Electronic Supplementary Information

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

Keitaro Yamamoto,[a,b] Sergio Moles Quintero,[c] Seihou Jinnai,[a] Eunjeong Jeong,[d] Kyohei Matsuo,[d] Mitsuharu Suzuki,[e] Hiroko Yamada,[d] Juan Casado,*[, c] and Yutaka Ie*[,a, f]

[a]*The Institute of Scientific and Industrial Research (SANKEN), Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan*

[b]*Tokyo Metropolitan Industrial Technology Research Institute, 2-4-10 Aomi, Koto-ku, Tokyo 135-0064, Japan*

[c]*Department of Physical Chemistry, University of Malaga, Campus de Teatinos s/n 29071 Malaga, Spain*

[d]*Division of Materials Science, Nara Institute of Science and Technology (NAIST), 8916-5 Takayama-cho, Ikoma, Nara 630-0192, Japan*

[e]*Division of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan*

[f]*Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives (OTRI), Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan*

Table of Contents

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–θ 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_4NPF_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_4NPF_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

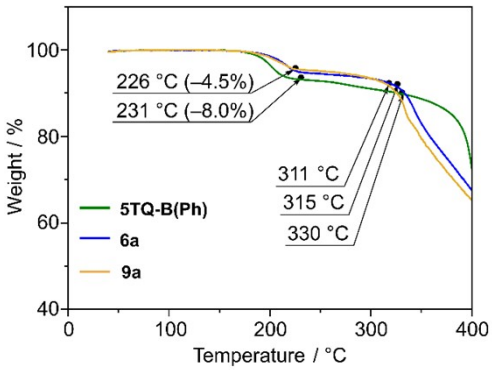


Fig. S1 TGA curves for **5TQ-B(Ph)**, **6a**, and **9a** with a heating rate of 10 °C min^{-1} in N_2.

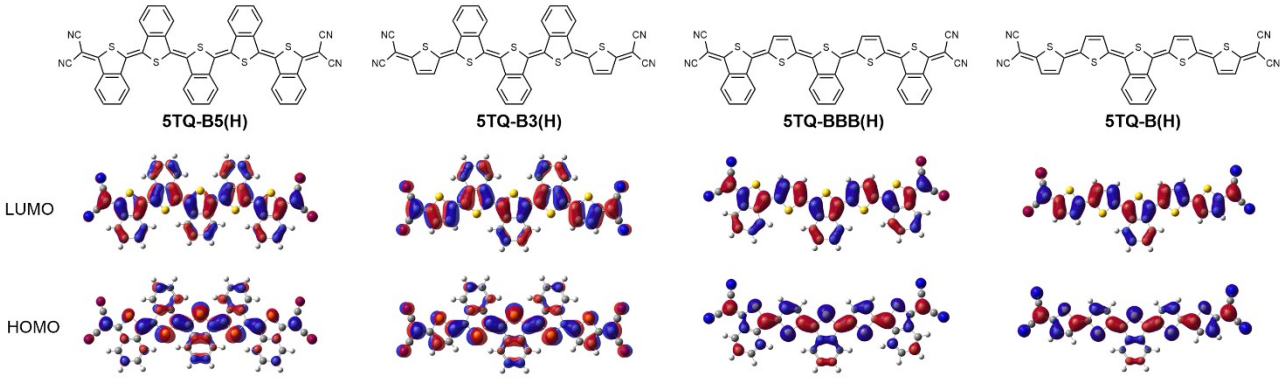
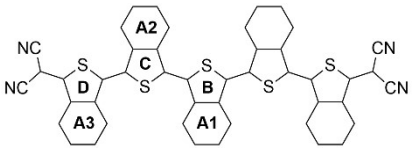


Fig. S2 Calculated HOMOs and LUMOs of **5TQ-B5(H)**, **5TQ-B3(H)**, **5TQ-BBB(H)**, and **5TQ-B(H)**.

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



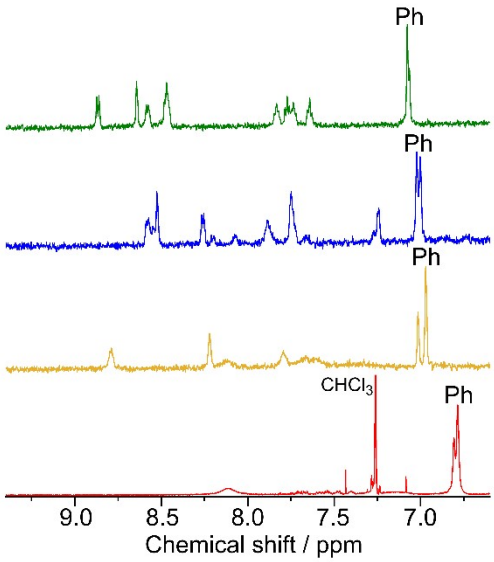


Fig. S3 ^{1}H NMR spectra of **5TQ-B5(Ph)** (green), **5TQ-B3(Ph)** (blue), and **5TQ-BBB(Ph)** (yellow) in 1,1,2,2,-tetrachloroethane-d_2 at 130 °C, and **5TQ-B(Ph)** (red) in $CDCl_3$ at 25 °C in the aromatic regions. Several minor peaks in the spectrum of **5TQ-B3(Ph)** are attributed to *syn*-, *anti*-isomers.

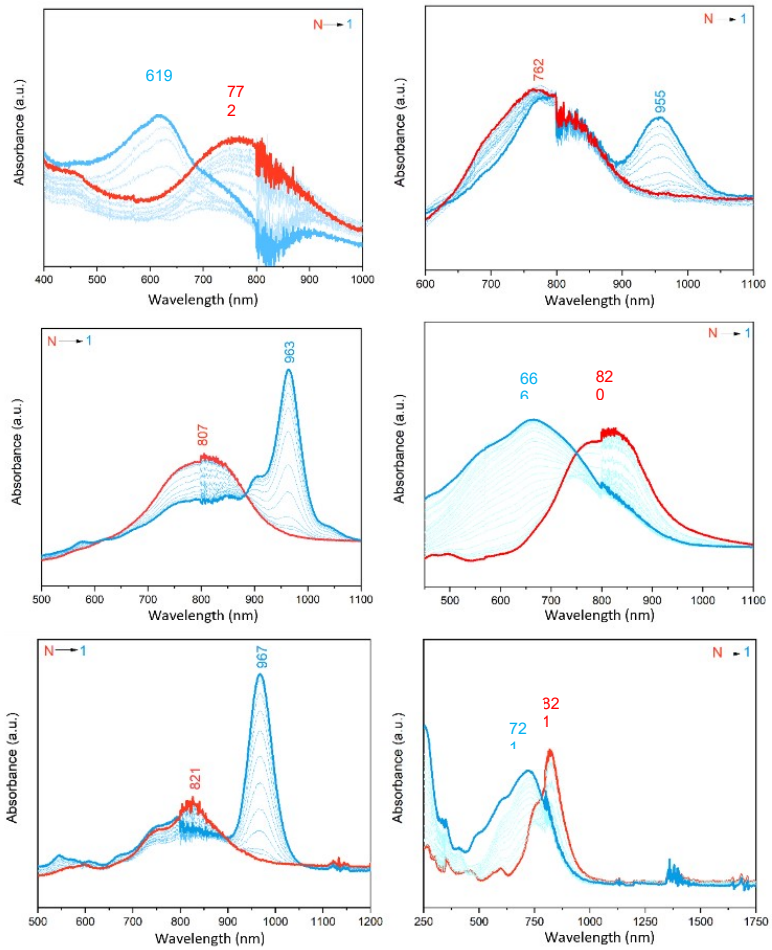


Fig. S4 From the bottom: **5TQ-BBB(Ph)**, **5TQ-B3(Ph)**, **5TQ-B5(Ph)**. UV-Vis-NIR spectroelectrochemical reduction/oxidation (right/left) processes in 0.1 M $TBAPF_6$ in dichloromethane at room temperature. Red lines correspond to the spectra of neutral species, blue lines correspond to the reduced/oxidized species. Dashed light color lines correspond to the intermediate spectra between the former species.

