Electronic Supplementary Information

Cross-conjugated isothianaphthene quinoids: a versatile strategy for controlling electronic structures

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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. 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. UV-vis-NIR spectra were recorded on a Shimadzu UV-3600 spectrophotometer. All spectra were obtained in spectrograde solvents. Photoelectron spectroscopy in air (PESA) was carried out using a Riken Keiki Co. Ltd. AC-3 with a light intensity of 20 mW. High-resolution mass spectrum (HRMS) was obtained atmospheric pressure chemical ionization (APCI) method using a Thermo scientific LTQ Orbitrap XL. 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–2θ scans between 2º–30º with scanning steps of 0.01º.

Electrochemical experiments have been conducted in dichloromethane or 1,1,2,2-tetrachloroethane at room temperature by using 0.1 M tetrabutyl ammonium hexafluorophosphate (Bu$_4$NPF$_6$) as the supporting electrolyte. DPV measurement 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$^{-1}$. In situ UV-Vis-NIR spectroelectrochemical studies were conducted on the the Varian Cary 5000 UV-Vis-NIR Spectrophotometer, respectively. A C3 epsilon potentiostat from BASi was used for the electrolysis using a thin layer cell from a demountable omni cell from Specac. In this cell, a three electrodes system was coupled to conduct in situ spectroelectrochemistry. A Pt gauze was used as the working electrode, a Pt wire was used as the counter electrode, and an Ag wire was used as the pseudo-reference electrode. The spectra were collected a constant potential electrolysis and the potentials were changed in interval of 15 mV. The electrochemical medium used was 0.1 M Bu$_4$NPF$_6$ in fresh distilled dichloromethane, at room temperature with sample concentrations of 10$^{-3}$ M.

The 1064 nm FT–Raman spectra were obtained with an FT–Raman accessory kit (FRA/106–S) of a Bruker Equinox 55 FT–IR interferometer. A continuous–wave Nd–YAG laser working at 1064 nm was employed for excitation. A germanium detector operating at liquid nitrogen temperature was used. Raman scattering radiation was collected in a back–scattering configuration with a standard spectral resolution of 4 cm$^{-1}$. For these measurements, 1000–3000 scans were averaged for each spectrum.
Supplementary figures

Fig. S1 TGA curves for 5TQ-B(Ph), 6a, and 9a with a heating rate of 10 °C min⁻¹ in N₂.

Fig. S2 Calculated HOMOs and LUMOs of 5TQ-B₅(H), 5TQ-B₃(H), 5TQ-BBB(H), and 5TQ-B(H).

Table S1. NICS(1.7)zz values calculated at the B3LYP/6-31G(d,p) level of theory by using the Guassian09.

| Ring | 5TQ-B₅(H) | 5TQ-B₃(H) | 5TQ-BBB(H) | 5TQ-B(H) |
|------|-----------|-----------|------------|----------|
| A1   | −17.9349  | −17.0315  | −15.6762   | −13.7215 |
| A2   | −16.9591  | −19.1305  | -          | -        |
| A3   | −18.5761  | -         | −17.1780   | -        |
| B    | −6.5389   | −5.5824   | −7.1950    | −12.9392 |
| C    | −6.4646   | −7.0087   | −8.2827    | −10.5878 |
| D    | −7.8669   | −7.7546   | −8.3854    | −8.0972  |
Fig. S3 $^1$H NMR spectra of 5TQ-B5(Ph) (green), 5TQ-B3(Ph) (blue), and 5TQ-BBB(Ph) (yellow) in 1,1,2,2,-tetrachloroethane-$d_2$ at 130 °C, and 5TQ-B(Ph) (red) in CDCl$_3$ at 25 °C in the aromatic regions. Several minor peaks in the spectrum of 5TQ-B3(Ph) are attributed to syn-, anti-isomers.

Fig. S4 From the bottom: 5TQ-BBB(Ph), 5TQ-B3(Ph), 5TQ-B5(Ph). UV-Vis-NIR spectroelectrochemical reduction/oxidation (right/left) processes in 0.1 M TBAPF$_6$ in dichloromethane at room temperature. Red lines correspond to the spectra of neutral species, blue lines correspond to the reduced/oxidized species. Dashed light color lines correspond to the intermediate spectra between the former species.
Fig. S5 XRD profiles of (a) 5TQ-B5(EH), (b) 5TQ-B3(EH), and (c) 5TQ-BBB(EH) in thin films.

Fig. S6 AFM height images of (a) 5TQ-B5(EH), (b) 5TQ-B3(EH), and (c) 5TQ-BBB(EH) in thin films.

Fig. S7 Transfer characteristics of the OFETs based on (a) 5TQ-B5(EH), (b) 5TQ-B3(EH), and (c) 5TQ-BBB(EH).

Fig. S8 Output characteristics of the OFETs based on (a) 5TQ-B5(EH), (b) 5TQ-B3(EH), and (c) 5TQ-BBB(EH).
Fig. S9 Transfer characteristics of OFETs based on (a) 5TQ-B5(EH), (b) 5TQ-B3(EH), and (c) 5TQ-BBB(EH) with repeated biases up to 100 cycles.

Fig. S10 UV-vis-NIR absorption spectra of 5TQ-B5(EH) (green), 5TQ-B3(EH) (blue), 5TQ-BBB(EH) (yellow), and 5TQ-B(EH) (red) in thin films.

Fig. S11 PESA spectra of (a) 5TQ-B5(EH), (b) 5TQ-B3(EH), and (c) 5TQ-BBB(EH) in thin films.

Table S2. Properties of the molecules in thin films.

| Compounds    | $\lambda_{\text{max}}$ /nm | $\Delta E_{\text{opt}}$ /eV | $I_p$ /eV $^a$ |
|--------------|----------------------------|----------------------------|----------------|
| 5TQ-B5(EH)   | 840                        | 1.16                       | -5.5           |
| 5TQ-B3(EH)   | 959                        | 1.13                       | -5.8           |
| 5TQ-BBB(EH)  | 1043                       | 0.94                       | -5.8           |

$^a$ Determined by PESA measurements.
Materials

Unless stated otherwise, all reagents were purchased from commercial sources and used without purification. Compounds 1b, 2, 7b, S1, S2, and S7 were prepared by the reference procedures.1-3

Scheme S1. Synthetic route of 5TQ-B(Ph), 5TQ-B(EH), 5TQ-B5(Ph), and 5TQ-B5(EH).

Synthesis of 3a: 1a (110 mg, 0.092 mmol), 2 (80 mg, 0.28 mmol), Pd$_2$(dba)$_3$·CHCl$_3$ (9.5 mg, 0.0092 mmol), SPhos (15 mg, 0.037 mmol), and K$_2$PO$_4$ (78 mg, 0.37 mmol) were placed in a reaction vial and dissolved in THF (1.4 mL)/H$_2$O (0.23 mL). The reaction vial was purged with nitrogen and allowed to warm to 65 °C. After stirring for 2 h, the reaction mixture was extracted with EtOAc, washed with water, and the organic layer was dried using MgSO$_4$. The extraction was passed through pad of celite and the solvent was removed under reduced pressure, followed by purification with preparative GPC (CHCl$_3$) to give the intermediate A (77 mg, 66%) as a dark red solid.

$^1$H NMR (600 MHz, CDCl$_3$, TMS): δ 7.84 (d, J = 8.2 Hz, 2H), 6.79 (s, 4H), 6.77 (s, 2H), 6.75 (s, 2H), 6.64-6.53 (m, 8H), 4.27-4.25 (m, 2H), 4.19-4.16 (m, 4H), 3.89-3.86 (m, 4H), 2.49 (t, J = 7.6 Hz, 8H), 1.84-1.63 (m, 16H), 1.42-1.37 (m, 8H), 1.29-1.23 (m, 24H), 0.88 (t, J = 6.9 Hz, 12H); $^{13}$C NMR (150 MHz, CDCl$_3$, TMS): δ 147.6, 145.3, 144.6, 144.6, 143.8, 143.8, 142.1, 141.3, 139.1, 135.8, 135.7, 135.6, 135.5, 135.4, 135.4, 135.3, 127.2, 126.7, 125.6, 124.1, 124.0, 122.5, 122.3, 121.8, 112.3, 112.3, 112.6, 36.9, 36.6, 35.9, 35.8, 35.7, 31.8, 31.6, 29.0, 26.2, 26.1, 25.9, 22.6, 14.2; HRMS (APCI) m/z: [M+H]$^+$ calcd. for C$_{64}$H$_{64}$N$_2$S$_6$, 1263.6032; found, 1263.6034.

