

Synthesis

***tert*-Butyl thiophene-3-carboxylate (4).** To a THF solution containing potassium *tert*-butoxide (1M, 50 mL), methyl thiophene-3-carboxylate (1.75 g, 12.3 mmol) was added slowly at room temperature. After 2 hours, the reaction mixture was poured into dilute HCl solution (0.1M, 500 mL) and extracted by CH₂Cl₂. The organic solution was washed with saturated NH₄Cl and water. After the solvent was distilled out under reduced pressure, the residue was purified by column chromatography using 4:1 hexane/ethyl acetate as the eluent to yield a yellow liquid (1.51 g, 67%). ¹H_NMR (300 MHz, CDCl₃), 8.01 (m, 1H), 7.47 (m, 1H), 7.27 (m, 1H), 1.57 (s, 9H); ¹³C_NMR (75 MHz, CDCl₃), 162.05, 135.66, 131.83, 127.95, 125.53, 80.87, 28.25; EI-Mass, calculated: 184.056; found: 184.061.

***tert*-Butyl 2-(trimethylstannyl)thiophene-3-carboxylate (5).** To a solution of **4** (1.07 g, 5.86 mmol) in anhydrous ether (35 mL) at -78 °C, a solution of lithium diisopropylamine (LDA) (4.4 mL, 2 M in THF) was added dropwise and stirred for 30 minutes at -78 °C. The mixture was warmed slowly to room temperature and stirred for another two hours before cooled again to -78 °C. Trimethyltin chloride (1.87 g, 9.4mmol) was added under argon flow. The mixture was stirred at -78 °C for 4 hours, warmed to room temperature and stirred overnight. The reaction mixture was filtered through silica gel treated with triethylamine, and washed with hexane (400 mL). The solvent was distilled out to give a thick brown oil (1.25 g, 91%). ¹H_NMR (300 MHz, CDCl₃), 7.57 (d, 1H), 7.51 (d, 1H), 1.56 (s, 9H), 0.37 (s, 9H); EI_Mass, calculated: 348.021; found: 348.026.

Di-tert-butyl 2,2'-(benzo[d][2,1,3]thiadiazole-4,7-diyl)bis(thiophene-3-carboxylate) (6). A mixture containing 4,7-dibromobenzothiadiazole (0.59 g, 2.1 mmol), THF (20 mL), DMF (20 mL), Pd(PPh₃)₄ (0.22 g, 0.2 mmol) and **5** (1.98 g, 5.7 mmol) was bubbled with nitrogen for 15 minutes. The mixture was stirred overnight at 90 °C under nitrogen. After the reaction was completed, the mixture was added to water and extracted by CH₂Cl₂, washed by water and dried over anhydrous Na₂SO₄. After the solvent was distilled out under reduced pressure, the residue was purified through column chromatography using 1:4 hexane/CH₂Cl₂ as the eluent to yield a green yellow solid (0.68 g, 64%). ¹H_NMR (300 MHz, CDCl₃), 7.71 (s, 2H), 7.59 (d, 2H), 7.39 (d, 2H), 1.21 (s, 18H); ¹³C_NMR (75 MHz, CDCl₃), 160.96, 153.37, 143.51, 133.59, 132.37, 129.21, 126.99, 112.37, 81.37, 27.78; EI_Mass, calculated: 500.09; found: 500.081.

Di-tert-butyl 2,2'-(benzo[d][1,2,3]thiadiazole-4,7-diyl)bis(5-iodothiophene-3-carboxylate) (7). A mixture containing **6** (0.16 g, 0.32 mmol), N-iodosuccinimide (NIS) (0.4 g, 1.78 mmol), CHCl₃ (10 mL) and acetic acid (2 mL) was stirred overnight at 50 °C. The mixture was poured into water, extracted by CHCl₃ and washed by water. After the solvent was distilled out under reduced pressure, the residue was purified by column using 1:5 hexane/CH₂Cl₂ as the eluent to yield a yellow solid (0.20 g, 83%). ¹H_NMR (300 MHz, CDCl₃), 7.71 (s, 2H), 7.67 (s, 2H), 1.22 (s, 18H); ¹³C_NMR (75 MHz, CDCl₃), 160.65, 153.32, 147.94, 139.37, 134.83, 129.16, 126.93, 81.32, 73.64, 27.78; EI_Mass, calculated: 751.883; found: 751.890.