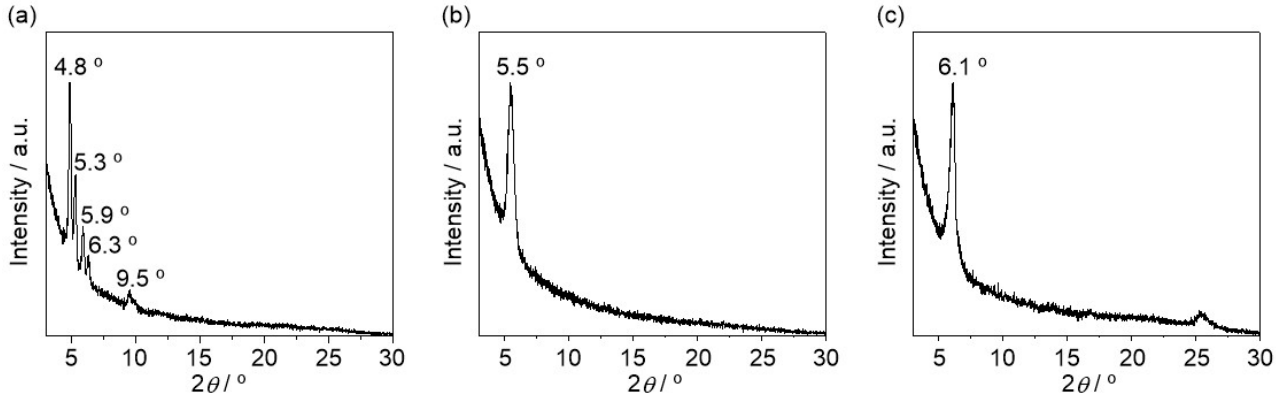


Fig. S5 XRD profiles of (a) **5TQ-B5(EH)**, (b) **5TQ-B3(EH)**, and (c) **5TQ-BBB(EH)** in thin films.

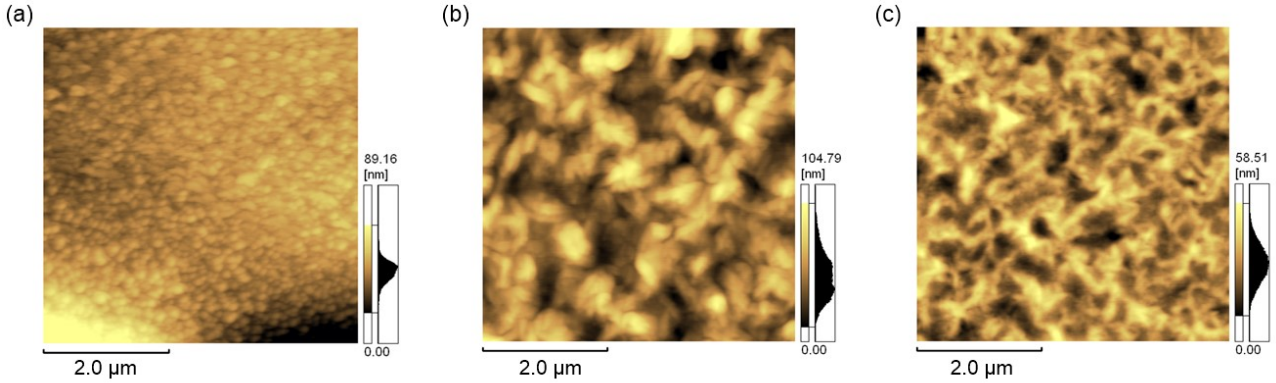


Fig. S6 AFM height images of (a) **5TQ-B5(EH)**, (b) **5TQ-B3(EH)**, and (c) **5TQ-BBB(EH)** in thin films.

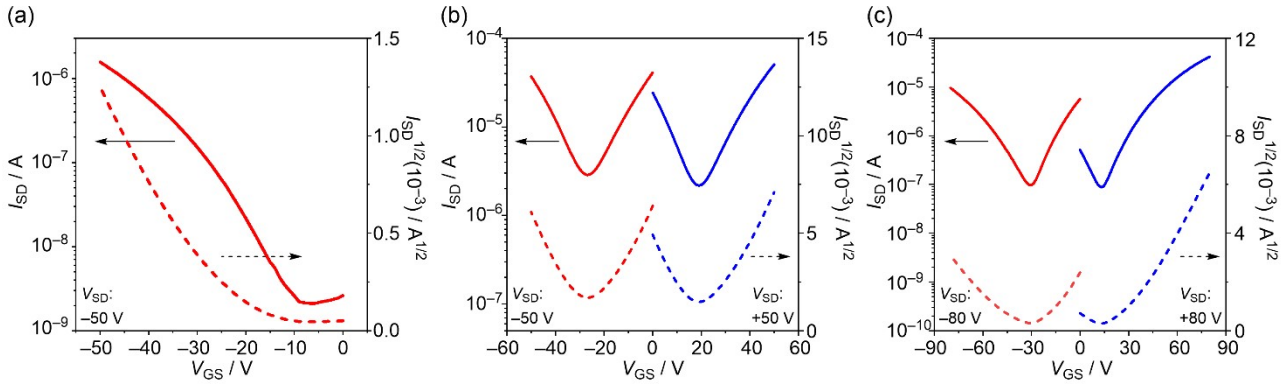


Fig. S7 Transfer characteristics of the OFETs based on (a) **5TQ-B5(EH)**, (b) **5TQ-B3(EH)**, and (c) **5TQ-BBB(EH)**.

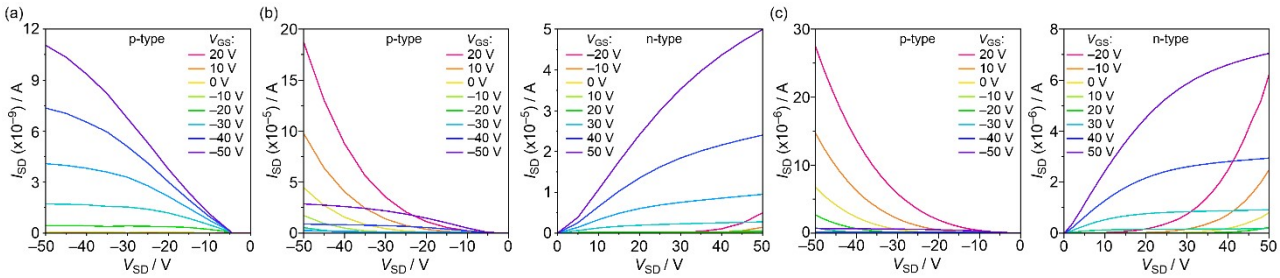


Fig. S8 Output characteristics of the OFETs based on (a) **5TQ-B5(EH)**, (b) **5TQ-B3(EH)**, and (c) **5TQ-BBB(EH)**.

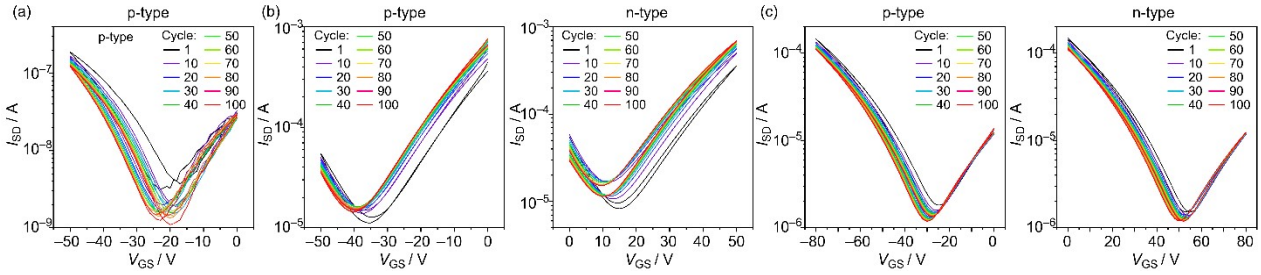


Fig. S9 Transfer characteristics of OFETs based on (a) **5TQ-B5(EH)**, (b) **5TQ-B3(EH)**, and (c) **5TQ-BBB(EH)** with repeated biases up to 100 cycles.

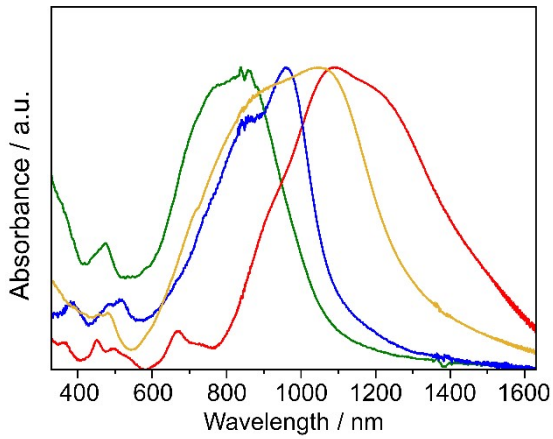


Fig. S10 UV-vis-NIR absorption spectra of **5TQ-B5(EH)** (green), **5TQ-B3(EH)** (blue), **5TQ-BBB(EH)** (yellow), and **5TQ-B(EH)** (red) in thin films.

