

From Benzobisthiadiazole, Thiadiazoloquinoxaline To Pyrazinoquinoxaline Based Polymers: Effects Of Aromatic Substituents On The Performance of Organic Photovoltaics

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Supporting Information

Experimental Section

Synthesis and Characterization

Column chromatography was carried out with Merck silica-gel (230 – 400 mesh) 1H and 13C data were performed on a Bruker DPX 400 MHz spectrometer with chemical shifts referenced to CDCl₃. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Shimadzu Biotech AXIMA-TOF². Elemental analysis was obtained via a Thermo Scientific Flash 2000 Series CHNS/O Analyzer. Differential scanning calorimetry (DSC) was carried out under nitrogen on a DSC Q100 instrument from TA Instruments using a scanning rate of 10 °C·min⁻¹. 2 cycles were performed, with the 1st cycle from 40 °C to 300 °C to 0 °C and 2nd cycle from 0 °C to 300 °C to 0 °C. Thermogravimetric analysis (TGA) was carried out on a TA Instrument Q500 Thermogravimetric Analyzer at a heating rate of 20 °C/min up to 900 °C. UV-Vis-NIR absorption spectra were recorded in CHCl₃ on a UV-1800 UV-Vis Spectrophotometer from Shimadzu. Cyclic voltammetry experiments were performed using a Multichannel Potentiostat (Model 1470E) from Solartron Analytical. All CV measurements were recorded in CHCl₃ with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte (scan rate of 100 mV·s⁻¹). The experiments were performed at room temperature with a conventional 3 electrodes configuration consisting of a platinum wire working electrode, a gold counter electrode and an Ag/AgCl in 3 M KCl reference electrode. The measured potentials (onset) were converted to orbital energies by using value of SCE (saturated calomel electrode) having potential of -4.4 eV relative to vacuum. Molecular weights of the polymers were measured using a GPC system consisting of an Agilent 1100 Series solvent delivery, sample injector, refractive index detector, and a 300mm by 7.8mm PLgel Mixed-C, 5µm column fitted with a guard column (Agilent Technologies, CA, USA). Tetrahydrofuran at a flow rate of 1ml/min was used and 50µl was injected per sample. EasiVial PS-M polystyrene standards (Agilent Technologies, CA, USA) were used for calibration. Thin film of the polymers were dropcasted on untreated Si wafers using 1,2-dichlorobenzene as solvent and XRD was performed using D8 ADVANCE from Bruker AXS with beam cutter to minimize air scattering.

5. **1** (0.30 g, 0.852 mmol) and iron powder (0.95 g, 17.04 mmol) were suspended in acetic acid (50 mL) and the mixture was stirred at 80 °C for four hours. The excess iron was removed using a magnetic retriever, followed by addition of **3** (0.43 g, 0.852 mmol) in one portion. The reaction was stirred at 80 °C for 2 days, poured into water, and extracted with dichloromethane. The organic extract was then washed with water, dried over anhydrous MgSO₄, concentrated and absorbed onto silica gel chromatography. Elution with hexane:dichloromethane (3:2) yielded **5** as a brown solids (0.480 g, 71 %). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 7.88 (d, ³J(H,H) = 8.4 Hz, 4H; Ph-H), 7.61 (m, 8H; Ph-H), 6.99 (d, ³J(H,H) = 8.8 Hz, 4H; Ph-H), 4.02 (t, ³J(H,H) = 6.4 Hz, 4H; OCH₂), 1.81 (quintet, ³J(H,H) = 6.4 Hz, 4H; CH₂), 1.50 (m, 4H; CH₂), 1.01 ppm (t, ³J(H,H) = 7.6 Hz, 6H; CH₃). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 160.0, 156.3, 153.0, 143.6, 138.8, 136.5, 132.8, 131.5, 128.8, 127.2, 115.6, 114.6, 68.5, 32.0, 20.2, 14.6 ppm. MALDI-TOF-MS: *m/z*: 794.04 (*M*⁺). elemental analysis: calcd (%) for C₄₀H₃₄Br₂N₄O₂S (794.07): C 60.46, H 4.31, N 7.05, S 4.04; found: C 60.29, H 4.36, N 7.23, S 3.82.

6. Reduction of **1** with iron followed by addition of **4** using same procedure for the preparation of **5** afforded **6** as a dark purple solids in 52 % yield. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 7.63 (d, ³J(H,H) = 4.0 Hz, 2H; Th-H), 7.19 (d, ³J(H,H) = 3.6 Hz, 2H; Th-H), 7.03 (d, ³J(H,H) = 4.0 Hz, 2H; Th-H), 6.74 (d, ³J(H,H) = 3.2 Hz, 2H; Th-H), 2.82 (t, ³J(H,H) = 7.2 Hz, 4H; Th-CH₂), 1.69 (quintet, ³J(H,H) = 7.2 Hz, 4H; CH₂), 1.53 (m, 12H; CH₂), 0.91 ppm (t, ³J(H,H) = 5.2 Hz, 6H; CH₃). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 147.93, 147.85, 144.8, 140.0, 138.7, 134.8, 132.7, 126.0, 125.8, 124.1, 32.3, 31.0, 29.5, 23.3, 14.8 ppm. MALDI-TOF-MS: *m/z*: 842.00 (*M*⁺). elemental analysis: calcd (%) for C₃₆H₃₄Br₂N₄S₅ (841.97): C 51.30, H 4.07, N 6.65, S 19.02; found: C 51.15, H 4.19, N 6.91, S 18.72.

7. **PQ1** (0.364 g, 0.29 mmol) was dissolved in chloroform (100 mL). The solution was then cooled to 0 °C in an ice-bath. NBS (0.104 g, 0.58 mmol) was dissolved in 50 ml of chloroform and was added dropwisely. After the addition of NBS, the reaction was allowed to warm up to room temperature overnight. Aqueous Na₂S₂O₃ was added to the reaction mixture and the organics were extracted using dichloromethane. The organic layer was collected, dried over anhydrous MgSO₄, concentrated and precipitated in methanol to afford **7** as dark brown solids (0.370 g, 90 %). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 8.49 (d, ³J(H,H) = 4.0 Hz, 2H; Th-H), 7.63 (d, ³J(H,H) = 8.0 Hz, 8H; Ph), 7.60 (d, ³J(H,H) = 8.8 Hz, 8H; Ph), 7.31 (d, ³J(H,H) = 4.4 Hz, 2H; Th-H), 6.99 (d, ³J(H,H) = 7.6 Hz, 8H; Ph), 4.02 (t, ³J(H,H) = 6.4 Hz, 8H; OCH₂), 1.81 (quintet, ³J(H,H) = 6.8 Hz, 8H; CH₂), 1.51 (m, 8H; CH₂), 1.00 ppm (t, ³J(H,H) = 7.6 Hz, 12H; CH₃). MALDI-TOF-MS: *m/z*: 1400.98 (*M*⁺). elemental analysis: calcd (%) for C₈₂H₇₂Br₂N₄O₄S₂ (1401.41): C 70.28, H 5.18, Br 11.40, N 4.00, O 4.57, S 4.58; found: C 70.46, H 5.16, N 4.01, S 4.61.

8. Bromination of **PQ2** was carried out using same procedure for the preparation of **7** afforded **8** as dark green solids in 96 % yield. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 8.29 (d, ³J(H,H) = 3.6 Hz, 2H; Th-H), 7.62 (d, ³J(H,H) = 4.0 Hz, 4H; Th-H), 7.34 (d, ³J(H,H) = 4.4 Hz, 2H; Th-H), 7.19 (d, ³J(H,H) = 3.2 Hz, 4H; Th-H), 7.05 (d, ³J(H,H) = 4.0 Hz, 4H; Th-H), 6.77 (d, ³J(H,H) = 3.2 Hz, 4H; Th-H), 2.84 (t, ³J(H,H) = 7.6 Hz, 8H; Th-CH₂), 1.72 (quintet, ³J(H,H) = 7.6 Hz, 8H; CH₂), 1.32 (m, 24H; CH₂), 0.91 ppm (t, ³J(H,H) = 6.8 Hz, 12H; CH₃). MALDI-TOF-MS: *m/z*: 1496.21 (*M*⁺). elemental analysis: calcd (%) for C₇₄H₇₂Br₂N₄S₁₀ (1497.85): C 59.34, H 4.85, Br 10.67, N 3.74, S 21.41; found: C 59.49, H 4.88, N 3.71, S 21.33.

pTQ1F. **5** (0.40 g, 0.50 mmol), **2** (0.57 g, 0.50 mmol) and Pd[PPh₃]₂Cl₂ (21 mg, 6 mol %) were added to a 50 mL round bottom flask purged with N₂ gas, followed by addition of anhydrous THF (25 mL). The reaction was stirred under reflux for 2 days, then cooled down, precipitated in methanol and filtered. The resulting solid was thoroughly washed with methanol, hexane and acetone. The residue was dissolved in chloroform and precipitated from acetone twice to obtain the polymer as a dark green solid (0.44 g, 73 %). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 9.14 (br, Ar-H), 8.04 (br, Ar-H), 7.57-7.79 (m, br, Ar-H), 7.00-7.02 (br, Ar-H), 4.02 (br, OCH₂), 2.08 (br, fluorine-CH₂), 1.81 (br, CH₂), 1.51-1.53 (br, CH₂), 0.98-1.25 (m, br, CH₂), 0.87 (br, CH₂, CH₃), 0.75-0.77 ppm (br, CH₃).

pBBTF. This polymer was synthesized by copolymerization of **1** and **2** by the same method as for polymer **pTQ1F** as a dark green solid in 50 % yield. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 8.65 (br, Th-H), 8.55 (br, Th-H), 7.49-7.70 (m, br, Ar-H), 2.10 (br, fluorene-CH₂), 1.73 (br, CH₂), 1.01-1.35 (m, br, CH₂), 0.77-0.87 ppm (m, br, CH₃).

pTQ2F. This polymer was synthesized by copolymerization of **6** and **2** by the same method as for polymer **pTQ1F** as a black solid in 55 % yield. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 8.99 (br, Ar-H), 7.31-7.76 (m, br, Ar-H), 6.99-7.12 (m, br, Ar-H), 6.78 (br, Ar-H), 2.86 (br, Th-CH₂), 2.04 (br, -fluorene-CH₂), 1.73 (br, CH₂), 1.11-1.32 (m, br, CH₂), 0.89 (br, CH₃), 0.78 ppm (br, CH₃).

