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Electronic Supplementary Information

Effects of fluorine substitution in quinoidal oligothiophenes for use as organic semiconductors

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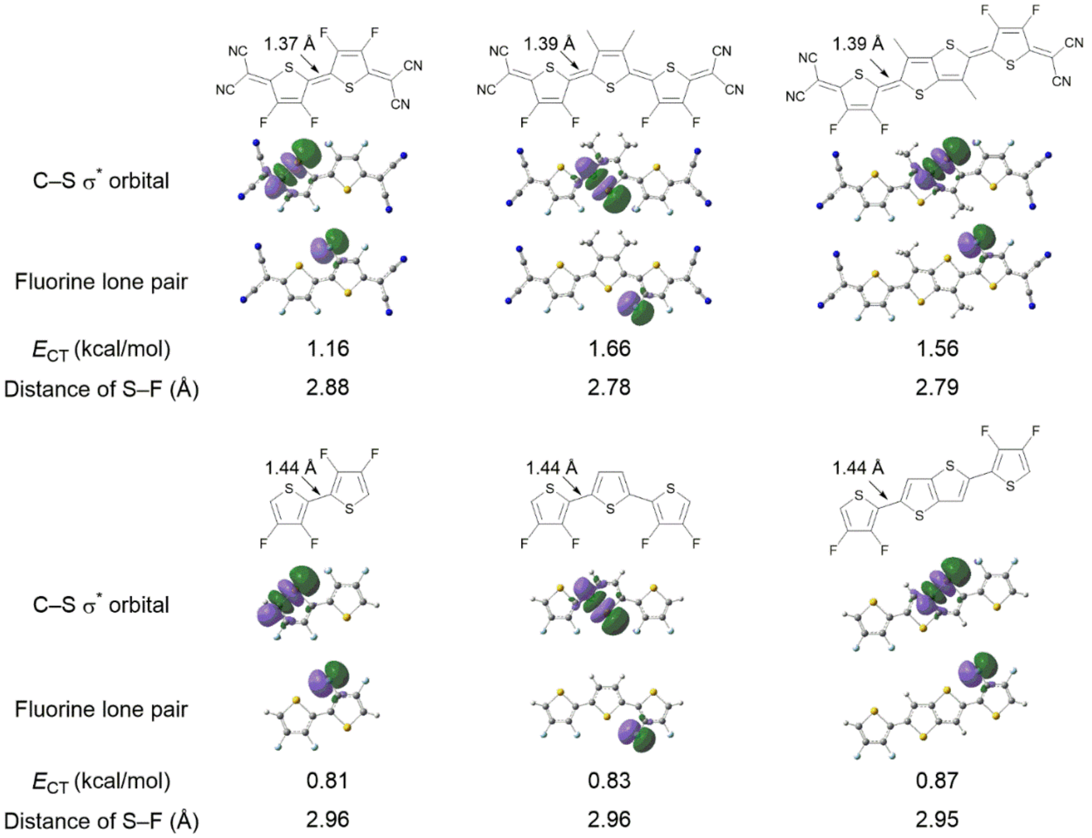


Fig. S1 Depiction of the NBO orbitals for the optimized structures.

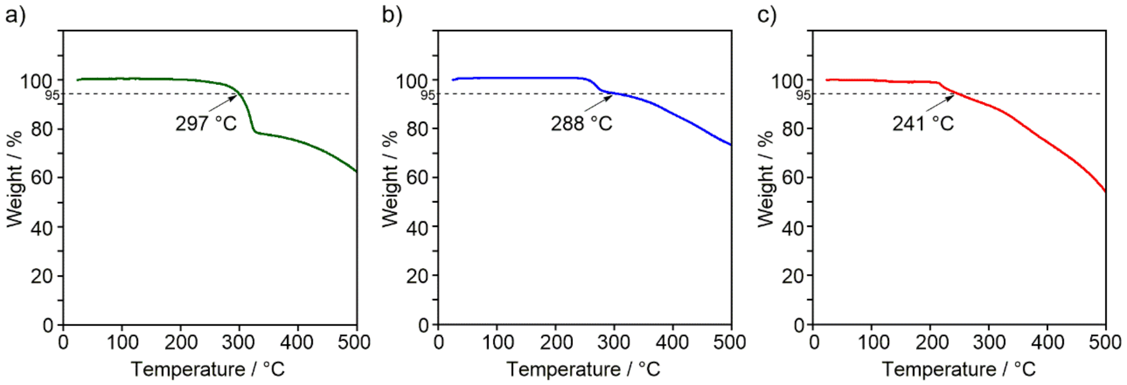


Fig. S2 TGA curves for (a) **FTQ-1**, (b) **FTQ-2**, and (c) **FTQ-3** with a heating rate of 10 °C min^{-1} in a N_2 atmosphere.

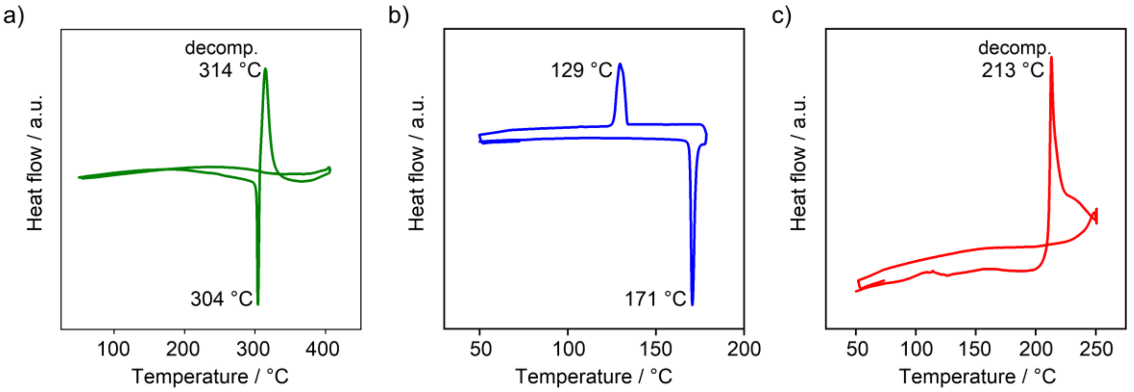
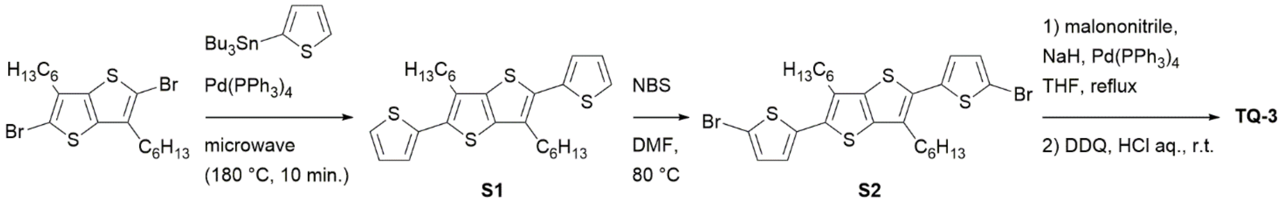
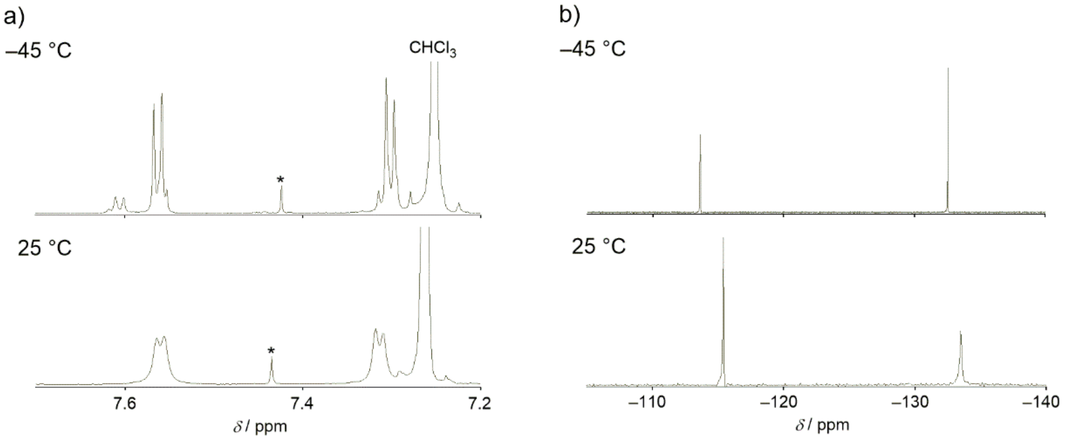


Fig. S3 DSC curves of (a) **FTQ-1**, (b) **FTQ-2**, and (c) **FTQ-3** for a heating rate of 10 °C min^{-1} in a N_2 atmosphere.



