Electronic Supplementary Information

Oligothiophene quinoids containing benzo[*c*]thiophene unit for stabilization of quinoidal electronic structure

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Supplementary Figures

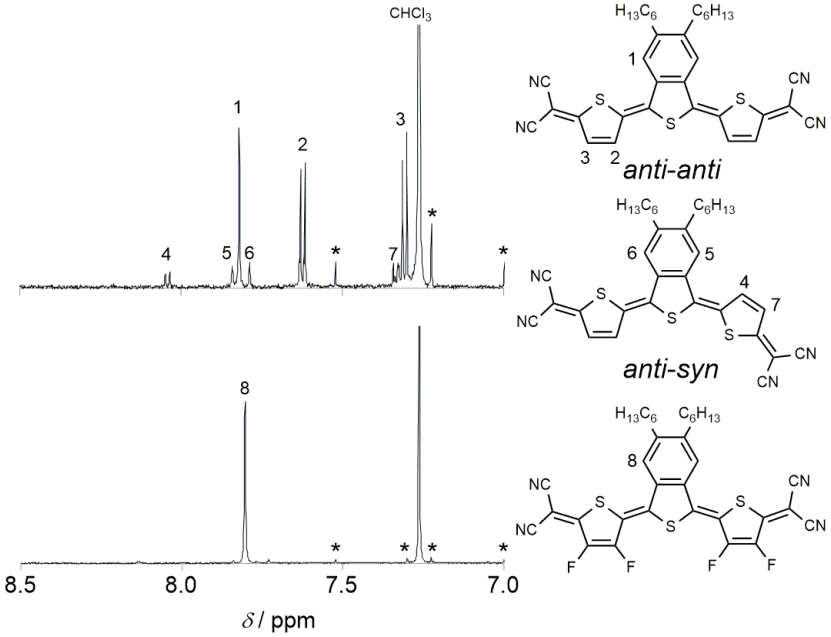


Fig. S1 Maginified ^{1}H NMR spectra of **BTQ** and **BTQ-F** at room temperature in $CDCl_3$.

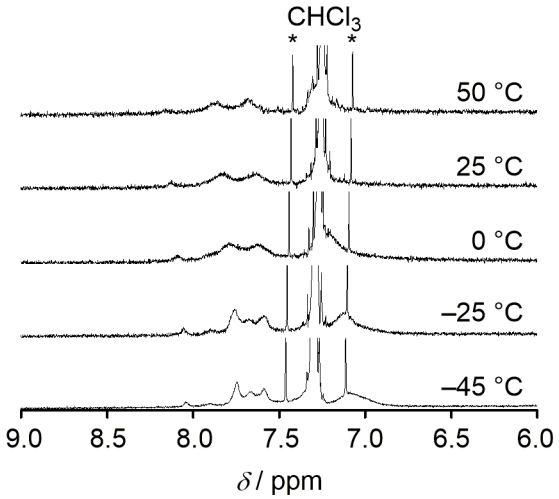


Fig. S2 VT-NMR spectra of **BTQ-6** in aromatic regions in $CDCl_3$. Signals pointed by asterisk are satellite peak of $CHCl_3$.

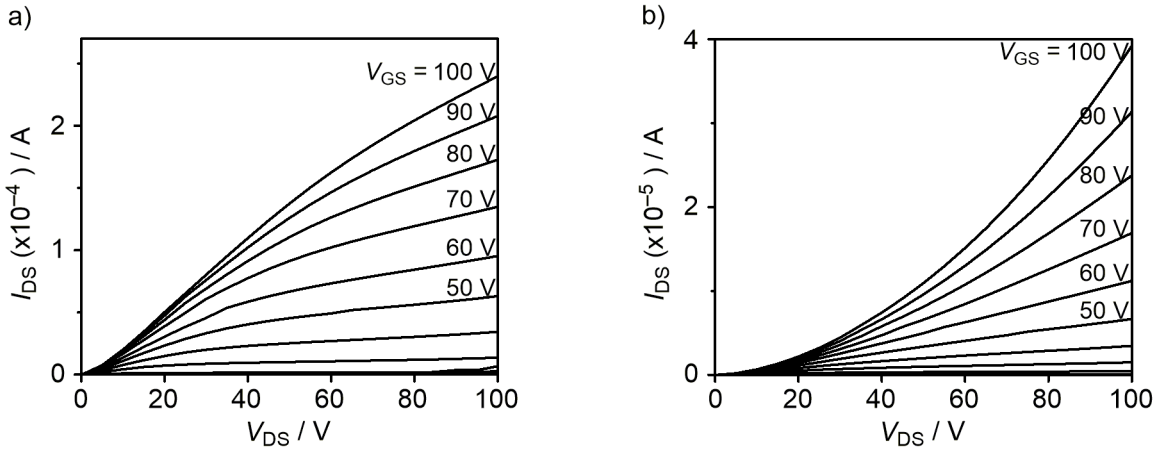


Fig. S3 Output characteristics of the OFET using (a) **BTQ** and (b) **BTQ-F** at source–drain voltage of 100 V. I_{DS}, and V_{DS} denotes source–drain current and source–drain voltage, respectively.

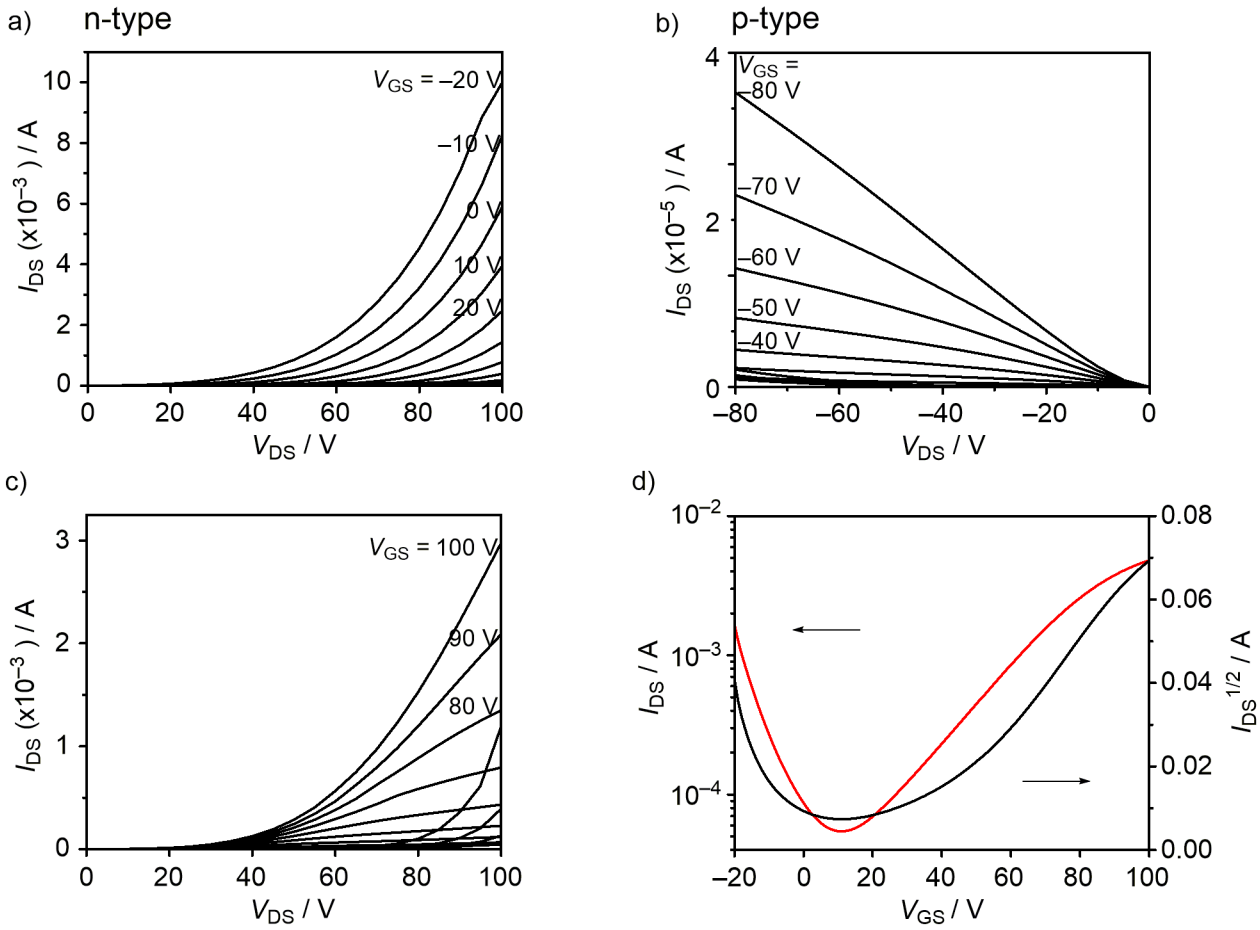


Fig. S4 Output characteristics of (a) **BTQ-6**, (b) **BTQ-6**, and (c) **TQ**. (d) Transfer characteristics of OFETs using **TQ**.

