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Effect of electron-withdrawing groups on molecular properties of naphthyl and anthryl bithiophenes as potential n-type semiconductors

Electronic Supporting Information

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1. Synthetic procedures

5-(Naphthalen-2-yl)-5'-(perfluorohexyl)-2,2'-bithiophene (IIA)

1.6 M Solution of *n*-butyl lithium (0.90 mL, 1.39 mmol, 1.05 equiv.) in hexanes was added dropwise to a solution of 5-(perfluorohexyl)-2,2'-bithiophene (643 mg, 1.33 mmol) in 3.3 mL of dry THF at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and then ZnBr₂ (357 mg, 1.58 mmol, 1.2 equiv.) in 1 mL of dry THF was added. The reaction mixture was stirred for 1h at 0 °C. Then the cooling bath was removed and this solution was added to solution of 2-bromonaphthalene (250 mg, 1.21 mmol, 0.90 equiv.) and Pd(PPh₃)₄ (70 mg, 0.061 mmol, 0.05 equiv.) in 3.5 mL of THF. The stirring continued under reflux for 24 h. After cooling the reaction mixture, 3 mL of water were added, and precipitate was formed. Precipitate was filtered and washed with hexanes, then it was dissolved in hot chloroform and filtered through a silica pad. The solution was evaporated and the residue was crystallized twice from toluene/methanol mixture (3/2, 2 x 30 ml) and pure compound IIA (354 mg, 48%) was obtained as ochre solid. M. p. = 173.2-175.6 °C. ¹H **NMR** (300 MHz, $C_2D_2Cl_4$): δ 8.07 (s, 1H), 7.88 (m, 3H, overlapping peaks), 7.75 (d, J = 8.7 Hz, 1H), 7.58-7.48 (m, 2H), 7.44-7.38 (m, 2H), 7.31 (d, J = 3.7 Hz, 1H), 7.25 (d, J = 3.1 Hz, 1H) ppm. ¹³C NMR (151 MHz, C₂D₂Cl₄): δ 146.3, 143.8, 136.0, 134.7, 134.2, 132.6, 132.2, 130.2, 129.4, 129.2, 128.3, 128.3, 127.8, 127.8, 125.9, 125.6, 125.3, 124.9, 124.8, 121.7 ppm. ¹⁹F NMR (282 MHz, C₂D₂Cl₄): δ -79.11 (3F), -99.59 (2F), -119.92 (4F), -121.22 (2F), -124.51 (2F) ppm. FTIR (solid): v 3053, 1193 (C-F), 1138, 1120, 794, 704, 623 cm⁻¹. **HRMS** (APPI): m/z for C₂₄H₁₁F₁₃S₂ calculated 610.0095, found 610.0090.

5-(Anthracen-2-yl)-5'-(perfluorohexyl)-2,2'-bithiophene (IIIA)

This compound was obtained by the method described for compound (**IIA**) using 1.6 M *n*-BuLi (0.40 mL, 0.65 mmol, 1.05 equiv.) in hexanes, 5-(perfluorohexyl)-2,2'-bithiophene (300 mg, 0.62 mmol) in 1.5 mL of dry THF, ZnBr₂ (167 mg, 0.74 mmol, 1.2 equiv.) in 1 mL of dry THF, 2-bromoanthracene (145 mg, 0.56 mmol, 0.9 equiv.) and Pd(PPh₃)₄ (36 mg, 0.031 mmol, 0.05 equiv.) in 3.5 mL of dry THF. After cooling the reaction mixture, 1 mL of water was added, and precipitate was formed. Precipitate was filtered and washed with hexanes. The precipitate was filtered and washed with hexanes, then it was dissolved in hot chloroform and filtered through a silica pad. The solution was evaporated and the residue was recrystallized from toluene (1 g/ 140 ml) and pure compound **IIIA** (149 mg, 40%) was obtained as ochre solid. **M. p.** = 239.2-242.2 °C. ¹**H NMR** (300 MHz, C₂D₂Cl₄): δ 7.79 (d, *J* = 10.9 Hz, 2H), 7.58 (s, 1H), 7.44–7.34 (m, 3H), 7.09 (dd, *J* = 8.9, 1.6 Hz, 1H), 6.87–6.82 (m, 2H), 6.81 (d, *J* = 3.9 Hz, 1H), 6.76 (d, *J* = 4.0 Hz, 1H), 6.68 (d, *J* = 3.8 Hz, 1H), 6.61 (d, *J* = 3.8 Hz, 1H) ppm. ¹³**C NMR** – low solubility. ¹⁹**F NMR** (282 MHz, C₂D₂Cl₄): δ ,): -79.1 (3F), -99.6 (2F), -120.0 (4F), -121.3 (2F), -124.5 (2F) ppm. **FTIR** (solid): *v* 3051, 1458, 1363, 1195 (C-F), 1141, 1121, 792, 704 cm⁻¹. **HRMS** (APPI): *m/z* for C₂₈H₁₃F₁₃S₂ calculated 660.0251, found 660.0243.

1-[5'-(Naphthalen-2-yl)-2,2'-bithiophen-5-yl]hexan-1-one (IIB)

Compound was obtained by method described for compound **IIC** using 1-(5'-bromo-2,2'bithiophen-5-yl)hexan-1-one (664 mg, 1.94 mmol), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)naphthalene (590 mg, 2.32 mmol, 1.2 equiv.) and Pd(PPh₃)₄ (224 mg, 0.194 mmol, 0.1 equiv.) in degassed toluene (19 mL) and 1 M solution of Na₂CO₃ (19 mL, 10 equiv.). After cooling, the precipitate was formed. Precipitate was filtered off and washed with water and hexanes. Precipitate was dissolved in chloroform and filtered through a silica pad. Solvent was evaporated and the product was obtained as yellow solid (610 mg, 81%). **M. p.** = 190.8–192.1 °C. ¹**H NMR** (600 MHz, CDCl₃): δ 8.06 (s, 1H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.74 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.63 (d, *J* = 3.9 Hz, 1H), 7.50 (ddd, *J* = 14.8, 13.5, 6.7 Hz, 2H), 7.39 (d, *J* = 3.8 Hz, 1H), 7.34 (d, *J* = 3.8 Hz, 1H), 7.22 (d, *J* = 3.9 Hz, 1H), 2.88 (t, *J* = 7.5 Hz, 2H), 1.81–1.74 (m, 2H), 1.43–1.35 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H) ppm. ¹³C **NMR** (151 MHz, CDCl₃): δ 193.2, 145.4, 145.3, 142.3, 135.7, 133.5, 133.0, 132.6, 131.0, 128.7, 128.1, 127.7, 126.8, 126.6, 126.3, 124.4, 124.3, 123.9, 123.9, 39.0, 31.5, 24.7, 22.5, 13.9 ppm. **FTIR** (solid): *v* 2956, 2927, 1649, 1436, 794 cm⁻¹. **HRMS** (pESI): *m/z* [M + H]⁺ for C₂₄H₂₃OS₂H calculated 391.1192, found 391.1185.

