$ (30 ml 2), and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by flash column chromatograph with 6:1 petroleum / ethyl acetate as eluent. (5a: olorless solid, 91% yield, 6a: colorless solid, 89% yield). **5a** M.p.= 72 – 73 C, ^{1}H-NMR ($CDCl_3$)(ppm): 6.61(s, 1H, thiophene-H), 6.59 (s, 1H, thiophene-H), 4.61(s, 2H, CH_2-OH), 4.23-4.16 (m, 4H, CH_2-S), 2.50 (s, 1H, OH), 2.01 (s, 3H, CH_3), 1.84 (s, 3H, CH_3). MS (m/z): 342 (M$^+$ 100). **6a** M.p.= 100 – 101 C, ^{1}H-NMR ($CDCl_3$)(ppm): 6.60(s, 2H, thiophene-H), 4.60 (s, 4H, CH_2-O), 4.01 (s, 4H, CH_2-S), 2.52 (s, 2H, OH), 1.94 (s, 6H, CH_3). MS (m/z): 338 (M$^+$ 100).

Diarylethenes 7a or 8a: To a solution of 2a (100mg, 0.3 mmol) or 3a (100mg, 0.3 mmol) in 15 ml of EtOH was added 2-aminophenol (35mg, 0.3 mmol for 2a; 70mg, 0.3 mmol for 3a). The mixture was refluxed for 8h, After concentration of the solvent, the compound was recrystallized from EtOH. (7a: yellow solid, 94% yield, 8a: yellow solid, 87% yield). **7a** M.p.= 178-179 C, ^{1}H-NMR ($CDCl_3$)(ppm): 8.65 (s, 1H, OH), 7.41 (s, 1H, CH=N), 7.38 (s, 1H, thiophene-H), 7.30-7.10 (m, 4H, aromatic-H), 6.76 (s, 1H, thiophene-H), 4.28-4.20 (m, 4H, CH_2-S), 2.10 (s, 3H, CH_3), 1.88 (s, 3H, CH_3). MS (m/z): 431 (M$^+$ 23), 109 (100). **8a** M.p.= 201 – 202 C, ^{1}H-NMR ($CDCl_3$)(ppm): 8.71 (s, 2H, OH), 7.43 (s, 2H, CH=N), 7.41(s, 2H, thiophene-H), 7.39-7.30 (d, 2H, aromatic-H), 7.14-7.09 (t, 2H, aromatic-H), 7.02-7.00 (d, 2H, aromatic-H), 6.84-6.80 (t, 2H, aromatic-H), 4.16 (s, 4H, CH_2-S), 2.14 (s, 6H, CH_3). MS (m/z): 516 (M$^+$ 10), 109 (100).