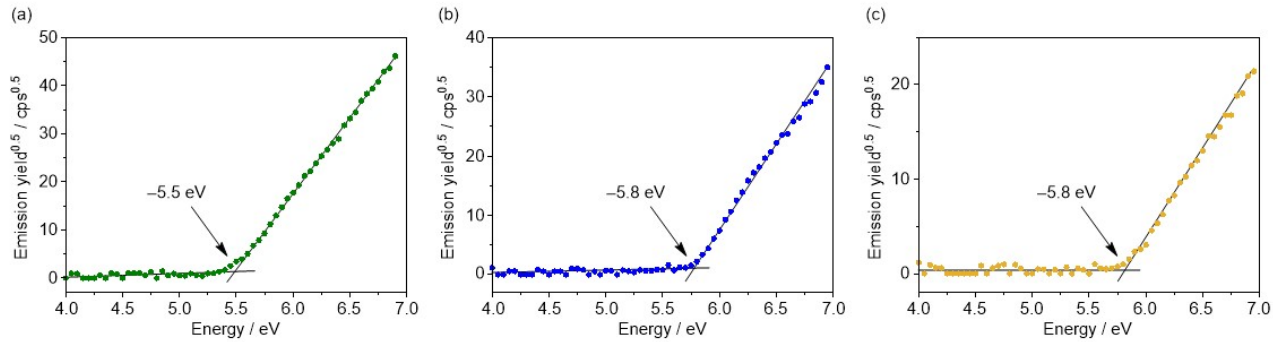


Fig. S11 PESA spectra of (a) **5TQ-B5(EH)**, (b) **5TQ-B3(EH)**, and (c) **5TQ-BBB(EH)** in thin films.

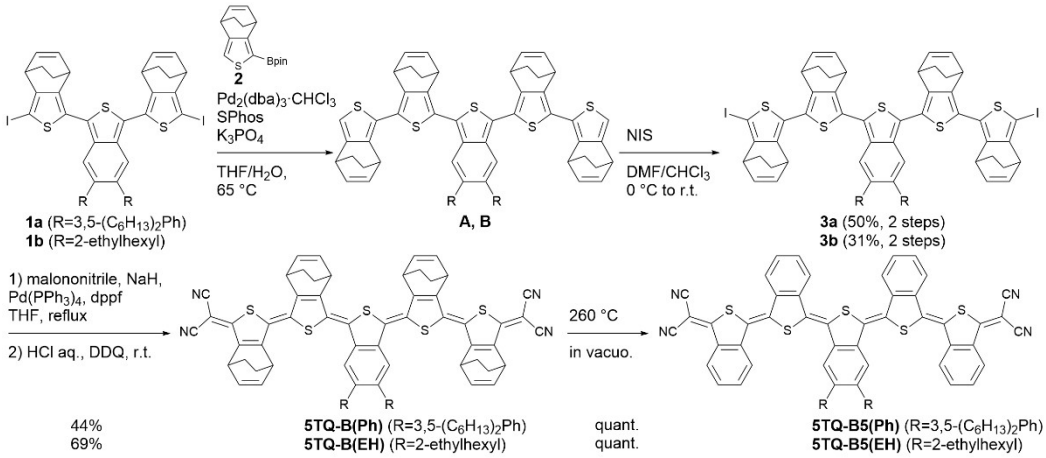
Table S2. Properties of the molecules in thin films.

Compounds	λ_{max} /nm	ΔE_g^{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), $Pd_2(dba)_3{\cdot}CHCl_3$ (9.5 mg, 0.0092 mmol), SPhos (15 mg, 0.037 mmol), and K_3PO_4 (78 mg, 0.37 mmol) were placed in a reaction vial and dissolved in THF (1.4 mL)/H_2O (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, 2H), 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, 122.5, 122.3, 121.8, 112.3, 36.9, 36.3, 35.9, 35.8, 35.7, 31.8, 31.6, 29.0, 26.2, 26.1, 26.0, 25.9, 22.6, 14.2; HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{84}H_{94}S_5$, 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_2SO_3 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:CH_2Cl_2 = 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, 6H), 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, 135.5, 135.4, 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, 31.5, 28.9, 25.8, 25.5, 25.3, 22.5, 14.0; HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{84}H_{92}I_2S_5$, 1515.3965; found, 1515.3973.

*Synthesis of **3b***: **1b** (180 mg, 0.19 mmol), **2** (120 mg, 0.43 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (20 mg, 0.019 mmol), SPhos (32 mg, 0.077 mmol), and K_3PO_4 (160 mg, 0.77 mmol) were placed in a reaction vial and dissolved in THF (2.6 mL)/H_2O (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, 123.7, 123.6, 122.7, 122.6, 122.2, 121.3, 112.2, 40.1, 40.0, 37.8, 36.9, 36.2, 36.0, 35.9, 35.8, 35.7, 32.6, 32.5, 29.0, 28.9, 26.2, 26.1, 26.0, 26.0, 26.0, 25.6, 23.2, 14.2, 14.2, 11.0, 10.9; HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{64}H_{70}S_5$, 999.4154; found, 999.4147.

NIS (76 mg, 0.34 mmol) was added to a solution of intermediate **B** (160 mg, 0.16 mmol) in DMF (17 mL) and

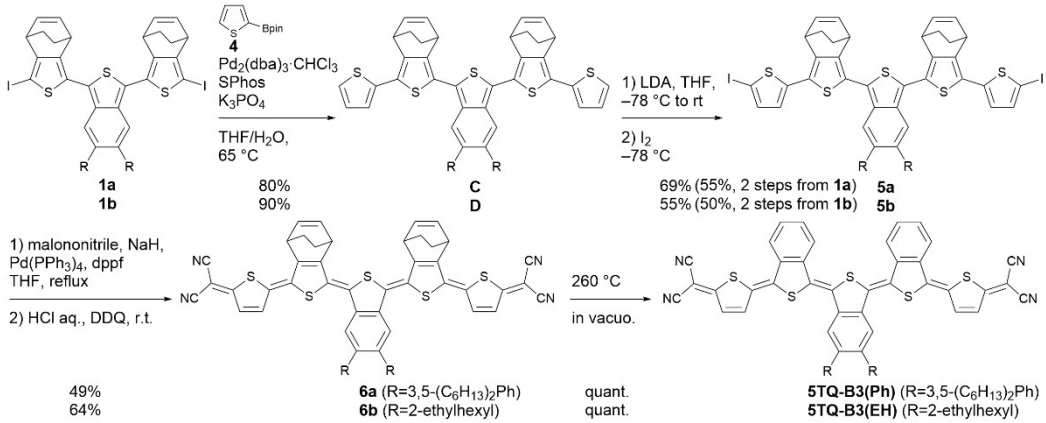
$CHCl_3$ (1.6 mL) at 0 °C. Then, this reaction was allowed to warm to room temperature. After stirring overnight, the reaction was quenched by addition of Na_2SO_3 aq.. The combined organic was extracted with EtOAc and washed with water. After drying with $MgSO_4$, the extraction was passed through pad of celite and the solvent was removed under reduced pressure, followed by purification with preparative GPC ($CHCl_3$) to give the intermediate **3b** (75 mg, 31%, 2 steps) as a dark red solid. ^{1}H NMR (400 MHz, $CDCl_3$, 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); ^{13}C NMR (150 MHz, $CDCl_3$, 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*: $[M+H]^+$ calcd. for $C_{64}H_{68}I_2S_5$, 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), $Pd(PPh_3)_4$ (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 $CHCl_3$, washed with water, and the organic layer was dried using $MgSO_4$. The organic solvent was removed under reduced pressure. Then the resultant precipitate was dissolved in CH_2Cl_2 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 (CH_2Cl_2) to give **5TQ-B(Ph)** (12 mg, 44%) as a green solid. ^{1}H NMR (600 MHz, $CDCl_3$, 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 $C_{90}H_{92}N_4S_5$, 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; ^{1}H NMR (600 MHz, $CDCl_3$, 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 $C_{70}H_{68}N_4S_5$, 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. ^{1}H NMR (600 MHz, 130 °C, 1,1,2,2-tetrachloroethane-d_2): 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). ^{13}C NMR spectrum of this compound was not observed due to the limited solubility. HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{82}H_{76}N_4S_5$, 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; ^{1}H NMR (600 MHz, 130 °C, 1,1,2,2-tetrachloroethane-d_2): 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 $C_{62}H_{52}N_4S_5$, 1013.2869; found, 1013.2869.



Scheme S2. Synthetic route of **5TQ-B3(Ph)** and **5TQ-B3(EH)**.