1-[5'-(Anthracen-2-yl)-2,2'-bithiophen-5-yl]hexan-1-one (IIIB)

Compound was obtained by method described for compound **IIIC** using 1-(5'-bromo-2,2'-bithiophen-5-yl)hexan-1-one (400 mg, 1.17 mmol), anthracen-2-ylboronic acid (310 mg, 1.39 mmol, 1.2 equiv.), and Pd(PPh₃)₄ (135 mg, 0.117 mmol, 0.1 equiv.) were placed into two-necked flask and degassed toluene (12 mL) was added. Then, 1 M solution of Na₂CO₃ (12 mL, 10 equiv.) was added and the reaction mixture was stirred under reflux for 24 h. After cooling, the precipitate was formed. Precipitate was filtered off and washed with water and hexanes. Precipitate was dissolved in hot chloroform and filtered through a silica pad. Solvent was evaporated and the product was obtained as yellow solid (375 mg, 73%). **M. p.** = 256.1–258.0 °C. ¹**H NMR** (600 MHz, CDCl₃): δ 8.45 (s, 1H), 8.41 (s, 1H), 8.22 (s, 1H), 8.05–7.98 (m, 3H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.64 (d, *J* = 3.9 Hz, 1H), 7.50–7.46 (m, 2H), 7.44 (d, *J* = 3.7 Hz, 1H), 7.36 (d, *J* = 3.6 Hz, 1H), 7.24 (d, *J* = 3.9 Hz, 2H), 2.89 (t, *J* = 7.5 Hz, 2H), 1.81–1.74 (m, 2H), 1.39 (m, 4H), 0.93 (t, *J* = 6.9 Hz, 3H) ppm. ¹³C **NMR** – low solubility. **FTIR** (solid): *v* 927, 2868, 1653, 1435, 896, 792 cm⁻¹. **HRMS** (pESI) *m/z* [M + H]⁺ for C₂₈H₂₄OS₂H calculated 441.1349, found 441.1341.

1-[5'-(Naphthalen-2-yl)-2,2'-bithiophen-5-yl]pentadecafluorooctan-1-one (IIC)

1-(5'-Bromo-2,2'-bithiophen-5-yl)pentadecafluorooctan-1-one (150 mg, 0.23 mmol), 2-(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (72 mg, 0.28 mmol, 1.2 equiv.), and Pd(PPh₃)₄ (23 mg, 0.023 mmol, 0.1 equiv.) were placed into two-necked flask and degassed toluene (10 mL) was added. Then, 1 M solution of Na₂CO₃ (2.3 mL, 10 equiv.) was added and the reaction mixture was stirred under reflux for 24 h. After cooling to room temperature, yellow precipitate was formed. Precipitate was filtered off and washed with water and hexanes. Solvent was evaporated and the residue was washed with chloroform (20 mL). Organic phase was washed with brine, dried over sodium sulfate, filtered, and solvent was evaporated under reduced pressure. Residue was purified by flash chromatography on silica gel (gradient hexanes:chloroform $0 \rightarrow 100\%$ of chloroform). The overall yield of yellow crystalline solid was 45% (104 mg). M. p. = 151.6-152.2 °C. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3)$: δ 8.08 (br s, 1H), 7.93-7.87 (m, 2H), 7.85 (dd, J = 9.9, 2.7 Hz, 2H), 7.74 (dd, J = 8.6, 1.7 Hz, 1H), 7.54–7.49 (m, 2H), 7.46 (d, J = 3.9 Hz, 1H) 7.43 (d, J = 3.9 Hz, 1H) (dd, J = 3.9 3.9, Hz, 2H), 7.31 (d, J = 4.2 Hz, 1H).ppm. ¹³C NMR (75 MHz, CDCl₃): δ 174.8, 150.6, 147.5, 137.9, 135.4, 134.4, 133.5, 133.2, 130.6, 128.9, 128.2, 128.1, 127.8, 126.9, 126.6, 124.9, 124.8, 124.7, 123.8 ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ -80.7 (3F), -114.5 (2F), -121.2 (4F, overlapped peaks), -121.9 (2F), -122.7 (2F), -126.1 (2F) ppm. FTIR (solid): v 1667 (CO), 1426, 1200 (C-F), 1147, 797 cm⁻¹. **HRMS** (APPI): m/z for C₂₆H₁₁F₁₅OS₂ calculated 688.0012, found 688.0003.

1-[5'-(Anthracen-2-yl)-2,2'-bithiophene-5-yl]pentadecafluorooctan-1-one (IIIC)

1-(5'-Bromo-2,2'-bithiophen-5-yl)pentadecafluorooctan-1-one (100 mg, 0.16 mmol), anthracene-2-ylboronic acid (42 mg, 0.19 mmol, 1.2 equiv.), and Pd(PPh₃)₄ (18 mg, 0.016 mmol, 0.1 equiv.) were placed into two-necked flask and degassed toluene (8 mL) was added. Then, 1 M solution of Na₂CO₃ (1.6 mL, 10 equiv.) was added and the reaction mixture was stirred under reflux for 24 h. After cooling to room temperature, dark precipitate was formed. Precipitate was filtered off and washed with water and hexanes, then it was dissolved in hot chloroform and filtered through a silica pad. The solution was evaporated and the residue was recrystallized from toluene (1 g/75 mL) and product was obtained as orange solid (90 mg, 70%). **M. p.** = 218.5–219.3 °C. ¹**H NMR** (600 MHz, C₂D₂Cl₄, 50 °C): δ 8.50 (s, 1H), 8.45 (s, 1H), 8.28 (s, 1H), 8.09 (d, *J* = 9.1 Hz, 1H), 8.05–8.04 (m, 2H), 7.95–7.94 (m, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.53–7.52 (m, 4H), 7.37 (d, *J* = 4.1 Hz, 1H) ppm. ¹³C NMR – low solubility. ¹⁹F NMR (282 MHz, C₂D₂Cl₄) δ : -79.1 (3F), -113.0 (2F), -119.7 (4F), -120.4 (2F), -121.1 (2F), -124.5 (2F) ppm. **FTIR** (solid): *v* 1655 (CO), 1427, 1196 (C-F), 1145, 798, 748 cm⁻¹. **HRMS** (APPI): *m/z* for C₃₀H₁₃F₁₅OS₂ calculated 738.0168, found 738.0162.

5-(Naphthalene-2-yl)-5'-nitro-2,2'-bithiophene (IID)

This compound was obtained by the method described for compound IIC using 2-bromo-2'-nitro-5.5'-bithiophene (600 mg. 2.07 mmol), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)naphthalene (2.48 mmol, 631 mg, 1.2 equiv.), and Pd(PPh₃)₄ (0.207 mmol, 239 mg, 0.1 equiv.) in degassed toluene (20 mL) and 1 M solution of Na₂CO₃ (20 mL, 10 equiv.). After cooling, the precipitate was formed. Precipitate was filtered off and washed with water and hexanes, then it was dissolved in hot chloroform and filtered through a silica pad. The solution was evaporated and the residue was purified by crystallization from hexanes/toluene (4.5:1). The overall yield of dark red solid was 51% (355 mg). **M. p**. = 165.7–168.9°C. ¹**H NMR** (300 MHz, CDCl₃): δ 8.07 (d, J = 1.5 Hz, 1H), 7.88 (dd, J = 7.9, 3.6 Hz, 4H), 7.72 (dd, J = 8.6, 1.9 Hz, 1H), 7.56–7.47 (m, 2H), 7.42 (d, J = 3.9 Hz, 1H), 7.38 (d, J = 3.9 Hz, 1H), 7.13 (d, J = 4.3 Hz, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃): *δ* 147.2, 145.2, 134.1, 133.5, 133.2, 130.5, 129.8, 128.9, 128.1, 127.8, 127.7, 126.9, 126.6, 124.7, 123.8, 122.2 ppm. FTIR (solid): v 1489, 1321, 794 cm⁻¹. HRMS (APPI): m/z for C₁₈H₁₁NO₂S₂ calculated 337.0231, found 337.0229.