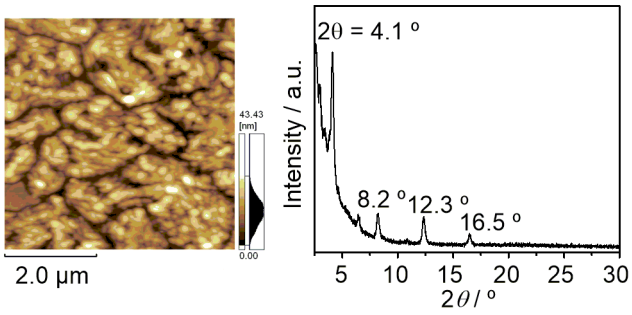


Fig. S5 AFM images and XRD data of **TQ**.

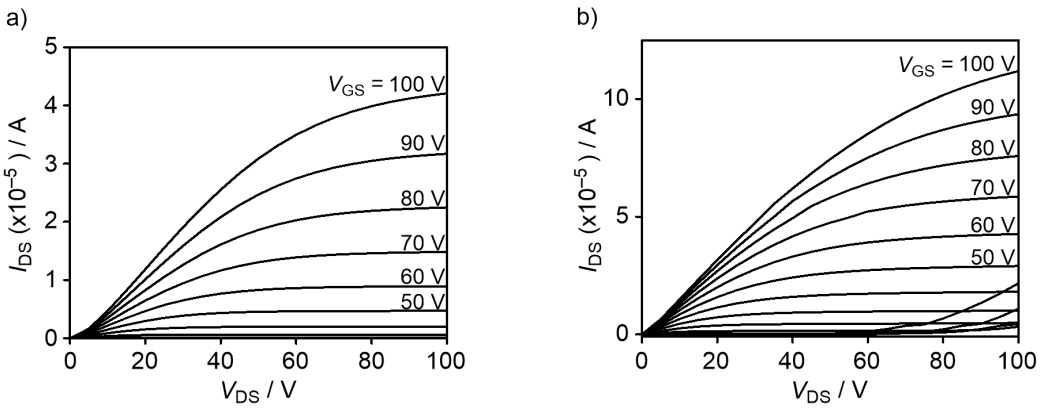


Fig. S6 Output characteristics of the 1-hexadecanethiol-treated OFETs using (a) **BTQ** and (b) **TQ**.

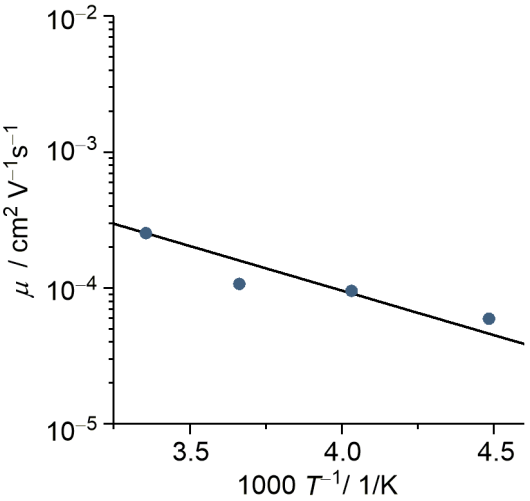


Fig. S7 Temperature dependence of carrier mobility for **BTQ**. Black solid lines were fitted from the equation $\mu = \mu_0 \exp(-E_a k^{-1}T^{-1})$, where E_a is an activation energy, k is Boltzmann's constant, and μ_0 is the mobility at $1000/T = 0$.

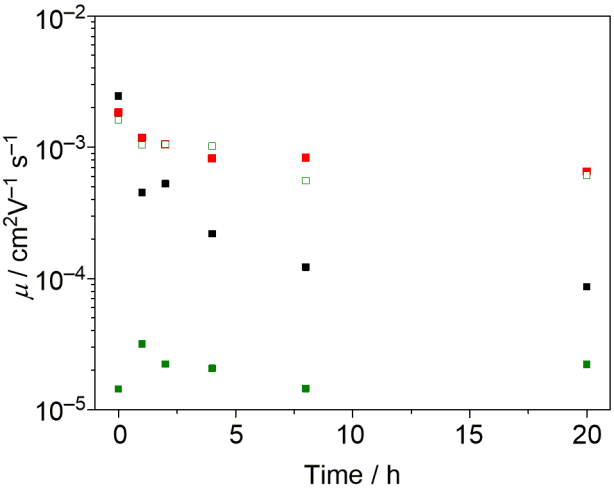


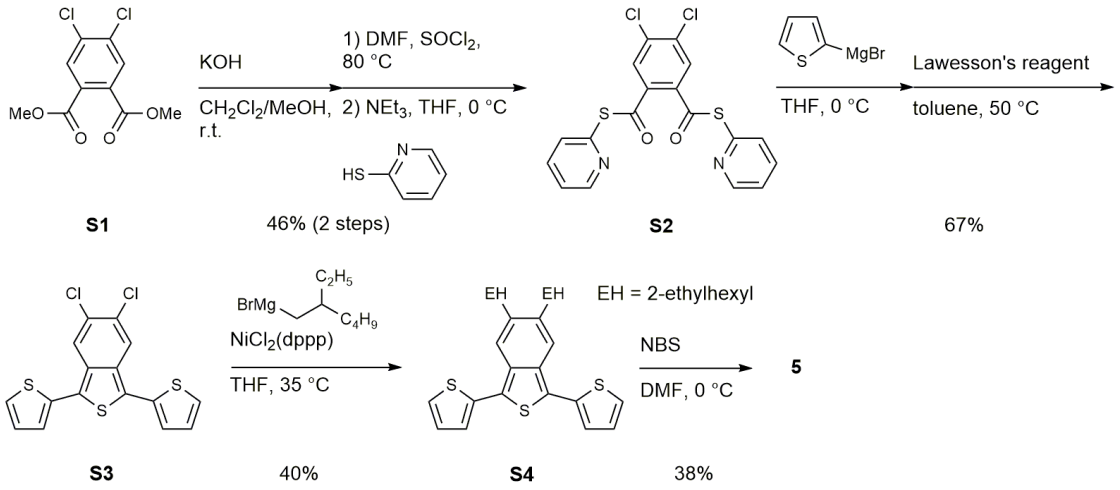
Fig. S8 Plots of electron mobility against time for **BTQ** (red square), **TQ** (black square), and **BTQ-6** (green square). Hole mobility of **BTQ-6** is represented as empty green square.

General Information

Column chromatography was performed on silica gel. KANTO Chemical silica gel 60N (40–50 μm). Thin-layer Chromatography (TLC) plates were visualized with UV light. Preparative gel-permeation chromatography (GPC) was performed on a Japan Analytical LC-918 equipped with JAI-GEL 1H/2H. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 or JEOL JNM-ECA600 spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. ^{19}F NMR spectra were recorded on a JEOL JNM-ECA600 spectrometer in $CDCl_3$. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triple, m = multiplet, br = broad), coupling constant (Hz), and integration. Mass spectra were obtained on a Shimadzu AXIMA-TOF. UV-vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. All spectra were obtained in spectrograde solvents. Cyclic voltammetry was carried out on a BAS CV-620C voltammetric analyzer using a platinum disk as the working electrode, platinum wire as the counter electrode, and $Ag/AgNO_3$ as the reference electrode at a scan rate of 100 mV s^{-1}. Elemental analyses were performed on PerkinElmer LS-50B by the elemental analysis section of the Comprehensive Analysis Center (CAC) of ISIR, Osaka University. The surface structures of the deposited organic film were observed by atomic force microscopy (Shimadzu, SPM9600), and the film crystallinity was evaluated by an X-ray diffractometer (Rigaku, SmartLab). X-ray diffraction patterns were obtained using Bragg-Brentano geometry with CuKα radiation as an X-ray source with an acceleration voltage of 45 kV and a beam current of 200 mA. The scanning mode was set to 2θ–θ scans between 2º–30º with scanning steps of 0.01º.