*Synthesis of the intermediate **C***: **1a** (91 mg, 0.076 mmol), thiophene-2-boronic acid pinacol ester (**4**) (48 mg, 0.23 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (7.9 mg, 0.0076 mmol), SPhos (13 mg, 0.030 mmol), and K_3PO_4 (65 mg, 0.30 mmol) were placed in a reaction vial and dissolved in THF (1.2 mL)/H_2O (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 $MgSO_4$. 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 **C** (67 mg, 80%) as a dark red solid. ^{1}H NMR (400 MHz, $CDCl_3$, 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, 40H), 0.88 (t, J = 6.9 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 145.8, 143.7, 142.1, 141.2, 139.2, 135.8, 135.6, 135.3, 135.3, 127.6, 127.2, 126.8, 125.5, 125.3, 125.1, 124.7, 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 $C_{72}H_{82}S_5$, 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 N_2, and dissolved in THF (3.5 mL). 1 M LDA (0.16 mL) was added slowly to a solution of S**1a** at –78 °C and allowed to warm to 0 °C, then cooled to –78 °C. A solution of I_2 (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 Na_2SO_3 aq.. 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 **5a** (29 mg, 69%) as a dark red solid. ^{1}H NMR (400 MHz, $CDCl_3$, 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); ^{13}C NMR (150 MHz, $CDCl_3$, 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 $C_{72}H_{80}I_2S_5$, 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; ^{1}H NMR (400 MHz, $CDCl_3$, 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), 4.20 (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); ^{13}C NMR (100 MHz, $CDCl_3$, 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, 25.6, 23.2, 14.2, 11.0, 10.9; HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{52}H_{58}S_5$, 843.3215; found, 843.3208.

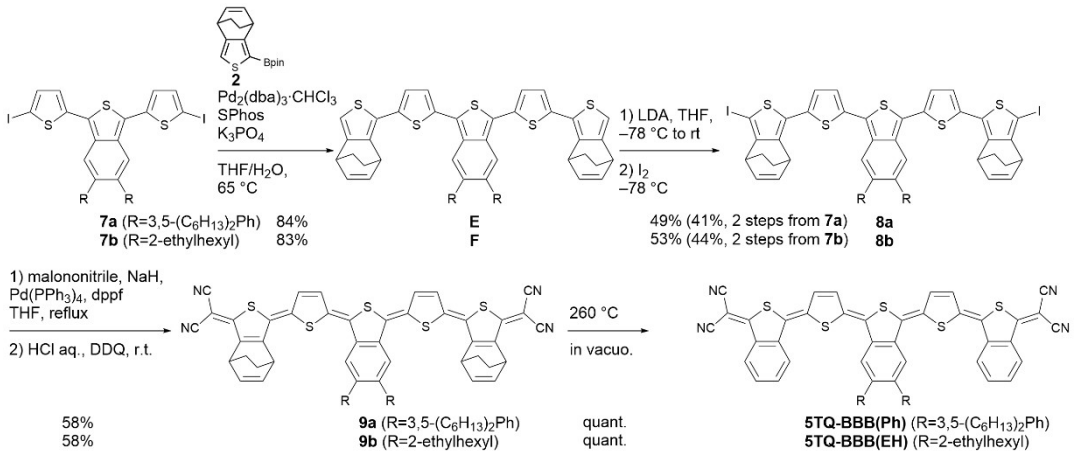
*Synthesis of **5b***: Compound **5b** was synthesized from the intermediate **D** (95 mg, 0.11 mmol) with a yield of 55% by following the procedure used for the preparation of **S2a**. Dark red solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.50 (s, 2H), 7.21 (d, *J* = 3.7 Hz, 2H), 6.84 (d, *J* = 3.7 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); ^{13}C NMR (150 MHz, $CDCl_3$, 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 $C_{52}H_{56}I_2S_5$, 1095.1148; found, 1095.1150.

*Synthesis of **6a***: Compound **6a** was synthesized from **S2a** (34 mg, 0.025 mmol) with a yield of 49% by following the procedure used for the preparation of **5TQ-B(Ph)**. Green solid; ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 8.25 (s, 2H), 7.83-7.55 (br), 6.92 (s, 2H), 6.81 (s, 4H), 6.78-6.70 (br), 4.90 (s, 2H), 4.67 (s, 2H), 2.49 (t, J = 7.9 Hz, 8H), 1.85-1.72 (br), 1.48-1.42 (m, 8H), 1.34-1.24 (m, 24H), 0.89 (t, J = 6.9 Hz, 12H); HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{78}H_{80}N_4S_5$, 1233.5060; found as thermally converted structure, 1177.4440 ($C_{54}H_{48}N_4S_5$).

*Synthesis of **6b***: Compound **6b** was synthesized from **S2b** (65 mg, 0.059 mmol) with a yield of 64% by following the procedure used for the preparation of **5TQ-B(Ph)**. Green solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.99 (s, 2H), 7.63 (br), 6.69 (br), 4.92 (s, 2H), 4.63 (s, 2H), 2.77 (br, 4H), 1.88-1.65 (br), 1.44-1.30 (m, 16H), 0.99-0.89 (m, 12); HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{58}H_{56}N_4S_5$, 969.3182; found, 979.3192.

*Synthesis of **5TQ-B3(Ph)***: Compound **5TQ-B3(Ph)** was synthesized from **6a** (15 mg, 0.012 mmol) quantitatively, by following the procedure used for the preparation of **5TQ-B5(Ph)**. Blue solid; ^{1}H NMR (600 MHz, 130 °C, 1,1,2,2-tetrachloroethane-d_2): δ 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 $C_{74}H_{72}N_4S_5$, 1177.4434; found, 1177.4425.

*Synthesis of **5TQ-B3(EH)***: Compound **5TQ-B3(EH)** was synthesized from **6b** (15 mg, 0.015 mmol) quantitatively, by following the procedure used for the preparation of **5TQ-B5(Ph)**. Blue solid; ^{1}H NMR (600 MHz, 130 °C, 1,1,2,2-tetrachloroethane-d_2): δ 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 $C_{54}H_{48}N_4S_5$, 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), $Pd_2(dba)_3{\cdot}CHCl_3$ (10 mg, 0.0096 mmol), SPhos (16 mg, 0.039 mmol), and K_3PO_4 (82 mg, 0.39 mmol) were placed in a reaction vial and dissolved in THF (1.3 mL)/H_2O (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. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 8.01 (s, 2H), 7.33 (d, J = 3.4 Hz, 2H), 7.14 (d, J = 3.4 Hz, 2H), 6.82 (s, 2H), 6.80 (s, 6H), 6.68 (s, 2H), 6.55-6.52 (m, 4H), 4.38-4.34 (m, 2H), 3.88-3.84 (m, 2H), 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); ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 148.2, 142.9, 142.3, 141.2, 139.8, 136.5, 135.5, 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, 31.8, 31.6, 29.1, 26.0, 25.9, 22.6, 14.2; HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{72}H_{82}S_5$, 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; ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 7.99 (s, 2H), 7.32 (d, J = 4.1 Hz, 2H), 7.09 (d, J = 3.4 Hz, 2H), 6.82 (s, 2H), 6.80 (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), 0.88 (t, J = 6.9 Hz, 12H); ^{13}C NMR (151 MHz, $CDCl_3$, TMS): δ 153.2, 146.4, 144.2, 143.0, 142.3, 141.0, 140.0, 135.2, 135.1, 134.8, 129.4, 127.2, 127.0, 126.2, 126.0, 125.8, 122.0, 62.5, 38.0, 36.3, 35.9, 31.8, 31.6, 29.1, 25.5, 25.3, 22.6, 14.2; HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{72}H_{80}I_2S_5$, 1359.3026; found, 1359.3030.

*Synthesis of the intermediate **F***: **7b** (180 mg, 0.19 mmol), **2** (120 mg, 0.43 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (20 mg, 0.019 mmol), SPhos (32 mg, 0.077 mmol), and K_3PO_4 (160 mg, 0.77 mmol) were placed in a reaction vial and dissolved in THF (2.6 mL)/H_2O (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 $MgSO_4$. 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 **F** (160 mg, 83%) as a dark red solid. ^{1}H NMR (400 MHz, $CDCl_3$, 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); ^{13}C NMR (100 MHz, $CDCl_3$, 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, 26.0, 25.9, 25.4, 25.3, 23.2, 14.2, 10.8, 10.7; HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{52}H_{58}S_5$, 843.3215; found, 843.3217.