2,2'-(3,4-Dioctylthiophene-2,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (8). A mixture containing 2,5-dibromo-3,4-dioctylthiophene (1.19 g, 2.55 mmol), bis(pinacolato)diboron (1.6 g, 6.37 mmol), Pd(dppf)Cl₂ (0.1 g), CH₃COOK (1.8 g, 17.8

mmol), and DMF (20 mL) was degassed with argon for 20 mins, and then heated to 85 °C for 12 hours. After the reaction was completed, water was added and extracted by CH₂Cl₂. After the organic solvent was distilled out under reduced pressure, the crude was purified with column using 1:1 hexane/CH₂Cl₂ to yield a colorless liquid (0.45 g, 31%). ¹H_NMR (300 MHz, CDCl₃), 2.78 (t, 4H), 1.47 (m, 4H), 1.40-1.20 (m, 44H), 0.88 (t, 6H); EI_Mass, calculated: 560.424; found: 560.431.

2,2'-(Benzo[*d*][1,2,3]thiadiazole-4,7-diyl)bis(thiophene-3-carboxylic acid) (1). A solution containing **3** (35 mg, 0.07 mmol), trifluoroacetic acid (TFA, 2 mL) and CHCl₃ (20 mL) was stirred overnight at room temperature. After the solvent was distilled out under reduced pressure, the residue was washed by water for 3 times and dissolved in a small amount of ethyl acetate. The solution was dropped into hexane to yield a green yellow solid (16 mg, 59%). ¹H_NMR (300 MHz, CD₃OD), 7.77 (s, 2H), 7.60 (m, 4H); HR_Mass, calculated: [M+H]⁺ 388.9719; found [M+H]⁺ 388.9725.

2b. A solution containing **7** (75 mg, 0.1 mmol), 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (56 mg, 0.1 mmol) in toluene (2 mL) was bubbled with argon for 15 minutes. A K₂CO₃ solution (1 mL, 2 M) was added and bubbled with argon for another 15 minutes. After Pd(PPh₃)₄ (4 mg) was added, the reaction mixture was heated to 85 °C and stirred for 2 hours under argon protection. Another portion of Pd(PPh₃)₄ (5 mg) was added. The mixture was heated to 100 °C and stirred overnight. After cooled to room temperature, the reaction mixture was poured into 1:4 H₂O/MeOH (50 mL) to yield a brown precipitate. After filtration, the obtained solid was re-dissolved in a small amount of THF and filtered again through a 0.5 μm microfilm, then precipitated from MeOH. Further purification was conducted through a Bio-beads (200-400 mesh resin,

Bio-Rad Laboratories) column with THF as the eluent. The filtrate was concentrated and precipitated from MeOH to yield an orange solid (70 mg, 79%). Mn, 6400, PDI, 1.62; $^1\text{H_NMR}$ (300 MHz, CDCl_3), 7.79-7.58 (m, 10H), 2.01-1.75 (br, 4H), 1.40 (br, 4H), 1.21 (s, 18H), 1.06 (br, 16H), 0.82-0.78 (m, 6H), 0.64 (br, 4H).