Synthesis

Unless stated otherwise, all reagents were purchased from commercial sources and used without purification. Compounds **1** and 2-bromo-3,4-difluoro-5-trimethylsilyl-thiohene were prepared by the reported procedures.[1,2]



Scheme S1. Synthetic route of **5**.

*Synthesis of **S2***: Compound **S2** was synthesized from **S1** with a yield of 46% by following the procedure used for the preparation of **2**. Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.31-7.35 (m, 2H), 7.73-7.80 (m, 4H), 7.96 (s, 2H), 8.64 (m, 2H). This compound was used for next step without further purification.

*Synthesis of **S3***: Compound **S2** (6.9 g, 16.4 mmol) was placed in a two-necked-bottomed flask and dissolved in THF (112 mL). 2-Thienyl magnesium bromide (32.8 mmol, 0.5 M in THF) was added slowly to the solution at 0 °C. The reaction mixture was stirred for 30 min. and then quenched by addition of 10% HCl aq.. The resultant mixture was extracted with $CHCl_3$, and the combined organic layer was washed with 5% NaOH aq., $NaHCO_3$ aq., and water. After drying over with $MgSO_4$, the solvent was removed under reduced pressure to give **D** as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.11 (dd, J = 5.0, 3.7 Hz, 2H), 7.47 (dd, J = 3.7, 0.9 Hz, 2H), 7.71 (dd, J = 5.0, 0.9 Hz, 2H), 7.82 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 128.3, 131.0, 135.2, 135.3, 135.8, 138.7, 143.2, 185.7.

Lawesson's reagent (9.4 g, 23.4 mmol) was added to a solution of **D** in toluene (260 mL) and stirred at 50 °C. After stirring for 1 h, the solvent was removed under reduced pressure and purified by column chromatography on silica gel ($CHCl_3$). Then obtained solid was recrystallized from $CHCl_3$/hexance to give **S3** (4.0 g, 67%) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.16 (dd, J = 5.0, 3.7 Hz, 2H), 7.32 (dd, J = 3.7, 0.9 Hz, 2H), 7.42 (dd, J = 5.0, 0.9 Hz, 2H), 8.03 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 122.2, 126.6, 126.7, 127.1, 128.5, 130.3, 133.6, 134.7; HRMS (APCI) *m/z* 366.9232 ($[M+H]^+$) ($[M+H]^+$, Calcd 366.9238).

*Synthesis of **S4***: Compound **S3** (1.13 g, 3.08 mmol) and $NiCl_2$(dppp) (85 mg, 0.157 mmol) were placed in a two-necked-bottomed flask and dissolved in THF (10.8 mL). (2-Ethylhexyl)magnesium bromide (9.38 mmol, 1.0 M in Et_2O) was added slowly to the solution at 0 °C. The reaction mixture was stirred for 1h at 0 °C, 11 h at 35 °C, and then quenched by addition of water. The resultant mixture was extracted with EtOAc, and the combined organic layer was washed with water. After drying over with $MgSO_4$, the solvent was removed under reduced pressure and purified by column chromatography on silica gel (hexane), followed by purification with preparative GPC ($CHCl_3$) to give **S4** (660 mg, 40%) as a red oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.85-0.93 (m, 12H), 1.22-1.42 (m, 16H), 1.63 (m, 2H), 2.59 (m, 4H), 7.14 (d, J = 5.0, 3.7 Hz, 2H), 7.32 (dd, J = 3.7, 1.4 Hz, 2H), 7.35 (dd, J = 5.0, 1.4 Hz, 2H), 7.66 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 10.8, 14.2, 23.2, 25.5, 28.8, 32.5, 37.7, 39.7, 121.0, 124.6, 124.9, 127.8, 134.6, 136.2, 138.4; HRMS (APCI) *m/z* 523.2512 ($[M+H]^+$) ($[M+H]^+$, Calcd 523.2521).

*Synthesis of **5***: NBS (224 mg, 1.26 mmol) was added in two portions to a solution of **S4** (660 mg, 1.26 mmol) in DMF (35 mL) at 0 °C. After stirring for 4 h at 0 °C, the reaction was quenched by addition of water. The combined organic was extracted with EtOAc and washed with water. After drying over with $MgSO_4$, the solvent was removed under reduced pressure and purified by column chromatography on silica gel (hexane) to give **5** (290 mg, 38%) as a red oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.82-0.93 (m, 12H), 1.22-1.42 (m, 16H), 1.62 (m, 2H), 2.59 (m, 4H), 7.04 (d, J = 4,4 Hz, 1H), 7.08 (d, J = 4,4 Hz, 1H), 7.14 (dd, J = 5.0, 3.8 Hz, 1H), 7.32 (dd, J = 3.8, 1.0 Hz, 1H), 7.36 (dd, J = 5.0, 1.0 Hz, 1H), 7.56 (s, 1H), 7.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 10.9, 14.2, 23.2, 25.6, 28.8, 32.5, 37.7, 40.0, 111.4, 120.7, 121.1, 123.3, 125.2, 125.3, 125.4, 127.8,

130.6, 134.5, 134.8, 136.0, 137.8, 138.6, 138.9; HRMS (APCI) *m/z* 601.1626 ($[M+H]^+$) ($[M+H]^+$, Calcd 601.1627).

*Synthesis of **2***: Compound **1** (1.44 g, 4.41 mmol) was placed in a round-bottom flask and dissolved in methanol (4.8 mL). Potassium hydroxide (988 mg, 17.6 mmol) was added to the mixture at room temperature. After stirring for 5 min, water was poured into the reaction mixture. The aqueous layer was washed with ether to remove unreacted ester compounds and then acidified with 6 *N* hydrochloric acid (HCl). The precipitate was extracted with ether and dried over $MgSO_4$. The solvent was removed under reduced pressure to give dicarboxilic acid **A** as a white solid (1.3 g). ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.86 (t, J = 7.2 Hz, 6H), 1.21-1.39 (m, 12H), 1.45-1.57 (m, 4H), 2.58-2.66 (m, 4H), 7.43 (s. 2H), 12.5-13.2 (br, 2H). This compound was used for next step without further purification. **A** (550 mg, 1.64 mmol) was placed in a round-bottom flask. Thionyl chloride (10 mL) and DMF as a catalyst was added to the flask, and the reaction mixture was reflux for overnight. After removal of thionyl chloride and DMF under reduced pressure, the residue was resolved in THF (5.8 mL). Then, this solution was added to a solution of triethylamine (0.55 mL) and 2-mercaptopyridine (362 mg, 3.28 mmol) in THF (7.5 mL) at 0 °C. After vigorously stirring for 10 min., the reaction was quenched by addition of 2% HCl aq.. The resultant mixture was extracted with $CHCl_3$. The combined organic layer was washed with 10% sodium hydroxide (NaOH) aq., and water. After drying over with $MgSO_4$, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane:EtOAc = 5:3) to give **2** (810 mg, 84%, 2 steps) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.91 (t, J = 7.0 Hz, 6H), 1.30-1.46 (m, 12H), 1.55-1.65 (m, 4H), 2.66-2.72 (m, 4H), 7.28-7.32 (m, 2H), 7.65 (s, 2H), 7.74-7.82 (m, 4H), 8.62-8.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.4, 21.8, 28.6, 30.0, 30.9, 31.9, 122.9, 128.8, 129.7, 133.6, 136.5, 144.7, 149.6, 150.9, 189.4; HRMS (ESI) *m/z* 543.2107 ($[M+Na]^+$) ($[M+Na]^+$, Calcd 543.2110).

*Synthesis of **3a***: Compound **2** (810 mg, 1.56 mmol) was placed in a two-necked-bottomed flask and resolved in THF (11 mL). 2-Thienyl magnesium bromide (3.12 mmol, 0.5 M in THF) was added slowly to the solution at 0 °C. The reaction mixture was stirred for 30 min. and then quenched by addition of 10% HCl aq.. The resultant mixture was extracted with $CHCl_3$, and the combined organic layer was washed with 10% NaOH aq., $NaHCO_3$ aq., and water. After drying over with $MgSO_4$, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane:EtOAc = 8:1) to give **3a** (660 mg, 90%) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.90 (t, J = 7.0 Hz, 6H), 1.28-1.46 (m, 12H), 1.59-1.67 (m, 4H), 2.68-2.74 (m, 4H), 7.06 (dd, J = 5.0 and 3.6 Hz, 2H), 7.46 (dd, J = 3.6 and 1.2 Hz, 2H), 7.51 (s, 2H), 7.64 (dd, J = 5.0 and 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 22.6, 29.4, 30.9, 31.7, 32.7, 127.9, 130.2, 134.5, 134.8, 136.9, 143.8, 144.5, 188.5; MS MALDI-TOF (1,8,9-trihydroxyanthracene matrix) *m/*z 466.03 (M^+, Calcd 465.93); Anal. Calcd for $C_{28}H_{34}O_2S_2$: C 72.06, H 7.34; found: C 71.86, H 7.34.