pPQ1F. **7** (0.370 g, 0.26 mmol), 9,9-dioctylfluorene-2,7-diboronic acid pinacol ester (0.133 g, 0.28 mmol) and Pd[PPh₃]₄ (12 mg, 4 mol %) catalyst were added into a 100 mL round bottom flask purged with N₂ gas. Toluene (50 mL, 2 M K₂CO₃ (20 mL) and a few drops of ethanol, bubbled with N₂ prior use, were injected into the flask and the reaction was heated at 80 °C for 2 days. The reaction mixture was extracted using dichloromethane and water. The organic layer was collected, dried over anhydrous MgSO₄ and concentrated. The polymer was obtained by precipitation in methanol. The residue was dissolved in chloroform and precipitated from acetone to obtain the

polymer as dark green solids (0.287 g, 67 %). ^1H NMR (400 MHz, CDCl_3 , 25 °C): δ = 8.74 (br, Ar-H), 7.63-8.10 (m, br, Ar-H), 6.97-7.02 (br, Ar-H), 4.03 (br, OCH_2), 1.79 (br, CH_2), 1.58 (br, CH_2), 1.25 (br, CH_2), 0.71-1.06 ppm (m, br, CH_2 , CH_3).

pPQ2F. This polymer was synthesized by copolymerization of **8** and 9,9-dioctylfluorene-2,7-diboronic acid pinacol ester by the same method as for polymer **pPQ1F** as a black solid in 43 % yield. ^1H NMR (400 MHz, CDCl_3 , 25 °C): δ = 8.59 (br, Ar-H), 7.35-8.03 (m, br, Ar-H), 7.20 (br, Ar-H), 7.08 (br, Ar-H), 6.76 (br, Ar-H), 2.84 (br, Th- CH_2), 2.10 (br, fluorene- CH_2), 1.71 (br, CH_2), 1.33 (br, CH_2), 1.08 (br, CH_2), 0.90 (br, CH_3), 0.78 ppm (br, CH_3).

Computational Method

Atomistic simulation, using density function theory (DFT) at B3LYP^{1,2} (which includes the gradient corrected exchange and correlation functionals along with the exact exchange) method with double- ζ quality basis functions 6-31G* (augmented with polarized function for all non-hydrogen atoms), was used to optimize the geometry of the thiadiazoloquinoxaline and pyrazinoquinoxaline molecules. Geometry was fully relaxed and no symmetry constraints were imposed during optimization using Gaussian 09 code³ with a convergence criterion of 10^{-3} a.u. on the gradient and displacement and 10^{-6} a.u. on energy and electron density. Harmonic vibrational analyses showed no imaginary frequency, indicating these structures are a local minimum.

Device Fabrication and Characterization

OPV devices (ITO glass/PEDOT:PSS/Donor:PC[71]BM/Al) were fabricated using these polymers as donor materials and PC[71]BM as acceptor. Indium tin oxide (ITO)/glass substrates were purchased from Kintec Company (7 X/sq). The ITO/glass substrates were cleaned by detergent followed by deionized water, acetone and isopropanol for 10 min each in ultrasonic water bath. Before spincoating of PEDOT:PSS, the substrates were UV/ozone plasma cleaned for 2 min. A layer of 30 nm of PEDOT:PSS film was deposited on ITO and then baked at 150 °C for 20 min. The polymer:PC[71]BM blend solutions (total weight solids fixed with varying D/A ratio) which were stirred overnight at room temperature were spincoated onto the PEDOT:PSS layer at 500 rpm. Finally, 100 nm of aluminum was deposited in a vacuum (10^{-6} Torr) through a shadow mask on the active layer to form the cathode. The active area for each device was 0.07 cm^2 . J - V characteristics of the devices were measured using Agilent 4155C Semiconductor Parameter Analyzer under simulated AM 1.5G illumination (100 mW cm^{-2}). The external quantum efficiency (EQE) test was performed by Merlin radiometer (Newport) with calibrated Si photodiode (Hamamatsu) as reference. AFM images were recorded using the tapping mode on the MFP-3D-BIOTM AFM from Asylum Research.

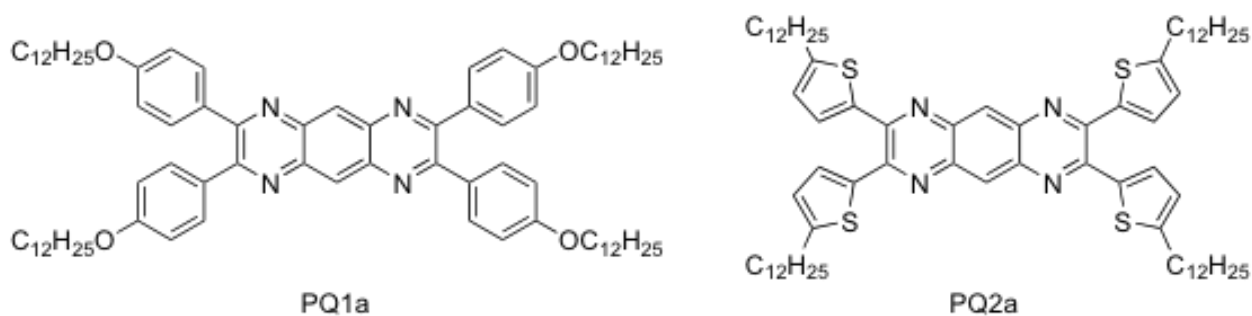


Figure S1. a) Chemical structures of the PQ small molecules discussed in reference 23 in the main text.

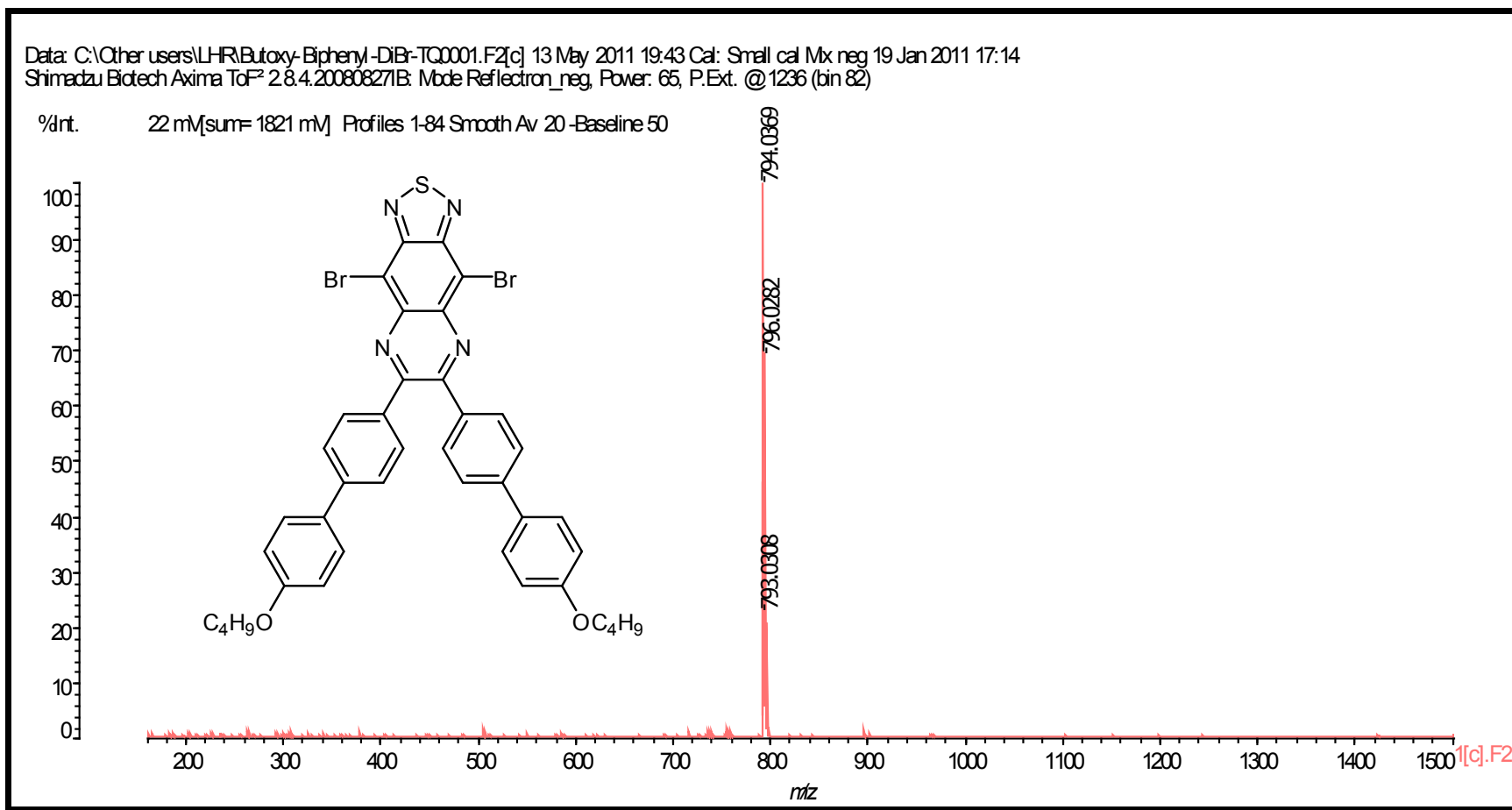


Figure S2. MALDI-TOF of **5**.