Scheme S1. Synthetic route for **TQ-3**.



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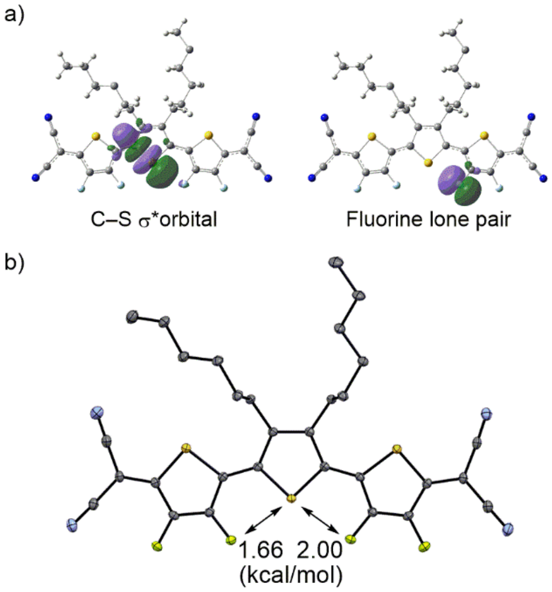


Fig. S5 (a) Depiction of NBO orbitals and (b) the estimated E_{CT} values for **FTQ-2** on the geometry of the single-crystal structure.

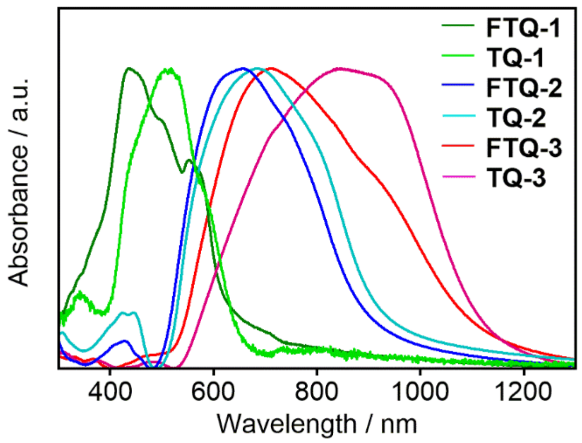
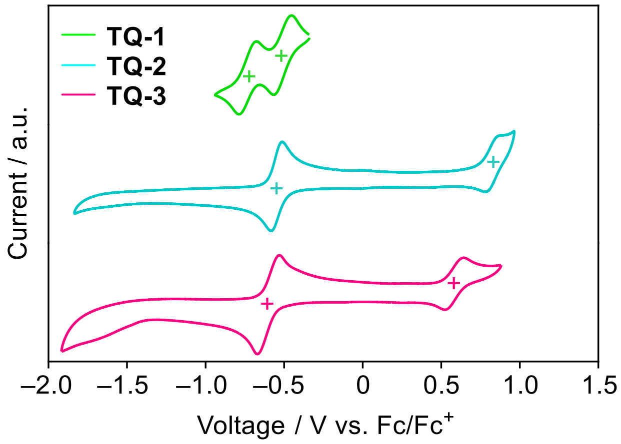


Fig. S6 UV-vis-NIR absorption spectra of thin films of **FTQ-1** (green), **TQ-1** (light green), **FTQ-2** (blue), **TQ-2** (light blue), **FTQ-3** (red), and **TQ-3** (light red).



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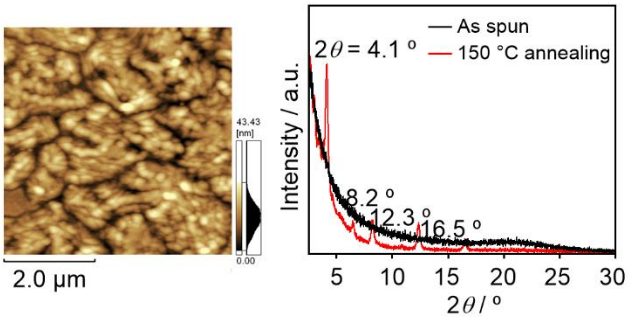


Fig. S8 AFM height image and XRD data for **TQ-2**.

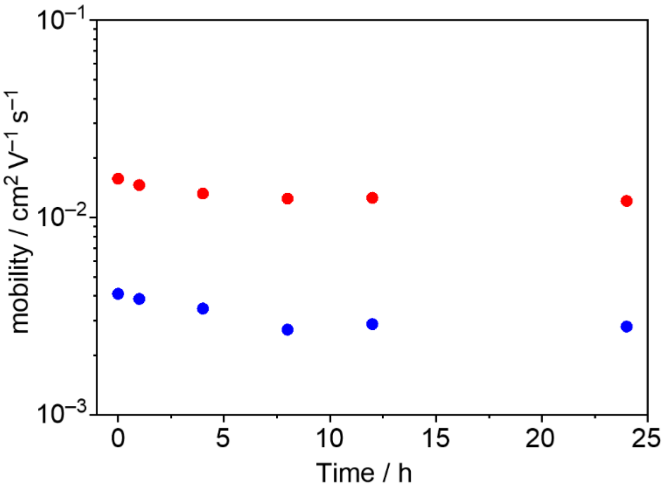
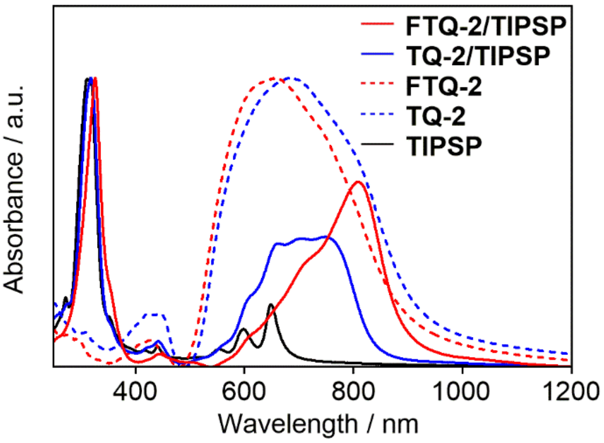


Fig. S9 Time-dependent electron mobilities under air-exposed conditions for **FTQ-2** (blue) and **FTQ-3** (red).