*Synthesis of **3b***: Compound **2** (433 mg, 0.831 mmol) was placed in a two-necked-bottomed flask and dissolved in THF (3.5 mL). The Grignard solution (1.83 mmol, 0.5 M in THF), which was generated in situ by refluxing of 2-bromo-3,4-difluoro-5-trimethylsilylthiophene and magnesium for 30 min., was added slowly to the solution at

0 °C. The reaction mixture was stirred for 2 h and then quenched by addition of 10% HCl aq.. Purification was conducted by following the same procedure as **3a** to give **3b** (420 mg 74%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.35(s, 18H), 0.90 (t, J = 6.8 Hz, 6H), 1.30-1.42 (m, 12H), 1.58-1.64 (m, 4H); ^{19}F NMR (565 MHz, $CDCl_3$): δ –125.7, –122.9; ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ –0.9, 14.4, 22.9, 29.7, 31.1, 32.0, 33.0, 125.2, 125.6, 130.3, 136.4, 144.8, 146.4, 149.7, 185.5; MS MALDI-TOF (1,8,9-trihydroxyanthracene matrix) *m/z* 681.88 (M^+, Calcd 682.24); Anal. Calcd for $C_{34}H_{46}F_4O_2S_2Si_2$: C 59.79, H 6.79; found: C 59.56, H 6.64.

*Synthesis of **4a***: Davy's reagent (623 mg, 2.19 mmol) was added to a solution of **3a** (930 mg, 1.99 mmol) in toluene (61 mL) and stirred at 50 °C. After stirring for 1 h, the solvent was removed under vacuum and ethanol (61 mL) was added. This solution was stirred at 50 °C for 30 min. The solvent was removed under reduced pressure and purified by column chromatography on silica gel (hexane) to give the intermediate **B** (810 mg) as a red solid. NBS (619 mg, 1.74 mmol) was added in four portions to a solution of the **B** (810 mg) in DMF (28 mL) at 0 °C. After stirring for 2 h at 0 °C, the reaction was quenched by addition of water. The combined organic was extracted with EtOAc and washed with water. The solvent was removed under reduced pressure and purified by column chromatography on silica gel (hexane:CH_2Cl_2 = 1:1), followed by purification with preparative GPC ($CHCl_3$) to give **4a** (760 mg, 61%) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.91 (t, J = 6.8 Hz, 6H), 1.29-1.49 (m, 12H), 1.60-1.68 (m, 4H), 2.62-2.68 (m, 4H), 7.05 (d, J = 2.0 Hz, 2H), 7.09 (d, J = 2.0 Hz, 2H), 7.60 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 22.7, 29.4, 30.8, 31.8, 33.1, 111.8, 119.4, 124.1, 125.4, 130.6, 134.9, 137.4, 140.0; MS MALDI-TOF (1,8,9-trihydroxyanthracene matrix) *m/z* 623.55 (M^+, Calcd 624.00); Anal. Calcd for $C_{28}H_{32}Br_2S_3$: C 53.85, H 5.16; found: C 53.76, H 5.29.

*Synthesis of **4b***: Compound **4b** was synthesized from 3**b** with a yield of 46% by following the procedure used for the preparation of **4a**. Red solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.91 (t, J = 6.8 Hz, 6H), 1.31-1.50 (m, 12H), 1.59-1.68 (m, 4H), 2.67 (t, J = 7.6 Hz ,4H), 7.50 (s, 2H); ^{19}F NMR (565 MHz, $CDCl_3$): δ –132.3, –131.4; ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 14.1, 22.7, 29.3, 30.7, 31.8, 33.1, 90.9, 114.2, 119.3, 120.2, 135.7, 140.6, 140.7, 144.9; MS MALDI-TOF (1,8,9-trihydroxyanthracene matrix) *m/z* 695.02 (M^+, Calcd 695.96); Calcd for $C_{28}H_{28}Br_2F_4S_3$: C 48.28, H 4.05; found: C 48.22, H 4.23.

*Synthesis of **BTQ***: Sodium hydride (60% in oil) (20 mg, 0.51 mmol) was added to a suspension of malononitrile (17 mg, 0.25 mmol) in anhydrous 1,4-dioxane (3.0 mL) under nitrogen atmosphere and stirred for 10 min at room temperature. To this mixture was added **4a** (66 mg, 0.11 mmol) and $Pd(PPh_3)_4$ (12 mg, 0.011 mmol). After stirring for 4 h at reflux, the reaction was quenched by adding 1.0 M HCl aq., and then DDQ (36 mg, 0.16 mmol) was added to the mixture. After stirring for 30 min. at room temperature, the resulting mixture was extracted with CH_2Cl_2. The combined organic was washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane:CH_2Cl_2 = 5:1) to give **BTQ** (25 mg, 40%) as a blue solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.92 (t, J = 7.0 Hz, 6H), 1.32-1.52 (m, 12H), 1.62-1.71 (m, 4H), 2.80-2.86 (m, 4H), 7.31 (d, J = 2.8 Hz, 2H), 7.62 (d, J = 2.8 Hz, 2H), 7.82 (s, 2H);

^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 14.1, 22.6, 29.3, 31.1, 31.6, 33.5, 67.9, 113.1, 114.0, 126.6, 129.8, 129.9, 137.1, 140.4, 141.7, 147.0, 172.6; MS MALDI-TOF (1,8,9-trihydroxyanthracene matrix) *m/z* 591.98 (M^+, Calcd 592.18); Calcd for $C_{34}H_{32}N_4S_3$: C 68.88, H 5.44, N 9.45; found: C 68.56, H 5.45, N 9.38.

*Synthesis of **BTQ-F***: Compound **BTQ-F** was synthesized from **4b** with a yield of 30% by following the procedure used for the preparation of **BTQ**. Blue solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.92 (t, J = 6.8 Hz, 6H), 1.30-1.52 (m, 12H), 1.63-1.72 (m, 4H), 2.84 (t, J = 7.6 Hz, 4H), 7.80 (s, 2H); ^{19}F NMR (565 MHz, $CDCl_3$): δ –135.8, –111.8; ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 14.1, 22.6, 29.2, 30.7, 31.6, 33.3, 67.7, 111.2, 111.3, 112.6, 112.9, 126.8, 136.6, 140.5, 142.4, 147.6, 152.0; MS MALDI-TOF (1,8,9-trihydroxyanthracene matrix) *m/z* 663.84 (M^+, Calcd 664.14); HRMS (APCI) *m/z* 665.1479 ($[M+H]^+$) ($[M+H]^+$, Calcd 665.1485).