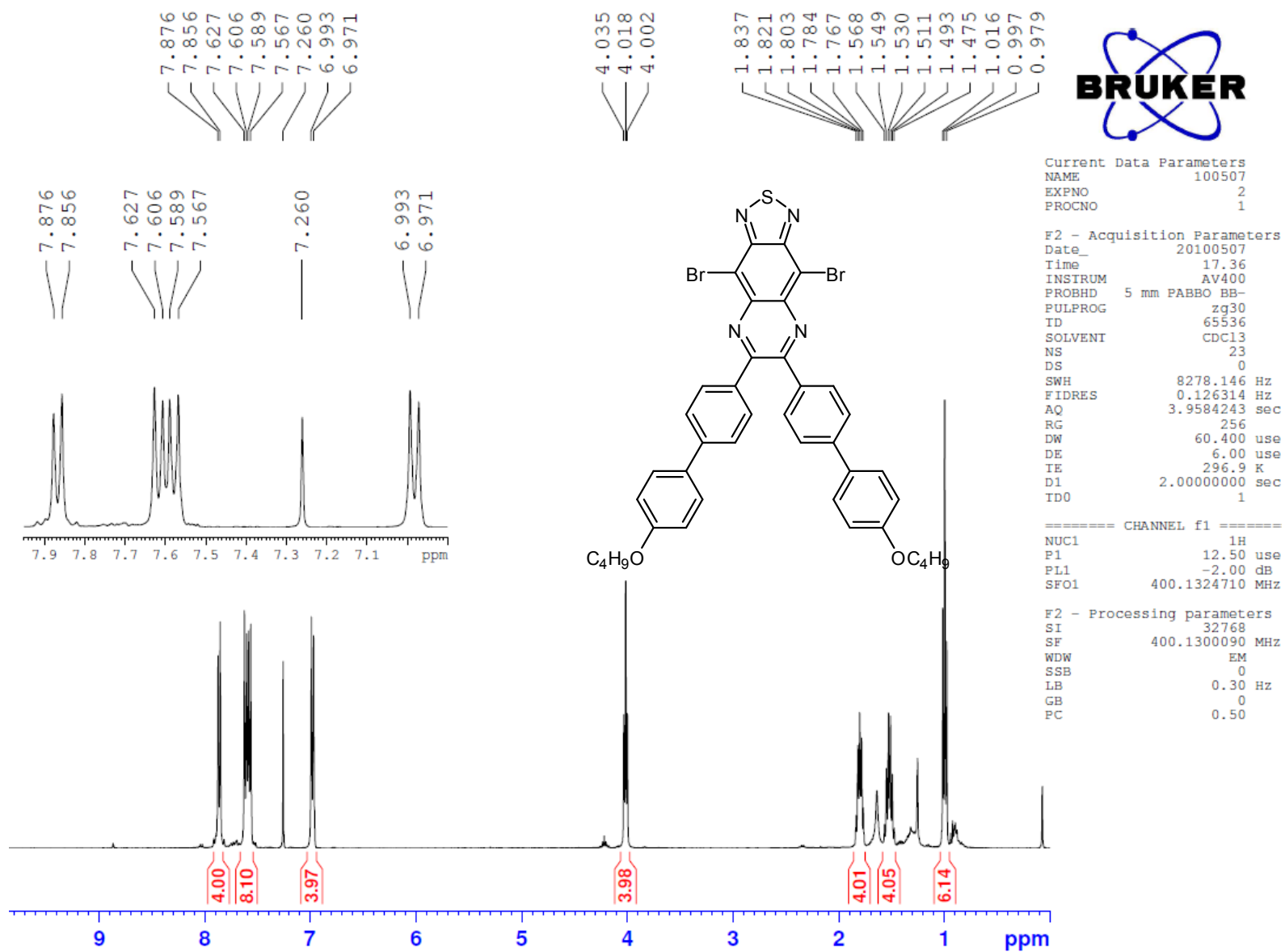


Figure S3. ¹H NMR of **5**.

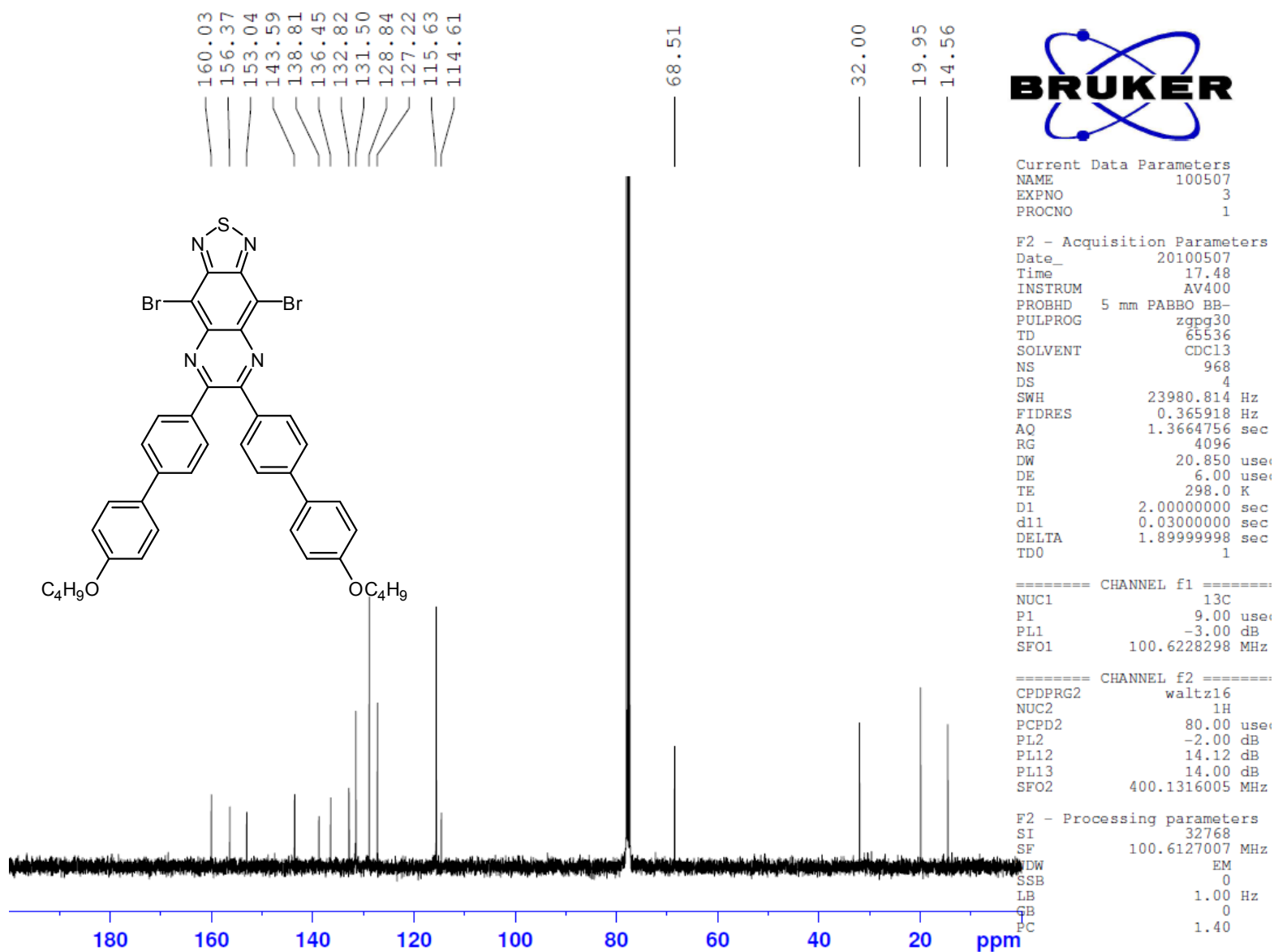


Figure S4. ¹³C NMR of **5**.

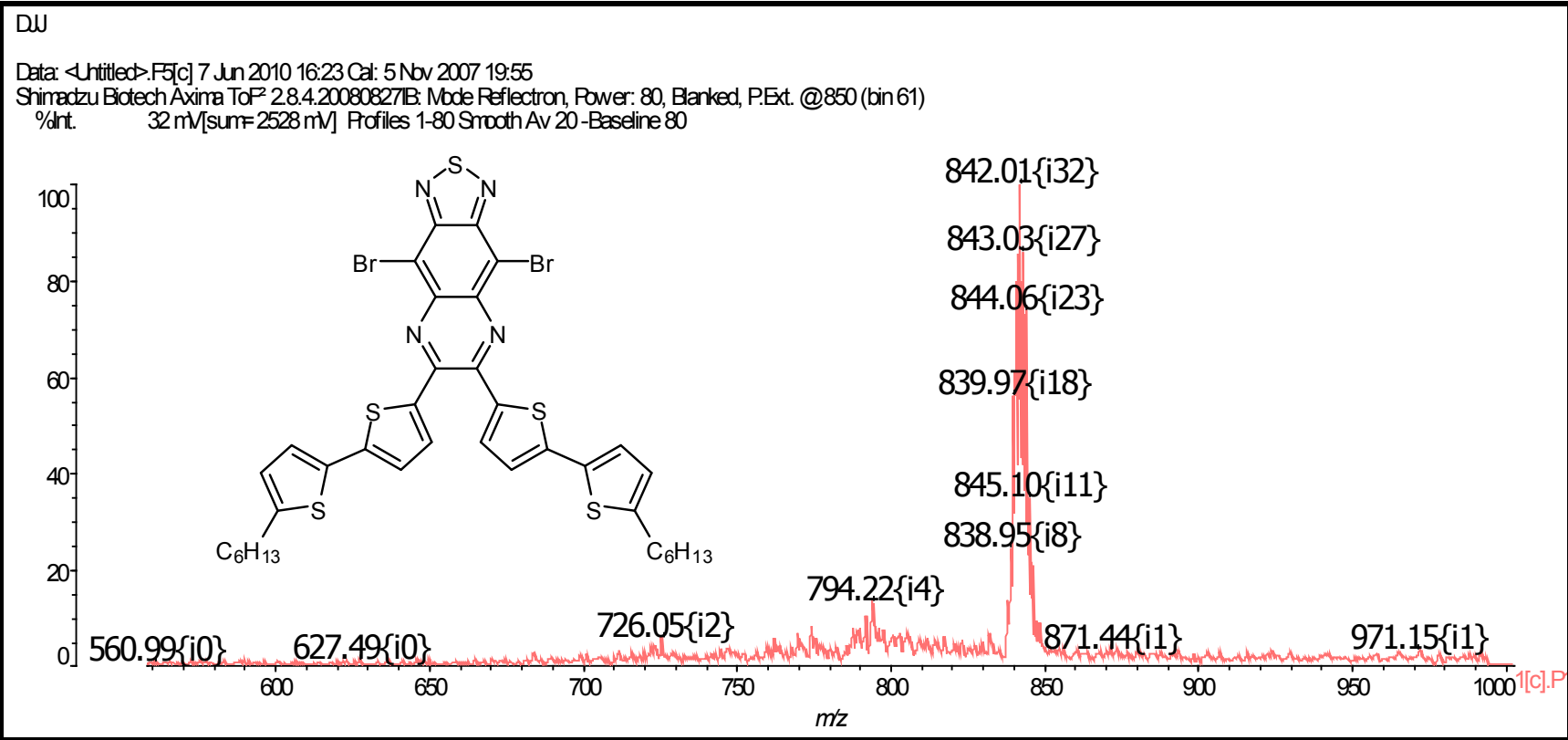


Figure S5. MALDI-TOF of **6**.