NIS (29 mg, 0.13 mmol) was added to a solution of intermediate A (77 mg, 0.061 mmol) in DMF (6.4 mL) and CHCl$_3$ (0.6 mL) at 0 °C. Then, this reaction was allowed to warm to room temperature. After stirring overnight, the reaction was quenched by addition of Na$_2$SO$_4$ aq.. The combined organic was extracted with EtOAc and washed with water. After drying with MgSO$_4$, the solvent was removed under reduced pressure and purified by column chromatography on silica gel (hexane:CHCl$_3$ = 10:1) to give 3a (70 mg, 50%, 2 steps) as a dark red solid.

$^1$H NMR (600 MHz, CDCl$_3$, TMS): δ 7.82 (s, 2H), 6.78 (s, 4H), 6.77 (s, 2H), 6.62-6.52 (m, 8H), 4.25-4.14 (m, 4H), 3.76 (s, 2H), 2.42 (t, J = 6.2 Hz, 8H), 1.80-1.61 (m, 16H), 1.42-1.37 (m, 8H), 1.27-1.24 (m, 24H), 0.90-0.86 (m, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$, TMS): δ 152.6, 145.2, 145.1, 145.0, 144.0, 143.9, 142.0, 141.1, 139.1, 135.5, 135.3, 135.3, 135.2, 127.6, 127.1, 126.7, 125.3, 122.7, 122.1, 62.9, 37.9, 36.1, 35.8, 31.7, 31.5, 28.9, 25.8, 25.5, 22.5, 14.0; HRMS (APCI) m/z: [M+H]$^+$ calcd. for C$_{64}$H$_{64}$I$_2$S$_6$, 1515.3965; found, 1515.3973.

Synthesis of 3b: 1b (180 mg, 0.19 mmol), 2 (120 mg, 0.43 mmol), Pd$_2$(dba)$_3$·CHCl$_3$ (20 mg, 0.019 mmol), SPhos (32 mg, 0.077 mmol), and K$_2$PO$_4$ (160 mg, 0.77 mmol) were placed in a reaction vial and dissolved in THF (2.6 mL)/H$_2$O (0.40 mL). The reaction vial was purged with nitrogen and allowed to warm to 65 °C. After stirring for 3 h, the reaction mixture was extracted with EtOAc, washed with water, and the organic layer was dried using MgSO$_4$. The extraction was passed through pad of celite and the solvent was removed under reduced pressure, followed by purification with preparative GPC (CHCl$_3$) to give the intermediate B (160 mg, 83%) as a dark red solid.

$^1$H NMR (400 MHz, CDCl$_3$, TMS): δ 7.55 (s, 2H), 6.76 (s, 2H), 6.60-6.54 (m, 8H), 4.21 (s, 6H), 3.88 (s, 2H), 2.59-2.55 (m, 4H), 1.77-1.63 (m, 18H), 1.42-1.29 (m, 16H), 0.93-0.86 (m, 12H); $^{13}$C NMR (150 MHz, CDCl$_3$, TMS): δ 147.6, 144.8, 144.5, 144.4, 143.7, 143.6, 137.8, 135.7, 135.7, 135.6, 135.5, 135.4, 135.4, 135.3, 135.2, 135.2, 135.3, 135.3, 127.6, 127.1, 126.7, 125.3, 122.7, 122.1, 62.9, 37.9, 36.1, 35.8, 31.7, 31.5, 31.5, 28.9, 25.8, 25.5, 22.5, 14.0; HRMS (APCI) m/z: [M+H]$^+$ calcd. for C$_{64}$H$_{64}$I$_2$S$_6$, 1515.3965; found, 1515.3973.

NIS (76 mg, 0.34 mmol) was added to a solution of intermediate B (160 mg, 0.16 mmol) in DMF (17 mL) and
CHCl₃ (1.6 mL) at 0 °C. Then, this reaction was allowed to warm to room temperature. After stirring overnight, the reaction was quenched by addition of Na₂SO₃ aq. The combined organic was extracted with EtOAc and washed with water. After drying with MgSO₄, the extraction was passed through pad of celite and the solvent was removed under reduced pressure, followed by purification with preparative GPC (CHCl₃) to give the intermediate 3b (75 mg, 31%, 2 steps) as a dark red solid. ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.53 (s, 2H), 6.60-6.53 (m, 8H), 4.25-4.10 (m, 6H), 3.78-3.75 (m, 2H), 2.59-2.56 (m, 4H), 1.73-1.61 (m, 18H), 1.41-1.26 (m, 16H), 0.93-0.84 (m, 12H); ¹³C NMR (150 MHz, CDCl₃, TMS): δ 152.7, 145.2, 145.1, 144.8, 144.0, 143.9, 138.0, 135.6, 135.4, 135.3, 127.9, 127.9, 123.6, 122.6, 122.4, 122.4, 121.2, 62.9, 40.1, 38.1, 37.8, 36.2, 36.0, 35.9, 32.6, 32.5, 29.0, 28.9, 25.9, 25.6, 25.5, 25.4, 23.2, 14.2, 11.0, 10.9; HRMS (APCI) m/z: [M+H]+= 7.6 Hz, 6H), 0.96 (t, J = 7.6 Hz, 2H), 8.59-8.57 (m, 4H), 8.50 (d, J = 7.6 Hz, 2H), 8.42 (s, 2H), 7.90-7.82 (m, 8H), 7.74 (t, J = 8.3 Hz, 2H), 7.68 (t, J = 8.3 Hz, 2H), 3.00-2.90 (m, 4H), 2.06-2.00 (m, 2H), 1.71-1.45 (m, 16H), 1.14 (t, J = 7.6 Hz, 6H), 0.96 (t, J = 7.6 Hz, 6H); HRMS (APCI) m/z: [M+H]⁺ calcd. for C₉₀H₆₈N₄S₅, 1251.2087; found, 1251.2076.

Synthesis of 5TQ-B(Ph): Sodium hydride (60% in oil) (7.5 mg, 0.18 mmol) was added to a suspension of malononitrile (6.2 mg, 0.093 mmol) in anhydrous THF (1.3 mL) under nitrogen atmosphere and stirred for 10 min at room temperature. This mixture was added to a mixture of 3a (30 mg, 0.020 mmol), Pd(PPh₃)₄ (2.3 mg, 0.0020 mmol), and 1,1'-bis(diphenylphosphino)ferrocene (dppf) (2.2 mg, 0.0040 mmol) in a reaction vial. The reaction vial was purged with nitrogen and allowed to warm to 75 °C. After stirring for 40 min, the reaction was cooled to 0 °C and diluted hydrochloric acid (1 M, 0.8 mL). The combined organic was extracted with CHCl₃, washed with water, and the organic layer was dried using MgSO₄. The organic solvent was removed under reduced pressure. Then the resultant precipitate was dissolved in CH₂Cl₂ and the oxidation reaction was conducted by adding DDQ. After confirming the disappearance of intermediate by TLC, the organic solvent was removed under reduced pressure. The resultant precipitate was washed with acetone and purified by column chromatography on silica gel (CH₂Cl₂) to give 5TQ-B(Ph) (12 mg, 44%) as a green solid. ¹H NMR (600 MHz, CDCl₃, TMS): δ 8.00-8.18 (br), 6.81 (s, 2H), 6.79 (s, 4H), 2.45 (t, J = 8.3 Hz, 8H), 1.45-1.35 (m, 8H), 1.20-1.31 (m, 24H), 0.92-0.85 (m, 12H); HRMS (APCI) m/z: [M+H]⁺ calcd. for C₇₉H₆₀N₄S₅, 1389.5999; found, 1389.6005.

Synthesis of 5TQ-B(EH): Compound 5TQ-B(EH) was synthesized from 3b (73 mg, 0.058 mmol) with a yield of 69% by following the procedure used for the preparation of 5TQ-B(Ph). Green solid; ¹H NMR (600 MHz, CDCl₃, TMS): δ 8.05-7.95 (br), 6.90-6.70 (br), 5.20-4.70 (br), 3.15-2.80 (br), 1.82-1.72 (br), 1.50-1.25 (m, 18H), 0.98 (t, J = 7.6 Hz, 6H), 0.90-0.86 (m, 6H); HRMS (APCI) m/z: [M+H]⁺ calcd. for C₇₀H₆₈N₄S₅, 1125.4121; found, 1125.4115.