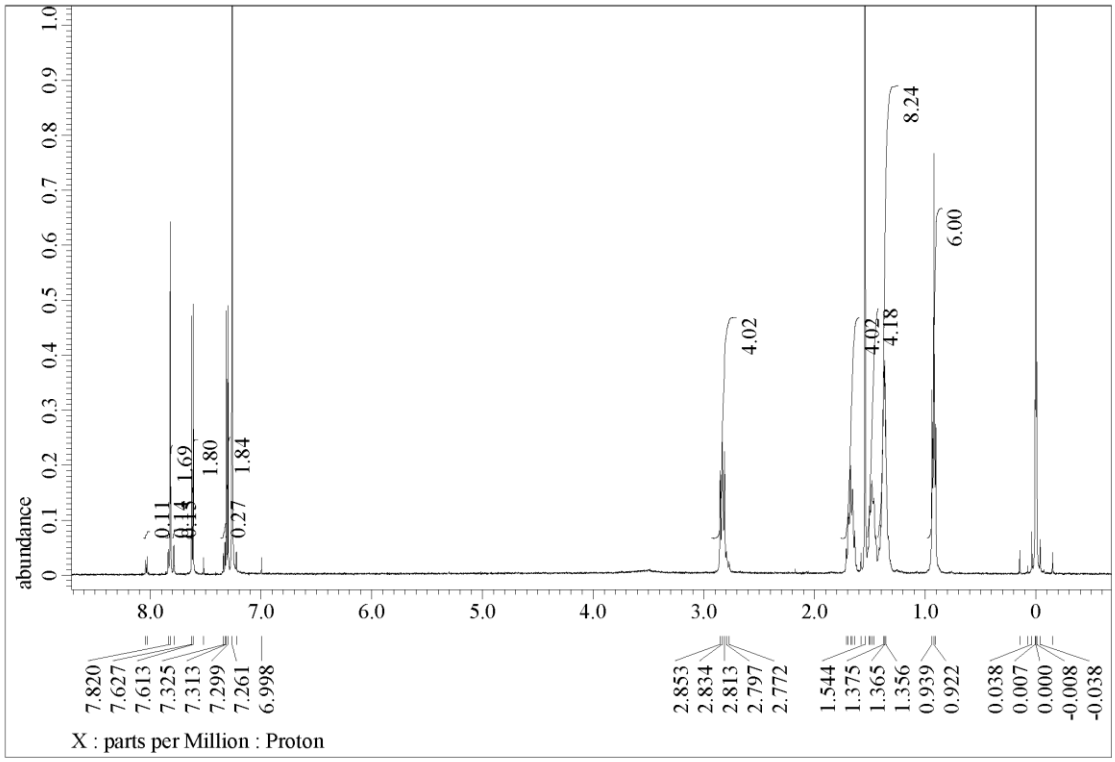
*Synthesis of **6***: **5** (110 mg, 0.183 mmol), bis(pinacolato)diboron (24.7 mg, 0.0967 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (15.0 mg, 0.0183 mmol), potassium fluoride (52.2 mg, 0.894 mmol), and toluene/methanol (2.5/2.5 mL) were placed in a microwave proof walled glass vial equipped with a snap cap. The glass vial was purged nitrogen, securely sealed, and heated in a microwave reactor with keeping a temperature at 70 °C for 15 min. The solvent was removed under reduced pressure and purified by column chromatography on silica gel (hexane:$CHCl_3$ = 1:1) to give **C** (87 mg, 91%) as a violet solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.86-0.96 (m, 24H), 1.22-1.46 (m, 32H), 1.60-1.70 (m, 4H), 2.54-2.70 (m, 8H), 7.15 (dd, J = 5.0, 3.7 Hz, 2H), 7.24 (d, J = 4.0 Hz, 2H), 7.27 (d, J = 4.0 Hz, 2H), 7.34 (dd, J = 3.7, 0.9 Hz, 2H), 7.37 (dd, J = 5.0, 0.9 Hz, 2H), 7.68 (s, 2H), 7.71 (s, 2H). NBS (39 mg, 0.220 mmol) was added in two portions to a solution of **C** (115 mg, 0.110 mmol) in THF (14 mL) at 0 °C. After stirring for 2 h at room temperature, the reaction was quenched by addition of water. The resulting mixture was extracted with EtOAc. The organic layer was washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and purified by column chromatography on silica gel ($CHCl_3$), followed by purification with preparative GPC ($CHCl_3$) to give **6** (111 mg, 84%) as a violet solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.85-0.96 (m, 24H), 1.24-1.46 (m, 32H), 1.59-1.69 (m, 4H), 2.54-2.68 (m, 8H), 7.06 (d, J = 4.1 Hz, 2H), 7.09 (d, J = 4.1 Hz, 2H), 7.24 (d, J = 3.7 Hz, 2H), 7.27 (d, J = 3.7 Hz, 2H), 7.56 (s, 2H), 7.02 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 10.9, 14.2, 23.2, 25.5, 28.8, 32.5, 37.7, 39.8, 111.6, 120.8, 121.2, 123.6, 124.3, 125.1, 125.7, 130.6, 134.5, 134.9, 135.1, 136.5, 137.6, 138.9, 139.1; HRMS (APCI) *m/z* 1201.2991 ($[M+H]^+$) ($[M+H]^+$, Calcd 1201.3003).

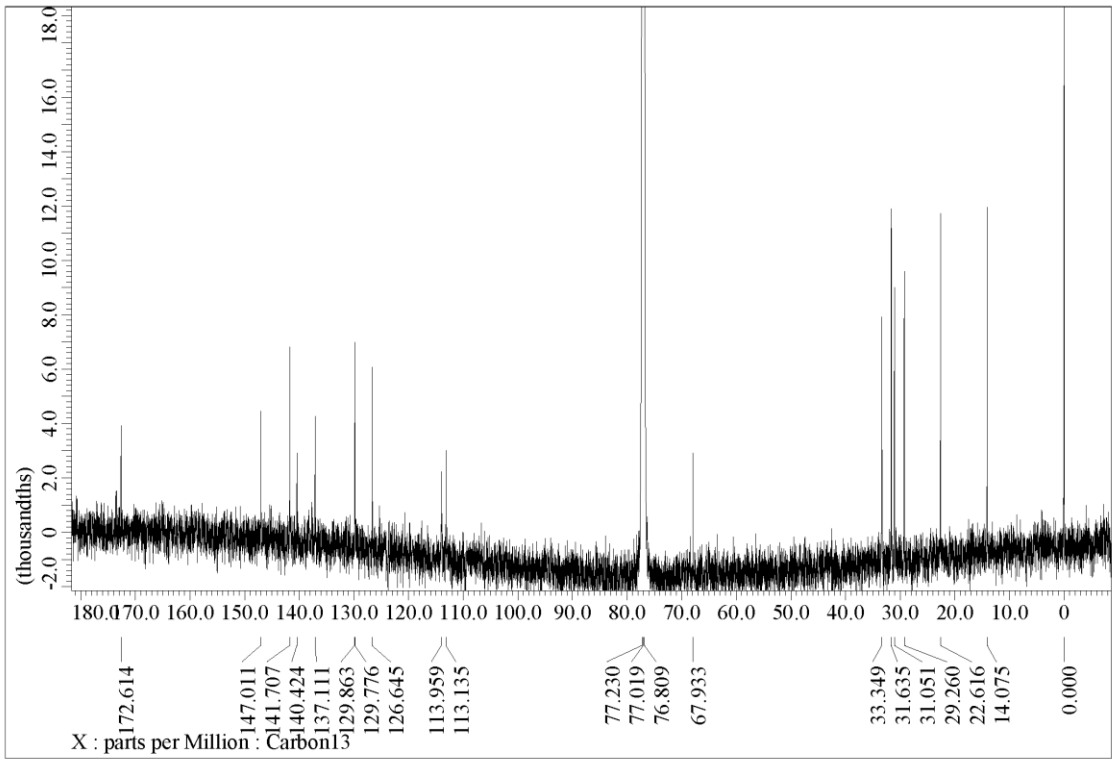
*Synthesis of **BTQ-6***: Sodium hydride (60% in oil) (15 mg, 0.37 mmol) was added to a suspension of malononitrile (13 mg, 0.19 mmol) in anhydrous THF (2.2 mL) under nitrogen atmosphere and stirred for 10 min. at room temperature. To this mixture was added compound **6** (92 mg, 0.077 mmol) and $Pd(PPh_3)_4$ (8.8 mg, 0.0077 mmol). After stirring at reflux temperature for 7 h, the reaction was quenched by adding 1.0 M HCl aq., and then DDQ (17 mg, 0.077 mmol) was added to the mixture. After stirring at room temperature for 30 min., the resulting mixture was extracted with $CHCl_3$. The combined organic was washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane:CH_2Cl_2 = 5:1), followed by purification with preparative GPC ($CHCl_3$) to give **BTQ-6** (8 mg, 9%) as

a black solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.78-1.04 (m, 24H), 1.14-1.48 (br, 32H), 1.60-1.74 (br, 4H), 2.62-2.84 (br, 8H). Proton signals of aromatic region were observed as broad signals; HRMS (APCI) *m/z* 1169.4767 ($[M+H]^+$) ($[M+H]^+$, Calcd 1169.4780).