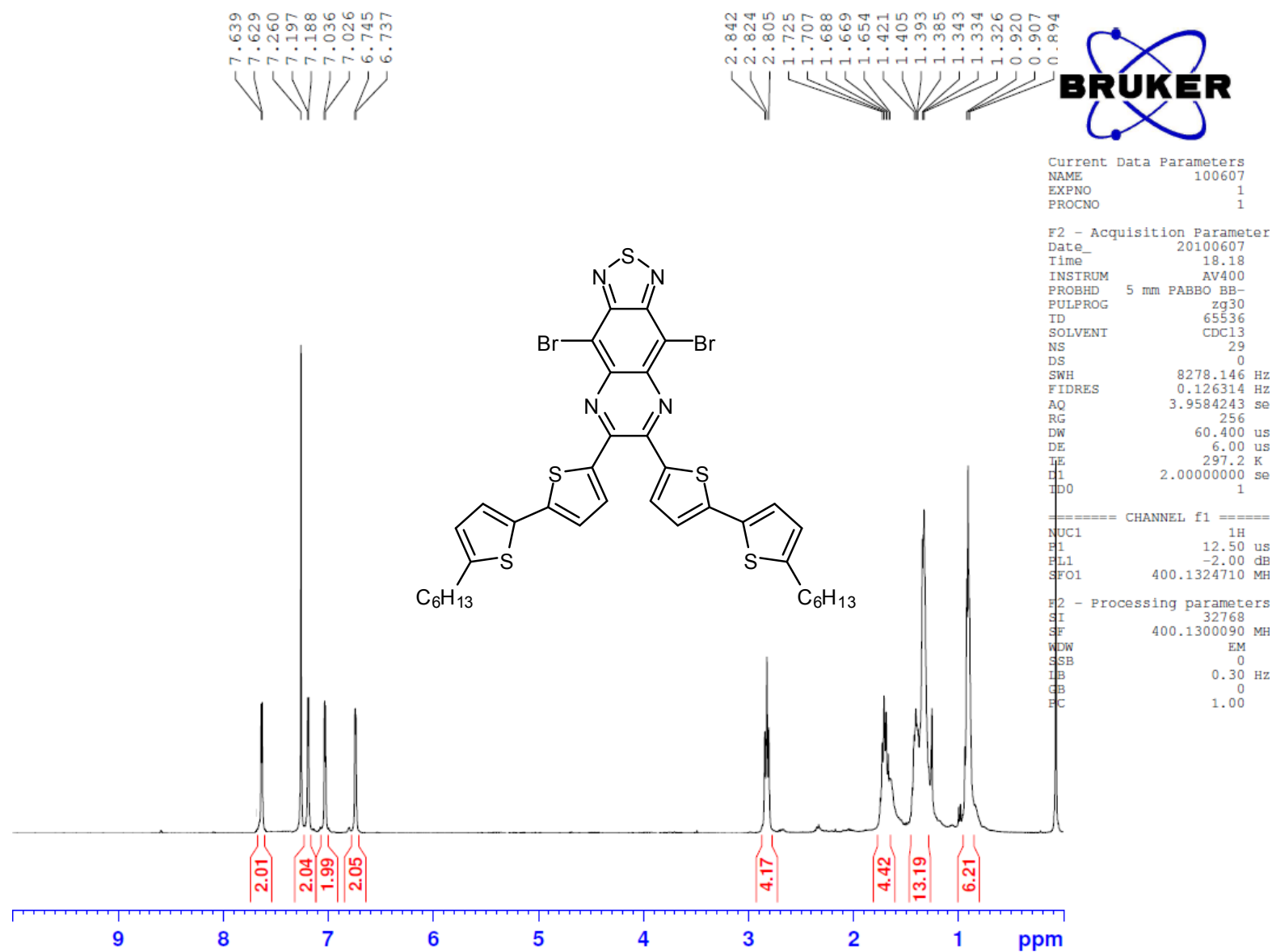


Figure S6. ¹H NMR of 6.

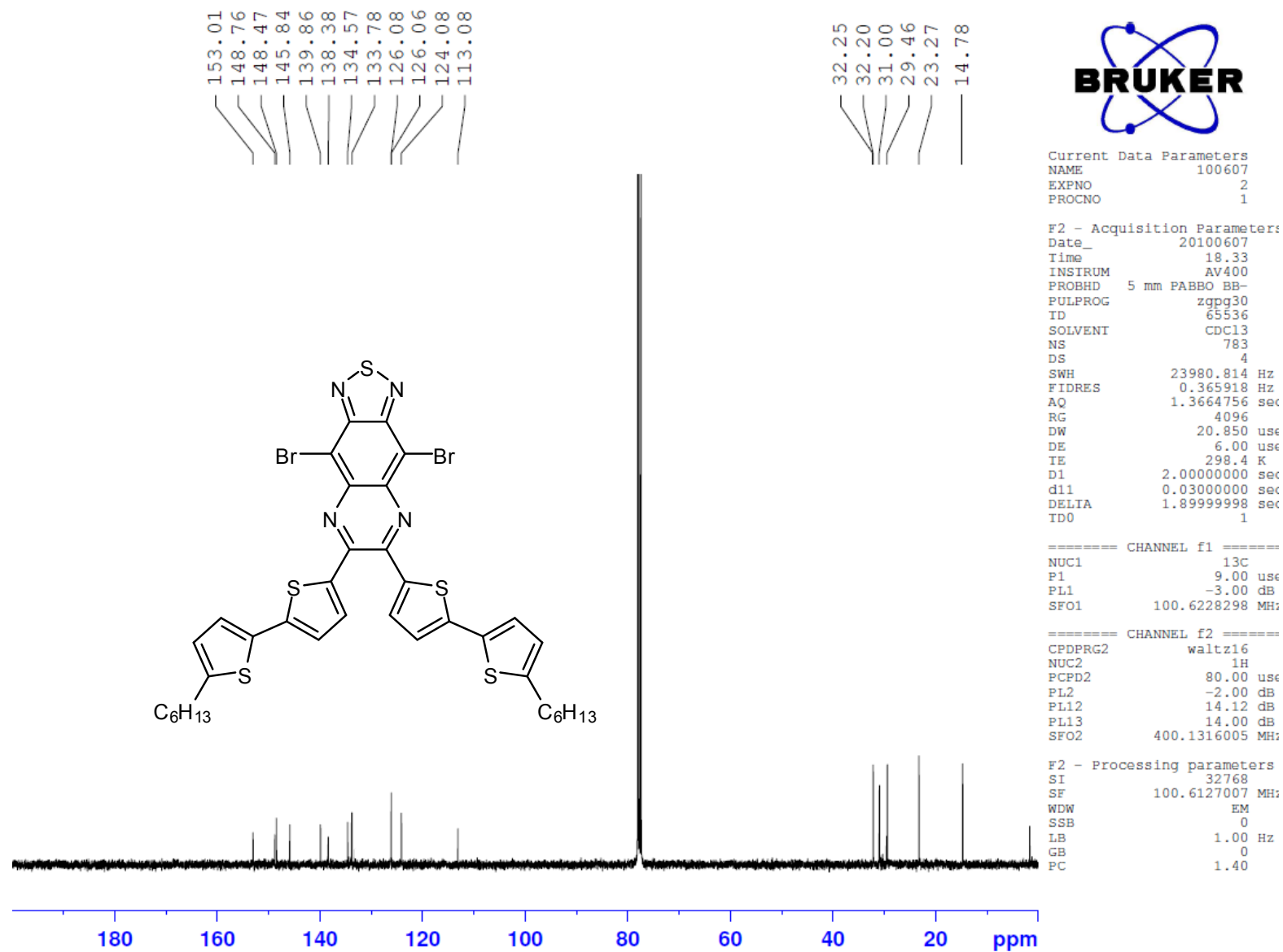


Figure S7. ¹³C NMR of **6**.