Synthesis of 5TQ-B5(Ph): 5TQ-B(Ph) (12 mg, 0.0086 mmol) was placed in a Kugelrohr setup and allowed to heated at 260 °C for 20 min under vacuum condition to give 5TQ-B5(Ph) as a blue solid, quantitatively. ¹H NMR (600 MHz, 130 °C, 1,1,2,2-tetrachloroethane-d₂): δ 8.87 (d, J = 8.3 Hz, 2H), 8.64 (s, 2H), 8.60-8.55 (m, 2H), 8.49-8.44 (m, 4H), 7.85-7.81 (m, 2H), 7.79-7.71 (m, 4H), 7.66-7.62 (m, 2H), 7.08 (s, 4H), 7.07 (s, 2H), 2.67 (t, J = 8.2 Hz, 8H), 1.63 (t, J = 6.5 Hz, 8H), 1.43-1.35 (m, 24H), 0.97 (t, J = 6.9 Hz, 12H). ¹³C NMR spectrum of this compound was not observed due to the limited solubility. HRMS (APCI) m/z: [M+H]⁺ calcd. for C₈₂H₇₀N₄S₅, 1277.4747; found, 1277.4747.

Synthesis of 5TQ-B5(EH): Compound 5TQ-B5(EH) was synthesized from 5TQ-B(EH) (19 mg, 0.017 mmol) quantitatively, by following the procedure used for the preparation of 5TQ-B5(Ph). Blue solid; ¹H NMR (600 MHz, 130 °C, 1,1,2,2-tetrachloroethane-d₂): δ 8.89 (d, J = 7.6 Hz, 2H), 8.59-8.57 (m, 4H), 8.50 (d, J = 7.6 Hz, 2H), 8.42 (s, 2H), 7.90-7.82 (m, 8H), 7.74 (t, J = 8.3 Hz, 2H), 7.68 (t, J = 8.3 Hz, 2H), 3.00-2.90 (m, 4H), 2.06-2.00 (m, 2H), 1.71-1.45 (m, 16H), 1.14 (t, J = 7.6 Hz, 6H), 0.96 (t, J = 7.6 Hz, 6H); HRMS (APCI) m/z: [M+H]⁺ calcd. for C₈₂H₇₀N₄S₅, 1013.2869; found, 1013.2869.
Synthesis of the intermediate C: 1a (91 mg, 0.076 mmol), thiophene-2-boronic acid pinacol ester (4) (48 mg, 0.23 mmol), Pd₂(dba)₃·CHCl₃ (7.9 mg, 0.0076 mmol), SPhos (13 mg, 0.030 mmol), and K₃PO₃ (65 mg, 0.30 mmol) were placed in a reaction vial and dissolved in THF (1.2 mL)/H₂O (0.2 mL). The reaction vial was purged with nitrogen and allowed to warm to 65 °C. After stirring for 2 h, the reaction mixture was extracted with EtOAc, washed with water, and the organic layer was dried using MgSO₄. The extraction was passed through pad of celite and the solvent was removed under reduced pressure, followed by purification with preparative GPC (CHCl₃) to give the intermediate C (67 mg, 80%) as a dark red solid. ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.84 (s, 2H), 7.29 (dd, J = 5.0, 0.9 Hz, 2H), 7.17 (dd, J = 3.7, 0.9 Hz, 2H), 7.06 (dd, J = 5.0, 3.7 Hz, 2H), 6.78 (s, 6H), 6.61-6.58 (m, 4H), 2.43 (t, J = 7.8 Hz, 8H), 1.80-1.20 (m, 8H), 1.44-1.35 (m, 8H), 1.30-1.20 (m, 24H), 0.88 (t, J = 6.9 Hz, 12H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 145.8, 143.7, 142.1, 141.2, 139.2, 135.8, 135.6, 135.3, 135.5, 127.6, 127.2, 126.8, 125.5, 125.3, 121.5, 124.3, 122.1, 121.0, 36.2, 35.9, 35.9, 31.8, 31.6, 29.0, 25.8, 22.6, 14.2; HRMS (APCI) m/z: [M+H]+ calcd. for C₁₇H₂₆S₅, 1107.5093; found, 1107.5107.

Synthesis of 5a: The intermediate C (42 mg, 0.031 mmol) was placed in a two-necked-bottomed flask, which was filled with N₂, and dissolved in THF (3.5 mL). 1 M LDA (0.16 mL) was added slowly to a solution of S2 (39 mg, 0.16 mmol) in THF 0.5 mL was added to the two-necked-bottomed flask and stirred 10 min at –78 °C. Then, the reaction was quenched by addition of Na₂S₂O₄·aq. The reaction mixture was extracted with EtOAc, washed with water, and the organic layer was dried using MgSO₄. The extraction was passed through pad of celite and the solvent was removed under reduced pressure, followed by purification with preparative GPC (CHCl₃) to give 5a (29 mg, 69%) as a dark red solid. ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.81 (s, 2H), 7.20 (d, J = 4.1 Hz, 2H), 6.84-6.82 (m, 2H), 6.78-6.76 (m, 8H), 6.63-6.56 (m, 4H), 4.32-4.23 (m, 4H), 2.42 (t, J = 7.6 Hz, 8H), 1.73-1.68 (m, 8H), 1.44-1.35 (m, 8H), 1.30-1.20 (m, 24H), 0.88 (t, J = 6.9 Hz, 12H); ¹³C NMR (150 MHz, CDCl₃, TMS): δ 145.8, 144.4, 142.1, 141.1, 139.4, 137.4, 135.4, 135.3, 127.2, 126.8, 126.4, 125.3, 124.2, 122.1, 121.5, 72.1, 36.2, 36.0, 35.9, 31.8, 31.6, 29.0, 25.7, 22.6, 14.2; HRMS (APCI) m/z: [M+H]+ calcd. for C₁₇H₈₂S₅, 1359.3026; found, 1359.3027.

Synthesis of the intermediate D: Compound the intermediate D was synthesized from 1b (220 mg, 0.24 mmol) with a yield of 90% by following the procedure used for the preparation of the intermediate C. Dark red solid; ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.53 (s, 2H), 7.30 (d, J = 5.0 Hz, 2H), 7.18 (d, J = 3.7 Hz, 2H), 7.08 (dd, J = 5.0, 3.7 Hz, 2H), 6.62-6.57 (m, 4H), 4.37 (s, 2H), 2.40 (s, 2H), 2.58 (d, J = 7.3 Hz, 4H), 1.75-1.63 (m, 10H), 1.40-1.28 (m, 16H), 0.93-0.85 (m, 12H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 145.3, 143.7, 138.0, 135.9, 135.5, 135.5, 135.3, 127.6, 124.9, 124.9, 124.6, 123.7, 121.5, 121.2, 40.1, 40.0, 37.9, 36.2, 36.0, 32.5, 32.4, 29.0, 28.8, 25.8, 25.8, 25.6, 23.2, 14.2, 11.0, 10.9; HRMS (APCI) m/z: [M+H]+ calcd. for C₁₇H₈₂S₅, 843.3215; found, 843.3208.

Synthesis of 5b: Compound 5b was synthesized from the intermediate D (95 mg, 0.11 mmol) with a yield of 55% by following the procedure used for the preparation of S2a. Dark red solid; ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.50 (s, 2H), 7.21 (d, J = 3.7 Hz, 2H), 6.84 (d, J = 3.7 Hz, 2H), 6.62-6.55 (m, 4H), 4.30 (s, 2H), 4.18 (s, 2H), 2.58 (d, J = 6.9 Hz, 4H), 1.75-1.58 (m, 10H), 1.40-1.28 (m, 16H), 0.92-0.85 (m, 12H); ¹³C NMR (150 MHz, CDCl₃, TMS): δ 145.3, 144.3, 141.8, 138.1, 137.3, 135.3, 126.2, 123.8, 123.5, 121.9, 121.1, 72.1, 40.0, 40.0, 37.8, 36.1, 36.0, 32.5, 32.4, 28.9, 28.8, 25.7, 25.6, 25.6, 23.2, 14.2, 11.0, 10.9; HRMS (APCI) m/z: [M+H]+ calcd. for C₂₁H₉₂S₅, 1095.1148; found, 1095.1150.

Scheme S2. Synthetic route of 5TQ-B3(Ph) and 5TQ-B3(EH).
Synthesis of 5TQ-B3(Ph): Compound 5TQ-B3(Ph) was synthesized from 5TQ-B5(Ph). Blue solid; \(^1H\) NMR (600 MHz, CDCl\(_3\), TMS): \(\delta 8.58-8.50\) (m, 4H), \(8.26-8.05\) (m, 2H), \(7.89\) (s, 2H), \(7.75\) (s, 4H), \(7.25\) (s, 2H), \(7.03-6.96\) (m, 6H), \(2.65-2.58\) (m, 8H), \(1.64-1.55\) (m, 8H), \(1.42-1.32\) (m, 24H), \(1.01-0.90\) (m, 12H); HRMS (APCI) \(m/z\): \([M+H]\)^+ calcd. for C\(_{74}\)H\(_{72}\)N\(_4\)S\(_5\)S, 1177.4434; found, 1177.4425.