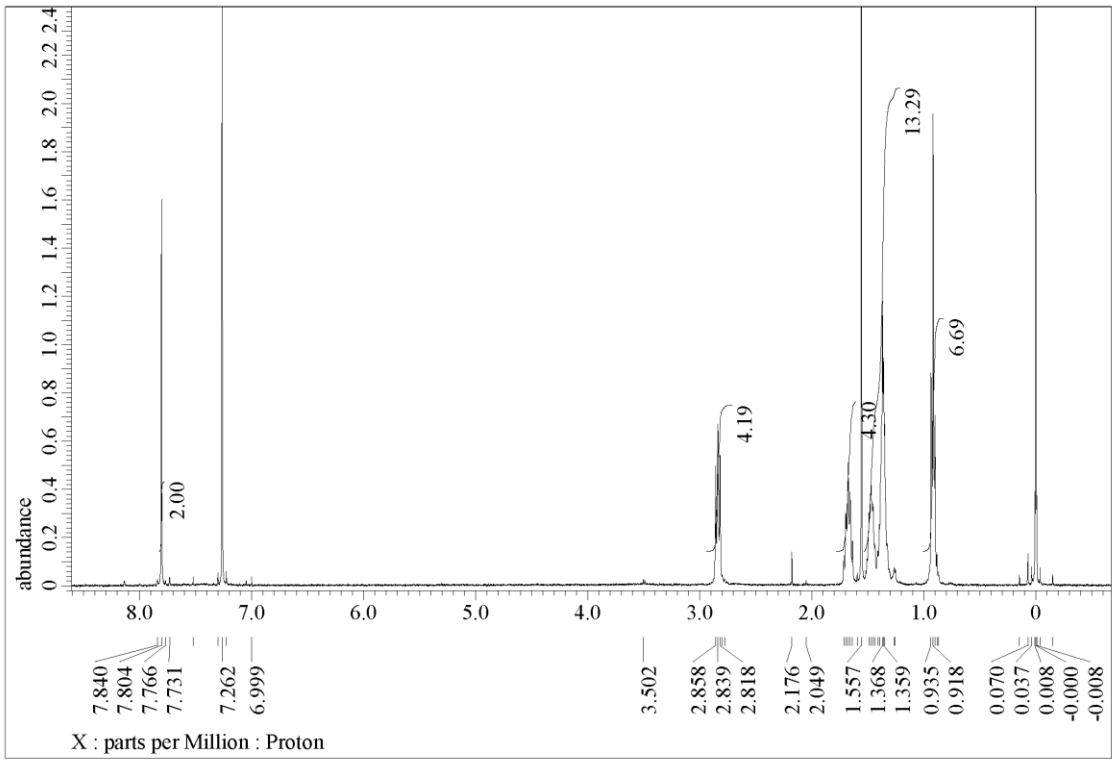
NMR Spectra

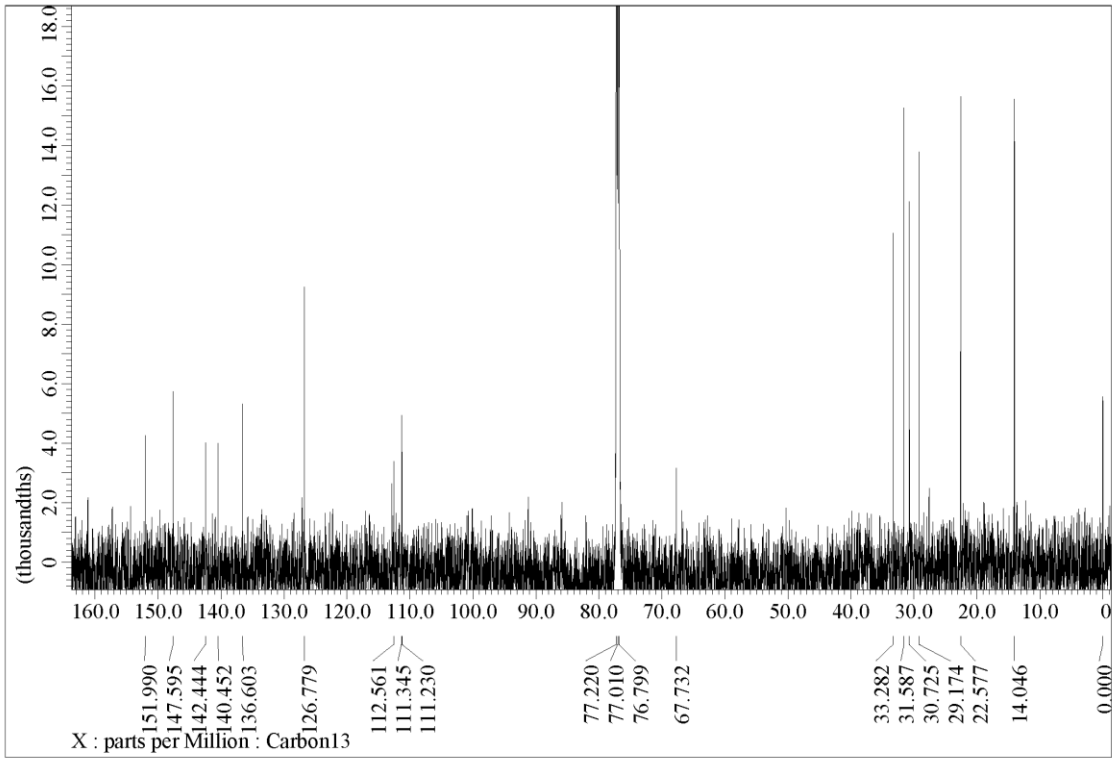
^{1}H NMR (400 MHz) and ^{13}C NMR (150 MHz) spectra of **BTQ** in $CDCl_3$.



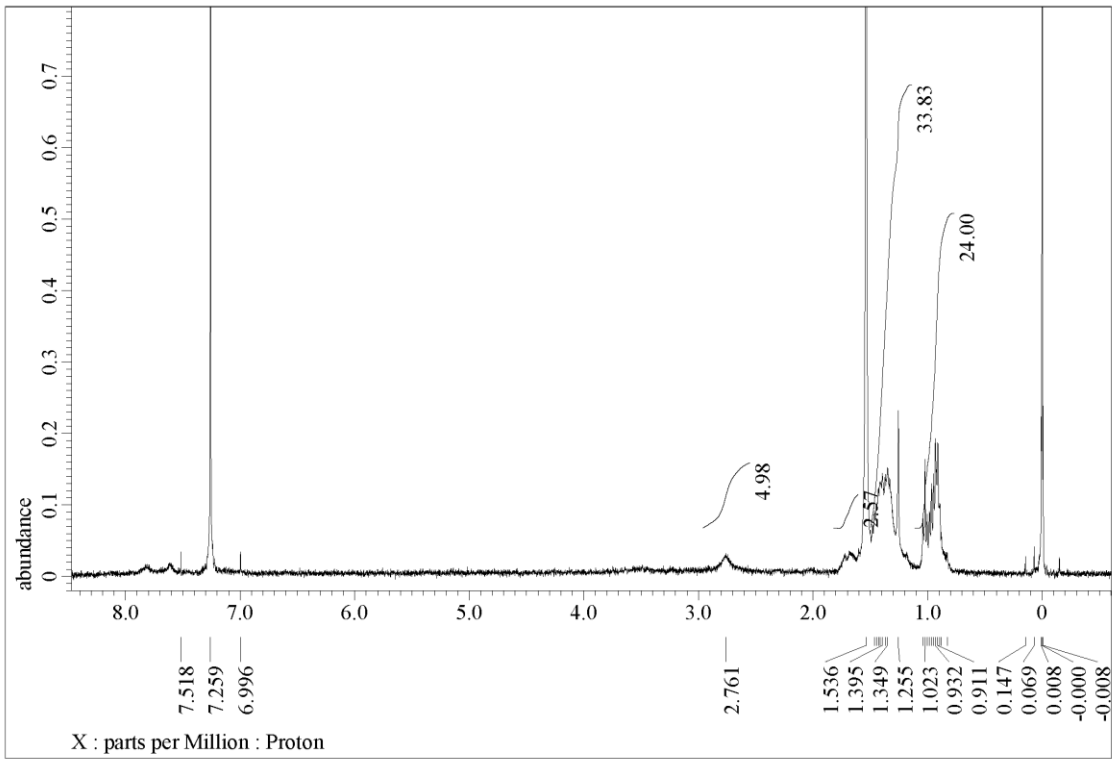


^{1}H NMR (400 MHz) and ^{13}C NMR (150 MHz) spectra of **BTQ-F** in $CDCl_3$.





^{1}H NMR (400 MHz) spectrum of **BTQ-6** in $CDCl_3$.