5-(Anthracene-2-yl)-5'-nitro-2,2'-bithiophene (IIID)

This compound was obtained by the method described for compound **IIIC** using 2-bromo-2'-nitro-5,5'-bithiophene (420 mg, 1.45 mmol), anthracene-2-ylboronic acid (386 mg, 1.73 mmol, 1.2 equiv.), and Pd(PPh₃)₄ (167 mg, 0.145 mmol, 0.1 equiv.) in degassed toluene (15 mL) and 1 M solution of Na₂CO₃ (14.5 mL, 10 equiv.). After cooling, the precipitate was formed. The precipitate was filtered off and washed with water and hexanes, then it was dissolved in hot chloroform and filtered through a silica pad. The solution was evaporated and the residue was purified by recrystallization from toluene (0.1 g/3 mL) Product was obtained as orange solid (336 mg, 60%). **M. p.** = 256.6–259.9 °C. ¹**H NMR** (600 MHz, CDCl₃): δ 8.46 (s, 1H), 8.42 (s, 1H), 8.24 (s, 1H), 8.05 (d, *J* = 8.9 Hz, 1H), 8.01 (dd, *J* = 9.2, 4.1 Hz, 2H), 7.89 (d, *J* = 4.2 Hz, 1H), 7.72 (dd, *J* = 8.6, 1.3 Hz, 1H), 7.52–7.45 (m, 3H), 7.41 (d, *J* = 3.8 Hz, 1H), 7.16 (d, *J* = 4.2 Hz, 1H) ppm. ¹³**C NMR** (151 MHz, CDCl₃): δ 132.4, 132.1, 131.0, 129.9, 129.9, 129.3, 129.0, 128.2, 128.2, 128.2, 127.8, 126.8, 126.3, 125.9, 125.9, 124.8, 124.6, 123.5, 122.2, 110.0 (due to lower solubility, quaternary C are not clearly visible) ppm. **FTIR** (solid): v 2355, 1489, 1423, 1322, 866, 795 cm⁻¹. **HRMS** (APPI): m/z for C₂₂H₁₃NO₂S₂ calculated 387.0388, found 387.0386.

{1-[5'-(Naphthalen-2-yl)-2,2'-bithiophen-5-yl]hexylidene}malononitrile (IIE)

This compound was obtained by the method described for compound IIC using [1-(5-bromo-2,2'bithiophen-5-yl)hexylidene]malononitrile (150 mg, 0.383 mmol), 2-(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)naphthalene (0.459 mmol, 117 mg, 1.2 equiv.), and Pd(PPh₃)₄ (0.038 mmol, 44 mg, 0.1 equiv.) in degassed toluene (4 mL) and 1 M solution of Na₂CO₃ (3.9 mL, 10 equiv.). After cooling, the precipitate was formed. Precipitate was filtered off and washed with water and hexanes. Filtrate was evaporated and the residue was washed with chloroform (20 mL). Organic phase was washed with brine, dried over sodium sulfate, filtered, and solvent was evaporated under reduced pressure. Crude material was purified by flash chromatography on reverse SiO₂ (eluent hexanes/toluene 1/2). Fractions containing excess of product were purified by preparation chromatography on SiO_2 with toluene as eluent. The overall yield of orange solid was 50% (84) mg). M. p. = 106.4-108.2 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.03 (s, 1H), 7.93 (d, J = 4.1 Hz, 1H), 7.88–7.79 (m, 3H), 7.70 (d, J = 7.9 Hz, 1H), 7.54–7.45 (m, 2H), 7.41–7.32 (m, 2H), 7.28– 7.23 (m, 1H), 2.92–2.82 (m, 2H), 1.75–1.63 (m, 2H), 1.48–1.32 (m, 4H), 1.02–0.83 (m, 3H) ppm. ¹³C NMR (151 MHz, CDCl₃): δ 166.4, 146.8, 146.7, 135.2, 135.1, 134.4, 133.5, 133.1, 130.6, 128.9, 128.1, 127.8, 127.6, 126.9, 126.6, 124.9, 124.7, 124.5, 123.7, 114.7, 113.9, 37.5, 31.6, 30.2, 22.3, 13.9 ppm. **FTIR** (solid): v 3051, 2929, 2851, 2223, 1429, 798 cm⁻¹. **HRMS** (pESI) m/z [M + Na]⁺ for C₂₇H₂₂N₂S₂Na calculated 461.1124, found 461.1117.

{1-[5'-(Anthracen-2-yl)-2,2'-bithiophen-5-yl]hexylidene}malononitrile (IIIE)

This compound was obtained by the method described for compound **IIIC** using [1-(5-bromo-2,2'bithiophen-5-yl)hexylidene]malononitrile (150 mg, 0,38 mmol), anthracene-2-ylboronic acid (79) (0.46 mmol, 102 mg, 1.2 equiv.), and Pd(PPh₃)₄ (0.038 mmol, 44 mg, 0.1 equiv.) in degassed toluene (4 mL) and 1 M solution of Na₂CO₃ (3.9 mL, 10 equiv.). After cooling, the precipitate was formed. Precipitate was filtered off and washed with water and hexanes, then it was dissolved in hot chloroform and filtered through a silica pad. The solution was evaporated and the residue was recrystallized twice from hexanes (0.1 g/2.25 mL) followed by recrystallization from toluene/hexanes 1/3 mixture to give pure compound (0.121 mg, 65% after purification) as dark red solid. **M. p.** = 170.4–171.6 °C. ¹**H NMR** (300 MHz, CDCl₃): δ 8.40 (d, J = 8.3 Hz, 1H), 8.20 (s, 1H), 8.03–7.98 (m, 3H), 7.95 (d, J = 4.0 Hz, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.50–7.47 (m, 2H), 7.44 (d, J = 3.7 Hz, 1H), 7.38 (d, J = 3.6 Hz, 1H), 7.29 (d, J = 4.0 Hz, 1H), 2.90 (t, J = 7.6 Hz, 2H), $1.76-1.66 (m, 2H), 1.48-1.35 (m, 4H), 0.93 (t, J = 6.9 Hz, 3H) ppm. {}^{13}C NMR (151 MHz, CDCl_3):$ δ 166.3, 146.9, 146.7, 135.2, 135.1, 134.4, 132.3, 132.1, 131.4, 130.94, 129.9, 129.2, 128.2, 128.1, 127.6, 126.7, 126.3, 125.9, 125.8, 125.0, 124.8, 124.5, 123.5, 114.7, 113.9, 37.5, 31.6, 30.2, 22.3, 13.9 ppm. **FTIR** (solid): v 3647, 3052, 2927, 2857, 2212, 1418, 892, 795 cm⁻¹. **HRMS** (APPI): m/z for C₃₁H₂₄N₂S₂ calculated 488.1381, found 488.1373.