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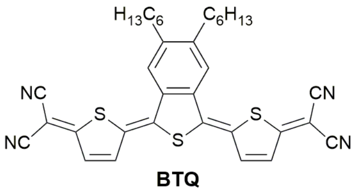
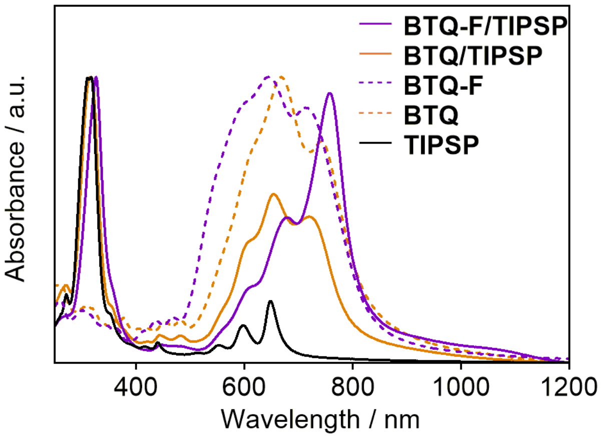


BTQ



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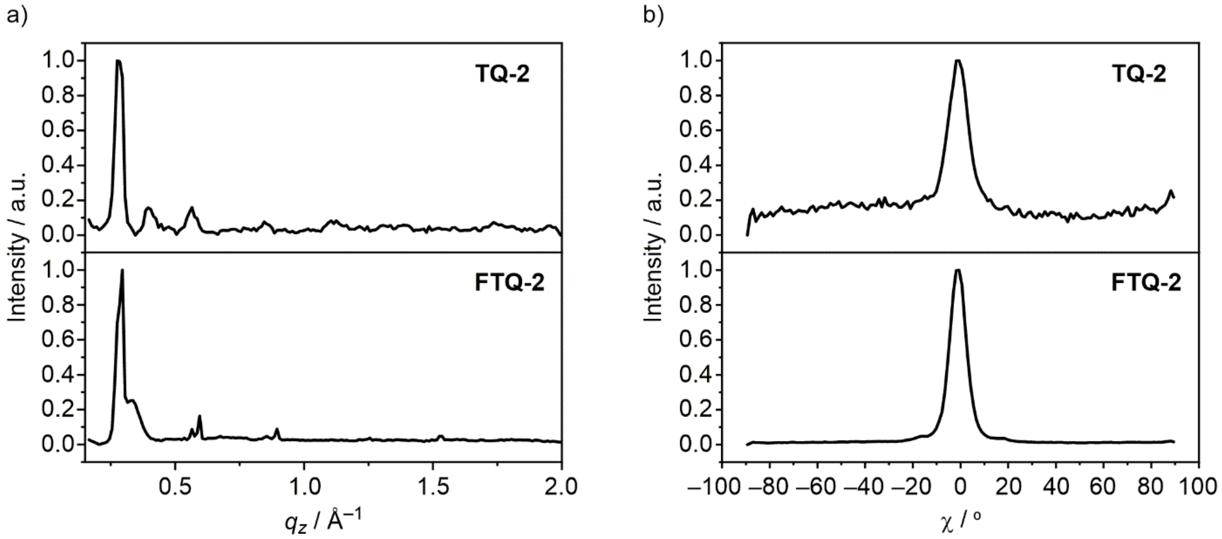


Fig. S12 (a) Meridional integration for **TQ-2** and **FTQ-2** obtained from GIWAXS patterns of spin-coated thin films; (b) azimuthal integration intensity containing (100) reflection for **TQ-2** and **FTQ-2**.

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 = triplet, 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}. High-resolution mass spectrum (HRMS) was obtained atmospheric pressure chemical ionization (APCI) or electrospray ionization (ESI) methods using a Thermo scientific LTQ Orbitrap XL.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 films 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.

Materials

Unless stated otherwise, all reagents were purchased from commercial sources and used without purification. Compounds **1**, **3**, 2,5-dibromo-3,4-dihexylthiophene and 2,5-dibromo-3,6-dihexylthieno[3,2-*b*]thiophene were prepared by the reference procedures.[1-4]

Synthesis of ***2***: NBS (226 mg, 1.27 mmol) was added to a solution of **1** (220 mg, 0.575 mmol) in AcOH (4.0 mL) at ambient temperature. The reaction was allowed to warm to 80 °C. After stirring for 4 h, the reaction mixture was poured into water. The resulting mixture was extracted with Et_2O. The organic layer was washed with 1 M aq. NaOH, water and dried over $MgSO_4$. The solvent was removed under reduced pressure, followed by purification with preparative GPC ($CHCl_3$) to give **2** (180 mg, 79%) as a white solid. ^{19}F NMR (565 MHz, $CDCl_3$): δ –133.3, –130.9; ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 92.2-92.4 (m), 111.1-111.3 (m), 141.1 (dd, J = 270.2 and 20.2 Hz), 144.3 (dd, J = 263.0 and 20.2 Hz).

Synthesis of ***FTQ-1***: Sodium hydride (60% in oil) (84 mg, 2.11 mmol) was added to a suspension of malononitrile (69 mg, 1.05 mmol) in anhydrous THF (12.5 mL) under nitrogen atmosphere and stirred for 10 min at room temperature. To this mixture was added compound **2** (174 mg, 0.439 mmol) and $Pd(PPh_3)_4$ (51 mg, 0.044 mmol), which was then heated to reflux. After 12 h, the reaction was cooled to 0 °C, and diluted hydrochloric acid (1M, 7.8 mL), $CHCl_3$ (7.8 mL), and DDQ (150 mg, 0.659 mmol) were added and stirred at 0 °C for 5 min. The resulting mixture was extracted with $CHCl_3$, washed with water, and dried over $MgSO_4$. The solvent was removed under reduced pressure and purified by column chromatography on silica gel ($CHCl_3$) to give **FTQ-1** (89 mg, 56%) as a red solid. ^{19}F NMR (565 MHz, $CDCl_3$): δ –127.5, –118.7; HRMS (APCI) *m/z*: $[M]^-$ calcd. for $C_{14}F_4N_4S_2$, 363.9501; found, 363.9503.

Synthesis of ***4a***: 2,5-Dibromo-3,4-dihexylthiophene (119 mg, 0.290 mmol), **3** (307 mg, 0.638 mmol), $Pd(PPh_3)_4$ (34 mg, 0.029 mmol), and toluene (3.5 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 180 °C for 10 min. The reaction mixture was passed through pad of celite and the solvent was removed under reduced pressure, followed by purification with preparative GPC ($CHCl_3$) to give **4a** (138 mg, 75%) as a pale yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 0.36 (s, 18H), 0.88 (t, J = 6.9 Hz, 6H), 1.25-1.38 (m, 12H), 1.47-1.52 (m, 4H), 2.62 (t, J = 8.3 Hz, 4H); ^{19}F NMR (565 MHz, $CDCl_3$): δ –134.1, –127.1; ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ –0.8, 14.1, 22.5, 28.1, 29.4, 30.4, 31.4, 114.6 (d, J = 24.6 Hz), 118.5 (d, J = 11.6 Hz), 126.6, 142.2, 142.4 (dd, J = 267.3 and 24.6 Hz), 149.6 (dd, J = 257.2 and 18.8 Hz); HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{30}H_{44}F_4S_3Si_2$, 633.2153; found, 633.2145.

Synthesis of ***5a***: NBS (85 mg, 0.475 mmol) was added to a solution of **4a** (137 mg, 0.216 mmol) in DMF (5.0 mL) at 0 °C. The reaction was allowed to warm to ambient temperature. After stirring for 4 h, the reaction mixture was poured into water. The resulting mixture was extracted with EtOAc. The organic layer was washed with water, brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, followed by purification with preparative GPC ($CHCl_3$) to give **5a** (134 mg, 96%) as a pale yellow solid. ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 0.89 (t, J = 6.2 Hz, 6H), 1.25-1.38 (m, 12H), 1.44-1.50 (m, 4H), 2.58 (t, J = 8.3 Hz, 4H); ^{19}F NMR (565 MHz, $CDCl_3$): δ –132.3, –130.9; ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 14.0, 22.5, 28.1, 29.5, 30.4, 31.4, 91.3-91.5 (m), 113.7 (d, J = 11.6 Hz), 125.4, 141.1 (dd, J = 265.7 and 18.6 Hz), 143.3, 144.3 (dd, J = 262.8 and 20.1 Hz); HRMS (APCI) *m/z*: $[M]^+$ calcd. for $C_{24}H_{26}Br_2F_4S_3$, 645.9479; found, 645.9468.