Synthesis of 5TQ-B3(EH): Compound 5TQ-B3(EH) was synthesized from 5TQ-B5(Ph). Blue solid; \(^1H\) NMR (600 MHz, 130 °C, 1,1,2,2-tetrachloroethane-d\(_2\)): \(\delta 8.55-8.50\) (m, 2H), \(8.30-8.05\) (m, 4H), \(7.88-7.64\) (m, 6H), \(7.32-7.26\) (m, 2H), \(2.94-2.88\) (m, 4H), \(1.93-1.86\) (m, 2H), \(1.63-1.48\) (m, 16H), \(1.11\) (t, \(J = 7.6\) Hz, 6H), \(1.01\) (t, \(J = 7.6\) Hz, 6H); HRMS (APCI) \(m/z\): \([M+H]\)^+ calcd. for C\(_{54}\)H\(_{48}\)N\(_4\)S\(_5\), 913.2556; found, 913.2561.

Scheme S3. Synthetic route of 5TQ-BBB(Ph) and 5TQ-BBB(EH).

Synthesis of the intermediate E: 7a (100 mg, 0.096 mmol), 2 (61 mg, 0.21 mmol), Pd\(_2\)(dba)\(_3\)-CHCl\(_3\) (10 mg, 0.0096 mmol), SPhos (16 mg, 0.039 mmol), and K\(_3\)PO\(_4\) (82 mg, 0.39 mmol) were placed in a reaction vial and dissolved in THF (1.3 mL)/H\(_2\)O (0.2 mL). The reaction vial was purged with nitrogen and allowed to warm to 50 °C. After stirring for 2 h, the reaction mixture was extracted with EtOAc, washed with water, and the organic layer was dried using MgSO\(_4\). The extraction was passed through pad of celite and the solvent was removed under reduced pressure, followed by purification with preparative GPC (CHCl\(_3\)) to give the intermediate E (89 mg, 84%) as a dark red solid. \(^1H\) NMR (600 MHz, CDCl\(_3\), TMS): \(\delta 8.01\) (s, 2H), \(7.33\) (d, \(J = 3.4\) Hz, 2H), \(7.14\) (d, \(J = 3.4\) Hz, 2H), \(6.82\) (s, 6H), \(6.80\) (s, 2H), \(6.55-6.52\) (m, 4H), \(4.38-4.34\) (m, 2H), \(3.89-3.87\) (s, 1H), \(2.45\) (t, \(J = 7.9\) Hz, 8H), \(1.66-1.60\) (m, 8H), \(1.46-1.38\) (m, 8H), \(1.30-1.26\) (m, 24H), 0.89-0.87 (m, 12H); \(^13C\) NMR (150 MHz, CDCl\(_3\), TMS): \(\delta 148.2, 142.9, 142.3, 141.2, 139.8, 136.5, 135.1, 134.7, 127.3, 126.9, 126.3, 125.8, 125.5, 124.3, 122.1, 111.6, 36.8, 35.9, 35.8, 31.6, 29.1, 26.0, 25.9, 22.6, 14.2; HRMS (APCI) \(m/z\): \([M+H]\)^+ calcd. for C\(_{72}\)H\(_{72}\)S\(_5\)S, 1107.5093; found, 1107.5093.

Synthesis of 8a: Compound 8a was synthesized from the intermediate E (84 mg, 0.076 mmol) with a yield of 49% by following the procedure used for the preparation of 6a. Dark red solid; \(^1H\) NMR (600 MHz, CDCl\(_3\), TMS): \(\delta 7.99\) (s, 2H), 7.16 (t, \(J = 4.1\) Hz, 2H), \(7.09\) (d, \(J = 3.4\) Hz, 2H), \(6.32\) (s, 2H), \(6.08\) (s, 4H), \(6.55-6.52\) (m, 4H), 4.36-4.35 (m, 2H), \(3.76-3.73\) (m, 2H), 2.45 (t, \(J = 7.9\) Hz, 8H), 1.64-1.59 (m, 8H), 1.45-1.38 (m, 8H), 1.32-1.22 (m, 24H), 0.89-0.87 (m, 12H); HRMS (APCI) \(m/z\): \([M+H]\)^+ calcd. for C\(_{37}\)H\(_{38}\)NaS\(_2\), 969.3182; found, 970.3192.

Scheme S3. Synthetic route of 5TQ-BBB(Ph) and 5TQ-BBB(EH).
Synthesis of the intermediate F: 7b (180 mg, 0.19 mmol), 2 (120 mg, 0.43 mmol), Pd2(dba)3·CHCl3 (20 mg, 0.019 mmol), SPhos (32 mg, 0.077 mmol), and K2PO4 (160 mg, 0.77 mmol) were placed in a reaction vial and dissolved in THF (2.6 mL)/H2O (0.4 mL). The reaction vial was purged with nitrogen and allowed to warm to 65 °C. After stirring for 3 h, the reaction mixture was extracted with EtOAc, washed with water, and the organic layer was dried using MgSO4. The extraction was passed through pad of celite and the solvent was removed under reduced pressure, followed by purification with preparative GPC (CHCl3) to give the intermediate F (160 mg, 83%) as a dark red solid. 1H NMR (400 MHz, CDCl3, TMS): δ 7.72 (s, 2H), 7.14 (d, J = 4.1 Hz, 2H), 6.69 (s, 2H), 6.59-6.54 (m, 4H), 4.39-4.35 (m, 2H), 3.88-3.84 (m, 2H), 2.68-2.57 (m, 4H), 1.71-1.59 (m, 10H), 1.44-1.31 (m, 16H), 0.95-0.87 (m, 12H); 13C NMR (100 MHz, CDCl3, TMS): δ 148.1, 142.7, 138.6, 135.9, 135.5, 135.2, 135.1, 134.6, 125.4, 125.1, 124.6, 124.4, 121.2, 111.5, 39.7, 37.6, 36.8, 35.8, 32.6, 32.5, 28.9, 28.9, 25.9, 25.4, 25.3, 23.2, 14.2, 10.8, 10.7; HRMS (APCI) m/z: [M+H]+ calcd. for C27H39I2S3, 843.3215; found, 843.3217.

Synthesis of 8b: Compound 8b was synthesized from the intermediate F (120 mg, 0.14 mmol) with a yield of 53% by following the procedure used for the preparation of 8a. dark red solid; 1H NMR (400 MHz, CDCl3, TMS): δ 7.70 (s, 2H), 7.25 (d, J = 3.7 Hz, 2H), 7.09 (d, J = 3.7 Hz, 2H), 6.58-6.50 (m, 4H), 4.39-4.34 (m, 2H), 3.78-3.73 (m, 2H), 2.69-2.54 (m, 4H), 1.69-1.61 (m, 8H), 1.46-1.25 (m, 16H), 0.95-0.85 (m, 12H); 13C NMR (100 MHz, CDCl3, TMS): δ 153.2, 142.8, 138.7, 135.6, 135.2, 135.1, 134.6, 129.5, 125.8, 125.1, 124.5, 121.1, 62.4, 39.7, 38.0, 37.5, 36.3, 32.6, 32.5, 28.9, 28.9, 25.5, 25.4, 25.3, 23.1, 14.2, 10.8, 10.7; HRMS (APCI) m/z: [M+H]+ calcd. for C52H56I2S3, 1095.1148; found, 1095.1134.

Synthesis of 9a: Compound 9a was synthesized from 8a (34 mg, 0.025 mmol) with a yield of 58% by following the procedure used for the preparation of 5TQ-BBB(Ph). Green solid; 1H NMR (600 MHz, CDCl3, TMS): δ 8.14-8.10 (br), 7.65-7.62 (br), 6.94 (s, 2H), 6.87 (s, 4H), 6.65-6.57 (br), 6.52-6.46 (br), 4.92-4.85 (m, 2H), 4.60-4.55 (m, 2H), 2.51 (t, J = 7.6 Hz, 8H), 1.78-1.65 (m, 8H), 1.50-1.42 (m, 8H), 1.33-1.25 (m, 24H), 0.90 (t, J = 6.5 Hz, 12H); HRMS (APCI) m/z: [M+H]+ calcd. for C78H80I4S8, 1233.5060; found, 1233.5052.