OFET Device Fabrication

The field-effect electron mobility was measured using bottom-gate bottom-contact OFET devices. The p-doped silicon substrate functions as the gate electrode. A thermally grown silicon oxide (SiO_2) dielectric layer on the gate substrate has 300 nm thick and a capacitance of 10.0 nF cm^{-2}. Interdigital source and drain electrodes were constructed with gold (30 nm) that were formed on the SiO_2layer. The channel width (*W*) and channel length (*L*) are 38 mm and 5 μm, respectively. The silicon oxide surface was first washed with toluene, acetone, purified water and 2-propanol. It was then activated by ozone treatment and pretreated with ODTS or HMDS. The semiconducting layer was fabricated by spin coating from 0.3 wt% chloroform solution at 1000 rpm for 1 min onto the substrate in air for **BTQ**, **BTQ-F** and **TQ**, 0.1 wt% chloroform solution at 1000 rpm for 1 min onto the substrate in air for **BTQ-6**, followed by annealing for 90 min at various temperatures under a vacuum condition (10^{-3}Pa). The characteristics of the OFETs were measured at room temperature under a pressure of 10^{-3} Pa by using a KEITHLEY 4200 semiconductor parameter analyzer. The μ_e was calculated in the saturated region by the following equation.

$$I_{DS} = \frac{W}{2L} C_i \mu (V_{GS} - V_{th})^2$$

Current on/off ratio was determined from the I_D sat V_{GS}= 0 V (I_{off}) and V_{GS}= 100 V (I_{on}).

Computational Details

All calculations were conducted using Gaussian 09 program. The geometry was optimized with the restricted Becke Hybrid (B3LYP) at 6-31 G(d,p) level.

TD-DFT Calculation

BTQ(Me)

Excited State 1: Singlet-A 2.30 eV 538 nm *f* = 1.84 <S**2>=0.000
HOMO–1 > LUMO+1 0.11515
HOMO > LUMO 0.69738

BTQ-F(Me)

Excited State 1: Singlet-A 2.30 eV 538 nm *f* = 2.01 <S**2>=0.000
HOMO–1 > LUMO+1 0.10961
HOMO > LUMO 0.69954

TQ(Me)

Excited State 1: Singlet-A 2.11 eV 589 nm *f* = 1.98 <S**2>=0.000
HOMO > LUMO 0.70613
HOMO < LUMO 0.11819

Optimized structure of **BTQ(Me)** at B3LYP/6-31G(d, p).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.710659	-0.929266	-0.000205
2	6	0	0.710668	-0.929254	0.000209
3	6	0	1.393079	-2.156493	0.000588
4	6	0	0.709751	-3.369713	0.000354
5	6	0	-0.709693	-3.369726	-0.000351
6	6	0	-1.393044	-2.156519	-0.000584
7	6	0	-1.293391	0.400017	-0.000191
8	16	0	-0.000014	1.613434	0.000003
9	6	0	1.293380	0.400036	0.000195
10	6	0	2.605915	0.819597	0.000127
11	6	0	-2.605928	0.819572	-0.000124
12	16	0	-4.025543	-0.257431	0.000037
13	6	0	-5.135406	1.108919	0.000020
14	6	0	-4.409230	2.345767	-0.000054
15	6	0	-3.057306	2.183488	-0.000125
16	6	0	5.135391	1.108935	-0.000021
17	16	0	4.025525	-0.257413	-0.000039
18	6	0	3.057295	2.183511	0.000129
19	6	0	4.409219	2.345786	0.000056
20	6	0	6.511742	0.952553	-0.000087
21	6	0	-6.511757	0.952541	0.000084
22	6	0	1.479300	-4.665762	0.000821
23	6	0	-1.479217	-4.665790	-0.000821
24	6	0	7.361178	2.096432	-0.000097
25	7	0	8.033352	3.048273	-0.000063
26	6	0	7.108472	-0.339658	-0.000142
27	7	0	7.561333	-1.413674	-0.000191
28	6	0	-7.361190	2.096422	0.000095
29	7	0	-8.033363	3.048264	0.000057
30	6	0	-7.108491	-0.339668	0.000135
31	7	0	-7.561354	-1.413683	0.000185
32	1	0	2.475092	-2.185980	0.001141
33	1	0	-2.475056	-2.186030	-0.001136
34	1	0	-4.919868	3.300826	-0.000050
35	1	0	-2.361039	3.014610	-0.000208
36	1	0	2.361030	3.014636	0.000215
37	1	0	4.919860	3.300843	0.000053
38	1	0	1.237838	-5.273732	0.880350
39	1	0	1.238698	-5.273878	-0.878840
40	1	0	2.556748	-4.487818	0.001330
41	1	0	-1.237752	-5.273747	-0.880359
42	1	0	-1.238595	-5.273910	0.878832
43	1	0	-2.556668	-4.487866	-0.001318

Optimized structure of **BTQ-F(Me)** at B3LYP/6-31G(d, p).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.710292	-1.264901	0.000455

2	6	0	-0.710222	-1.265004	-0.000418
3	6	0	-1.391100	-2.493209	-0.001185
4	6	0	-0.709135	-3.707140	-0.000686
5	6	0	0.709624	-3.707027	0.000730
6	6	0	1.391386	-2.492984	0.001228
7	6	0	1.288388	0.067899	0.000451
8	16	0	-0.000129	1.285444	0.000030
9	6	0	-1.288488	0.067733	-0.000411
10	6	0	-2.610684	0.459847	-0.000335
11	6	0	2.610568	0.460063	0.000359
12	16	0	4.016260	-0.641065	-0.000225
13	6	0	5.174901	0.692507	-0.000056
14	6	0	4.470885	1.931814	0.000317
15	6	0	3.111844	1.799893	0.000519
16	6	0	-5.175015	0.692390	0.000026
17	16	0	-4.016422	-0.641224	0.000194
18	6	0	-3.111916	1.799690	-0.000481
19	6	0	-4.470952	1.931669	-0.000307
20	6	0	-1.479384	-5.002553	-0.001580
21	6	0	1.480085	-5.002314	0.001628
22	9	0	5.090710	3.107892	0.000475
23	9	0	2.297843	2.855678	0.000926
24	9	0	-2.297858	2.855432	-0.000848
25	9	0	-5.090728	3.107773	-0.000456
26	6	0	-6.541643	0.478231	0.000232
27	6	0	6.541521	0.478297	-0.000297
28	6	0	-7.488163	1.543542	0.000181
29	7	0	-8.293456	2.384876	0.000153
30	6	0	-7.045406	-0.854687	0.000506
31	7	0	-7.412886	-1.960778	0.000737
32	6	0	7.488078	1.543574	-0.000247
33	7	0	8.293406	2.384876	-0.000213
34	6	0	7.045235	-0.854640	-0.000607
35	7	0	7.412682	-1.960741	-0.000849
36	1	0	-2.472482	-2.527679	-0.002358
37	1	0	2.472780	-2.527251	0.002410
38	1	0	-1.237430	-5.610372	-0.880995
39	1	0	-1.239224	-5.610537	0.878209
40	1	0	-2.556821	-4.824650	-0.002658
41	1	0	1.238225	-5.610174	0.881041
42	1	0	1.240027	-5.610338	-0.878163
43	1	0	2.557493	-4.824237	0.002710

Optimized structure of **BTQ-6(Me)** at B3LYP/6-31G(d, p).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	6.744390	-1.167844	-0.000300
2	6	0	5.330323	-1.339137	-0.000485
3	6	0	7.161247	0.219019	-0.000034
4	16	0	5.732728	1.262760	-0.000102
5	6	0	4.594265	-0.097743	-0.000377
6	6	0	3.235099	0.169142	-0.000425
7	6	0	8.418140	0.797659	0.000273

