

Scheme S1. Synthesis of quaterthiophene amphiphile.

Synthesis of quaterthiophene amphiphile.

5-Bromo-2-thiophene methanol (5). 5-bromo-2-thiophene carboxaldehyde (7.23 g, 39 mmol) was dissolved in dry THF (100 mL). The solution was cooled to 0°C. Lithium aluminum hydride in a 1 M solution of THF (12 mL, 12 mmol) was slowly dripped into the solution. The reaction was stirred at 0°C for 10 min. Water (7 mL), aqueous 2M NaOH (7 mL), and then water (21 mL) was added and allowed to stir for 20 min. during which time a gray precipitate was observed to form. The precipitate was filtered off, and the resulting solution was evaporated, dissolved in dichloromethane, and dried with MgSO₄. The solution was evaporated to give 6.63 g (34 mmol, 88% yield) of **5** as a black oil. ¹H NMR (CDCl₃, ppm): δ 6.90 (d, 1H, *J* = 3.5 Hz), 6.72 (d, 1H, *J* = 4.0 Hz), 4.68 (s, 2H), 2.58 (s, 1H). ¹³C NMR (120 MHz, CDCl₃): δ 145.8, 129.8, 125.9, 112.4, 60.2.

(5-bromothiophen-2-yl)methyl methanesulfonate. A mixture of compound 5 (3.0 g, 15.5 mmol), triethylamine (2.26g, 23.3 mmol), and methanesulfonyl chloride (2.13 g, 18.6 mmol) in 150 mL of dichloromethane was stirred overnight at room temperature. The solution

was extracted twice with HCl (2 M) and once with saturated NaCl. The organic layer was dried with MgSO₄, filtered, and concentrated in vacuo to give the product as a brown oil (3.60 g, 85% yield). ¹H NMR (CDCl₃, ppm): δ 6.92 (d, 1H, *J* = 4 Hz), 6.85 (d, 1H, *J* = 4.5 Hz), 4.72 (s, 2H), 3.69 (s, 3H).

2-((5-bromothiophen-2-yl)methoxy)-N,N-dimethylethanamine (6). In a dry flask, NaH (0.76 g, 31.8 mmol) was added to 100 mL of dry THF. The solution was cooled to 0°C. 2-(Dimethylamino)ethanol (2.83 g, 31.8 mmol) was added and the mixture was stirred for 30 min. 5-bromothiophen-2-yl)methyl methanesulfonate (3.60 g, 13.3 mmol) dissolved in 20 mL dry THF was dripped into the solution and let stir at room temperature overnight. The reaction mixture was diluted with dichloromethane and washed three times with 2 M HCl. 4 M NaOH was added to the aqueous layer until a white precipitate was obtained. The aqueous layer was then washed three times with dichloromethane. The combined organic layer was dried with MgSO₄, evaporated, and the crude product was purified by column chromatography (silica gel; CH₂Cl₂/MeOH, 85:15) to give **6** (1.00 g, 28% yield) as a black oil. ¹H NMR (CDCl₃, ppm): δ 6.90 (d, 1H, *J* = 3.5 Hz), 6.73 (d, 1H, *J* = 3.5 Hz), 3.54 (t, 2H, *J* = 5.5 Hz), 2.51 (t, 2H, *J* = 5.5 Hz), 2.26 (s, 6H). ¹³C NMR (120 MHz, CDCl₃): δ 143.2, 129.5, 126.9, 112.6, 67.9, 58.9, 46.0. ACPI-MS *m*/z calculated for C₉H₁₄BrNOS, 263.00; found, 263.99 (M⁺).

2-(5-(5-5-5-((2-(Dimethylamino)ethoxy)methyl)tetrathiophene)methoxy)-N,N-

dimethylethanamine (7). In a dry flask that was purged with nitrogen, compound **6** (0.77 g, 2.9 mmol), 5,5'-bis(tributylstannyl)-2,2'-bithiophene (0.98 g, 1.3 mmol), tetrakis(triphenylphosphine)palladium (0.0015 g, 0.013 mmol) was dissolved in 10 mL DMF. The mixture was degassed by three freeze-pump-thaw cycles and then heated to 100°C overnight. The mixture was cooled to room temperature and diluted with dichloromethane. The

organic layer was extracted with saturated NaHCO₃ three times, dried with MgSO₄, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel; CH₂Cl₂/MeOH, 80/20) to give the desired product (0.26 g, 39%) as a red solid. ¹H NMR (CDCl₃, ppm): δ 7.07 (m, 4H), 7.04 (d, 2H, *J* = 4 Hz), 6.92 (d, 2H, *J* = 3.5 Hz), 4.69 (t, 4H, *J* = 6.0 Hz), 2.56 (t, 4H, *J* = 5.5 Hz), 2.30 (s, 12H). ¹³C NMR not possible due to poor solubility. MALDI-TOF MS *m*/*z* calculated for C₂₇H₃₂N₂O₂S₄, 533.81; found, 533.89 (M + H⁺).

Cationic quaterthiophene (2). Compound **7** (0.1 g 0.19 mmol) was dissolved in 20 mL of dry THF. A 2 M solution of methylbromide in *t*-butyl methyl ether (5 mL, 10 mmol) was added and the mixture was stirred for 1 day to room temperature. During the stirring a yellow-orange suspension was formed. The suspension was filtered to give the desired compound quantitatively as a yellow-orange solid. ¹H NMR (DMSO-*d*₆, ppm): δ 7.32 (d, 2H, *J* = 3.5 Hz), 7.29 (d, 2H, *J* = 4.0 Hz), 7.26 (d, 2H, *J* = 3.5 Hz), 7.09 (d, 2H, *J* = 4.0 Hz), 4.73 (s, 4H), 3.90 (t, 4H, *J* = 5.0 Hz), 3.60 (t, 4H, *J* = 5.0 Hz), 3.13 (s, 18H). ¹³C NMR (DMSO-*d*₆, ppm): δ 140.5, 135.9, 136.1, 135.4, 128.9, 126.0, 125.8, 124.6, 67.1, 63.9, 53.7. ESI-MS *m*/*z* calculated for C₂₈H₃₈N₂O₂S₄²⁺ 281.09; found, 281.49 (M²⁺).