Synthesis of 9b: Compound 9b was synthesized from 8b (70 mg, 0.064 mmol) with a yield of 58% by following the procedure used for the preparation of 5TQ-BBB(Ph). Green solid; 1H NMR (400 MHz, CDCl3, TMS): δ 7.85 (s, 2H), 7.55-7.52 (m, 2H), 6.65-6.58 (m, 2H), 6.55-6.48 (m, 2H), 4.90-4.86 (m, 2H), 4.63-4.57 (m, 2H), 2.78-2.75 (m, 4H), 1.78-1.65 (m, 8H), 1.48-1.30 (m, 16H), 1.00 (t, J = 7.3 Hz, 6H), 0.91 (t, J = 6.2 Hz, 6H); HRMS (APCI) m/z: [M+H]+ calcd. for C38H38I4S8, 969.3182; found, 979.3184.

Synthesis of 5TQ-BBB(Ph): Compound 5TQ-BBB(Ph) was synthesized from 9a (17 mg, 0.014 mmol) quantitatively, by following the procedure used for the preparation of 5TQ-B5S(Ph). Blue solid; 1H NMR (600 MHz, 130 °C, 1,1,2,2-tetrachloroethane-d2): δ 8.83-8.77 (m, 2H), 8.22 (s, 2H), 8.18-8.05 (br), 7.84-7.55 (br), 7.02 (s, 2H), 6.97 (s, 4H), 2.65-2.58 (m, 8H), 1.64-1.55 (m, 8H), 1.42-1.32 (m, 24H), 1.01-0.90 (m, 12H); HRMS (APCI) m/z: [M+H]+ calcd. for C47H72N4S4, 1177.4434; found, 1177.4438.

Synthesis of 5TQ-BBB(EH): Compound 5TQ-BBB(EH) was synthesized from 9b (17 mg, 0.018 mmol) quantitatively, by following the procedure used for the preparation of 5TQ-B5S(Ph). Blue solid; 1H NMR (600 MHz, 130 °C, 1,1,2,2-tetrachloroethane-d2): δ 8.82-8.77 (m, 2H), 8.20-8.10 (br), 7.99 (s, 2H), 7.85-7.78 (m, 2H), 7.65-7.55 (br), 7.40-7.25 (br), 2.91-2.87 (m, 4H), 1.92-1.86 (m, 2H), 1.63-1.48 (m, 16H), 1.12 (t, J = 7.6 Hz, 6H), 0.99 (t, J = 6.9 Hz, 6H); HRMS (APCI) m/z: [M+H]+ calcd. for C54H48S4N4S, 913.2556; found, 913.2549.
Synthesis of S3: S1 (653 mg, 1.55 mmol) was placed in a two-necked-bottomed flask, which was filled with N₂ and dissolved in THF (10.4 mL). Grignard reagent S2 (3.47 mmol, 0.33 M in THF), which was prepared by a reaction of 1-iodo-4,7-dihydro-4,7-ethanobenzothiophene and isopropylmagnesium chloride in THF at –10 °C for 1 h, was added slowly to a solution of S1 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 CHCl₃, and the combined organic layer was washed with 5% NaOH aq., NaHCO₃ aq., and water. After drying with MgSO₄, the solvent was removed under reduced pressure. The residue was isolated by column chromatography on silica gel (hexane:EtOAc = 5:1) to give S3 (580 mg, 72%) as a pale yellow solid.

1H NMR (400 MHz, CDCl₃, TMS): δ 7.77-7.75 (m, 2H), 7.04-7.02 (m, 2H), 6.55-6.50 (m, 2H), 6.45-6.38 (m, 2H), 4.14-4.08 (m, 2H), 3.93-3.88 (m, 2H), 1.54-1.48 (m, 8H). This compound was used for next step without further purification.

Synthesis of S5: S3 (580 mg, 1.11 mmol), S4 (990 mg, 2.66 mmol), Pd₂(dbq)₃·CHCl₃ (115 mg, 0.111 mmol), SPhos (182 mg, 0.444 mmol), and K₃PO₄ (942 mg, 4.44 mmol) were placed in a reaction vial and dissolved in 1,4-dioxane (7.4 mL)/H₂O (2.1 mL). The reaction vial was purged with nitrogen and allowed to warm to 100 °C. After stirring for 14 h, the reaction mixture was extracted with EtOAc, washed with water, and the organic layer was dried using MgSO₄. The extraction was passed through pad of celite and the solvent was removed under reduced pressure, followed by purification by column chromatography on silica gel (hexane:EtOAc = 7:1) to give S5 (580 mg, 55%) as a pale yellow oil.

1H NMR (400 MHz, CDCl₃, TMS): δ 7.73-7.71 (m, 2H), 7.02-6.98 (m, 2H), 6.81 (s, 2H), 6.78 (s, 4H), 6.51-6.47 (m, 2H), 4.30-4.26 (m, 2H), 3.90-3.86 (m, 2H), 2.43 (t, J = 7.6 Hz, 8H), 1.55-1.50 (m, 8H), 1.45-1.36 (m, 8H), 1.33-1.18 (m, 24H), 0.88 (t, J = 6.9 Hz, 12H); 13C NMR (150 MHz, CDCl₃, TMS): δ 188.4, 153.3, 148.8, 143.0, 142.5, 139.7, 139.5, 135.7, 134.7, 131.5, 131.1, 127.5, 127.1, 120.1, 36.6, 36.5, 35.8, 31.7, 31.5, 29.0, 26.0, 25.1, 22.6, 14.1; HRMS (APCI) m/z: [M+H]+ calcd. for C₇₂H₇₅O₂S₂, 943.5516; found, 943.5505.

Synthesis of S6: Davy’s reagent (p-tolyl) (143 mg, 0.327 mmol) was added to a solution of intermediate S5 (280 mg, 0.297 mmol) in toluene (4.3 mL) and stirred at 50 °C for 1 h. The reaction mixture was passed through pad of celite and the solvent was removed under reduced pressure, followed by purification by column chromatography on silica gel (hexane:CH₂Cl₂ = 5:1) to give S5 (140 mg, 50%) as an orange oil. 1H NMR (400 MHz, CDCl₃, TMS): δ 7.79 (s, 2H), 6.84 (s, 2H), 6.76 (s, 6H), 6.58-6.55 (m, 4H), 4.25-4.20 (m, 2H), 3.94-3.88 (m, 2H), 2.42 (t, J = 7.8 Hz, 8H), 1.75-1.62 (m, 8H), 1.44-1.34 (m, 8H), 1.28-1.22 (m, 22H), 0.88 (t, J = 6.9 Hz, 12H); 13C NMR (100 MHz, CDCl₃, TMS): δ 147.9, 144.5, 142.0, 141.3, 139.0, 135.8, 135.3, 135.2, 129.8, 128.5, 127.2, 126.7, 125.9, 122.4, 122.1, 113.4, 77.3, 77.0, 76.7, 37.0, 36.0, 35.9, 31.8, 31.6, 29.0, 26.2, 26.1, 22.6, 14.2; HRMS (APCI) m/z: [M+H]+ calcd. for C₆₅H₇₄S₃, 943.5339; found, 943.5330.

Synthesis of 1a: NIS (100 mg, 0.445 mmol) was added to a solution of intermediate S6 (200 mg, 0.212 mmol) in DMF (16 mL) and CHCl₃ (1.6 mL) at 0 °C. Then, this reaction was allowed to warm to room temperature. After stirring overnight, the reaction was quenched by addition of Na₂SO₃ aq.. The combined organic was extracted with EtOAc and washed with water. After drying with MgSO₄, the solvent was removed under reduced pressure and purified by column chromatography on silica gel (hexane:CH₂Cl₂ = 10:1) to give 1a (190 mg, 75%) as an orange solid. 1H NMR (400 MHz, CDCl₃, TMS): δ 7.73 (s, 2H), 6.77 (s, 2H), 6.74 (s, 4H), 6.57-6.53 (m, 4H),
4.24-4.20 (m, 2H), 3.83-3.78 (m, 2H), 2.42 (t, J = 7.8 Hz, 8H), 1.71-1.62 (m, 8H), 1.44-1.20 (m, 32H), 0.88 (t, J = 6.9 Hz, 12H); H NMR (101 MHz, CDCl₃, TMS): δ 153.1, 145.1, 142.2, 141.1, 139.7, 135.6, 135.5, 135.3, 127.5, 127.3, 127.0, 125.3, 121.9, 64.3, 38.2, 36.5, 36.0, 31.9, 31.7, 29.1, 25.8, 25.6, 22.7, 14.3; HRMS (APCI) m/z: [M+H]+ calc. for C₆₄H₇₆I₂S₃, 1195.3272; found, 1195.3274.