*Synthesis of **FTQ-2***: Sodium hydride (60% in oil) (40 mg, 0.94 mmol) was added to a suspension of malononitrile (33 mg, 0.50 mmol) in anhydrous 1,4-dioxane (5.9 mL) under nitrogen atmosphere and stirred for 10 min at room temperature. To this mixture was added compound **5a** (134 mg, 0.207 mmol) and $Pd(PPh_3)_4$ (24 mg, 0.021 mmol), which was then heated to reflux. After 12 h, the reaction was cooled to 0 °C, and diluted hydrochloric acid (1M, 6.0 mL), $CHCl_3$ (6.0 mL) and DDQ (71 mg, 0.31 mmol) were added and stirred at 0 °C for 5 min. The resulting mixture was extracted with $CHCl_3$, washed with water, and dried over $MgSO_4$. The solvent was removed under reduced pressure and purified by column chromatography on silica gel (hexane/CH_2Cl_2, 1:2) to give **FTQ-2** (62 mg, 49%) as a blue solid. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.93 (t, J = 6.9 Hz, 6H), 1.30-1.42 (m, 8H), 1.48-1.62 (m, 8H), 2.78-2.84 (m, 4H); ^{19}F NMR (565 MHz, $CDCl_3$): δ –133.3, –112.6; HRMS (APCI) *m/z*: $[M]^-$ calcd. for $C_{30}H_{26}F_4N_4S_3$, 614.1256; found, 614.1224.

*Synthesis of **4b***: 2,5-Dibromo-3,6-dihexylthieno[3,2-*b*]thiophene (152 mg, 0.326 mmol), **3** (345 mg, 0.717 mmol), $Pd(PPh_3)_4$ (38 mg, 0.033 mmol), and toluene (5.0 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 180 °C for 10 min. The reaction mixture was passed through pad of celite and the solvent was removed under reduced pressure, followed by purification with preparative GPC ($CHCl_3$) to give **4b** (200 mg, 89%) as a yellow solid. ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 0.37 (s, 18H), 0.87 (t, J = 6.2 Hz, 6H), 1.25-1.40 (m, 12H), 1.71-1.76 (m, 4H), 2.79 (t, J = 8.3 Hz, 4H); ^{19}F NMR (565 MHz, $CDCl_3$): δ –134.1, –126.8; ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ –0.7, 14.2, 22.7, 28.9, 29.0, 29.4, 31.6, 115.3 (d, J = 24.6 Hz), 119.1 (d, J = 11.6 Hz), 126.4, 134.5, 139.9, 142.6 (dd, J = 267.3 and 24.6 Hz), 149.8 (dd, J = 258.7 and 18.8 Hz); HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{32}H_{44}F_4S_4Si_2$, 689.1874; found, 689.1864.

*Synthesis of **5b***: NBS (114 mg, 0.638 mmol) was added to a solution of **4b** (200 mg, 0.290 mmol) in DMF (13.6 mL) at 0 °C. The reaction was allowed to warm to ambient temperature. After stirring for 14 h, the reaction mixture was poured into water. The resulting mixture was extracted with EtOAc. The organic layer was washed with water, brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, followed by purification with preparative GPC ($CHCl_3$) to give **5b** (165 mg, 81%) as a pale yellow solid. ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 0.88 (t, J = 6.2 Hz, 6H), 1.25-1.40 (m, 12H), 1.68-1.73 (m, 4H), 2.75 (t, J = 8.3 Hz, 4H); ^{19}F NMR (565 MHz, $CDCl_3$): δ –132.1, –131.2; ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 14.1, 22.6, 28.7, 28.8, 29.3, 31.5, 91.6-91.8 (m), 114.4 (d, J = 11.6 Hz), 124.8, 135.5, 139.9, 141.1 (dd, J = 265.8 and 20.1 Hz), 144.4 (dd, J = 261.5 and 20.3 Hz); HRMS (APCI) *m/z*: $[M]^+$ calcd. for $C_{26}H_{26}Br_2F_4S_4$, 701.9200; found, 701.9193.

*Synthesis of **FTQ-3***: Sodium hydride (60% in oil) (23 mg, 0.57 mmol) was added to a suspension of malononitrile (19 mg, 0.28 mmol) in anhydrous 1,4-dioxane (3.5 mL) under nitrogen atmosphere and stirred for 10 min at room temperature. To this mixture was added compound **5b** (83 mg, 0.12 mmol) and $Pd(PPh_3)_4$ (14 mg, 0.012 mmol), which was then heated to reflux. After 18 h, the reaction was cooled to 0 °C, and diluted hydrochloric acid (1M, 3.6 mL), $CHCl_3$ (3.6 mL) and DDQ (40 mg, 0.18 mmol) were added and stirred at 0 °C for 10 min. The resulting mixture was extracted with $CHCl_3$, washed with water, and dried over $MgSO_4$. The solvent was removed under reduced pressure and purified by column chromatography on silica gel (hexane/CH_2Cl_2, 1:2) to give **FTQ-3** (50 mg, 63%) as a blue solid. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.92 (t, J = 6.9 Hz, 6H), 1.32-1.52 (m, 12H), 1.70-1.78 (m, 4H), 2.89 (t, J = 7.8 Hz, 4H); ^{19}F NMR (565 MHz, $CDCl_3$): δ –127.5, –118.7; HRMS (APCI) *m/z*: $[M]^-$ calcd. for $C_{32}H_{26}F_4N_4S_4$, 670.0976; found, 670.0941.