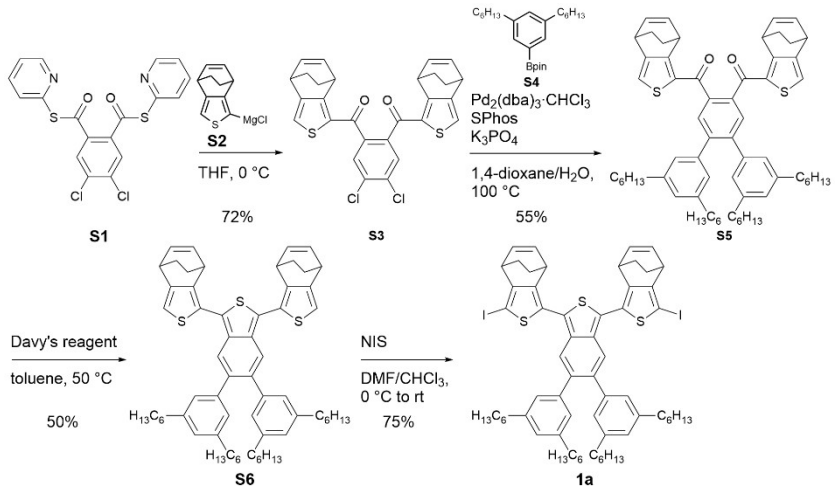
*Synthesis of **8b***: Compound **8b** was synthesized from the intermediate **F** (120 mg, 0.14 mmol) with a yield of 53% by following the procedure used for the preparation of **8a**. dark red solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.70 (s, 2H), 7.25 (d, J = 3.7 Hz, 2H), 7.09 (d, J = 3.7 Hz, 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); ^{13}C NMR (100 MHz, $CDCl_3$, 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, 25.3, 23.1, 14.2, 10.8, 10.7; HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{52}H_{56}I_2S_5$, 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-B(Ph)**. Green solid; ^{1}H NMR (600 MHz, $CDCl_3$, 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 $C_{78}H_{80}N_4S_5$, 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-B(Ph)**. Green solid; ^{1}H NMR (400 MHz, $CDCl_3$, 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 $C_{58}H_{56}N_4S_5$, 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-B5(Ph)**. Blue solid; ^{1}H NMR (600 MHz, 130 °C, 1,1,2,2-tetrachloroethane-d_2): 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 $C_{74}H_{72}N_4S_5$, 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-B5(Ph)**. Blue solid; ^{1}H NMR (600 MHz, 130 °C, 1,1,2,2-tetrachloroethane-d_2): 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 $C_{54}H_{48}N_4S_5$, 913.2556; found, 913.2549.



Scheme S4. Synthetic route of **1a**.

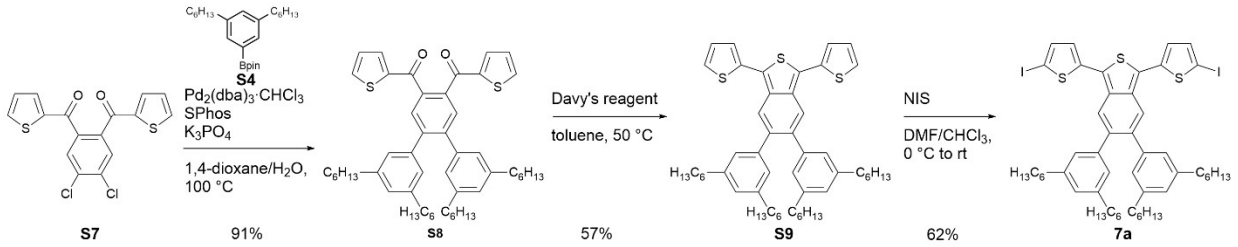
*Synthesis of **S3***: **S1** (653 mg, 1.55 mmol) was placed in a two-necked-bottomed flask, which was filled with N_2 and dissolved in THF (10.4 mL). Grignard reagent **S2** (3.47 mmol, 0.33 M in THF), which was prepared by a reaction of 1-iodo-4,7-dihydro-4,7-ethanobenzo[*c*]thiophene and isopropylmagnesium 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 $CHCl_3$, and the combined organic layer was washed with 5% NaOH aq., $NaHCO_3$ aq., and water. After drying with $MgSO_4$, 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. ^{1}H NMR (400 MHz, $CDCl_3$, 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), $Pd_2(dba)_3{\cdot}CHCl_3$ (115 mg, 0.111 mmol), SPhos (182 mg, 0.444 mmol), and K_3PO_4 (942 mg, 4.44 mmol) were placed in a reaction vial and dissolved in 1,4-dioxance (7.4 mL)/H_2O (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 $MgSO_4$. 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. ^{1}H NMR (400 MHz, $CDCl_3$, 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), 6.40-6.37 (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 = 7.2 Hz, 12H); ^{13}C NMR (150 MHz, $CDCl_3$, 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 $C_{64}H_{78}O_2S_2$, 943.5516; found, 943.5505.

*Synthesis of **S6***: Davy's reagent (*p*-tolyl) (143 mg, 0.327 mmol) was added to a solution of **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 silica gel and the solvent was removed under reduced pressure, followed by purification by column chromatography on silica gel (hexane:CH_2Cl_2 = 5:1) to give **S5** (140 mg, 50%) as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$, 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, 24H), 0.88 (t, J = 6.9 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 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 $C_{64}H_{78}S_3$, 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 $CHCl_3$ (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 Na_2SO_3 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:CH_2Cl_2 = 10:1) to give **1a** (190 mg, 75%) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$, 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); ^{13}C NMR (101 MHz, $CDCl_3$, 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*: $[M+H]^+$ calcd. for $C_{64}H_{76}I_2S_3$, 1195.3272; found, 1195.3274.

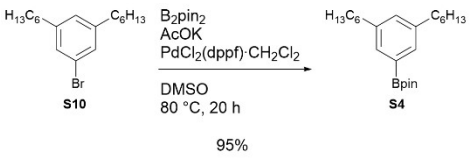


Scheme S5. Synthetic route of **6a**.

*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; ^{1}H NMR (600 MHz, $CDCl_3$, 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); ^{13}C NMR (150 MHz, $CDCl_3$, 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*: $[M+H]^+$ calcd. for $C_{52}H_{66}O_2S_2$, 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.; ^{1}H NMR (400 MHz, $CDCl_3$, 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); ^{13}C NMR (100 MHz, $CDCl_3$, 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*: $[M+H]^+$ calcd. for $C_{52}H_{66}S_3$, 787.4400; 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; ^{1}H NMR (600 MHz, $CDCl_3$, 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); ^{13}C NMR (151 MHz, $CDCl_3$, 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*: $[M+H]^+$ calcd. for $C_{52}H_{64}I_2S_3$, 1039.2333; found, 1039.2338.



Scheme S6. Synthetic route of **S4**.

*Synthesis of **S4***: **S10** (1.43 g, 4.40 mmol), B_2pin_2 (1.24 g, 4.90 mmol), AcOK (1.31 g, 13.4 mmol), and $PdCl_2(dppf)\cdot CH_2Cl_2$ (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 $MgSO_4$. 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. ^{1}H NMR (400 MHz, $CDCl_3$, 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 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 drop coating from 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 the 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 μ 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_{SD} sat V_{GS}= 0 V (I_{off}) and V_{GS}= ±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 Number	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	-0.392436
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	16	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	-2.619454	0.473794	-0.588914
31	16	0	-3.857376	-0.778460	-0.329517
32	6	0	-4.595185	1.725813	0.029411
33	6	0	-3.234190	1.780497	-0.390767
34	6	0	10.348549	0.207435	0.536836
35	6	0	-5.258944	2.921404	0.358773
36	6	0	-4.626058	4.147220	0.196117
37	6	0	-3.322424	4.204315	-0.305530
38	6	0	-2.629673	3.034709	-0.590603
39	6	0	1.398969	-2.339265	-1.473862
40	6	0	0.698535	-3.499999	-1.780106
41	6	0	-0.698859	-3.500052	-1.779678
42	6	0	-1.399202	-2.339372	-1.473022
43	6	0	9.043833	-2.699925	0.644999
44	6	0	8.301460	-3.871011	0.715142
45	6	0	6.902926	-3.818185	0.690428
46	6	0	6.235879	-2.604848	0.568306
47	6	0	-10.348606	0.207641	0.535603
48	6	0	10.716748	1.585566	0.499462
49	7	0	10.989527	2.718269	0.470143
50	6	0	11.421114	-0.725053	0.621105
51	7	0	12.314943	-1.470276	0.689769
52	6	0	-10.716711	1.585797	0.498239
53	7	0	-10.989422	2.718517	0.468942
54	6	0	-11.421270	-0.724806	0.619079
55	7	0	-12.315181	-1.469985	0.687151
56	1	0	1.627838	3.107462	-0.991806
57	1	0	2.841617	5.164025	-0.468637
58	1	0	5.155407	5.059829	0.448518
59	1	0	6.263366	2.911609	0.756264
60	1	0	-5.155570	-2.600880	0.597020
61	1	0	-6.325949	-4.733506	0.778059
62	1	0	-8.810787	-4.824732	0.806610
63	1	0	-10.123851	-2.745296	0.688790
64	1	0	-6.262898	2.911161	0.759051
65	1	0	-5.154965	5.059529	0.451714
66	1	0	-2.841383	5.163948	-0.465939
67	1	0	-1.627726	3.107559	-0.989944
68	1	0	2.477274	-2.347854	-1.552791
69	1	0	1.244165	-4.398725	-2.049579
70	1	0	-1.244586	-4.398822	-2.048810
71	1	0	-2.477554	-2.348056	-1.551286
72	1	0	10.123554	-2.745411	0.690373
73	1	0	8.810353	-4.824803	0.807579