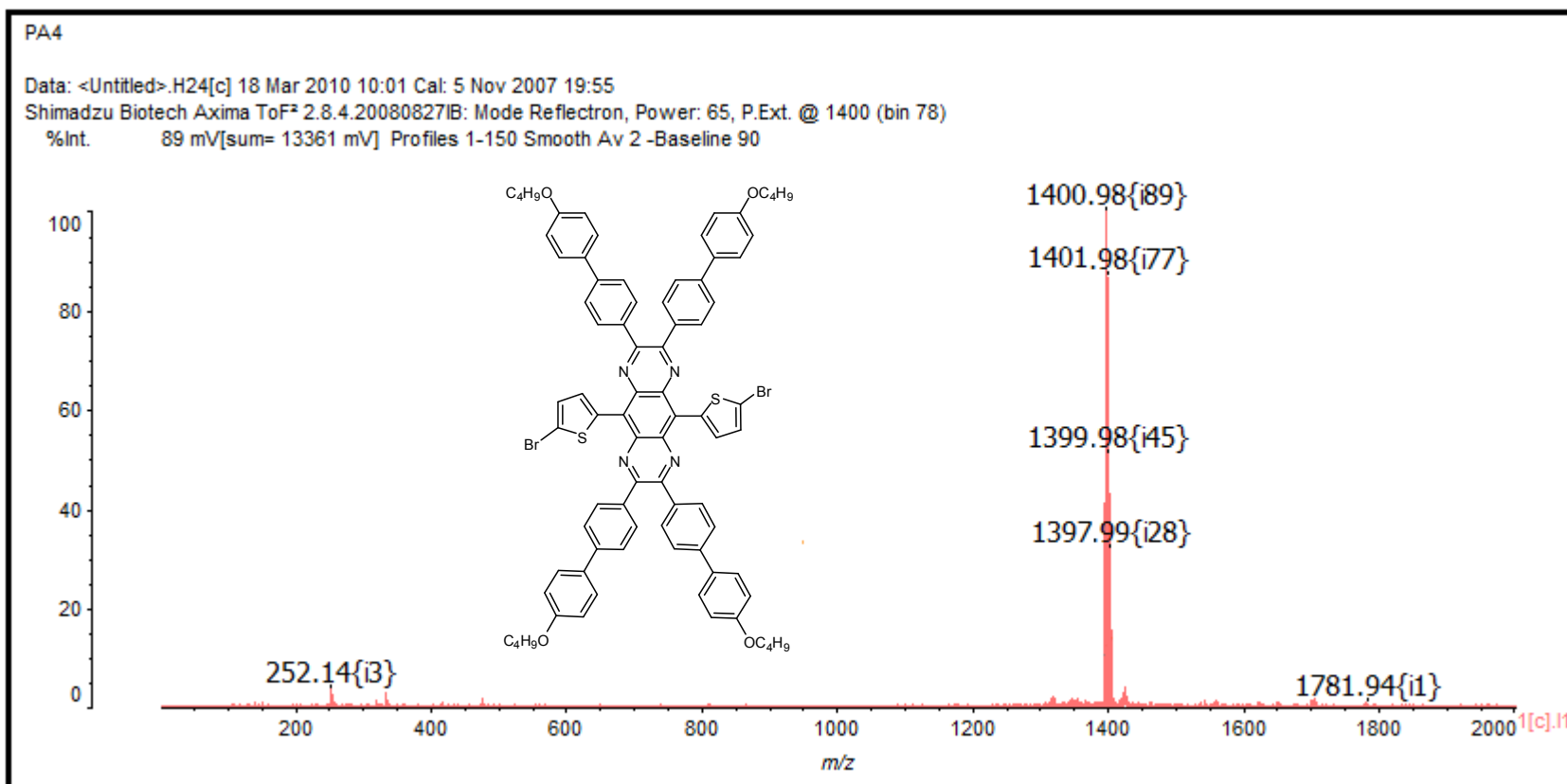


Figure S8. MALDI-TOF of **7**.

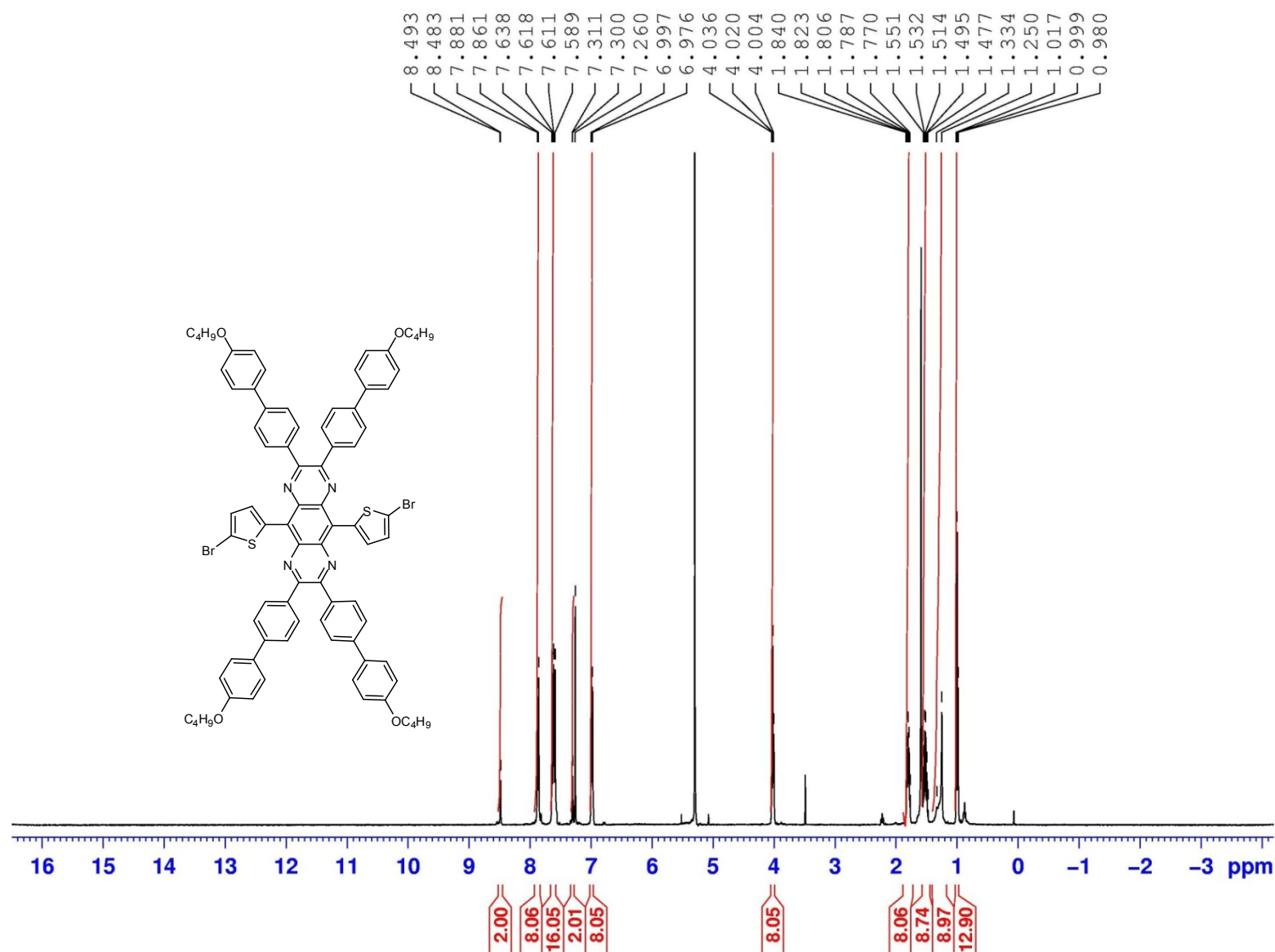


Figure S9. ^1H NMR of 7.

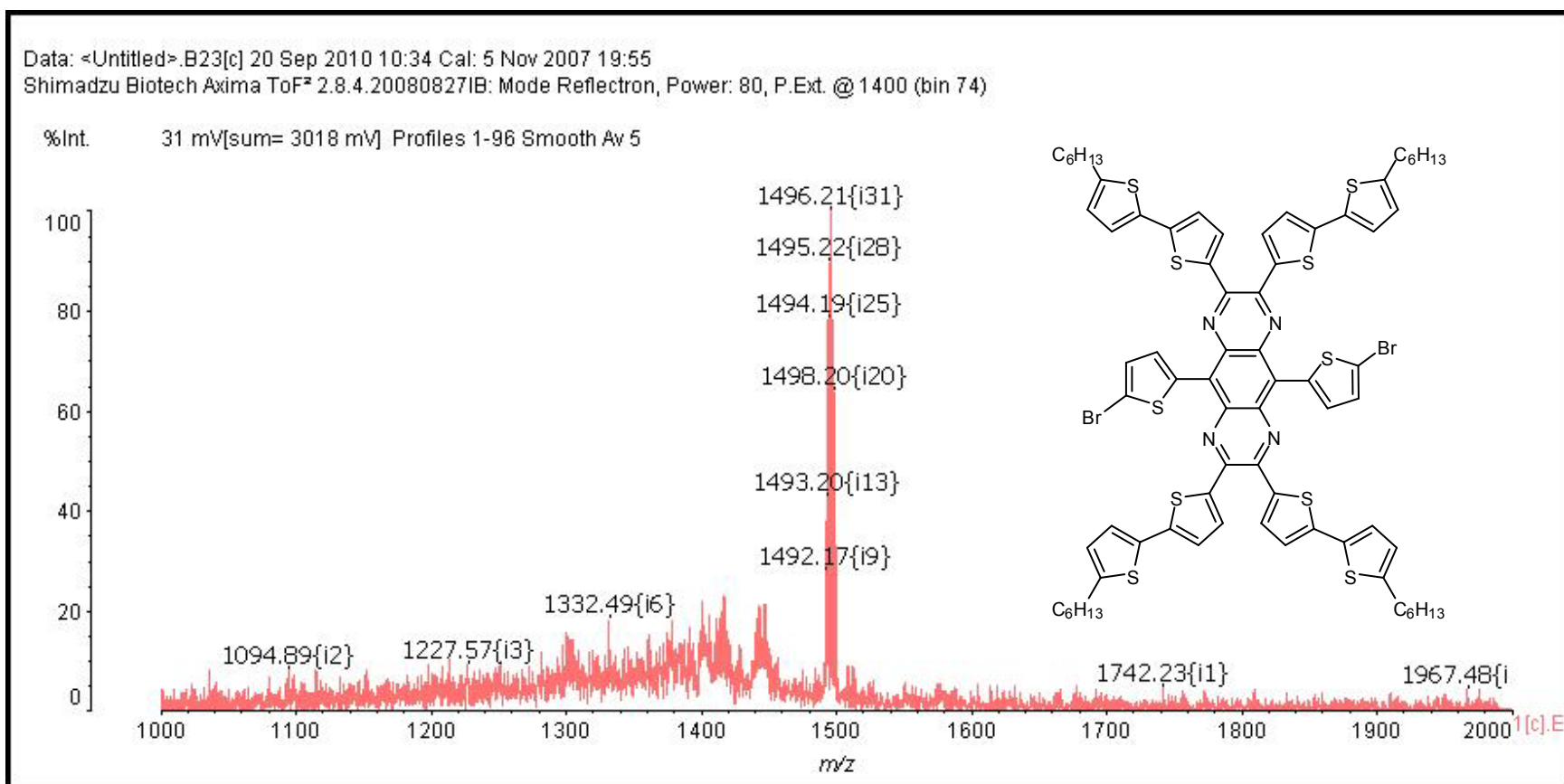


Figure S10. MALDI-TOF of **8**.