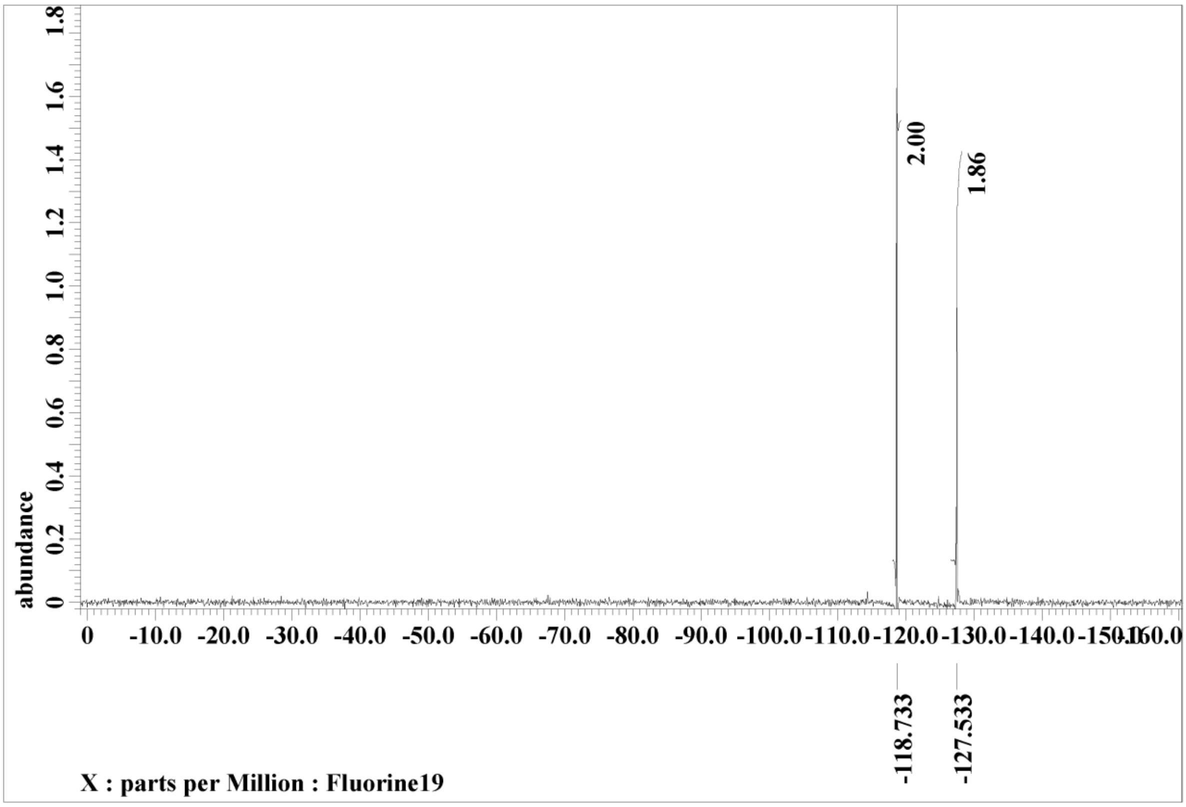
*Synthesis of **S1***: 2-(Tributylstannyl)thiophene (230 mg, 0.616 mmol), 2,5-dibromo-3,6-dihexylthieno[3,2-*b*]thiophene (130 mg, 0.279 mmol), $Pd(PPh_3)_4$ (32 mg, 0.028 mmol), and toluene (4.3 mL) were placed in a microwave proof walled glass vial equipped with a snap cap. The glass vial was purged nitrogen, securely sealed, and heated in a microwave reactor with keeping a temperature at 180 °C for 10 min. The reaction mixture was passed through pad of celite and the solvent was removed under reduced pressure, followed by purification with preparative GPC ($CHCl_3$) to give **S1** (200 mg, 89%) as a brown solid. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.88 (t, J = 6.9 Hz, 6H), 1.25-1.45 (m, 12H), 1.71-1.80 (m, 4H), 2.87 (t, J = 8.2 Hz, 4H), 7.09 (dd, J = 5.0, and 3.7 Hz, 2H), 7.17 (dd, *J* = 3.7 and 0.9 Hz, 2H), 7.35 (dd, *J* = 5.0 and 0.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 22.6, 28.8, 29.1, 29.4, 31.6, 125.7, 126.2, 127.5, 131.3, 132.0, 136.6, 138.5; HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{26}H_{32}S_4$, 473.1460; found, 473.1446.

Synthesis of ***S2***: NBS (166 mg, 0.930 mmol) was added to a solution of **S1** (220 mg, 0.465 mmol) in DMF (24 mL) and THF (6 mL) at 0 °C. The reaction was allowed to warm to ambient temperature. After stirring for 10 h, the reaction mixture was poured into water. The resulting mixture was extracted with EtOAc. The organic layer was washed with water, brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, followed by purification with preparative GPC ($CHCl_3$) to give **S2** (250 mg, 85%) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.88 (t, *J* = 6.9 Hz, 6H), 1.22-1.45 (m, 12H), 1.65-1.80 (m, 4H), 2.82 (t, *J* = 8.2 Hz, 4H), 6.90 (d, *J* = 3.7 Hz, 2H), 7.04 (d, *J* = 3.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 22.6, 28.7, 29.1, 29.3, 31.6, 126.5, 130.3, 130.7, 132.5, 137.9, 138.6; HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{26}H_{30}Br_2S_4$, 630.9650; found, 630.9644.

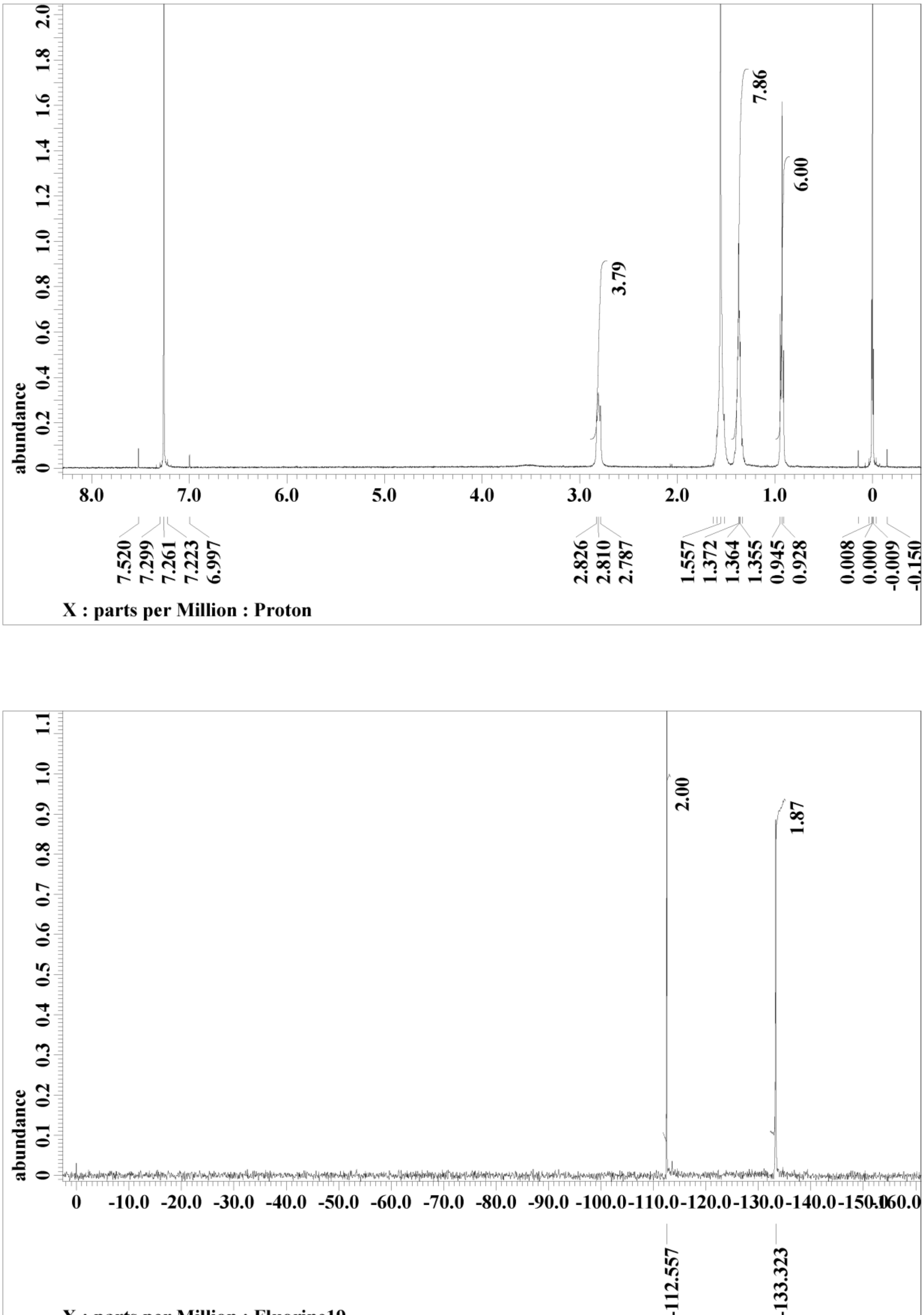
Synthesis of ***TQ-3***: Sodium hydride (60% in oil) (43 mg, 1.07 mmol) was added to a suspension of malononitrile (35 mg, 0.53 mmol) in anhydrous THF (6.4 mL) under nitrogen atmosphere and stirred for 10 min at room temperature. To this mixture was added compound **S2** (140 mg, 0.222 mmol) and $Pd(PPh_3)_4$ (26 mg, 0.022 mmol), which was then heated to reflux. After 12 h, the reaction was cooled to 0 °C, and diluted hydrochloric acid (1M, 6.0 mL), $CHCl_3$ (6.0 mL) and DDQ (76 mg, 0.33 mmol) were added and stirred at 0 °C for 10 min. The resulting mixture was extracted with $CHCl_3$, washed with water, and dried over $MgSO_4$. The solvent was removed under reduced pressure and purified by column chromatography on silica gel (hexane/$CHCl_3$, 1:10) to give **TQ-3** (50 mg, 38%) as a blue solid. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 0.92 (t, *J* = 7.3 Hz, 6H), 1.32-1.52 (m, 12H), 1.70-1.78 (m, 4H), 2.86 (t, *J* = 8.2 Hz, 4H), 7.31 (d, *J* = 5.5 Hz, 2H), 7.56 (d, *J* = 5.5 Hz, 2H); HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{32}H_{30}N_4S_4$, 599.1426; found, 599.1422.