8	16	0	9.957658	-0.099346	0.000511
9	6	0	10.896424	1.389140	0.000833
10	6	0	10.028341	2.525685	0.000764
11	6	0	8.702033	2.199874	0.000467
12	6	0	0.672356	0.167424	-0.000462
13	16	0	1.953010	-1.061614	-0.000448
14	6	0	2.628625	1.464720	-0.000419
15	6	0	1.260099	1.462867	-0.000446
16	6	0	12.286015	1.395690	0.001116
17	6	0	-12.286011	-1.395707	0.001113
18	6	0	-10.028332	-2.525692	0.000761
19	6	0	-8.702025	-2.199875	0.000465
20	16	0	-9.957661	0.099339	0.000510
21	6	0	-10.896420	-1.389151	0.000831
22	6	0	-2.628625	-1.464711	-0.000421
23	6	0	-1.260099	-1.462858	-0.000447
24	6	0	-0.672356	-0.167415	-0.000462
25	16	0	-1.953010	1.061623	-0.000447
26	6	0	-3.235100	-0.169133	-0.000425
27	6	0	-8.418138	-0.797659	0.000271
28	6	0	-7.161247	-0.219015	-0.000035
29	16	0	-5.732727	-1.262754	-0.000104
30	6	0	-4.594265	0.097751	-0.000378
31	6	0	-6.744392	1.167850	-0.000301
32	6	0	-5.330325	1.339144	-0.000485
33	6	0	7.571250	-2.305480	-0.000429
34	6	0	4.804400	-2.644392	-0.000790
35	6	0	7.041968	-3.591033	-0.000714
36	6	0	5.630907	-3.762219	-0.000898
37	6	0	-4.804404	2.644399	-0.000790
38	6	0	-5.630912	3.762226	-0.000897
39	6	0	-7.041972	3.591038	-0.000713
40	6	0	-7.571253	2.305484	-0.000429
41	6	0	5.027552	-5.144183	-0.001219
42	6	0	7.961392	-4.786395	-0.000845
43	6	0	-5.027558	5.144191	-0.001217
44	6	0	-7.961398	4.786400	-0.000844
45	6	0	12.992232	2.631619	0.001377
46	7	0	13.544974	3.658116	0.001576
47	6	0	13.030671	0.184334	0.001150
48	7	0	13.607989	-0.828934	0.001171
49	6	0	-12.992223	-2.631640	0.001372
50	7	0	-13.544960	-3.658139	0.001594
51	6	0	-13.030672	-0.184355	0.001148
52	7	0	-13.607995	0.828911	0.001169
53	1	0	10.418851	3.535753	0.000936
54	1	0	7.910931	2.941487	0.000375
55	1	0	3.221601	2.371859	-0.000412
56	1	0	0.659605	2.365408	-0.000453
57	1	0	-10.418837	-3.535762	0.000933
58	1	0	-7.910920	-2.941484	0.000372
59	1	0	-3.221602	-2.371850	-0.000414
60	1	0	-0.659605	-2.365399	-0.000454
61	1	0	8.648809	-2.201514	-0.000336
62	1	0	3.733479	-2.803288	-0.000984

63	1	0	-3.733484	2.803297	-0.000983
64	1	0	-8.648812	2.201518	-0.000336
65	1	0	5.341664	-5.718438	-0.880570
66	1	0	5.341363	-5.718707	0.878067
67	1	0	3.936093	-5.099882	-0.001396
68	1	0	7.796302	-5.419575	0.878735
69	1	0	7.796525	-5.419211	-0.880729
70	1	0	9.009645	-4.479944	-0.000649
71	1	0	-5.341674	5.718447	-0.880566
72	1	0	-5.341367	5.718713	0.878071
73	1	0	-3.936100	5.099890	-0.001397
74	1	0	-7.796306	5.419581	0.878734
75	1	0	-7.796534	5.419213	-0.880730
76	1	0	-9.009650	4.479947	-0.000644

Optimized structure of **TQ(Me)** at B3LYP/6-31G(d, p).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	6.505729	-0.375527	0.000033
2	6	0	-0.692708	1.466632	0.000078
3	6	0	0.692491	1.466767	-0.000167
4	6	0	-1.274003	0.146056	0.000073
5	16	0	0.000117	-1.080914	-0.000077
6	6	0	1.274028	0.146272	-0.000178
7	6	0	2.598819	-0.259257	0.000081
8	6	0	-2.598770	-0.259519	-0.000158
9	16	0	-4.014150	0.824757	-0.000057
10	6	0	-5.128142	-0.536825	-0.000065
11	6	0	-4.409344	-1.775886	-0.000229
12	6	0	-3.055114	-1.618984	-0.000283
13	6	0	5.128196	-0.536755	0.000085
14	16	0	4.014294	0.824901	0.000073
15	6	0	3.055087	-1.618747	0.000180
16	6	0	4.409304	-1.775758	0.000177
17	6	0	-6.505662	-0.375496	0.000052
18	6	0	-1.552299	2.699845	0.000224
19	6	0	1.551747	2.700211	-0.000304
20	6	0	-7.358060	-1.516588	0.000030
21	7	0	-8.032415	-2.467043	0.000112
22	6	0	-7.099804	0.917408	0.000191
23	7	0	-7.552939	1.991417	0.000256
24	6	0	7.358046	-1.516680	0.000047
25	7	0	8.032325	-2.467189	0.000070
26	6	0	7.099964	0.917334	-0.000035
27	7	0	7.553166	1.991315	-0.000087
28	1	0	-4.923657	-2.729025	-0.000342
29	1	0	-2.362870	-2.453371	-0.000490
30	1	0	2.362777	-2.453080	0.000329
31	1	0	4.923542	-2.728939	0.000277
32	1	0	-0.957716	3.612254	0.000612
33	1	0	-2.199218	2.733271	-0.882906
34	1	0	-2.199609	2.732816	0.883072

35	1	0	2.199091	2.733340	-0.883117
36	1	0	0.956910	3.612457	-0.000762
37	1	0	2.198588	2.733863	0.882871

Optimized structure of **TQ-6(Me)** at B3LYP/6-31G(d, p).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.625669	-1.597949	0.000541
2	6	0	-5.229574	-1.662036	0.000701
3	6	0	-7.136385	-0.262289	0.000198
4	16	0	-5.805602	0.898051	0.000023
5	6	0	-4.594822	-0.385277	0.000499
6	6	0	-3.237852	-0.028743	0.000604
7	6	0	-8.448675	0.218218	-0.000018
8	16	0	-9.911094	-0.796261	-0.000470
9	6	0	-10.962606	0.613580	-0.000671
10	6	0	-10.189785	1.810642	-0.000386
11	6	0	-8.837041	1.587939	-0.000039
12	6	0	-0.688512	0.129761	0.000618
13	16	0	-1.881589	-1.172412	0.000578
14	6	0	-2.722604	1.292243	0.000642
15	6	0	-1.346801	1.378129	0.000650
16	6	0	-4.434307	-2.938701	0.001101
17	6	0	-7.538555	-2.793539	0.000750
18	6	0	4.434259	2.938645	0.001105
19	6	0	7.538527	2.793526	0.000756
20	6	0	10.189818	-1.810603	-0.000381
21	6	0	8.837071	-1.587925	-0.000034
22	16	0	9.911081	0.796294	-0.000467
23	6	0	10.962618	-0.613527	-0.000668
24	6	0	2.722607	-1.292299	0.000643
25	6	0	1.346803	-1.378184	0.000650
26	6	0	0.688514	-0.129816	0.000618
27	16	0	1.881591	1.172358	0.000577
28	6	0	3.237853	0.028688	0.000604
29	6	0	8.448680	-0.218211	-0.000015
30	6	0	7.136383	0.262275	0.000199
31	16	0	5.805617	-0.898084	0.000020
32	6	0	4.594821	0.385229	0.000499
33	6	0	6.625650	1.597928	0.000544
34	6	0	5.229554	1.661996	0.000703
35	6	0	12.352920	-0.508316	-0.001044
36	6	0	-12.352910	0.508394	-0.001047
37	6	0	13.153524	-1.683651	-0.001218
38	7	0	13.784508	-2.664489	-0.001329
39	6	0	12.999621	0.756510	-0.001268
40	7	0	13.497967	1.811333	-0.001456
41	6	0	-13.153493	1.683743	-0.001221
42	7	0	-13.784458	2.664593	-0.001325
43	6	0	-12.999634	-0.756420	-0.001269
44	7	0	-13.498001	-1.811234	-0.001434
45	1	0	-10.656377	2.787937	-0.000421

46	1	0	-8.107119	2.389803	0.000250
47	1	0	-3.369881	2.161396	0.000700
48	1	0	-0.806511	2.317933	0.000709
49	1	0	-3.789224	-3.005086	0.884074
50	1	0	-5.075445	-3.819252	0.001507
51	1	0	-3.789447	-3.005778	-0.881989
52	1	0	-6.984714	-3.731844	0.001416
53	1	0	-8.188118	-2.799897	0.882693
54	1	0	-8.187441	-2.800727	-0.881691
55	1	0	3.789173	3.005013	0.884078
56	1	0	5.075375	3.819210	0.001512
57	1	0	3.789395	3.005706	-0.881984
58	1	0	6.984682	3.731828	0.001423
59	1	0	8.188090	2.799887	0.882699
60	1	0	8.187415	2.800719	-0.881684
61	1	0	10.656429	-2.787891	-0.000415
62	1	0	8.107163	-2.389803	0.000256
63	1	0	3.369882	-2.161453	0.000702
64	1	0	0.806512	-2.317988	0.000710

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