1-(5'-Bromo-2,2'-bithiophen-5-yl)hexan-1-one IVB

To 5'-bromo-2,2'-bithiophene (1 g, 4.8 mmol) in dry dichloromethane (10 mL), hexanoyl chloride (0.65 ml, 4.49 mmol, 1.1 equiv.) was added and the reaction mixture was cooled to 0 °C. Then,

AlCl₃ (0.65 g, 4.89 mmol, 1.2 equiv.) was added gradually, and after 15 min the cooling bath was removed, and reaction mixture was stirred at room temperature for 3 h. Then the mixture was cooled down and 10 mL of a saturated aqueous solution of NaHCO₃ were added. The mixture was extracted with dichloromethane (3 x 15 ml), the combined organic phases were washed with brine, and dried over Na₂SO₄. The solvent was evaporated under vacuum, and the crude product was purified by flash column chromatography on silica gel (eluent hexanes/dichloromethane 1:1) to give a pure product (1.01 g, 72%) as light yellow solid. **M. p.** = 95.8–97.5 °C. ¹**H NMR** (600 MHz, CDCl₃): δ 7.57 (d, *J* = 4.0 Hz, 1H), 7.09 (d, *J* = 3.9 Hz, 1H), 7.05 (d, *J* = 3.9 Hz, 1H), 7.01 (d, *J* = 3.9 Hz, 1H), 2.87–2.83 (m, 2H), 1.75 (dq, *J* = 14.8, 7.4 Hz, 2H), 1.39–1.32 (m, 4H), 0.94–0.88 (m, 3H) ppm. ¹³**C NMR** (151 MHz, CDCl₃): δ 193.2, 144.0, 142.8, 137.8, 132.4, 131.0, 125.5, 124.2, 113.3, 39.0, 31.5, 24.6, 22.5, 13.9 ppm. **FTIR** (solid): *v* 2926, 2866, 1648, 1421, 789 cm⁻¹. **HRMS** (pESI): *m/z*: [M + H]⁺ calcd for C₁₄H₁₅BrOS₂H 342.9826, found 342.9821.

1-(5'-Bromo-2,2'-bithiophen-5-yl)pentadecafluorooctan-1-one (IVC)

To 5'-bromo-2,2'-bithiophene (1.50 g, 6.12 mmol) in dry dichloromethane (15 mL), pentadecafluorooctanoyl chloride (2.28 ml, 9.18 mmol, 1.5 equiv.) was added and the reaction mixture was cooled to 0 °C. Then, AlCl₃ (0.98 g, 7.34 mmol, 1.2 equiv.) was added gradually, and after 15 min the cooling bath was removed, and reaction mixture was stirred at room temperature for 3 h. The mixture was cooled down and 10 mL of a saturated aqueous solution of NaHCO₃ were added. The mixture was filtered through silica gel, filtrate was washed with water and brine, then dried over Na₂SO₄. Solvent was evaporated under vacuum, and the crude product was purified by column chromatography on silica gel (eluent hexanes/chloroform $0\rightarrow100\%$) to give a pure product (1.28 g, 33%) as yellow solid. **M. p.** = 128.1–129.3 °C. ¹**H NMR** (300 MHz, CDCl₃): δ 7.89–7.84 (m, 1H), 7.20 (d, J = 4.2 Hz, 1H), 7.17 (d, J = 3.9 Hz, 1H), 7.07 (d, J = 3.9 Hz, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 175.4–174.7 (t, CO), 149.2, 137.8, 136.7, 135.9, 131.5, 127.1, 127.1, 125.2, 119.5–118.6 (m), 119.0, 115.5, 115.2–113.9 (m), 111.7–110.2 (m), 108.6–106.6 (m) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ -85.5 (3F), -119.4 (2F), -126.0 (4F), -126.7 (2F), -127.5 (2F), -130.9 (2F) ppm. **FTIR** (solid): v 1659 (CO), 1443, 1196 (C-F), 1142 cm⁻¹. **HRMS** (APPI): m/z for C₁₆H4BrF₁₅OS₂ calculated 639.8647, found 639.8648.

[1-(5-Bromo-2,2'-bithiophen-5-yl)hexylidene]malononitrile (IVE)

IVB (0.2 g, 0.583 mmol) and malononitrile (0.115 g, 1.75 mmol, 3 equiv.) in 12 mL of dry pyridine was refluxed for 18 h. After cooling, the solvent was evaporated and the residue was extracted twice with chloroform. Combined organic phases were washed with brine, dried over Na₂SO₄. After evaporation of chloroform, the product was further purified by recrystallization from ethanol (12 mL) and was obtained as orange crystalline solid (0.199 mg, 84%). **M. p.** = 103.8–104.8 °C. ¹**H NMR** (600 MHz, CDCl₃): δ 7.93 (d, *J* = 4.2 Hz, 1H), 7.20 (d, *J* = 4.2 Hz, 1H), 7.11 (d, *J* = 3.9 Hz, 1H), 7.05 (d, *J* = 3.9 Hz, 1H), 2.92 (t, J = 7.9 Hz, 1H), 1.73–1.66 (m, 1H), 1.48–1.41 (m, 1H), 1.41–1.33 (m, 1H), 0.92 (t, *J* = 7.2 Hz, 1H) ppm. ¹³**C NMR** (151 MHz, CDCl₃): δ 166.5, 145.2, 136.6, 135.7, 134.8, 131.4, 126.5, 125.2, 114.8, 114.39, 113.6, 37.6, 31.6, 30.1, 22.2, 13.8 ppm. **FTIR** (solid): *v* 3647, 3104, 2951, 2928, 2863, 2218 (CN), 1523, 1421, 1236, 781 cm⁻¹. **HRMS** (APPI): *m*/*z* for C₁₇H₁₅BrN₂S₂ calculated 389.9860, found 389.9853.

2. Computational analysis

Table S1. Calculated distribution of frontier orbitals and optimized geometry of naphthalene bithiophenes IIA-IIE.





Table S2. Calculated distribution of frontier orbitals and optimized geometry of anthracene bithiophenes IIIA-IIIE.

IIB'

Job type: Geometry optimization.

Method: RB3LYP

Basis set: 6-31G**

Cartesian coordinates:

Н	2.906508	-2.736930	-0.697490
С	3.382204	-1.798444	-0.432147
Н	5.353376	-2.540699	-0.773294
С	4.748492	-1.685302	-0.484142
С	3.182857	0.518602	0.237242
С	5.398400	-0.458361	-0.179280
С	2.565018	-0.686076	-0.063645
С	4.590994	0.666779	0.187308
С	6.808443	-0.309083	-0.225794
Н	4.619387	2.749487	0.780722
Н	2.585036	1.373146	0.543244
С	7.399013	0.896742	0.080977
Н	7.416368	-1.165321	-0.506044
Н	8.479444	0.999354	0.043804
С	6.602517	2.008985	0.448058
Н	7.080129	2.954073	0.689070
С	5.231808	1.896700	0.499924
С	1.110546	-0.847070	-0.007916
S	0.029443	0.510456	-0.257728

С	-1.393481	-0.491210	-0.022182
С	-1.018189	-1.796723	0.222618
С	0.383026	-1.994897	0.227264
Н	-1.734824	-2.590724	0.400352
Н	0.847701	-2.952301	0.430622
С	-2.722523	0.070786	-0.102048
С	-3.083823	1.377706	-0.391990
С	-4.480730	1.581941	-0.389888
С	-5.201298	0.440759	-0.100811
S	-4.137586	-0.919275	0.178787
Н	-2.361103	2.158236	-0.601237
Н	-4.945964	2.539277	-0.595736
С	-6.650744	0.228443	0.001257
С	-7.557305	1.424524	-0.239544
Н	-7.341046	2.227306	0.473325
Н	-8.593472	1.105567	-0.124228
Н	-7.410311	1.829110	-1.246684
0	-7.105296	-0.876714	0.272344