NMR Spectra

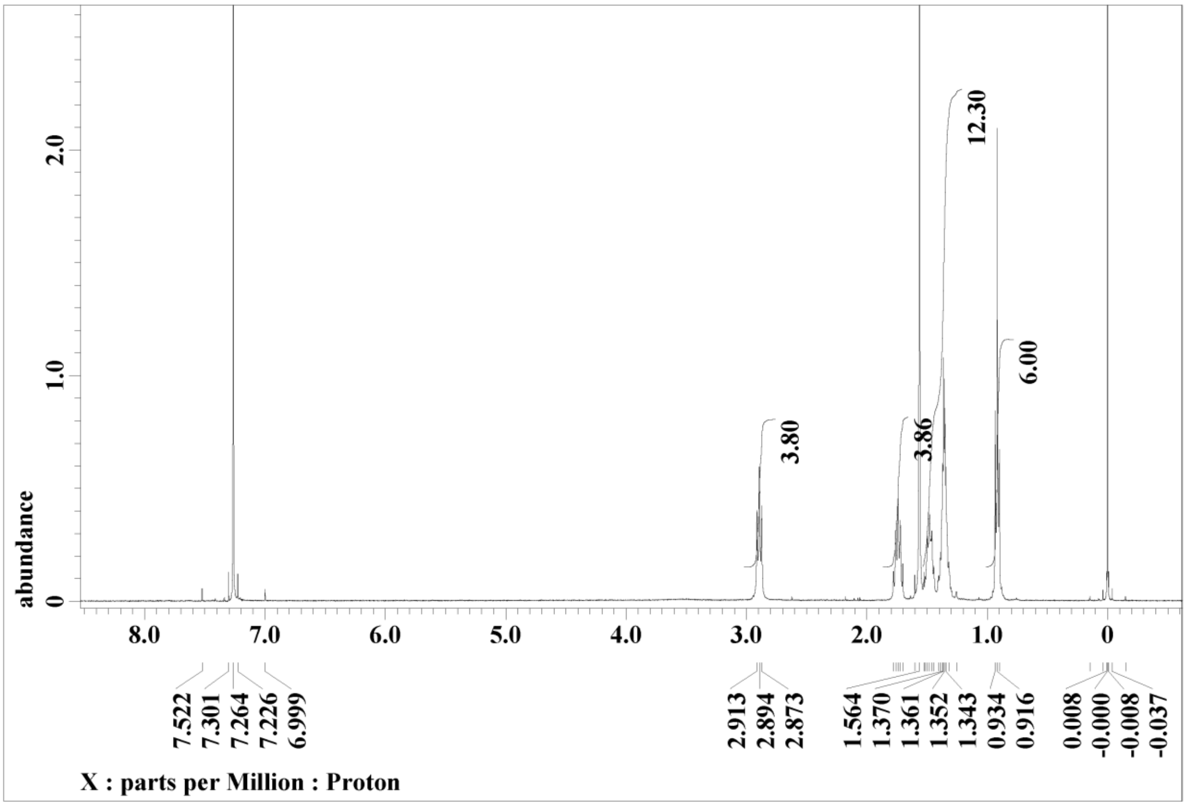
^{19}F NMR (565 MHz) spectrum of **FTQ-1** in $CDCl_3$.

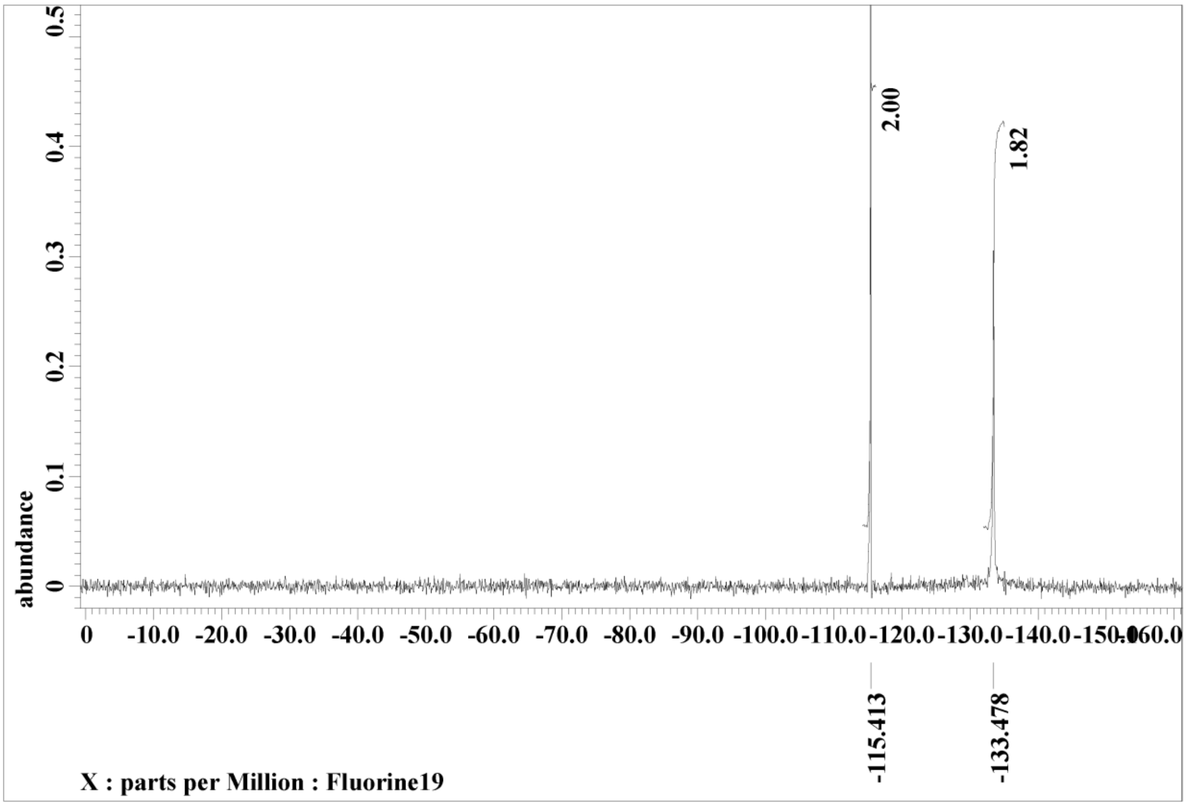


^{1}H NMR (400 MHz) and ^{19}F NMR (565 MHz) spectra of **FTQ-2** in $CDCl_3$.