Scheme S5. Synthetic route of 6a.

**Synthesis of S8:** Compound S8 was synthesized from S7 (440 mg, 0.840 mmol) with a yield of 91% by following the procedure used for the preparation of S5. Pale yellow oil; H NMR (600 MHz, CDCl₃, TMS): δ 7.79 (s, 2H), 7.66 (d, J = 4.8 Hz, 2H), 7.58 (d, J = 4.1 Hz, 2H), 7.08 (dd, J = 4.1, 4.8 Hz, 2H), 6.84 (s, 2H), 6.79 (s, 4H), 2.44 (t, J = 7.9 Hz, 8H), 1.46-1.37 (m, 8H), 1.32-1.20 (m, 24H), 0.88 (t, J = 6.9 Hz, 12H); 13C NMR (150 MHz, CDCl₃, TMS): δ 188.2, 144.3, 143.6, 142.7, 139.5, 138.0, 135.2, 134.8, 131.1, 128.0, 127.6, 127.1, 35.8, 31.7, 31.5, 29.0, 22.6, 14.1; HRMS (APCI) m/z: [M+H]+ calc. for C₅₂H₆₆O₂S₂, 787.4577; found, 787.4562.

**Synthesis of S9:** Compound S9 was synthesized from S8 (600 mg, 0.764 mmol) with a yield of 57% by following the procedure used for the preparation of S6. Orange oil; H NMR (400 MHz, CDCl₃, TMS): δ 7.97 (s, 2H), 7.39-7.36 (m, 4H), 7.14 (dd, J = 5.3, 3.4 Hz, 2H), 6.80 (s, 2H), 6.77 (s, 4H), 2.44 (t, J = 7.6 Hz, 8H), 1.47-1.35 (m, 8H), 1.29-1.23 (m, 24H), 0.89 (t, J = 6.9 Hz, 12H); 13C NMR (100 MHz, CDCl₃, TMS): δ 142.2, 141.1, 139.7, 135.7, 134.7, 127.9, 127.3, 126.9, 126.3, 125.6, 125.4, 121.9, 35.9, 31.8, 31.6, 29.0, 22.6, 14.2; HRMS (APCI) m/z: [M+H]+ calc. for C₅₂H₆₆I₂S₂, 787.4395; found, 787.4395.

**Synthesis of 7a:** Compound 7a was synthesized from S9 (444 mg, 0.056 mmol) with a yield of 62% by following the procedure used for the preparation of 7a. Orange oil; H NMR (600 MHz, CDCl₃, TMS): δ 7.86 (s, 2H), 7.28 (d, J = 3.4 Hz, 2H), 7.04 (d, J = 3.4 Hz, 2H), 6.81 (s, 2H), 6.75 (s, 4H), 2.44 (t, J = 7.9 Hz, 8H), 1.45-1.38 (m, 8H), 1.33-1.22 (m, 24H), 0.89 (t, J = 6.9 Hz, 12H); 13C NMR (151 MHz, CDCl₃, TMS): δ 142.3, 141.4, 140.9, 140.3, 137.8, 134.9, 127.2, 127.1, 127.0, 125.6, 121.6, 73.3, 35.8, 31.8, 31.6, 29.0, 22.6, 14.2; HRMS (APCI) m/z: [M+H]+ calc. for C₅₂H₆₄I₂S₃, 1039.2333; found, 1039.2338.

Scheme S6. Synthetic route of S4.

**Synthesis of S4:** S10 (1.43 g, 4.40 mmol), B₂pin₂ (1.24 g, 4.90 mmol), AcOK (1.31 g, 13.4 mmol), and PdCl₂(dppf)-CH₂Cl₂ (180 mg, 0.220 mmol) were placed in a reaction vial and dissolved in DMSO (40 mL). The reaction vial was purged with nitrogen and allowed to warm to 80 °C. After stirring for 20 h, the reaction mixture was extracted with EtOAc, washed with water, and the organic layer was dried using MgSO₄. The extraction was passed through pad of celite and the solvent was removed under reduced pressure, followed by purification by column chromatography on silica gel (hexane:EtOAc = 15:1) to give S4 (1.55 g, 95%) as a pale yellow oil. H NMR (400 MHz, CDCl₃, TMS): δ 7.45 (s, 2H), 7.10 (s, 1H), 2.57 (t, J = 8.0 Hz, 4H), 1.65-1.58 (m, 4H), 1.35 (s, 12H), 1.33-1.24 (m, 12H), 0.90-0.86 (m, 6H). This compound was used for the next reaction without further purification.
OFET and NIR OPT device fabrication and evaluation

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 a thickness of 300 nm and a capacitance of 10.0 nF cm$^{-2}$. Interdigital source and drain electrodes were constructed with gold (30 nm) 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 drop coating from a 0.1 wt% 1,1,2,2-tetrachloroethane solution onto the substrate at 150 °C for 5TQ-B5(EH) and 5TQ-B3(EH) in N$_2$ atmosphere, followed by annealing for 20 min at the same temperature. The semiconducting layer of 5TQ-BBB(EH) was fabricated by thermal conversion (190 °C for 20 min in N$_2$ atmosphere) of 9b film, which was prepared by spin-coating (1000 rpm, 1 min) from a 0.3 wt% CHCl$_3$ solution of 9b onto the HMDS-modified Si/SiO$_2$ substrate. 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 $\mu$ was calculated in the saturated region by the following equation.

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

Current on/off ratio was determined from the $I_{DS}$ at $V_{GS} = 0$ V ($I_{off}$) and $V_{GS} = \pm 50$ V ($I_{on}$).

The NIR-OPT using bulk-heterojunction configuration of the 5TQ-B5(EH)/2CF$_3$BP was fabricated by the thermal conversion (200 °C for 20 min in N$_2$ atmosphere) of 5TQ-B(EH)/2CF$_3$BP film, which was prepared by spin-coating (1000 rpm, 1 min) from a 0.05/0.25 wt% CHCl$_3$ blended solution of 5TQ-B(EH)/2CF$_3$BP-pre onto the HMDS-modified Si/SiO$_2$ substrate. The photoresponse were evaluated by 810 nm LED light with the power of 143 mW cm$^{-2}$ under a pressure of 10$^{-3}$ Pa using a KEITHLEY 4200 semiconductor parameter analyzer.

Computational details

All calculations were conducted using Gaussian 09 program. The geometry was optimized with the unrestricted Becke Hybrid (UB3LYP) at 6-31G(d,p) level. The time-dependent density functional theory (TD-DFT) calculation was conducted for the estimation of excited singlet (S$_0$) and triplet (T$_1$) energies at the CAM-B3LYP/6-31G(d,p) level of theory with Tamm–Dancoff approximation. The frequencies calculations have been performed within the DFT framework with B3LYP energy functional and the 6-31G(d,p) basis set. NICS(1.7)zz values were calculated at the B3LYP/6-31G(d,p) level of theory.

Optimized structure of 5TQ-B5(H) at UB3LYP/6-31G(d,p).