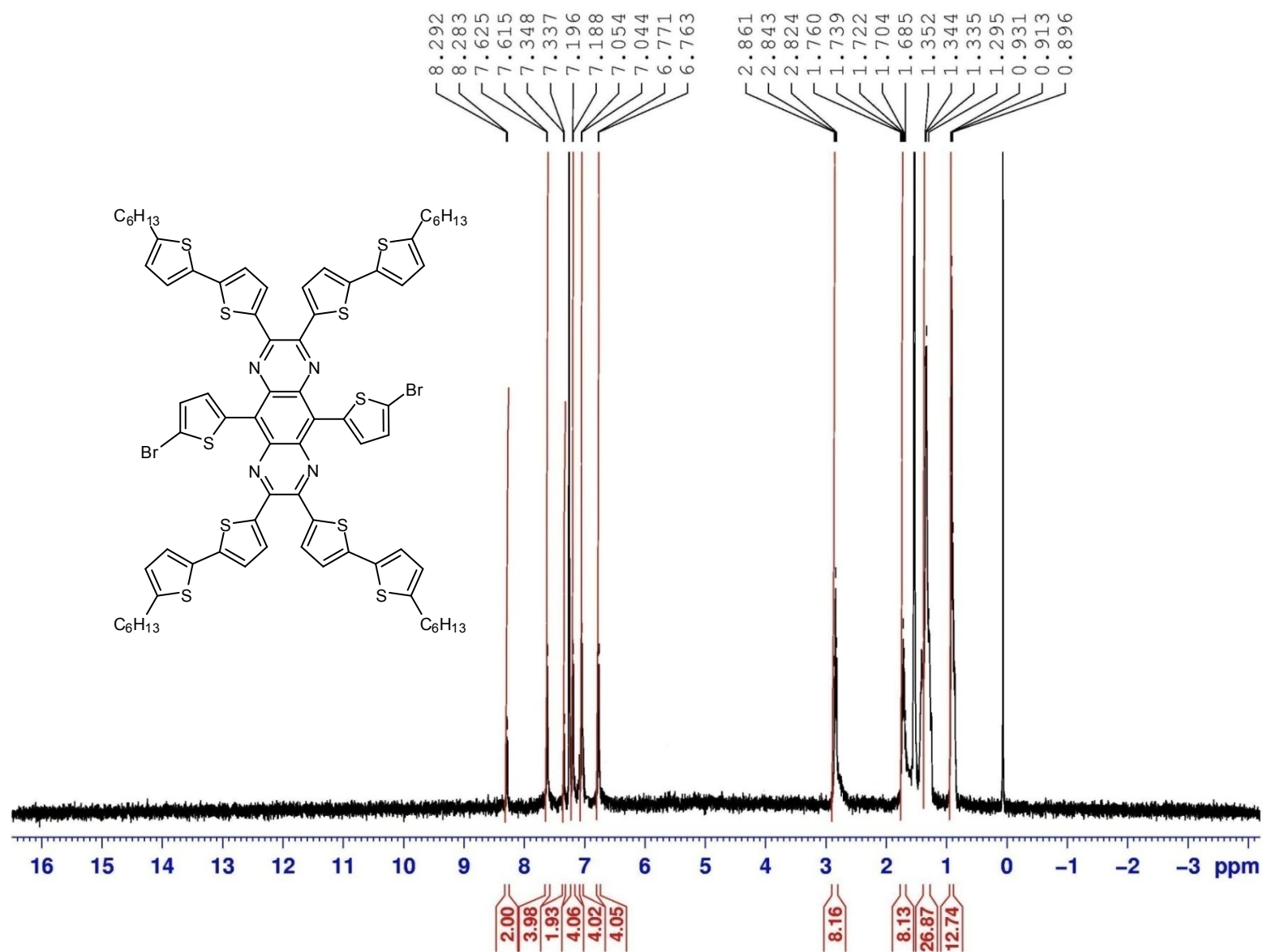


Figure S11. ^1H NMR of **8**.

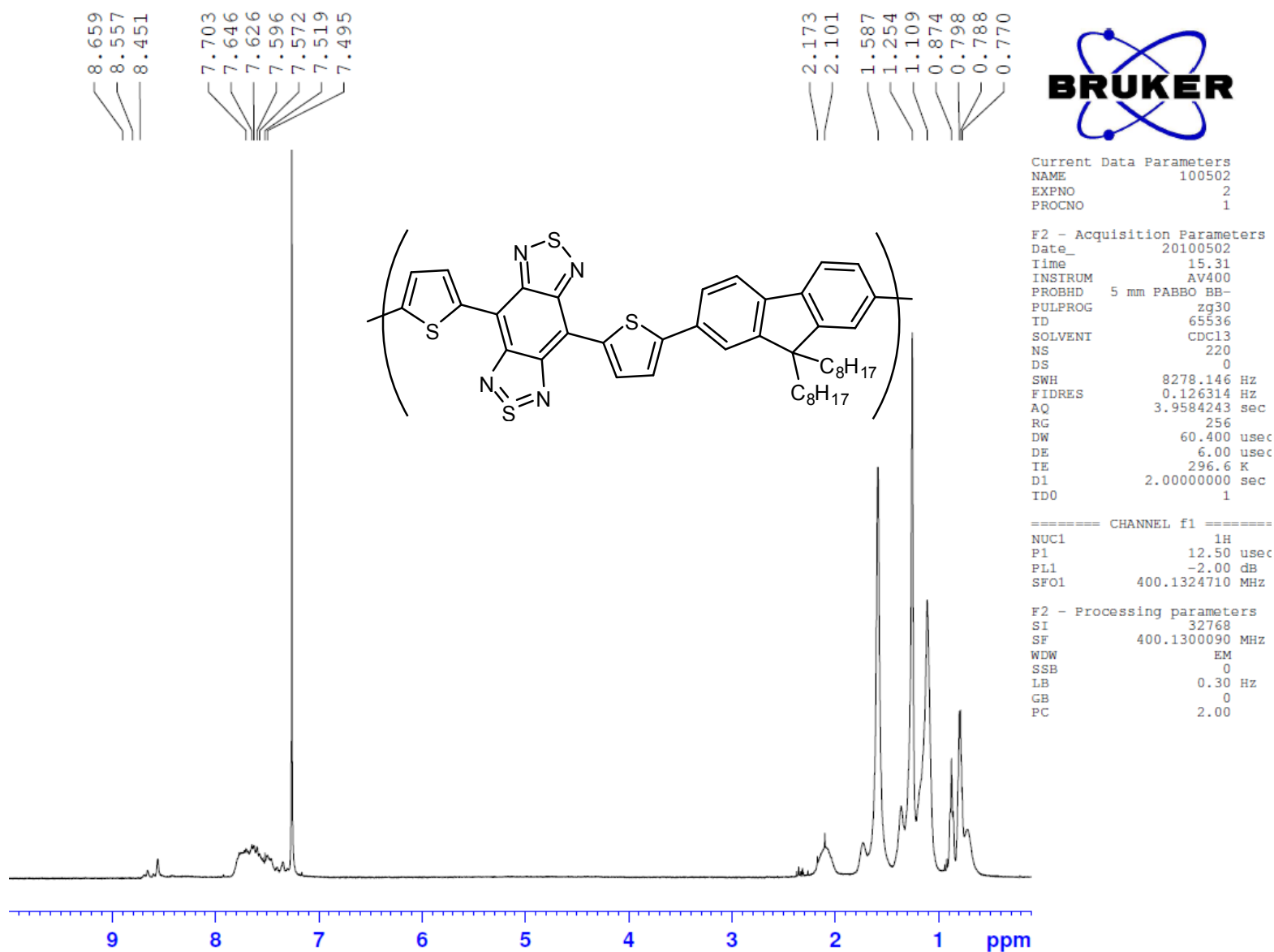


Figure S12. 1H NMR of pBBTF.

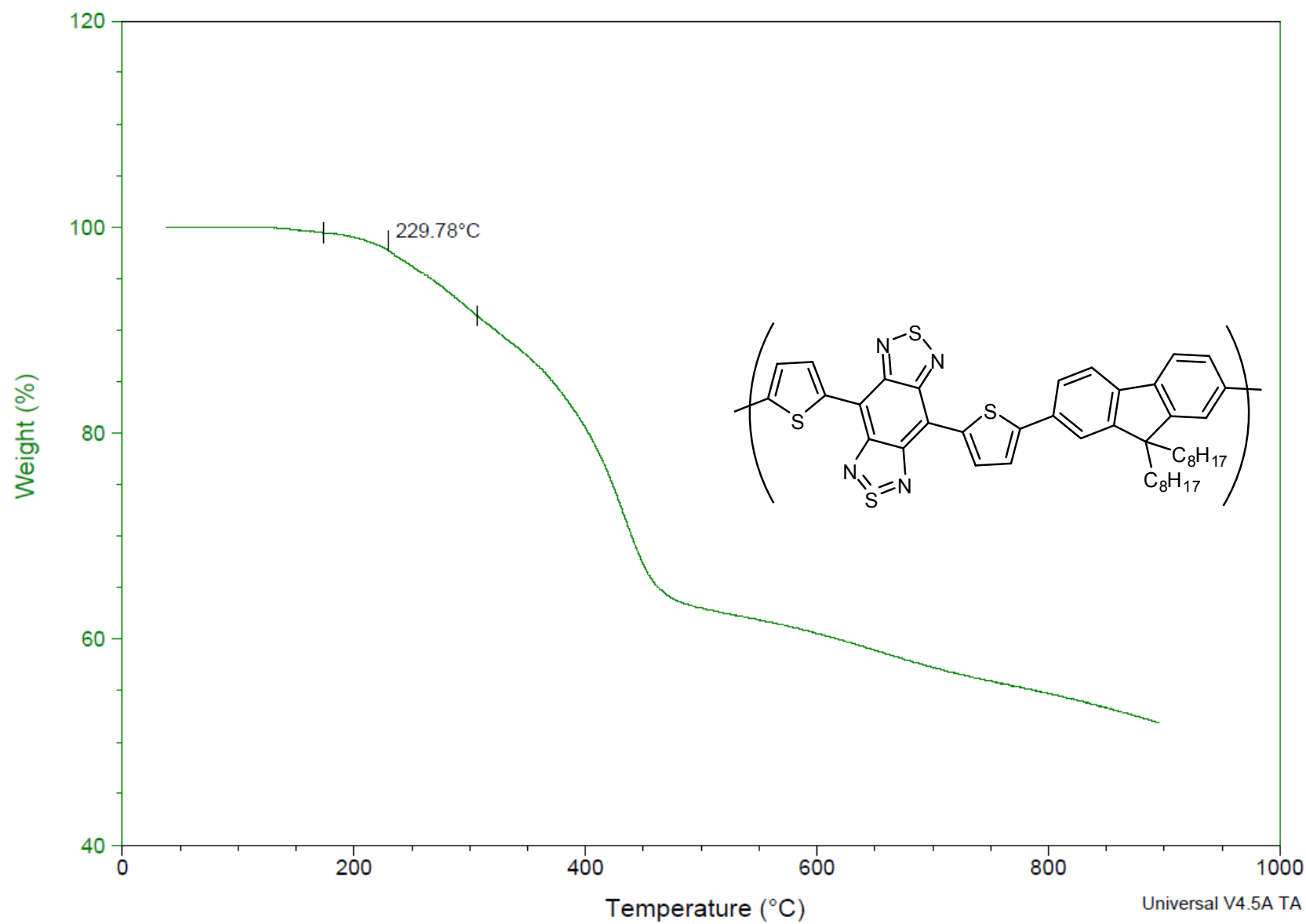


Figure S13. TGA of **pBBTF**.