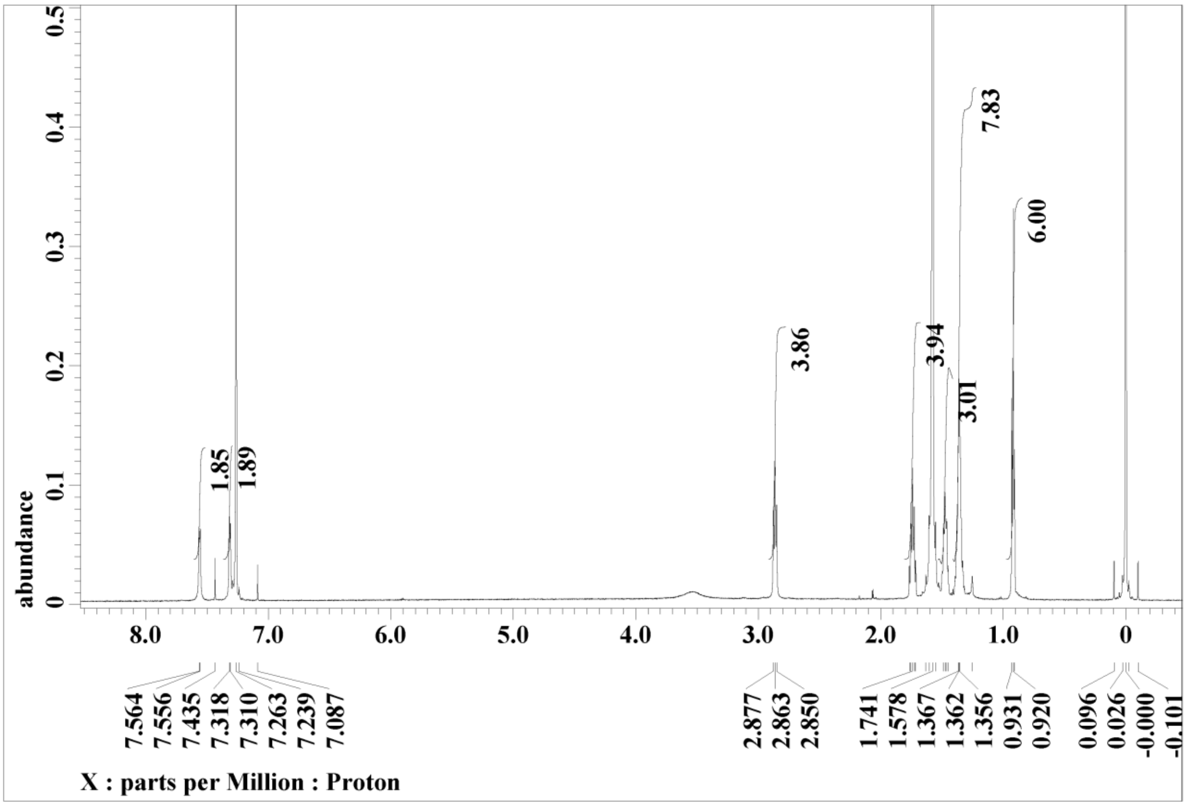


^{1}H NMR (400 MHz) and ^{19}F NMR (565 MHz) spectra of **FTQ-3** in $CDCl_3$.





^{1}H NMR (600 MHz) spectrum of **TQ-3** 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_2 layer. 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 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 **FTQ-2** and **FTQ-3**, 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}= 80 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

FTQ-1

```
Excited State   1:      Singlet-A      2.61 eV  474 nm  f = 1.58  <S**2>=0.000
     HOMO > LUMO           0.70776
     HOMO < LUMO           0.11597
```

FTQ-2(Me)

```
Excited State   1:      Singlet-A      2.12 eV  586 nm  f = 2.14  <S**2>=0.000
     HOMO > LUMO           0.70816
     HOMO < LUMO           0.12439
```

FTQ-3(Me)

```
Excited State   1:      Singlet-A      1.96 eV  632 nm  f = 2.63  <S**2>=0.000
     HOMO > LUMO           0.70965
     HOMO < LUMO           0.13242
```

TQ-1

```
Excited State   1:      Singlet-A      2.57 eV  483 nm  f = 1.37  <S**2>=0.000
     HOMO > LUMO           0.70399
     HOMO < LUMO           0.10769
```

TQ-2(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
```

TQ-3(Me)

```
Excited State   1:      Singlet-A      1.96 eV  634 nm  f = 2.51  <S**2>=0.000
     HOMO–1> LUMO+1     0.10533
     HOMO > LUMO           0.70790
     HOMO < LUMO           0.12771
```

Optimized structure of **FTQ-1** at B3LYP/6-31G(d, p).

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-2.693119	-1.335370	0.000001
2	6	0	-1.330513	-1.383311	0.000006
3	16	0	-1.907940	1.175286	0.000008
4	6	0	-3.225420	-0.005828	0.000002
5	6	0	4.552791	-0.370957	-0.000003
6	6	0	-0.677228	-0.112527	0.000010
7	6	0	0.677226	0.112529	0.000010
8	16	0	1.907940	-1.175288	0.000008
9	6	0	3.225420	0.005828	0.000003
10	6	0	2.693118	1.335369	0.000002
11	6	0	1.330512	1.383311	0.000007
12	9	0	3.466054	2.412100	-0.000002
13	9	0	0.635912	2.519361	0.000008
14	9	0	-3.466055	-2.412099	-0.000003
15	9	0	-0.635912	-2.519361	0.000008
16	6	0	-4.552790	0.370958	-0.000004
17	6	0	-5.623306	-0.571314	-0.000002
18	7	0	-6.526556	-1.305824	-0.000033
19	6	0	-4.898877	1.754589	-0.000005
20	7	0	-5.145427	2.893091	-0.000001
21	6	0	5.623307	0.571315	0.000000
22	7	0	6.526556	1.305825	-0.000036
23	6	0	4.898878	-1.754589	-0.000005
24	7	0	5.145429	-2.893091	0.000001

Optimized structure of **FTQ-2(Me)** at B3LYP/6-31G(d, p).

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.691723	1.757533	0.000062
2	6	0	-0.691789	1.757483	-0.000119
3	6	0	1.269400	0.433182	0.000134
4	16	0	0.000049	-0.797950	-0.000030
5	6	0	-1.269380	0.433101	-0.000184
6	6	0	-2.603835	0.057060	-0.000132
7	6	0	-5.168771	-0.157087	-0.000008
8	16	0	-4.003670	1.169089	0.000485
9	6	0	-3.112704	-1.276716	-0.000601
10	6	0	-4.474326	-1.400047	-0.000564
11	6	0	5.168793	-0.157073	0.000030
12	6	0	2.603862	0.057157	0.000098
13	16	0	4.003735	1.169140	-0.000481
14	6	0	4.474308	-1.400010	0.000560
15	6	0	3.112690	-1.276632	0.000568
16	6	0	-6.535994	0.064020	0.000205
17	6	0	6.536024	0.063989	-0.000148
18	6	0	1.547197	2.993854	0.000060
19	6	0	-1.547378	2.993724	-0.000127
20	9	0	5.099581	-2.572273	0.001027
21	9	0	2.308119	-2.340064	0.001055
22	9	0	-2.308177	-2.340182	-0.001118

23	9	0	-5.099640	-2.572289	-0.001028
24	6	0	-7.035427	1.398124	0.000790
25	7	0	-7.402393	2.504472	0.001272
26	6	0	-7.486686	-0.996848	-0.000135
27	7	0	-8.295150	-1.835352	-0.000374
28	6	0	7.035500	1.398077	-0.000713
29	7	0	7.402500	2.504414	-0.001184
30	6	0	7.486682	-0.996910	0.000210
31	7	0	8.295119	-1.835439	0.000468
32	1	0	0.949505	3.903968	0.000715
33	1	0	2.192890	3.031905	0.883855
34	1	0	2.191922	3.032493	-0.884429
35	1	0	-0.949774	3.903895	-0.000822
36	1	0	-2.193103	3.031684	-0.883904
37	1	0	-2.192087	3.032323	0.884377

Optimized structure of **FTQ-3(Me)** at B3LYP/6-31G(d, p).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.154613	0.694557	-0.000053
2	6	0	0.154612	-0.694559	-0.000052
3	16	0	-1.304338	-1.654387	-0.000036
4	6	0	-2.310088	-0.164602	-0.000013
5	6	0	-1.491993	1.023043	-0.000014
6	16	0	1.304337	1.654385	-0.000041
7	6	0	2.310087	0.164600	-0.000016
8	6	0	1.491993	-1.023045	-0.000015
9	6	0	-3.693062	-0.267384	-0.000004
10	6	0	3.693062	0.267384	-0.000011
11	6	0	-4.466956	-1.462655	0.000012
12	6	0	-5.825597	-1.295339	0.000010
13	6	0	-6.242055	0.065171	-0.000005
14	16	0	-4.822779	1.115512	-0.000027
15	6	0	4.466955	1.462655	0.000008
16	6	0	5.825596	1.295340	0.000010
17	6	0	6.242055	-0.065170	-0.000004
18	16	0	4.822780	-1.115511	-0.000033
19	6	0	-7.532792	0.571222	0.000009
20	6	0	7.532793	-0.571220	0.000011
21	6	0	-2.006759	2.434640	0.000020
22	6	0	2.006759	-2.434641	0.000020
23	9	0	-3.901842	-2.671736	0.000029
24	9	0	-6.683923	-2.310254	0.000024
25	9	0	3.901840	2.671736	0.000024
26	9	0	6.683921	2.310257	0.000029
27	6	0	-7.738617	1.980086	0.000009
28	7	0	-7.862247	3.139322	0.000037
29	6	0	-8.685147	-0.265478	0.000016
30	7	0	-9.651736	-0.915663	0.000047
31	6	0	7.738618	-1.980084	0.000008
32	7	0	7.862252	-3.139320	0.000037
33	6	0	8.685147	0.265481	0.000024
34	7	0	9.651742	0.915659	0.000052
35	1	0	-2.616966	2.645060	0.884656
36	1	0	-1.175419	3.143454	0.000095