| Center | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|--------|---------------|-------------|-------------------------|
|        |               |             | X          | Y          | Z          |
| 1      | 6             | 0           | 8.385454   | -1.463820  | 0.528032   |
| 2      | 6             | 0           | 6.962923   | -1.405073  | 0.457940   |
| 3      | 16            | 0           | 7.794270   | 1.101233   | 0.373892   |
| 4      | 6             | 0           | 9.011182   | -0.153785  | 0.489824   |
| 5      | 6             | 0           | 0.712586   | -1.161363  | -1.130207  |
| 6      | 6             | 0           | -0.712704  | -1.161410  | -1.129801  |
| 7      | 6             | 0           | -1.305302  | 0.138521   | -0.830533  |
| 8      | 16            | 0           | 0.000004   | 1.340356   | -0.705110  |
| 9      | 6             | 0           | 1.305291   | 0.138579   | -0.831236  |
| 10     | 6             | 0           | 6.433608   | -0.053234  | 0.315888   |
| 11     | 6             | 0           | 2.629831   | 3.034743   | -0.592559  |
| 12     | 6             | 0           | 3.322651   | 4.204429   | -0.307990  |
| 13     | 6             | 0           | 4.626391   | 4.147452   | 0.193385   |
| 14     | 6             | 0           | 5.259288   | 2.921677   | 0.356308   |
| 15     | 6             | 0           | 5.143651   | 0.372300   | 0.082015   |
| 16     | 16            | 0           | 3.857571   | -0.778312  | -0.331231  |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 17 | 6 | 0 | 2.619556 | 0.473864 | -0.590217 |
| 18 | 6 | 0 | 3.234364 | 1.780589 | -0.392392 |
| 19 | 6 | 0 | 4.595432 | 1.725973 | 0.027533 |
| 20 | 6 | 0 | -6.963036 | -1.405044 | 0.458546 |
| 21 | 6 | 0 | -8.385608 | -1.463729 | 0.527738 |
| 22 | 6 | 0 | -9.011234 | -0.153646 | 0.489338 |
| 23 | 6 | 0 | -7.794170 | 1.101343 | 0.374361 |
| 24 | 6 | 0 | -6.433562 | -0.053243 | 0.316892 |
| 25 | 6 | 0 | -6.236085 | -2.604835 | 0.569314 |
| 26 | 6 | 0 | -6.903248 | -3.818166 | 0.690870 |
| 27 | 6 | 0 | -8.301802 | -3.870944 | 0.714621 |
| 28 | 6 | 0 | -9.044101 | -2.699829 | 0.644123 |
| 29 | 6 | 0 | -5.143473 | 0.372172 | 0.083579 |
| 30 | 6 | 0 | -3.857376 | -0.778460 | -0.329517 |
| 31 | 6 | 0 | 10.348549 | 0.207435 | 0.536836 |
| 32 | 6 | 0 | -5.259444 | 2.921404 | 0.358773 |
| 33 | 6 | 0 | -4.626058 | 4.147220 | 0.196117 |
| 34 | 6 | 0 | -3.322424 | 4.204315 | -0.305530 |
| 35 | 6 | 0 | -2.629673 | 3.034709 | -0.590603 |
| 36 | 6 | 0 | 1.398969 | -2.339265 | -1.473862 |
| 37 | 6 | 0 | 0.698535 | -3.499999 | -1.780106 |
| 38 | 6 | 0 | -0.698859 | -3.500052 | -1.779678 |
| 39 | 6 | 0 | -1.399202 | -2.339372 | -1.473022 |
| 40 | 6 | 0 | 9.043833 | -2.699925 | 0.644999 |
| 41 | 6 | 0 | 8.301460 | -3.817011 | 0.715142 |
| 42 | 6 | 0 | 6.902926 | -3.818185 | 0.690428 |
| 43 | 6 | 0 | 6.235897 | -2.604848 | 0.568306 |
| 44 | 6 | 0 | -10.348606 | 0.207641 | 0.535603 |
| 45 | 6 | 0 | 10.716748 | 1.585566 | 0.499462 |
| 46 | 7 | 0 | 10.989527 | 2.718269 | 0.470143 |
| 47 | 6 | 0 | 11.421114 | -0.725053 | 0.621105 |
| 48 | 6 | 0 | 12.314943 | -1.470276 | 0.689769 |
| 49 | 7 | 0 | 10.989422 | 2.718517 | 0.468942 |
| 50 | 7 | 0 | 11.421270 | -0.724806 | 0.619079 |
| 51 | 7 | 0 | 12.315181 | -1.469985 | 0.687151 |
| 52 | 1 | 0 | 1.627838 | 3.107462 | -0.991806 |
| 53 | 1 | 0 | 2.841617 | 5.164025 | -0.468637 |
| 54 | 1 | 0 | 5.155407 | 5.059829 | 0.448518 |
| 55 | 1 | 0 | 6.263366 | 2.911609 | 0.756264 |
| 56 | 1 | 0 | -5.15570 | -2.600880 | 0.597020 |
| 57 | 1 | 0 | -6.325949 | -4.733506 | 0.778059 |
| 58 | 1 | 0 | -8.810787 | -4.824732 | 0.806610 |
| 59 | 1 | 0 | -10.123851 | -2.745296 | 0.688790 |
| 60 | 1 | 0 | -6.262898 | 2.911611 | 0.759051 |
| 61 | 1 | 0 | -5.154965 | 5.059529 | 0.451714 |
| 62 | 1 | 0 | -2.841383 | 5.163948 | -0.465939 |
| 63 | 1 | 0 | -1.627726 | 3.107559 | -0.989944 |
| 64 | 1 | 0 | 2.477274 | -2.347854 | -1.552791 |
| 65 | 1 | 0 | 1.244165 | -4.398725 | -2.049579 |
| 66 | 1 | 0 | -1.244586 | -4.398822 | -2.048810 |
| 67 | 1 | 0 | -2.477554 | -2.348056 | -1.551286 |
| 68 | 1 | 0 | 10.123554 | -2.745411 | 0.690373 |
| 69 | 1 | 0 | 8.810353 | -4.824803 | 0.807579 |
Optimized structure of 5TQ-B3(H) at UB3LYP/6-31G(d,p).

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | -8.082352 -1.970949 0.720721 |
| 2             | 6             | 0           | -6.789303 -1.76866 0.339353 |
| 3             | 16            | 0           | -7.768613 0.638793 0.693792 |
| 4             | 6             | 0           | -8.803758 -0.758012 0.966735 |
| 5             | 6             | 0           | -0.712746 -1.532192 -1.255405 |
| 6             | 6             | 0           | 0.712677 -1.532226 -1.255373 |
| 7             | 6             | 0           | 1.304604 -0.224239 -0.996467 |
| 8             | 16            | 0           | 0.000017 0.977091 -0.887737 |
| 9             | 6             | 0           | -1.304624 -0.224189 -0.996482 |
| 10            | 6             | 0           | -6.384696 -0.395440 0.252517 |
| 11            | 6             | 0           | -5.132329 0.060391 -0.105948 |
| 12            | 16            | 0           | -3.867014 -1.115010 -0.486251 |
| 13            | 6             | 0           | -2.620768 0.123229 -0.777000 |
| 14            | 6             | 0           | -3.233689 1.440089 -0.640213 |
| 15            | 6             | 0           | -4.604999 1.404142 -0.250190 |
| 16            | 6             | 0           | 6.789327 -1.768772 0.339426 |
| 17            | 6             | 0           | 8.082382 -1.907982 0.720800 |
| 18            | 6             | 0           | 8.803755 -0.758013 0.966765 |
| 19            | 16            | 0           | 7.768574 0.638755 0.693761 |
| 20            | 6             | 0           | 6.384688 -0.395538 0.252535 |
| 21            | 6             | 0           | 5.132320 0.060271 -0.105946 |
| 22            | 6             | 0           | 2.620768 0.123149 -0.777039 |
| 23            | 16            | 0           | 3.866982 -1.115110 -0.486220 |
| 24            | 6             | 0           | 4.605028 1.404027 -0.250242 |
| 25            | 6             | 0           | 3.233733 1.439997 -0.640310 |
| 26            | 6             | 0           | -10.128075 -0.641032 1.362740 |
| 27            | 6             | 0           | -1.399404 -2.720915 -1.559961 |
| 28            | 6             | 0           | -0.699080 -3.889736 -1.830964 |
| 29            | 6             | 0           | 0.698899 -3.889778 -1.830912 |
| 30            | 6             | 0           | 1.399278 -2.720997 -1.559874 |
| 31            | 6             | 0           | 10.128066 -0.640981 1.362768 |
| 32            | 6             | 0           | -2.632746 2.686939 -0.891591 |
| 33            | 6             | 0           | -3.351913 3.862099 -0.714200 |
| 34            | 6             | 0           | -4.685385 3.824930 -0.290405 |
| 35            | 6             | 0           | -5.311880 2.606642 -0.068694 |
| 36            | 6             | 0           | 5.311944 2.606506 -0.068755 |
| 37            | 6             | 0           | 4.685499 3.824805 -0.290543 |
| 38            | 6             | 0           | 3.352050 3.862000 -0.714410 |
| 39            | 6             | 0           | 2.632846 2.686857 -0.891775 |
| 40            | 6             | 0           | -10.728979 0.631758 1.569820 |
| 41            | 7             | 0           | -11.189289 1.690875 1.729843 |
| 42            | 6             | 0           | -10.916207 -1.809258 1.568999 |
| 43            | 7             | 0           | -11.538474 -2.781545 1.730168 |
| 44            | 6             | 0           | 10.728939 0.631834 1.569788 |
| 45            | 7             | 0           | 11.189226 1.690966 1.729774 |
| 46            | 6             | 0           | 10.916226 -1.809178 1.569084 |
| 47            | 7             | 0           | 11.538539 -2.781437 1.730248 |
| 48            | 1             | 0           | -8.551255 -2.940380 0.835329 |
| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|------------------------|
| 1             | 6             | 0           | 8.803306 0.407898 0.000250 |
| 2             | 6             | 0           | 7.419038 0.750541 0.000216 |
| 3             | 16            | 0           | 7.507982 -1.892908 0.000000 |
| 4             | 6             | 0           | 9.03687 -1.028051 0.000127 |
| 5             | 6             | 0           | 0.713664 1.553105 -0.000336 |
| 6             | 6             | 0           | -0.713664 1.553105 -0.000352 |
| 7             | 6             | 0           | -1.294895 0.224957 -0.000330 |
| 8             | 16            | 0           | 0.000000 -0.987203 -0.000405 |
| 9             | 6             | 0           | 1.294895 0.224957 -0.000312 |
| 10            | 6             | 0           | 6.539172 -0.398602 0.000065 |
| 11            | 6             | 0           | 5.164756 -0.503460 -0.000032 |
| 12            | 16            | 0           | 4.033746 0.867133 -0.000033 |
| 13            | 6             | 0           | 2.608225 -0.199067 -0.000224 |
| 14            | 6             | 0           | 3.056984 -1.560549 -0.000261 |
| 15            | 6             | 0           | 4.408701 -1.724311 -0.000164 |
| 16            | 6             | 0           | -7.419037 0.750541 0.000137 |
| 17            | 6             | 0           | -8.803307 0.407898 0.000176 |
| 18            | 6             | 0           | -9.033687 -1.028051 0.000162 |
| 19            | 16            | 0           | -7.507982 -1.892909 0.000110 |
| 20            | 6             | 0           | -6.539172 -0.398602 0.000074 |
| 21            | 6             | 0           | -7.051506 2.108932 0.000159 |
| 22            | 6             | 0           | -8.032127 3.092055 0.000211 |
| 23            | 6             | 0           | -9.391550 2.750618 0.000242 |
| 24            | 6             | 0           | -9.781027 1.417786 0.000225 |
| 25            | 6             | 0           | -5.164755 -0.503461 -0.000022 |
| 26            | 6             | 0           | -2.608225 -0.199067 -0.000227 |
| 27            | 16            | 0           | -4.033746 0.867132 -0.000069 |
| 28            | 6             | 0           | -4.408701 -1.724311 -0.000110 |
| 29            | 6             | 0           | -3.056984 -1.560549 -0.000218 |
| 30            | 6             | 0           | 10.219959 -1.746152 0.000091 |
| 31            | 6             | 0           | 1.403958 2.779221 -0.000369 |
| 32            | 6             | 0           | 0.700650 3.975804 -0.000410 |
| 33            | 6             | 0           | -0.700650 3.975804 -0.000431 |
| 34            | 6             | 0           | -1.403958 2.779220 -0.000409 |
| 35            | 6             | 0           | 9.781027 1.417786 0.000400 |
### Optimized structure of 5TQ-B(H) at UB3LYP/6-31G(d,p).