3b. Through a similar polymerization method with **2b**, **3b** was synthesized from **7** and 2,2'-(3,4-dioctylthiophene-2,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane). After the polymer was eluted through a Bio-Beads (200-400 mesh) column, three fractions with various molecular weights were obtained. The overall yield is 60%. All three polymers show deep purple color. The number average molecular weight and disperse index were: Mn, 8900, PDI, 1.32; Mn, 6200, PDI, 1.39; Mn, 4000, PDI, 1.15; $^1\text{H_NMR}$ (300 MHz, CDCl_3), 7.79 (s, 2H), 7.62 (s, 2H), 2.77 (br, 4H), 1.47-1.29 (m, 42H), 0.88 (br, 6H).

2a. 2b (45 mg) was dissolved in CHCl_3 (5 mL) and trifluoroacetic acid (15 mL), then stirred overnight at room temperature. The solvent was distilled out under reduced pressure. The residue was washed with MeOH and acetone. A purple solid was finally obtained (23 mg, 60%). $^1\text{H_NMR}$ (300 MHz, $\text{d}_6\text{-DMSO}$), 12.75 (br, 2H), 8.07-7.63 (m, 10H), 2.15 (br, 4H), 1.20-0.57 (m, 30H).

3a-DPs were prepared through a similar procedure with **2a**. $^1\text{H_NMR}$ (300 MHz, $\text{d}_6\text{-DMSO}$), 12.80 (br, 2H), 7.95-7.63 (m, 4H), 2.60 (br, 4H), 1.56-0.78 (m, 30H).

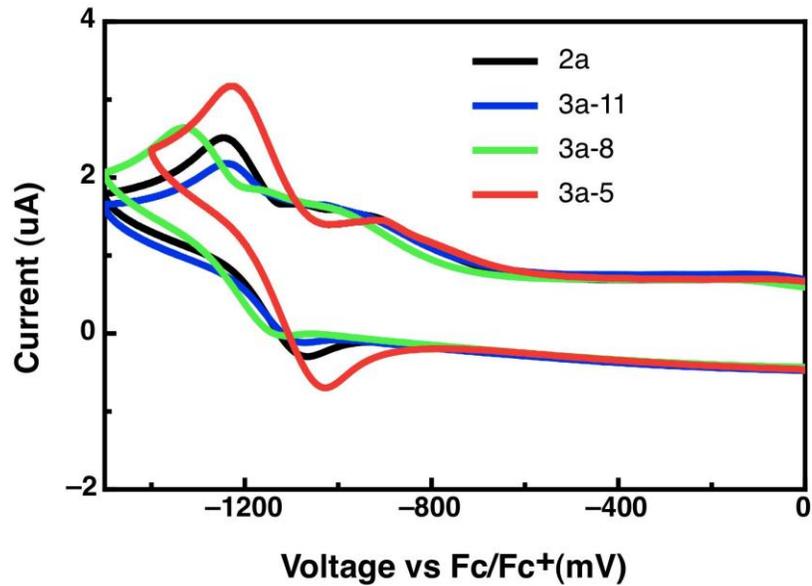


Figure S1. Cyclic voltammetry of polymers in DMF solutions.