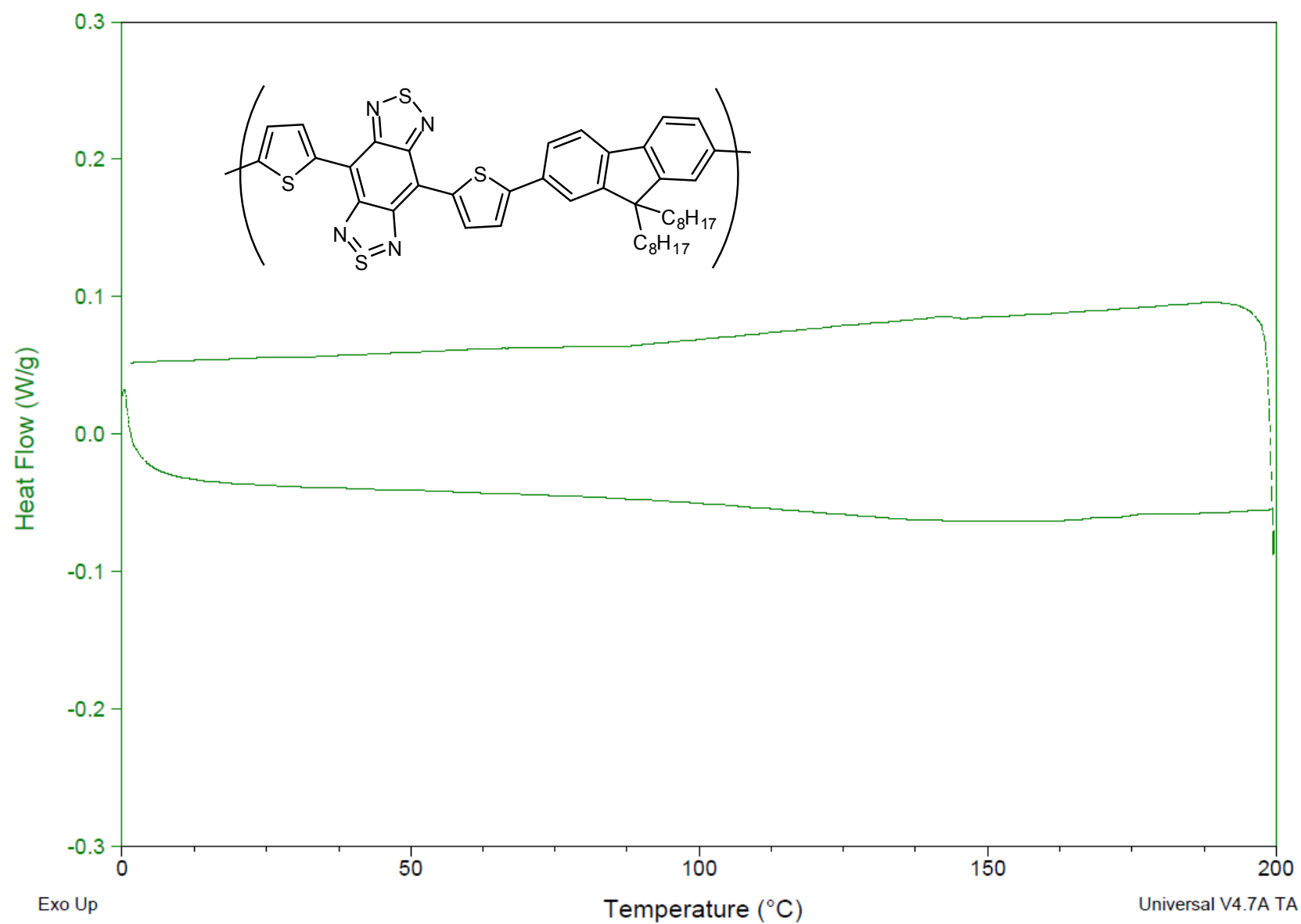


Figure S14. 2nd cycle DSC of pBBTF.

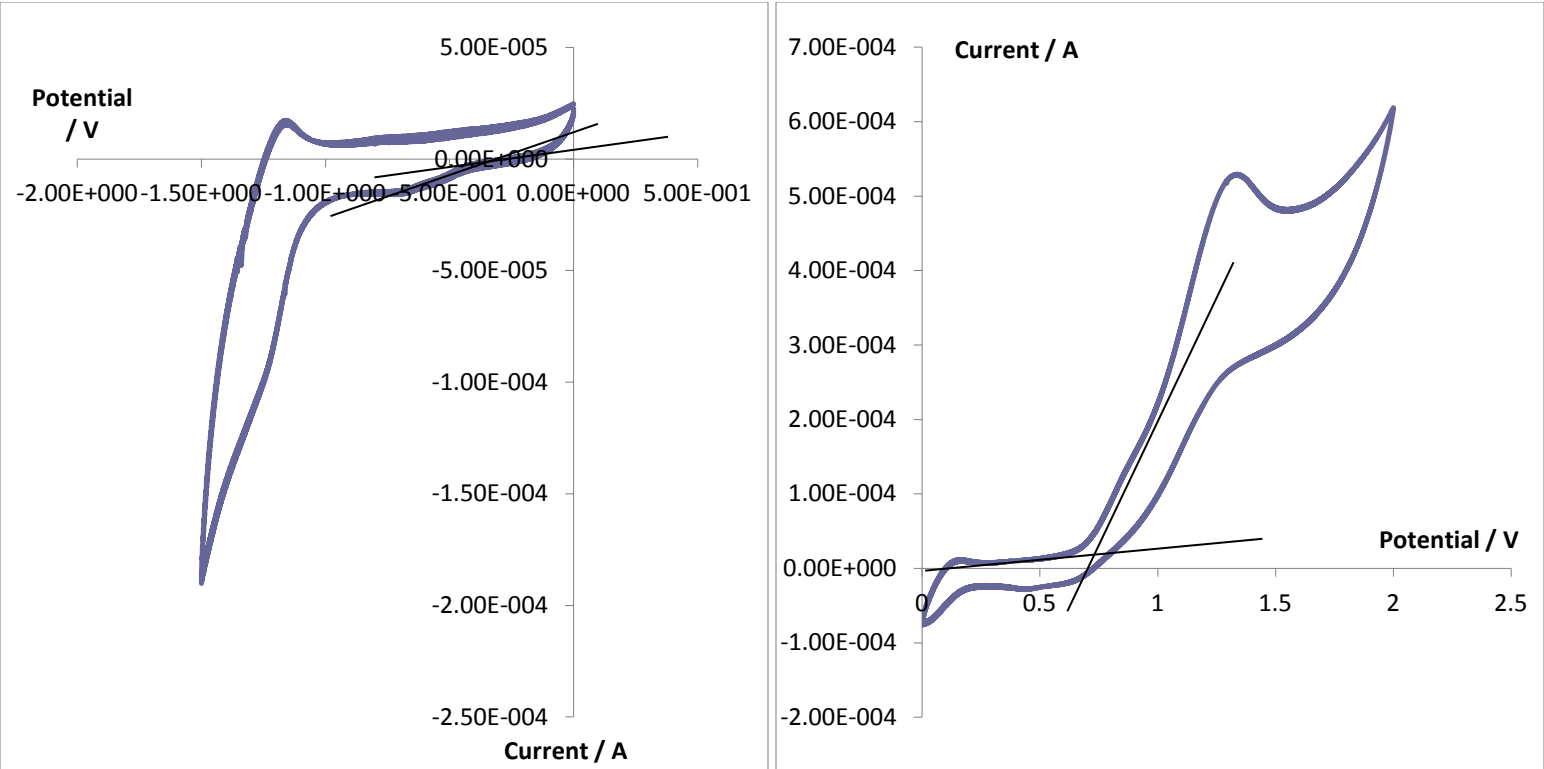
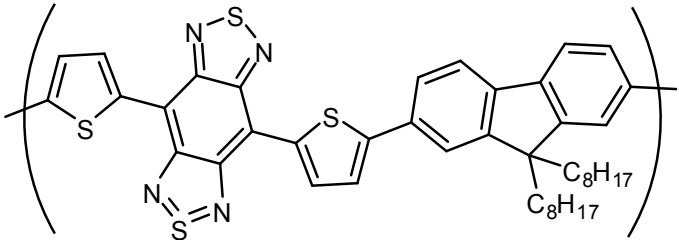


Figure S15. CV of pBBTF.