74	1	0	6.325534	-4.733498	0.777290
75	1	0	5.155349	-2.600891	0.595229

Optimized structure of **5TQ-B3(H)** at UB3LYP/6-31G(d,p).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-8.082352	-1.970949	0.720721
2	6	0	-6.789303	-1.768686	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	-1.970982	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

49	1	0	-6.105462	-2.579291	0.113974
50	1	0	6.105510	-2.579406	0.114078
51	1	0	8.551314	-2.940394	0.835445
52	1	0	-2.478123	-2.734673	-1.631238
53	1	0	-1.244496	-4.797440	-2.068402
54	1	0	1.244277	-4.797520	-2.068290
55	1	0	2.477999	-2.734834	-1.631079
56	1	0	-1.616504	2.749730	-1.254668
57	1	0	-2.873133	4.815324	-0.914738
58	1	0	-5.239504	4.747078	-0.149605
59	1	0	-6.350868	2.602241	0.232487
60	1	0	6.350918	2.602075	0.232487
61	1	0	5.239639	4.746941	-0.149745
62	1	0	2.873316	4.815232	-0.915022
63	1	0	1.616625	2.749663	-1.254904

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

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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	9.033687	-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

36	6	0	9.391550	2.750618	0.000513
37	6	0	8.032127	3.092055	0.000484
38	6	0	7.051506	2.108932	0.000341
39	6	0	-10.219959	-1.746152	0.000191
40	6	0	10.190620	-3.172254	-0.000041
41	7	0	10.137069	-4.336537	-0.000149
42	6	0	11.510198	-1.144736	0.000178
43	7	0	12.576269	-0.672903	0.000247
44	6	0	-10.190621	-3.172254	0.000168
45	7	0	-10.137070	-4.336537	0.000148
46	6	0	-11.510198	-1.144735	0.000244
47	7	0	-12.576268	-0.672900	0.000285
48	1	0	2.360686	-2.391118	-0.000359
49	1	0	4.890003	-2.695160	-0.000174
50	1	0	-6.010585	2.404256	0.000140
51	1	0	-7.738126	4.137120	0.000230
52	1	0	-10.147299	3.529125	0.000282
53	1	0	-10.833040	1.166345	0.000251
54	1	0	-4.890003	-2.695160	-0.000085
55	1	0	-2.360686	-2.391119	-0.000294
56	1	0	2.485401	2.807230	-0.000393
57	1	0	1.242906	4.915916	-0.000440
58	1	0	-1.242907	4.915916	-0.000479
59	1	0	-2.485401	2.807230	-0.000464
60	1	0	10.833040	1.166346	0.000432
61	1	0	10.147298	3.529126	0.000627
62	1	0	7.738126	4.137120	0.000580
63	1	0	6.010585	2.404255	0.000341

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

23	16	0	-4.030698	-1.065927	-0.000002
24	6	0	-4.414154	1.526594	0.000006
25	6	0	-3.057711	1.362385	0.000010
26	6	0	10.348302	0.929855	-0.000005
27	6	0	1.405054	-2.975551	0.000005
28	6	0	0.701177	-4.170857	0.000004
29	6	0	-0.701186	-4.170855	0.000004
30	6	0	-1.405060	-2.975547	0.000004
31	6	0	-10.348301	0.929855	-0.000012
32	6	0	10.632836	2.323019	0.000001
33	7	0	10.830570	3.472152	0.000005
34	6	0	11.436748	0.012221	-0.000009
35	7	0	12.308885	-0.761280	-0.000009
36	6	0	-10.632837	2.323018	-0.000006
37	7	0	-10.830573	3.472151	-0.000005
38	6	0	-11.436747	0.012219	-0.000021
39	7	0	-12.308883	-0.761282	0.000025
40	1	0	9.347942	-1.720631	-0.000014
41	1	0	6.781376	-2.043634	-0.000012
42	1	0	2.361064	2.192800	0.000017
43	1	0	4.903503	2.493622	0.000012
44	1	0	-6.781374	-2.043632	-0.000009
45	1	0	-9.347940	-1.720631	-0.000016
46	1	0	-4.903503	2.493624	0.000007
47	1	0	-2.361064	2.192804	0.000016
48	1	0	2.486458	-3.005464	0.000006
49	1	0	1.242885	-5.111177	0.000004
50	1	0	-1.242897	-5.111174	0.000004
51	1	0	-2.486465	-3.005456	0.000005

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

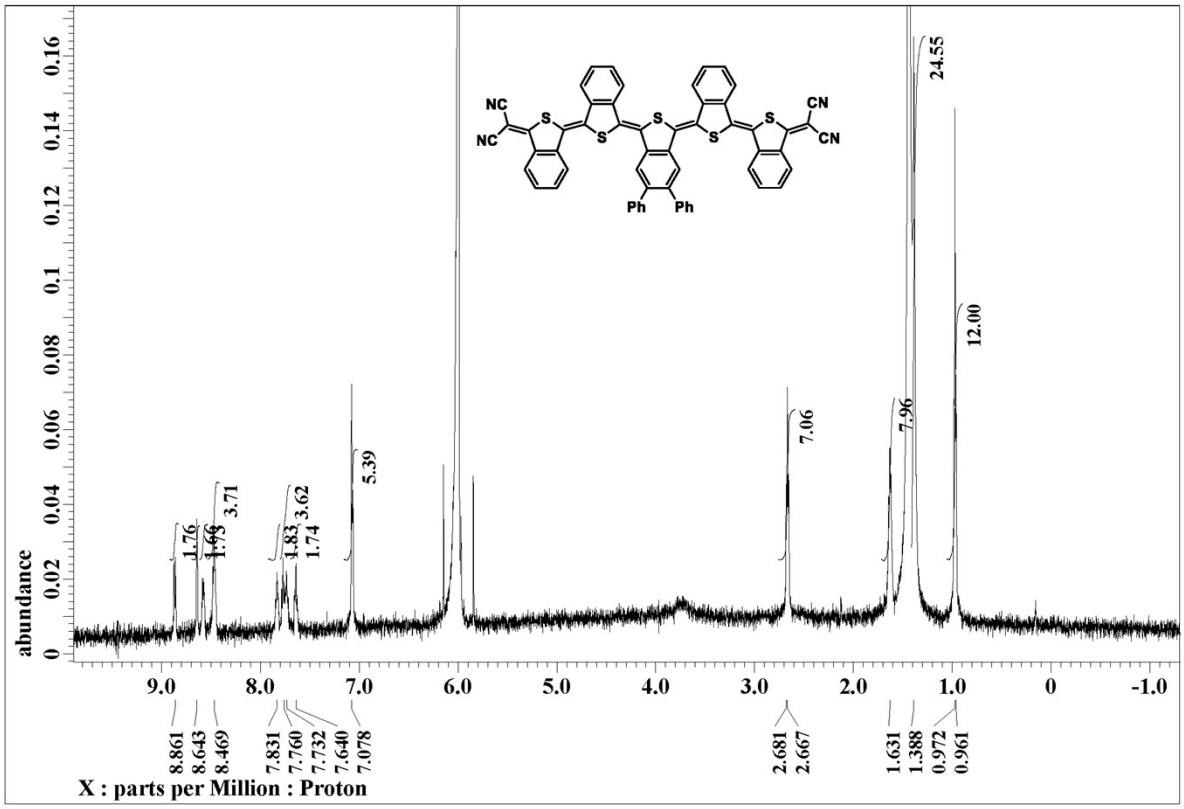
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.020722	7.787329	0.000000
2	6	0	0.224939	6.521956	0.000000
3	6	0	1.517113	7.116466	0.000000
4	6	0	1.512953	8.486429	0.000000
5	6	0	0.201525	9.055058	0.000000
6	6	0	-0.099704	5.171334	0.000000
7	6	0	-1.394849	4.584215	0.000000
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	1.131885	-3.898602	-0.000000
17	6	0	-0.099704	-5.171333	-0.000000
18	6	0	-1.394850	-4.584214	-0.000000
19	6	0	-1.391850	-3.210208	-0.000000
20	6	0	-0.099408	-2.625934	-0.000000
21	6	0	0.224939	-6.521956	-0.000000