IIC'

Job type: Geometry optimization.			Basis set: 6-31G**					
Meth	nod: RB3LY	P						
Carte	esian coordi	nates:						
С	2.103598	0.969754	0.001271		С	1.454894	2.160308	-0.258909

С	0.045323	2.054186	-0.263879
С	-0.415809	0.778453	-0.002176
S	0.935841	-0.307989	0.269588
Н	1.982856	3.080610	-0.477586
Н	-0.616544	2.886972	-0.474189
С	-1.776635	0.305669	0.067648
S	-3.120422	1.422456	0.025096
С	-4.269713	0.107161	0.140693
С	-3.625065	-1.116160	0.216695
С	-2.223559	-1.006005	0.175138
Η	-4.154012	-2.057213	0.295291
Н	-1.552598	-1.856418	0.210011
С	-5.683923	0.429559	0.144662
0	-6.132455	1.561579	0.069590
С	-6.668673	-0.766108	0.252179
F	-7.932954	-0.347480	0.251795
F	-6.499508	-1.619297	-0.783982
F	-6.448598	-1.465394	1.388682

С	3.543495	0.713889	0.071011
Η	3.423886	-1.360189	-0.471473
С	4.077905	-0.539502	-0.188384
С	5.787905	1.573172	0.474265
С	5.471891	-0.783013	-0.124706
С	4.433076	1.779136	0.409535
С	6.353083	0.295416	0.211709
С	6.027118	-2.063616	-0.394464
Η	4.023409	2.756623	0.641960
Η	8.414188	0.870771	0.529420
Η	6.449275	2.393294	0.740798
С	7.386420	-2.268532	-0.329563
Η	5.358254	-2.880375	-0.652512
Η	7.798436	-3.251644	-0.536684
С	8.255946	-1.202358	0.007122
Η	9.326560	-1.377566	0.054442
С	7.749139	0.050627	0.272057

IID

Job type: Geometry optimization.

Method: RB3LYP

Basis set: 6-31G**

Η	2.152956	-2.134192	0.669529
С	2.901314	-1.388901	0.417290
Н	4.526905	-2.748364	0.668053
С	4.230097	-1.731439	0.426071
С	3.457846	0.888273	-0.184534
С	5.238769	-0.773597	0.136819
С	2.486232	-0.058171	0.109312
С	4.836986	0.566919	-0.171798

С	6.620893	-1.094763	0.142376
Н	5.533737	2.547188	-0.705841
Н	3.165248	1.897977	-0.457256
С	7.566801	-0.136596	-0.146059
Н	6.921267	-2.112026	0.379304
Н	8.621822	-0.393478	-0.138823
С	7.171225	1.188268	-0.454798
Н	7.927031	1.934131	-0.682036

С	5.838742	1.531529	-0.468219
С	1.067689	0.305951	0.102890
С	0.493989	1.547668	0.291674
С	-0.917573	1.543117	0.219182
С	-1.456135	0.294396	-0.024963
Η	1.075165	2.434509	0.514223
Η	-1.525801	2.428190	0.370671
С	-2.841668	-0.088461	-0.147068
S	-4.096666	1.127426	-0.300294

С	-5.303851	-0.122449	-0.369850
С	-4.782634	-1.390603	-0.294578
С	-3.378667	-1.369359	-0.167205
Н	-5.402567	-2.276831	-0.323489
Н	-2.771735	-2.262604	-0.075320
S	-0.176274	-0.894401	-0.184848
N	-6.681363	0.227349	-0.492829
0	-6.954962	1.433732	-0.538567
0	-7.502527	-0.692957	-0.545975

IIE'

Job type: Geometry optimization.

Method: RB3LYP

Basis set: 6-31G**

С	3.633293	-0.686630	-0.064833
Η	3.538950	1.353115	0.600757
С	4.182596	0.543038	0.267605
С	5.866517	-1.546607	-0.523861
С	5.579204	0.773537	0.214923
С	4.509695	-1.740236	-0.468011
С	6.446865	-0.293072	-0.187787
С	6.149966	2.029730	0.557716
Н	4.088344	-2.697122	-0.757954
Н	8.500268	-0.872233	-0.546226
Н	6.517761	-2.356947	-0.840534
С	7.511362	2.222336	0.499972
Н	5.491507	2.837548	0.865830
Н	7.935593	3.186582	0.763404
С	8.367382	1.168090	0.097590
С	7.845363	-0.061365	-0.238514
Н	9.439769	1.333646	0.056671

С	2.191076	-0.931276	-0.008766
S	1.034747	0.371919	-0.189224
С	-0.327159	-0.719797	0.003871
С	0.124210	-2.014387	0.182614
С	1.532100	-2.131275	0.172393
Η	-0.543378	-2.857303	0.323353
Η	2.052405	-3.068876	0.326091
С	-1.680948	-0.230772	-0.039655
С	-2.125381	1.065807	-0.261862
С	-3.522201	1.201714	-0.239048
С	-4.205248	0.011727	-0.000884
S	-3.036626	-1.301575	0.202267
Η	-1.451666	1.896307	-0.438021
Η	-4.017580	2.149197	-0.395428
С	-5.613642	-0.281855	0.102741
С	-5.999312	-1.717142	0.378254
Н	-5.627041	-2.371532	-0.417485

Η	-7.078620	-1.844729	0.447924
Η	-5.552849	-2.058130	1.318621
С	-6.623543	0.657380	-0.031231
С	-8.001157	0.288219	0.086961

С	-6.417246	2.045753	-0.291691
N	-9.127114	0.004439	0.180567
Ν	-6.271017	3.182010	-0.503162

IIIA'

Job type: Geometry optimization.

Method: RB3LYP

Basis set: 6-31G**

Η	9.909826	1.148862	-0.056435
С	8.825380	1.148824	0.001121
Н	8.652517	-0.958677	-0.317221
С	8.128768	-0.022215	-0.143754
С	6.768801	2.400531	0.304195
С	6.702045	-0.041455	-0.072047
С	8.136400	2.375816	0.227909
С	6.003187	1.202094	0.157731
С	5.961278	-1.222667	-0.217874
Н	8.705460	3.293864	0.340874
Н	4.078156	2.131611	0.402209
Н	6.241203	3.334781	0.477586
С	4.565518	-1.226923	-0.147938
Н	6.486965	-2.158953	-0.391224
С	3.790800	-2.419547	-0.299537
С	3.864882	0.015072	0.078433
Н	1.930477	0.937434	0.347781
С	4.604427	1.195773	0.228498
С	2.427376	-2.393767	-0.236248
Н	4.310502	-3.356441	-0.481831
Н	1.863428	-3.307895	-0.387766

С	1.715617	-1.164966	-0.006954
С	2.441674	-0.000655	0.147534
С	0.254177	-1.186917	0.055485
S	-0.698280	0.253381	-0.258675
С	-2.206428	-0.599804	0.018431
С	-1.954968	-1.921035	0.324807
С	-0.577846	-2.248958	0.342375
Н	-2.741126	-2.638872	0.531806
Η	-0.207770	-3.237407	0.586926
С	-3.477316	0.080481	-0.096262
С	-3.735777	1.372885	-0.507198
С	-5.116060	1.700827	-0.510572
С	-5.908702	0.661135	-0.105715
S	-4.972758	-0.750318	0.299283
Η	-2.955977	2.062588	-0.808738
Η	-5.513875	2.664108	-0.804269
С	-7.391023	0.661128	0.039980
F	-7.925626	1.770667	-0.510204
F	-7.956208	-0.413233	-0.557384
F	-7.779991	0.625015	1.336050

IIIB'

Job type: Geometry optimization.