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y           | Z           |
| 1             | 6             | 0           | 8.626460    | -0.912900  | -0.000010   |
| 2             | 6             | 0           | 7.268859    | -1.074848  | -0.000009   |
| 3             | 16            | 0           | 7.643174    | 1.526866   | -0.000001   |
| 4             | 6             | 0           | 9.041786    | 0.457606   | -0.000006   |
| 5             | 6             | 0           | 0.714237    | -1.748679  | 0.000005    |
| 6             | 6             | 0           | -0.714239   | -1.748677  | 0.000005    |
| 7             | 6             | 0           | -1.292639   | -0.421993  | 0.000006    |
| 8             | 16            | 0           | 0.000002    | 0.787185   | 0.000009    |
| 9             | 6             | 0           | 1.292639    | -0.421995  | 0.000006    |
| 10            | 6             | 0           | 6.526126    | 0.142166   | -0.000004   |
| 11            | 6             | 0           | 5.153053    | 0.305803   | 0.000001    |
| 12            | 16            | 0           | 4.030699    | -1.065929  | -0.000002   |
| 13            | 6             | 0           | 2.610237    | 0.002819   | 0.000006    |
| 14            | 6             | 0           | 3.057712    | 1.362382   | 0.000011    |
| 15            | 6             | 0           | 4.414154    | 1.526592   | 0.000008    |
| 16            | 6             | 0           | -7.268858   | -1.074846  | -0.000008   |
| 17            | 6             | 0           | -8.626459   | -0.912899  | -0.000011   |
| 18            | 6             | 0           | -9.041786   | 0.457607   | -0.000009   |
| 19            | 16            | 0           | -7.643174   | 1.526868   | -0.000002   |
| 20            | 6             | 0           | -6.526124   | 0.142167   | -0.000003   |
| 21            | 6             | 0           | -5.153052   | 0.305805   | -0.000001   |
| 22            | 6             | 0           | -2.610236   | 0.002823   | 0.000006    |
Optimized structure of 5TQ(H) at UB3LYP/6-31G(d,p).

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X    | Y    | Z    |
| 1             | 16            | 0           | -1.020722 | 7.787329 | 0.000000 |
| 2             | 6             | 0           | 0.224939  | 6.521956 | 0.000000 |
| 3             | 6             | 0           | 1.517113  | 7.116466 | 0.000000 |
| 4             | 6             | 0           | 1.512953  | 8.486429 | 0.000000 |
| 5             | 6             | 0           | 0.201525  | 9.055058 | 0.000000 |
| 6             | 6             | 0           | -0.099704 | 5.171334 | 0.000000 |
| 7             | 6             | 0           | -1.394849 | 4.584215 | 0.000000 |
| 8             | 6             | 0           | -1.391849 | 3.210209 | 0.000000 |
| 9             | 6             | 0           | -0.099407 | 2.625935 | 0.000000 |
| 10            | 16            | 0           | 1.131886  | 3.898602 | 0.000000 |
| 11            | 6             | 0           | 0.232970  | 1.272359 | 0.000000 |
| 12            | 16            | 0           | -0.997644 | 0.000000 | -0.000000 |
| 13            | 6             | 0           | 0.232970  | -1.272359 | -0.000000 |
| 14            | 6             | 0           | 1.524974  | -0.687880 | -0.000000 |
| 15            | 6             | 0           | 1.524974  | 0.687880  | 0.000000 |
| 16            | 16            | 0           | 1.131886  | -3.898602 | -0.000000 |
| 17            | 6             | 0           | -0.099704 | -5.171333 | -0.000000 |
| 18            | 6             | 0           | -1.394849 | -4.584214 | -0.000000 |
| 19            | 6             | 0           | -1.391849 | -3.210208 | -0.000000 |
| 20            | 6             | 0           | -0.099407 | -2.625934 | -0.000000 |
| 21            | 6             | 0           | 0.224939  | -6.521956 | -0.000000 |
|   |   |
|---|---|
| 22 | 6 0  | 1.517113 -7.116466 -0.000000 |
| 23 | 6 0  | 1.512954 -8.486429 -0.000000 |
| 24 | 6 0  | 0.201525 -9.055059 -0.000000 |
| 25 | 16 0 | -1.020722 -7.787330 -0.000000 |
| 26 | 6 0  | -0.121974 -10.407974 -0.000000 |
| 27 | 6 0  | -0.121974 10.407974 0.000000 |
| 28 | 6 0  | -1.474190 10.846078 0.000000 |
| 29 | 7 0  | -2.594302 11.170567 0.000000 |
| 30 | 6 0  | 0.911218 11.386628 0.000000 |
| 31 | 7 0  | 1.777500 12.166863 0.000000 |
| 32 | 6 0  | 0.911218 -11.386628 -0.000000 |
| 33 | 7 0  | 1.777502 -12.166863 -0.000000 |
| 34 | 6 0  | -1.474190 -10.846079 -0.000000 |
| 35 | 7 0  | -2.594302 -11.170569 -0.000000 |
| 36 | 1 0  | 2.423195  6.520446 0.000000 |
| 37 | 1 0  | 2.398557  9.109831 0.000000 |
| 38 | 1 0  | -2.297362  5.184392 0.000000 |
| 39 | 1 0  | -2.294323  2.609379 0.000000 |
| 40 | 1 0  | 2.427751 -1.287959 -0.000000 |
| 41 | 1 0  | 2.427752  1.287959 0.000000 |
| 42 | 1 0  | -2.297363 -5.184391 -0.000000 |
| 43 | 1 0  | -2.294324 -2.609379 -0.000000 |
| 44 | 1 0  | 2.423195 -6.520446 -0.000000 |
| 45 | 1 0  | 2.398558 -9.109831 -0.000000 |

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$^1$H NMR spectra