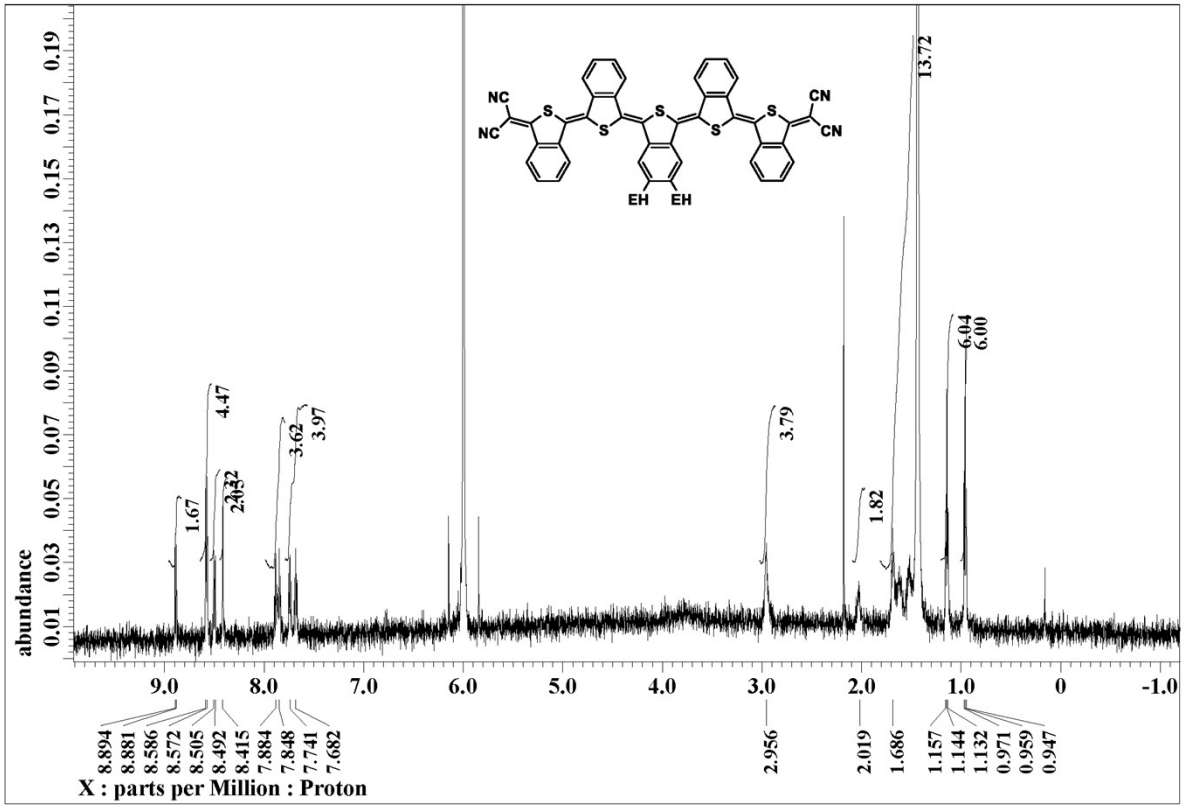
22	6	0	1.517113	-7.116466	-0.000000
23	6	0	1.512954	-8.486429	-0.000000
24	6	0	0.201525	-9.055059	-0.000000
25	16	0	-1.020722	-7.787330	-0.000000
26	6	0	-0.121974	-10.407974	-0.000000
27	6	0	-0.121974	10.407974	0.000000
28	6	0	-1.474190	10.846078	0.000000
29	7	0	-2.594302	11.170567	0.000000
30	6	0	0.911218	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

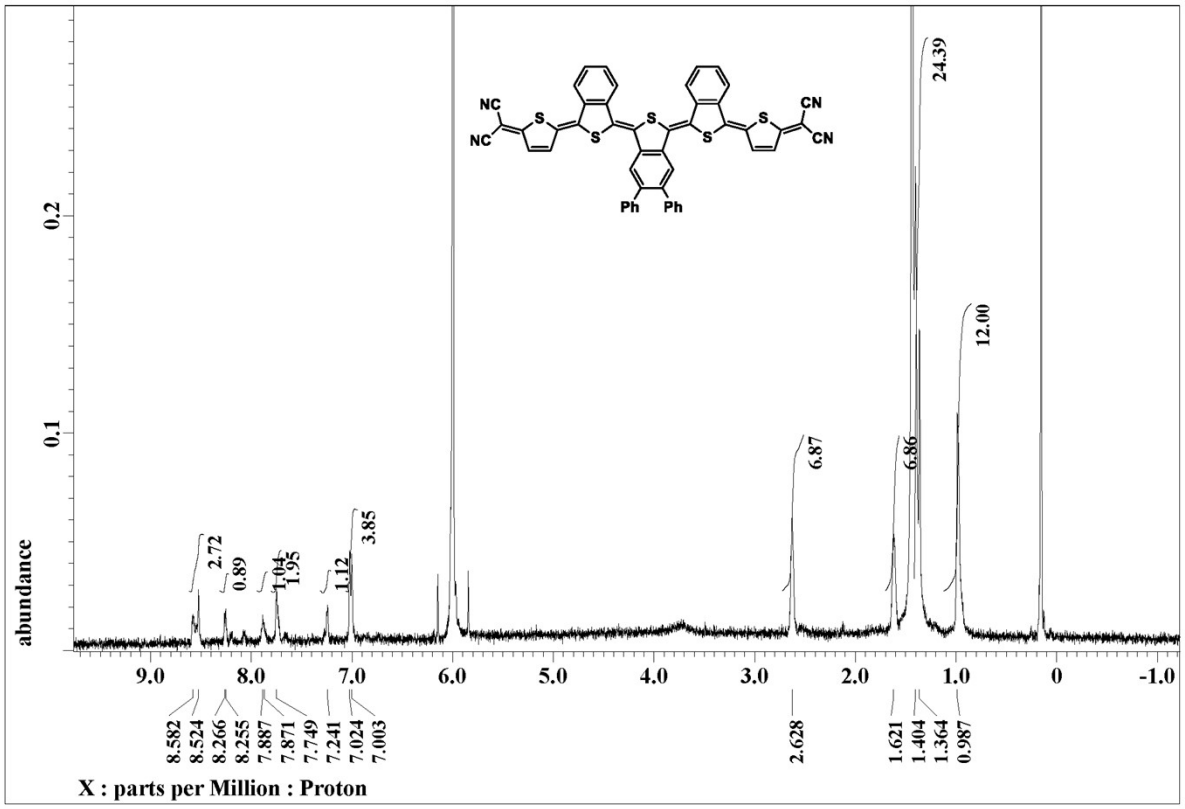
References

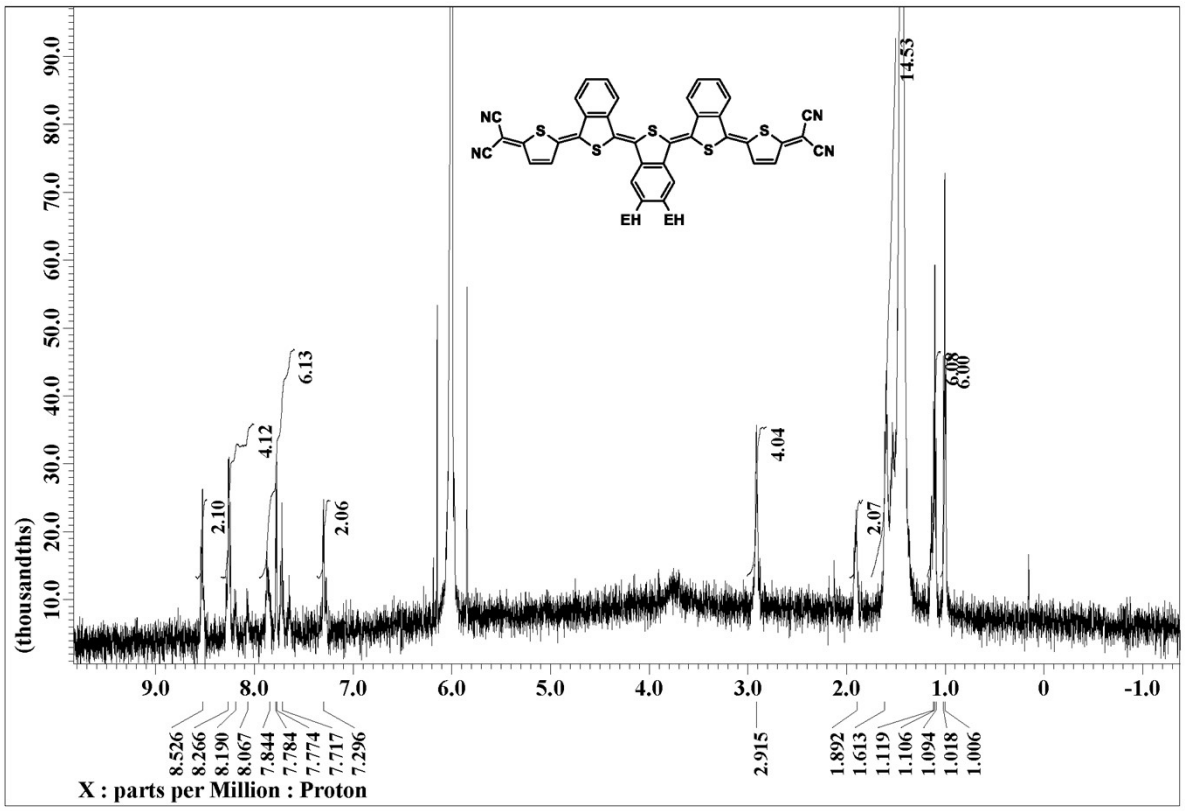
1) K. Yamamoto, S. Jinnai, T. Takehara, T. Suzuki, Y. Ie, *Org. Lett.,* 2020, **22**, 547–551.
2) Y. Shimizu, Z. Shen, S. Ito, H. Uno, J. Daub, N. Ono, *Tetrahedron Lett.,* 2002, **43**, 8485–8488.
3) K. Yamamoto, Y. Ie, M. Nitani, N. Tohnai, F. Kakiuchi, K. Zhang, W. Pisula, K. Asadi, P. W. M. Blom, Y. Aso, *J. Mater. Chem. C,* 2018, **6**, 7493–7500.