Method: RB3LYP

Basis set: 6-31G**

Cartesian coordinates:

Η	-1.470741	-3.307495	-0.365441
С	-2.038451	-2.393902	-0.225320
Η	-3.917537	-3.366901	-0.460312
С	-3.401655	-2.425840	-0.289013
С	-2.062435	0.003721	0.129029
С	-4.181246	-1.234661	-0.151503
С	-1.331577	-1.159622	-0.010376
С	-3.485604	0.012798	0.059846
С	-5.577086	-1.237101	-0.219651
Η	-3.707522	2.131935	0.359649
Η	-1.554783	0.945951	0.318420
С	-6.322775	-0.057526	-0.085955
Η	-6.099015	-2.177543	-0.381466
С	-7.749662	-0.045314	-0.154889
С	-5.628987	1.191527	0.128846
Η	-5.875813	3.326380	0.426101
С	-4.230091	1.191984	0.197325
С	-8.451210	1.124069	-0.021072
Η	-8.269614	-0.985896	-0.317117
Η	-9.535776	1.118562	-0.076170
С	-7.767259	2.356475	0.191037
Н	-8.340129	3.273163	0.295508

С	-6.399666	2.388019	0.263925
С	0.129428	-1.175012	0.054890
S	1.078342	0.261393	-0.282225
С	2.588136	-0.579595	0.026833
С	2.338899	-1.898706	0.348248
С	0.963846	-2.231185	0.360132
Η	3.126501	-2.603523	0.590442
Η	0.594944	-3.215811	0.621391
С	3.857125	0.102925	-0.079166
С	4.090458	1.464847	-0.196598
С	5.462653	1.788652	-0.273218
С	6.290343	0.685563	-0.214773
S	5.361315	-0.789364	-0.073159
Η	3.295370	2.201801	-0.210527
Η	5.833936	2.803240	-0.362116
С	7.755162	0.586388	-0.258600
0	8.311523	-0.502814	-0.183260
С	8.547160	1.874707	-0.410082
Η	8.321078	2.354604	-1.368533
Η	9.610415	1.636867	-0.368293
Η	8.299779	2.587731	0.383258

IIIC'

Job type: Geometry optimization. Method: RB3LYP Basis set: 6-31G** Cartesian coordinates:

Н	-2.615945	-3.405712	0.370996	
С	-3.123544	-2.456216	0.239619	
Н	-5.061344	-3.306467	0.470689	
С	-4.485633	-2.399558	0.305940	
С	-2.991446	-0.057882	-0.093398	
С	-5.185869	-1.158966	0.177385	
С	-2.339032	-1.268555	0.032171	
С	-4.410894	0.042803	-0.022834	
С	-6.579033	-1.072606	0.241865	
Н	-4.496492	2.175010	-0.305975	
Н	-2.423766	0.850828	-0.276041	
С	-7.247227	0.153178	0.113576	
Н	-7.159773	-1.979434	0.394646	
С	-8.670684	0.255327	0.175323	
С	-6.473962	1.356843	-0.088693	
Н	-6.583341	3.505742	-0.371203	
С	-5.077670	1.268650	-0.152239	
С	-9.295590	1.467776	0.045235	
Н	-9.249501	-0.651822	0.327689	
Н	-10.378564	1.531026	0.093922	
С	-8.533366	2.655613	-0.154126	
Н	-9.046280	3.607445	-0.255236	

С	-7.166126	2.601097	-0.218713
С	-0.883009	-1.381266	-0.046801
С	-0.127717	-2.487691	-0.384114
С	1.265484	-2.251996	-0.382225
С	1.608907	-0.959351	-0.036812
S	0.164951	-0.021980	0.308154
Η	-0.568617	-3.437118	-0.662657
Η	2.000128	-3.003075	-0.650489
С	2.922014	-0.370728	0.061325
S	4.356050	-1.367563	0.015652
С	5.387960	0.039047	0.160239
С	4.640067	1.201470	0.251714
С	3.253137	0.972157	0.196346
Η	5.084157	2.184137	0.347312
Η	2.510787	1.760804	0.235490
С	6.823818	-0.166841	0.168321
0	7.362619	-1.258008	0.081463
С	7.708833	1.101691	0.293468
F	9.002488	0.785040	0.288423
F	7.471256	1.951602	-0.731885
F	7.434682	1.766141	1.439127

IIID

Job type: Geometry optimization.

Method: RB3LYP

Basis set: 6-31G**

Η	-0.843961	-2.399995	-0.379481	C
С	-1.626360	-1.656652	-0.260516	C
Н	-3.188408	-3.102965	-0.307573	С

С	-2.933937	-2.049525	-0.229321
С	-2.269663	0.670638	-0.039606
С	-3.993490	-1.097309	-0.108040

С	-1.264722	-0.268752	-0.167726
С	-3.644700	0.301088	-0.013554
С	-5.340512	-1.469503	-0.077553
Н	-4.405531	2.304054	0.186097
Н	-2.019051	1.721765	0.069534
С	-6.364221	-0.519860	0.044338
Н	-5.601931	-2.522638	-0.150186
С	-7.744835	-0.886141	0.077077
С	-6.017001	0.879788	0.141934
Н	-6.805902	2.891251	0.340172
С	-4.667516	1.251195	0.111597
С	-8.723075	0.065497	0.197839
Н	-8.005014	-1.938826	0.003817
Н	-9.768347	-0.227963	0.221202
С	-8.380997	1.446052	0.293910
Н	-9.170319	2.185732	0.388619
С	-7.069408	1.839518	0.266748

С	0.138485	0.144255	-0.209124
С	0.668434	1.359860	-0.595664
С	2.076947	1.425414	-0.505088
С	2.658065	0.257197	-0.050249
S	1.422679	-0.940639	0.288597
Н	0.058073	2.171319	-0.973084
Н	2.654719	2.295375	-0.797346
С	4.055136	-0.041753	0.151236
S	5.244398	1.245776	0.205894
С	6.507535	0.073582	0.440220
С	6.049775	-1.220291	0.489854
С	4.650799	-1.284346	0.325271
Н	6.709522	-2.066430	0.628757
Н	4.089619	-2.211242	0.311453
N	7.862062	0.505057	0.559138
0	8.074505	1.722373	0.483347
0	8.725302	-0.360301	0.730721

IIIE'

Job type: Geometry optimization.