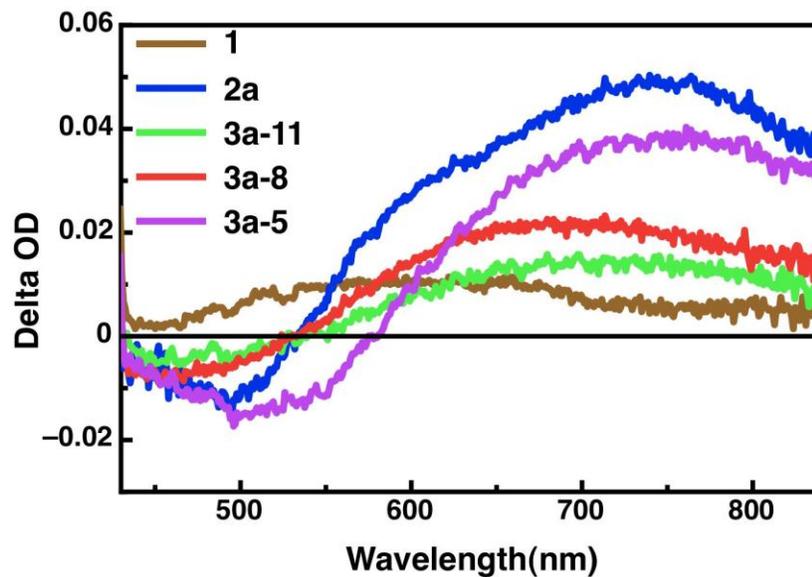


Figure S2. Transient absorption of 1, 2a and 3a-DPs in propylene carbonate. Excitation wavelength: 420 nm, 5 ns pulse; camera delay: 45 ns.

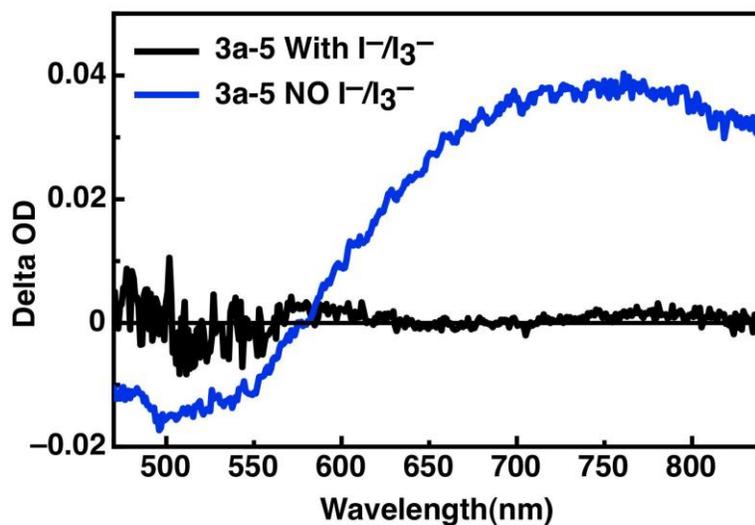


Figure S3. Transient absorption of **3a-5** in propylene carbonate with and without I^-/I_3^- , excitation wavelength: 420 nm, 5 ns pulse; camera delay: 45 ns.

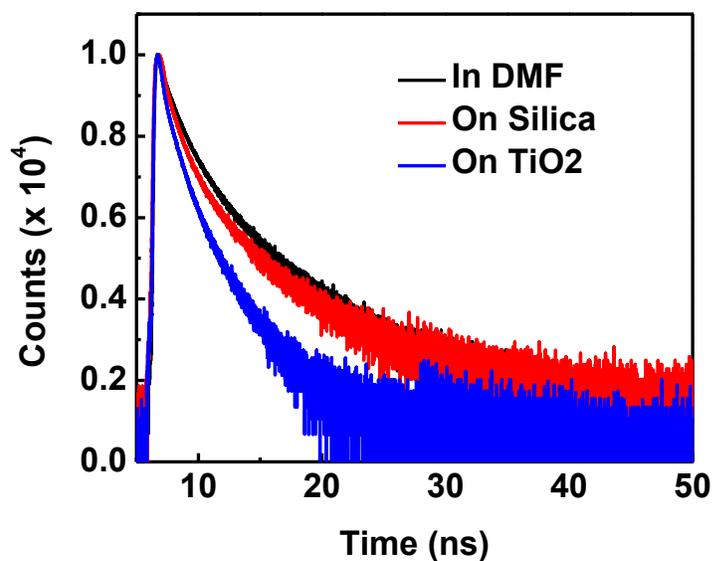


Figure S4. Fluorescence decay of **3a-5** in DMF solution, and adsorbed on SiO_2 and TiO_2 films measured by time-correlated single photon counting. Excitation at 370 nm and detection at $\lambda > 700$ nm. Y-axis is log (photon counts) and x-axis is time in nanoseconds.