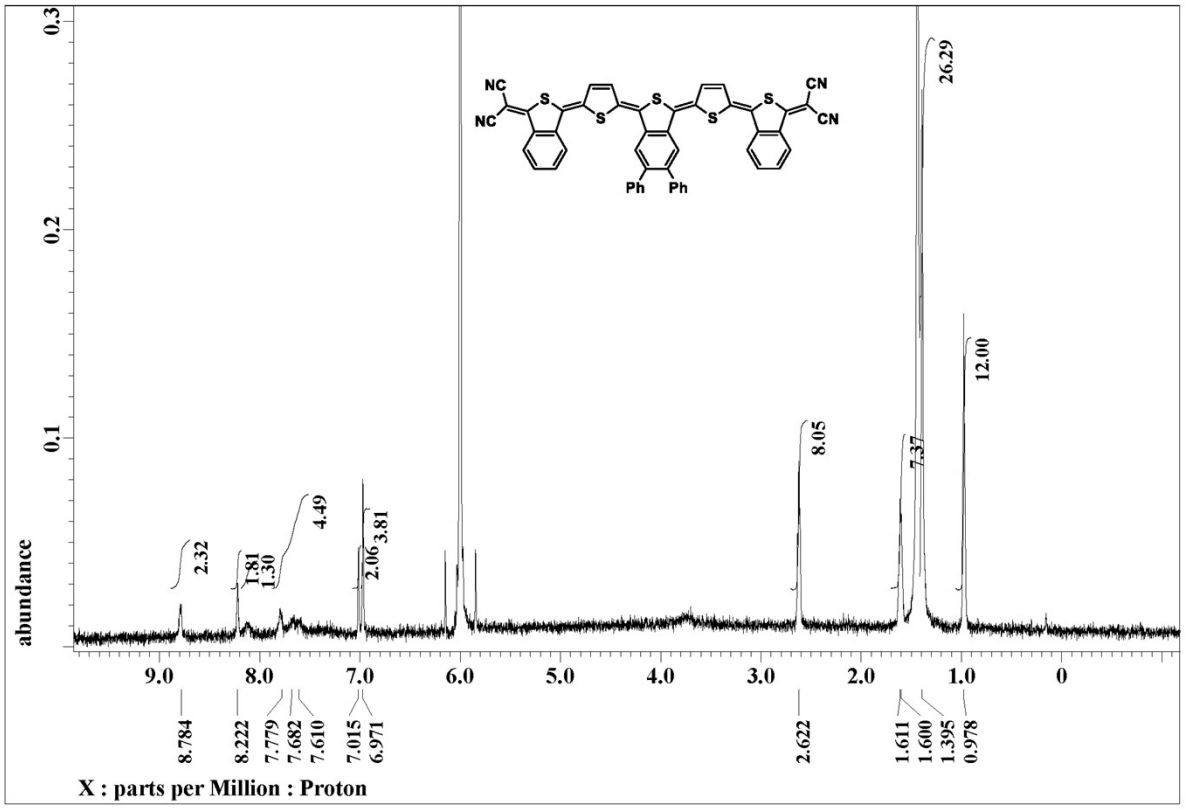
^{1}H NMR spectra

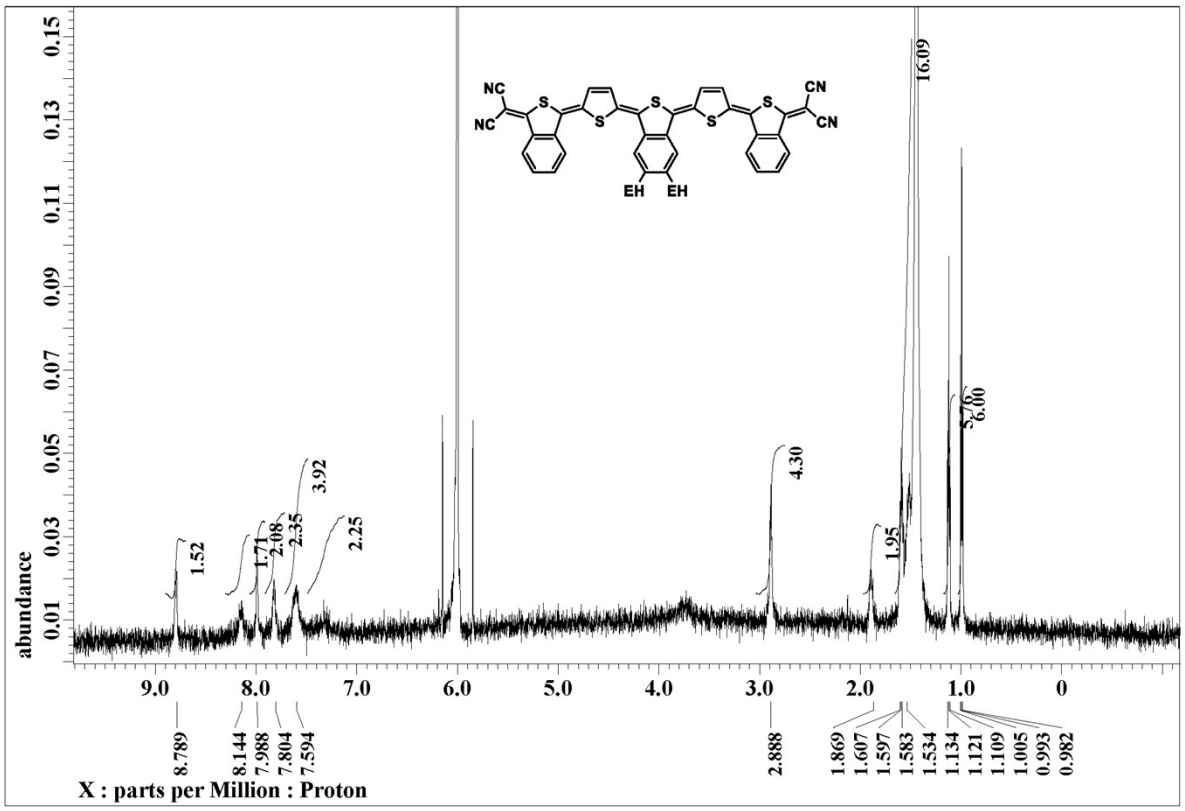





abundance
0.2
0.1
NC
NC
CN
CN
Ph Ph
24.39
12.00
6.87
6.86
3.85
2.72
0.89
1.04
1.95
1.12
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0
8.582 8.524 8.266 8.255 7.887 7.871 7.749 7.241 7.024 7.003
2.628
1.621 1.404 1.364 0.987
X : parts per Million : Proton


(thousandths)
90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
NC
NC
CN
CN
EH EH
14.53
6.13
4.12
4.04
2.10
2.06
2.07
6.08
6.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0
8.526 8.266 8.190 8.067 7.844 7.784 7.774 7.717 7.296
2.915
1.892 1.613 1.119 1.106 1.094 1.018 1.006
X : parts per Million : Proton


abundance
X : parts per Million : Proton
NC
NC
CN
CN
Ph
Ph
26.29
12.00
8.05
7.37
4.49
2.32
1.81
1.30
2.06
3.81
8.784
8.222
7.779
7.682
7.610
7.015
6.971
2.622
1.611
1.600
1.395
0.978


abundance
X : parts per Million : Proton
NC
NC
CN
CN
EH
EH
16.09
6.00
5.78
4.30
3.92
2.25
2.35
2.08
1.71
1.52
1.95
8.789
8.144
7.988
7.804
7.594
2.888
1.869
1.607
1.597
1.583
1.534
1.134
1.121
1.109
1.005
0.993
0.982