Method: RB3LYP

Basis set: 6-31G**

Η	-2.677508	-3.368595	-0.454562
С	-3.192946	-2.428059	-0.292358
Η	-5.122318	-3.279472	-0.582484
С	-4.554458	-2.376489	-0.374677
С	-3.081041	-0.043720	0.137301
С	-5.264358	-1.146175	-0.206086
С	-2.419188	-1.244643	-0.028170
С	-4.499945	0.051120	0.052866
С	-6.657091	-1.065275	-0.285404

Η	-4.602356	2.169781	0.420116
Н	-2.521755	0.860541	0.362739
С	-7.334539	0.150490	-0.116212
Н	-7.230203	-1.968557	-0.481601
С	-8.757786	0.246746	-0.191805
С	-6.571687	1.349425	0.145213
Н	-6.697843	3.484438	0.512777
С	-5.175829	1.266921	0.223219
С	-9.391739	1.449300	-0.020327

Н	-9.328892	-0.656850	-0.387893	C	5.322997	0.157536	-0.007881
Η	-10.474378	1.508352	-0.080250	S	4.278576	-1.265399	0.122829
С	-8.639685	2.632488	0.236872	Н	2.402705	1.823547	-0.169917
Η	-9.159940	3.576371	0.369943	Н	4.938104	2.295040	-0.218750
С	-7.273062	2.583358	0.316868	C	6.754336	-0.020225	0.018623
С	-0.963783	-1.349458	0.064336	C	7.675056	1.012103	-0.060586
S	0.075793	0.030336	-0.230019	C	9.082619	0.755906	-0.031727
С	1.524547	-0.906508	0.098141	C	7.341024	2.395675	-0.173216
С	1.188040	-2.214026	0.394729	Ν	10.231424	0.564037	-0.009291
С	-0.202546	-2.461179	0.371509	Ν	7.090590	3.529716	-0.264863
Η	1.925315	-2.969238	0.643690	C	7.269824	-1.435685	0.142781
Н	-0.638655	-3.423212	0.611383	Н	6.917987	-1.888446	1.076289
С	2.828890	-0.299886	0.033546	Н	8.358081	-1.477733	0.133235
С	3.151934	1.043409	-0.102002	Н	6.895498	-2.051881	-0.681568
С	4.532192	1.298167	-0.124582				

3. *Procedure for testing the solubility*

To 1 mg of each material was added 1 ml of CHCl₃. In the case of derivatives where the clear solution was observed after dissolving only 1 mg of material in 1 ml of chloroform, more material was added until a saturation point was reached. These solutions were transferred to a weighed vial through the syringe equipped by PTFE filters (0.45 μ m) to filter off the undissolved material. After spontaneous evaporation of the solvent, the vials were weighed, and the results are shown on the graph pictures.

4. Optical properties analysis



Figure S1. 10⁻⁴ M Toluene solution of **IIA-IIE** under ambient lighting (left) and under 365 nm UV light (right).



Figure S2. 10⁻⁴ M Toluene solution of **IIIA-IIIE** under ambient lighting (left) and under 365 nm UV light (right).

4.1. TD-DFT study

Table S3. The comparison of the calculated maximum absorption wavelengths λ_{max} (nm) of **IIA-IIE** by TD-DFT with 6-31G(d,p) base and various functional.

Compound	B3LYP	CAM-B3LYP	ω-B97XD	Experiment
Compound	λ_{\max} [nm]	λ_{\max} [nm]	λ_{\max} [nm]	λ_{\max} [nm]
IIA	391.92	351.85	347.28	363
IIB	425.71	376.09	370.31	395
IIC	456.86	394.62	387.02	426
IID	478.75	401.47	392.06	435
IIE	515.29	442.96	433.92	457

Table S4. The comparison of the calculated maximum absorption wavelengths λmax (nm) of **IIIA-IIIE** by TD-DFT with 6-31G(d,p) base and various functional.

Compound	B3LYP		CAM-B3LYP		ω-B97XD		Experiment
Compound	$\lambda_{\max 1}$ [nm]	λ_{max2} [nm]	λ_{max1} [nm]	λ_{max2} [nm]	λ_{max1} [nm]	λ_{max2} [nm]	λ_{\max} [nm]
IIIA	374.47	446.92	339.74	382.92	336.94	375.78	394
IIIB	391.60	470.55	-	394.54	346.29	386.16	421
IIIC	423.32	517.99	-	410.76	-	399.83	448
IIID	432.44	541.87	-	413.67	-	400.94	447
IIIE	468.90	577.84	-	452.87	-	440.60	469



Figure S3. Graphical comparison of functionals on maximum absorption wavelength λ max (nm) of **IIA-IIE** (left) and **IIIA-IIIE** (right).

	CAM-B3LYP						
comp	$S_0 \rightarrow S_1$		comp	$S_0 \rightarrow S_1$		$S_0 \rightarrow S_2$	
	f	MO composition		f	MO composition	f	MO composition
IIA	1.1175	HOMO-1→LUMO (3%)	IIIA	0.6804	HOMO-1→LUMO (21%)	0.9389	HOMO-2→LUMO+1 (20%)
		HOMO→LUMO (97%)			HOMO-1→LUMO+1 (27%)		HOMO-1→LUMO (43%)
					HOMO→LUMO (52%)		HOMO→LUMO+1 (37%)
IIB	1.2382	HOMO-1→LUMO (4%)	IIIB	1.0428	HOMO-1→LUMO (28%)	0.6307	HOMO-1→LUMO (40%)
		HOMO→LUMO (96%)			HOMO-1→LUMO+1 (24%)		HOMO-1→LUMO+1 (19%)
					HOMO→LUMO (48%)		HOMO→LUMO+1 (40%)
IIC	1.2474	HOMO-2→LUMO (2%)	IIIC	1.1801	HOMO-1→LUMO (33%)	0.4247	HOMO-1→LUMO (31%)
		HOMO-1→LUMO (6%)			HOMO→LUMO (44%)		HOMO-1→LUMO+1 (20%)
		HOMO→LUMO (92%)			HOMO→LUMO+1 (23%)		HOMO→LUMO (15%)
							HOMO→LUMO+1 (34%)
IID	1.2322	HOMO-2→LUMO (19%)	IIID	1.2924	HOMO-2→LUMO (16%)	0.2324	HOMO-2→LUMO (16%)
		HOMO-1→LUMO (22%)			HOMO-1→LUMO (28%)		HOMO-1→LUMO (29%)
		HOMO→LUMO (41%)			HOMO→LUMO (36%)		HOMO-1→LUMO+1 (19%)
		HOMO→LUMO+1 (18%)			HOMO→LUMO+1 (20%)		HOMO→LUMO+1 (36%)
IIE	1.5189	HOMO-1→LUMO (34%)	IIIE	1.5681	HOMO-1→LUMO (37%)	0.2495	HOMO-1→LUMO (28%)
		HOMO→LUMO (66%)			HOMO→LUMO (44%)		HOMO-1 \rightarrow LUMO+1 (20%)
					HOMO→LUMO+1 (19%)		HOMO→LUMO (20%)
							HOMO→LUMO+1 (32%)

Table S5. Summary of $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions and oscillator strength *f* of **II/IIIA-E**.



Figure S4. Calculated molecular orbitals of IIA-IIE.



Figure S5. Calculated molecular orbitals of IIIA-IIIE.



Figure S6. Calculated UV-Vis spectra of derivatives II/IIIA-E (TD-DFT, CAM-B3LYP,6-31G(d,p)).

5. Electrochemical analysis



Figure S7. Spectrum of energy-resolved electrochemical impedance spectroscopy (ER-EIS) of the supporting electrolyte (0.1 M TBAPF₆ in THF).

The LUMO level positions on the energetic scale indicated by arrows in the following graphs are obtained as the intercept point of the linear region of the DOS with the energy axis.



Figure S8. ER-EIS of naphthalene derivatives IIA-E.



Figure S9. ER-EIS of anthracene derivatives IIIA-E.