```
    37      1       0     -2.616878   2.645138  -0.884658
    38      1       0      2.616971  -2.645060   0.884652
    39      1       0      1.175419  -3.143456   0.000100
    40      1       0      2.616872  -2.645141  -0.884662
 ---------------------------------------------------------------------------------------------------
```

Optimized structure of **TQ-1** at B3LYP/6-31G(d, p).

```
---------------------------------------------------------------------------------------------------
 Center     Atomic      Atomic              Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------------------------------------
     1      6       0      2.579781   1.539159  -0.000001
     2      6       0      1.219715   1.500315  -0.000002
     3     16       0      1.971768  -1.029355  -0.000001
     4      6       0      3.195080   0.238572  -0.000001
     5      6       0     -4.551438   0.028047   0.000000
     6      6       0      0.664532   0.175956  -0.000002
     7      6       0     -0.664532  -0.175954  -0.000002
     8     16       0     -1.971767   1.029356  -0.000001
     9      6       0     -3.195080  -0.238573  -0.000001
    10      6       0     -2.579780  -1.539159  -0.000002
    11      6       0     -1.219714  -1.500314  -0.000002
    12      6       0      4.551437  -0.028048   0.000000
    13      6       0      5.493195   1.042445   0.000002
    14      7       0      6.243532   1.933381   0.000007
    15      6       0      5.044497  -1.364181  -0.000001
    16      7       0      5.414465  -2.468954  -0.000001
    17      6       0     -5.493196  -1.042446   0.000001
    18      7       0     -6.243533  -1.933382   0.000009
    19      6       0     -5.044498   1.364180  -0.000001
    20      7       0     -5.414467   2.468953  -0.000001
    21      1       0      3.175761   2.443708  -0.000001
    22      1       0      0.591681   2.384228  -0.000001
    23      1       0     -3.175759  -2.443709  -0.000002
    24      1       0     -0.591679  -2.384226  -0.000003
---------------------------------------------------------------------------------------------------
```

Optimized structure of **TQ-2** at B3LYP/6-31G(d, p).

```
---------------------------------------------------------------------------------------------------
 Center     Atomic      Atomic              Coordinates (Angstroms)
 Number     Number       Type              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-3** at B3LYP/6-31G(d, p).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.188863	-0.686961	-0.000258
2	6	0	-0.188863	0.686960	-0.000261
3	16	0	1.229801	1.706400	-0.000242
4	6	0	2.303434	0.265134	-0.000156
5	6	0	1.539958	-0.955486	-0.000186
6	16	0	-1.229801	-1.706401	-0.000239
7	6	0	-2.303434	-0.265135	-0.000160
8	6	0	-1.539958	0.955485	-0.000192
9	6	0	3.676019	0.460707	-0.000053
10	6	0	-3.676020	-0.460708	-0.000060
11	6	0	4.350429	1.722587	0.000091
12	6	0	5.713793	1.648152	0.000181
13	6	0	6.213575	0.307401	0.000111
14	16	0	4.885282	-0.847059	-0.000082
15	6	0	-4.350430	-1.722588	0.000088
16	6	0	-5.713794	-1.648151	0.000183
17	6	0	-6.213576	-0.307401	0.000114
18	16	0	-4.885281	0.847058	-0.000088
19	6	0	7.544955	-0.086223	0.000191
20	6	0	-7.544956	0.086225	0.000202
21	6	0	2.123261	-2.339842	-0.000134
22	6	0	-2.123262	2.339841	-0.000150
23	6	0	7.910027	-1.460883	0.000136
24	7	0	8.171753	-2.596994	0.000096
25	6	0	8.578309	0.893301	0.000330
26	7	0	9.404283	1.715638	0.000428
27	6	0	-7.910027	1.460885	0.000147
28	7	0	-8.171748	2.596998	0.000108
29	6	0	-8.578311	-0.893299	0.000350
30	7	0	-9.404283	-1.715638	0.000400
31	1	0	3.808202	2.661454	0.000137

```
  32          1           0        6.380974    2.501277    0.000300
  33          1           0       -3.808204   -2.661455    0.000131
  34          1           0       -6.380976   -2.501277    0.000305
  35          1           0        2.745213   -2.517368   -0.883759
  36          1           0        2.745197   -2.517307    0.883514
  37          1           0        1.328926   -3.090020   -0.000118
  38          1           0       -2.745196    2.517313    0.883498
  39          1           0       -1.328926    3.090019   -0.000140
  40          1           0       -2.745215    2.517360   -0.883775
 ---------------------------------------------------------------------
```

GIWAXS measurements of the films deposited by spin-coating were performed at the DELTA Synchrotron using beamline BL09 with a photon energy of 10 keV. The beam size was 1.0 mm × 0.2 mm (width x height), and samples were irradiated just below the critical angle for total reflection with respect to the incoming X-ray beam (~0.1°). The scattering intensity was detected on a 2-D image plate (MAR-345) with a pixel size of 150 μm (2300 × 2300 pixels), and the detector was placed 523 mm from the sample center. All X-ray scattering measurements were performed under vacuum (~1mbar) to reduce air scattering and beam damage to the sample. All 2DWAXS data processing and analysis was performed by using the software package Datasqueeze (http://www.datasqueezesoftware.com).

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