6. Crystallographic data

Identification code	IIB	IIC*	
Empirical formula	$C_{24}H_{22}OS_2$	$C_{26}H_{11}F_{15}OS_2$	
Formula weight	390.53	688.47	
Temperature/K	100.0(1)	100.0 (1)	
Crystal system	monoclinic	monoclinic	
Space group	P 2 ₁ /c	P 2 ₁ /c	
a/Å	41.2198(6)	29.2832(8)	
b/Å	5.82020(10)	5.93510(10)	
c/Å	8.0162(2)	14.6720(3)	
$lpha/^{\circ}$	90	90	
β/°	90.988(1)	97.692(2)	
$\gamma^{/\circ}$	90	90	
Volume/Å ³	1922.86(6)	2527.03(10)	
Ζ	4	4	
$\rho_{calc}g/cm^3$	1.349	1.810	
μ/mm^{-1}	2.583	3.175	
F(000)	824.0	1368.0	
Crystal size/mm ³	0.23 x 0.20 x 0.09	0.118	
Radiation	CuK(a)	Cu(Ka)	
20 range for data collection/°	6.434 to 143.794	6.092 - 133.192	
Index ranges	$-49 \le h \le 49, -6 \le k \le 7, -5 \le 1 \le 9$	$-34 \le h \le 34, -7 \le k \le 4, -17 \\ \le 1 \le 17$	
Reflections collected	33369	100040	
Independent reflections	3522	4428	
Data/restraints/parameters	3522 / 0 / 246	4270 / 0 / 398	
Goodness-of-fit on F ²	1.032	1.092	
Final R indexes [I>= 2σ (I)]	0.0296	0.1209	
Final R indexes [all data]	0.0307	0.1333	
Largest diff. peak/hole / e Å ⁻ $_{3}$	0.35 / -0.19	0.96/-0.61	

Table S6. Crystallographic data of derivatives IIB and IIC.

* Data of crystal structure **IIC** was integrated up to four orientation matrices. No improvement. Single crystal consists of small domains shifted in one direction.



Figure S10. Detailed view to intermolecular interaction distances d_i of derivative IIB.



Figure S11. Herringbone packing motif and molecular packing within the crystal structure of IIC.

7. NMR spectra



Figure S12. ¹H NMR (300 MHz, C₂D₂Cl₄) of 5-(naphthalen-2-yl)-5'-(perfluorohexyl)-2,2'-bithiophene (IIA).



Figure S13. ¹⁹F NMR (282 MHz, C₂D₂Cl₄) of 5-(naphthalen-2-yl)-5'-(perfluorohexyl)-2,2'-bithiophene (IIA).



Figure S14. ¹³C NMR (151 MHz, C₂D₂Cl₄) of 5-(naphthalen-2-yl)-5'-(perfluorohexyl)-2,2'-bithiophene (IIA).



Figure S15. ¹H NMR (300 MHz, C₂D₂Cl₄) of 5-(anthracen-2-yl)-5'-(perfluorohexyl)-2,2'-bithiophene (IIIA).



Figure S16. ¹⁹F NMR (282 MHz, C₂D₂Cl₄) of 5-(anthracen-2-yl)-5'-(perfluorohexyl)-2,2'-bithiophene (IIIA).



Figure S17. ¹H NMR (300 MHz, CDCl₃) of 1-[5'-(naphthalen-2-yl)-2,2'-bithiophen-5-yl]pentadecafluorooctan-1one (**IIC**).



Figure S18. ¹⁹F NMR (282 MHz, CDCl₃) of 1-[5'-(naphthalen-2-yl)-2,2'-bithiophen-5-yl]pentadecafluorooctan-1-one (**IIC**).



Figure S19. ¹³C NMR (75 MHz, CDCl₃) of 1-[5'-(naphthalen-2-yl)-2,2'-bithiophen-5-yl]pentadecafluorooctan-1-one (**IIC**).



1-one (IIIC).

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Figure S21. ¹⁹F NMR (282 MHz, C₂D₂Cl₄) of 1-[5'-(anthracen-2-yl)-2,2'-bithiophene-5-yl]pentadecafluorooctan-1-one (**IIIC**).



Figure S22. ¹H NMR (600 MHz, CDCl₃) of 1-[5'-(naphthalen-2-yl)-2,2'-bithiophen-5-yl]hexan-1-one (IIB).



Figure S23. ¹³C NMR (151 MHz, CDCl₃) of 1-[5'-(naphthalen-2-yl)-2,2'-bithiophen-5-yl]hexan-1-one (IIB).



Figure S24. ¹H NMR (600 MHz, CDCl₃) of 1-[5'-(anthracen-2-yl)-2,2'-bithiophen-5-yl]hexan-1-one (IIIB).



Figure S25. ¹H NMR (300 MHz, CDCl₃) of 5-(naphthalene-2-yl)-5'-nitro-2,2'-bithiophene (IID).



Figure S26. ¹³C NMR (75 MHz, CDCl₃) of 5-(naphthalene-2-yl)-5'-nitro-2,2'-bithiophene (IID).



Figure S27. ¹H NMR (600 MHz, CDCl₃) of 5-(anthracene-2-yl)-5'-nitro-2,2'-bithiophene (IIID).



Figure S28. ¹³C NMR (151 MHz, CDCl₃) of 5-(anthracene-2-yl)-5'-nitro-2,2'-bithiophene (IIID).



Figure S29. ¹H NMR (600 MHz, CDCl₃) of {1-[5'-(naphthalen-2-yl)-2,2'-bithiophen-5-yl]hexylidene}-malononitrile (**IIE**).



Figure S30. ¹³C NMR (151 MHz, CDCl₃) of {1-[5'-(naphthalen-2-yl)-2,2'-bithiophen-5-yl]hexylidene}-malononitrile (**IIE**).



Figure S31. ¹H NMR (300 MHz, CDCl₃) of {1-[5'-(anthracen-2-yl)-2,2'-bithiophen-5-yl]hexylidene}-malononitrile (**IIIE**).



Figure S32. ¹³C NMR (151 MHz, CDCl₃) of $\{1-[5'-(anthracen-2-yl)-2,2'-bithiophen-5-yl]hexylidene\}-malononitrile (IIIE).$



Figure S33. ¹H NMR (600 MHz, CDCl₃) of 1-(5'-bromo-2,2'-bithiophen-5-yl)hexan-1-one (IVB).



Figure S34. ¹³C NMR (151 MHz, CDCl₃) of 1-(5'-bromo-2,2'-bithiophen-5-yl)hexan-1-one (IVB).



Figure S35. ¹H NMR (600 MHz, CDCl₃) of [1-(5-bromo-2,2'-bithiophen-5-yl)hexylidene]malononitrile (IVE).



Figure S36. ¹³C NMR (151 MHz, CDCl₃) of [1-(5-bromo-2,2'-bithiophen-5-yl)hexylidene]malononitrile (IVE).



Figure S37. ¹H NMR (300 MHz, CDCl₃) of 5-bromo-5'-nitro-2,2'-bithiophene (IVD).



Figure S38. ¹⁹F NMR (282 MHz, CDCl₃) of 1-(5'-bromo-2,2'-bithiophen-5-yl)pentadecafluorooctan-1-one (IVC).



Figure S39. ¹H NMR (300 MHz, CDCl₃) of 1-(5'-bromo-2,2'-bithiophen-5-yl)pentadecafluorooctan-1-one (IVC).



Figure S40. ¹³C NMR (75 MHz, CDCl₃) of 1-(5'-bromo-2,2'-bithiophen-5-yl)pentadecafluorooctan-1-one (IVC).