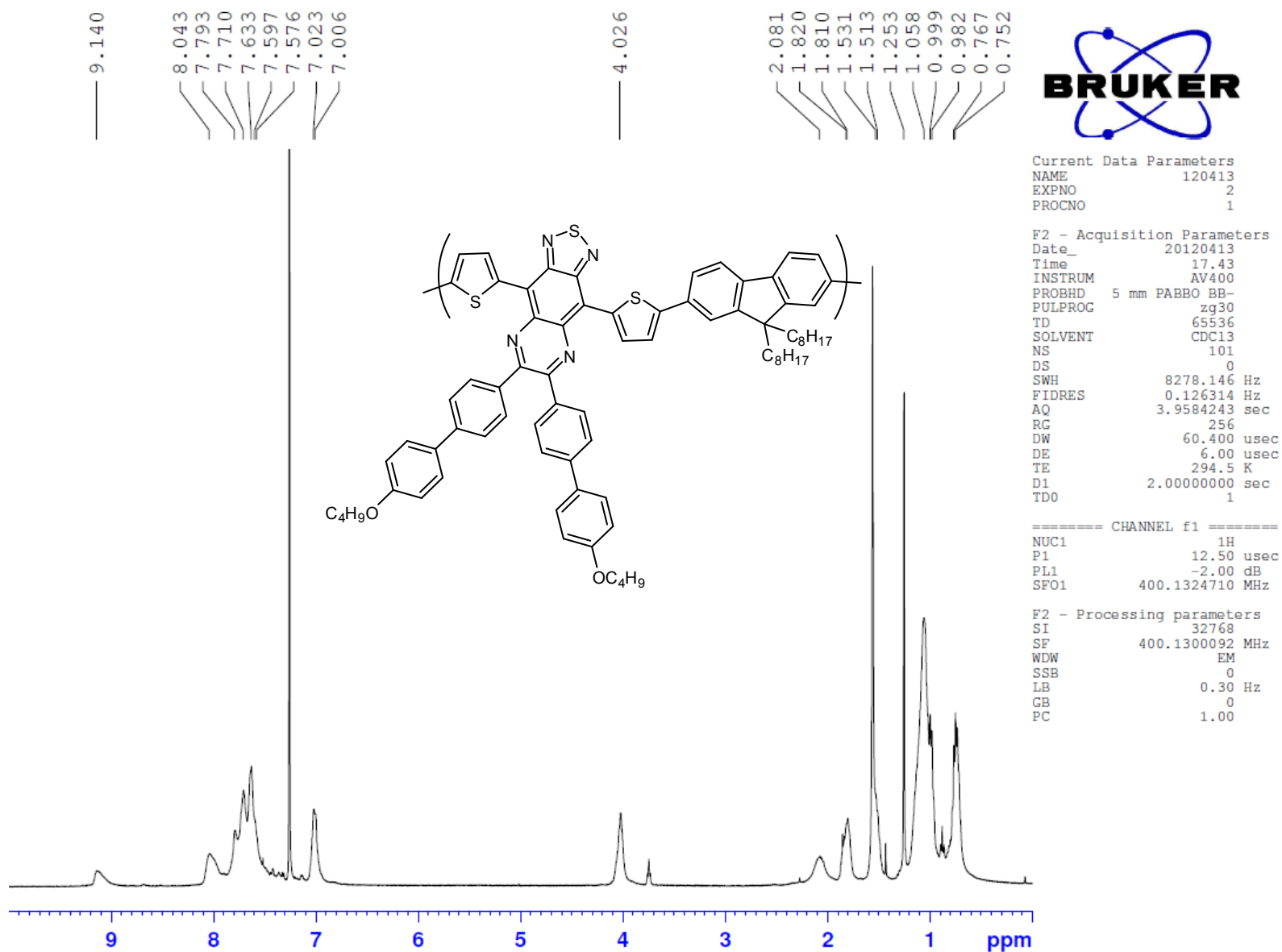


Figure S16. ¹H NMR of pTQ1F.

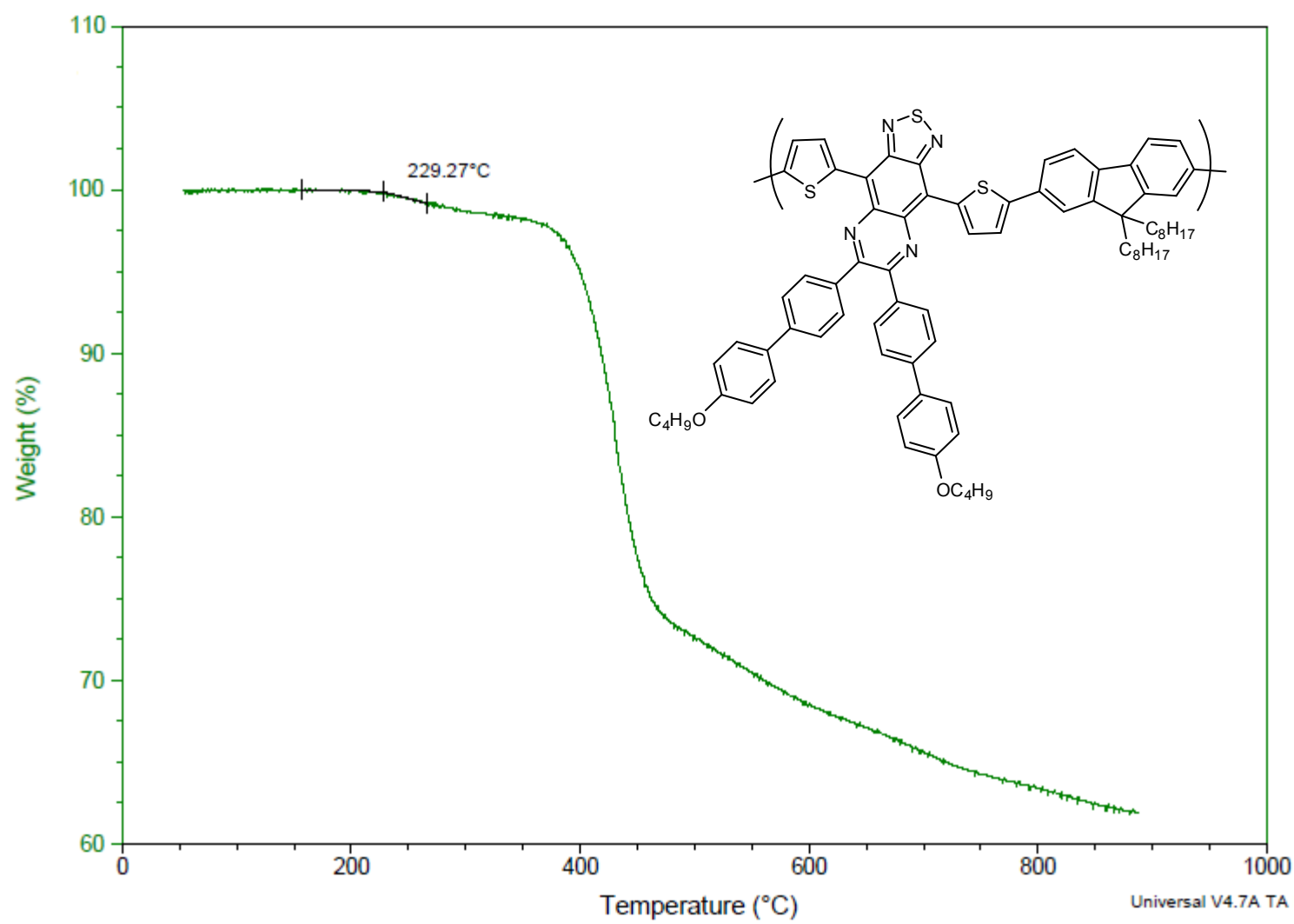


Figure S17. TGA of **pTQ1F**.

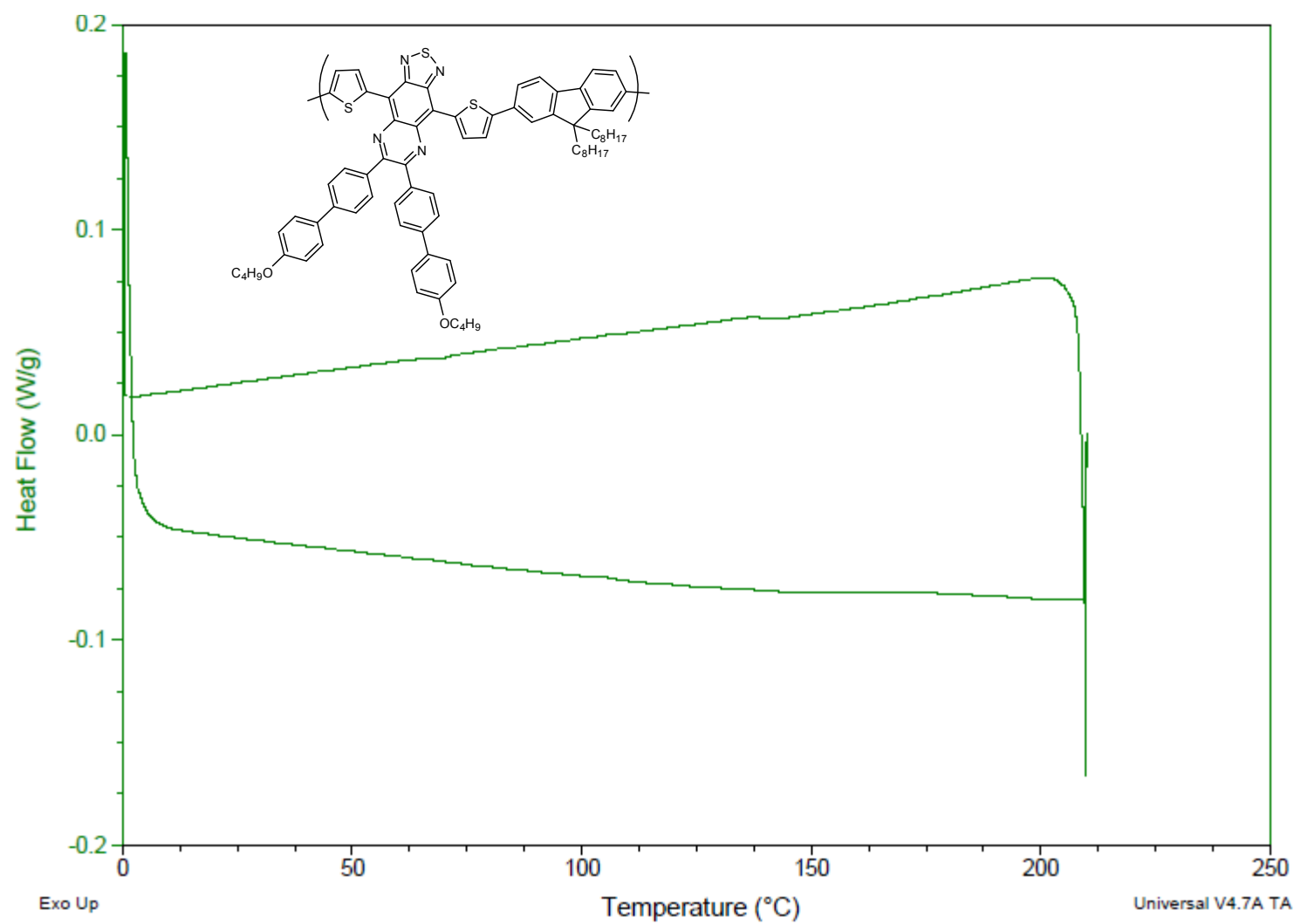


Figure S18. 2nd cycle DSC of pTQ1F.

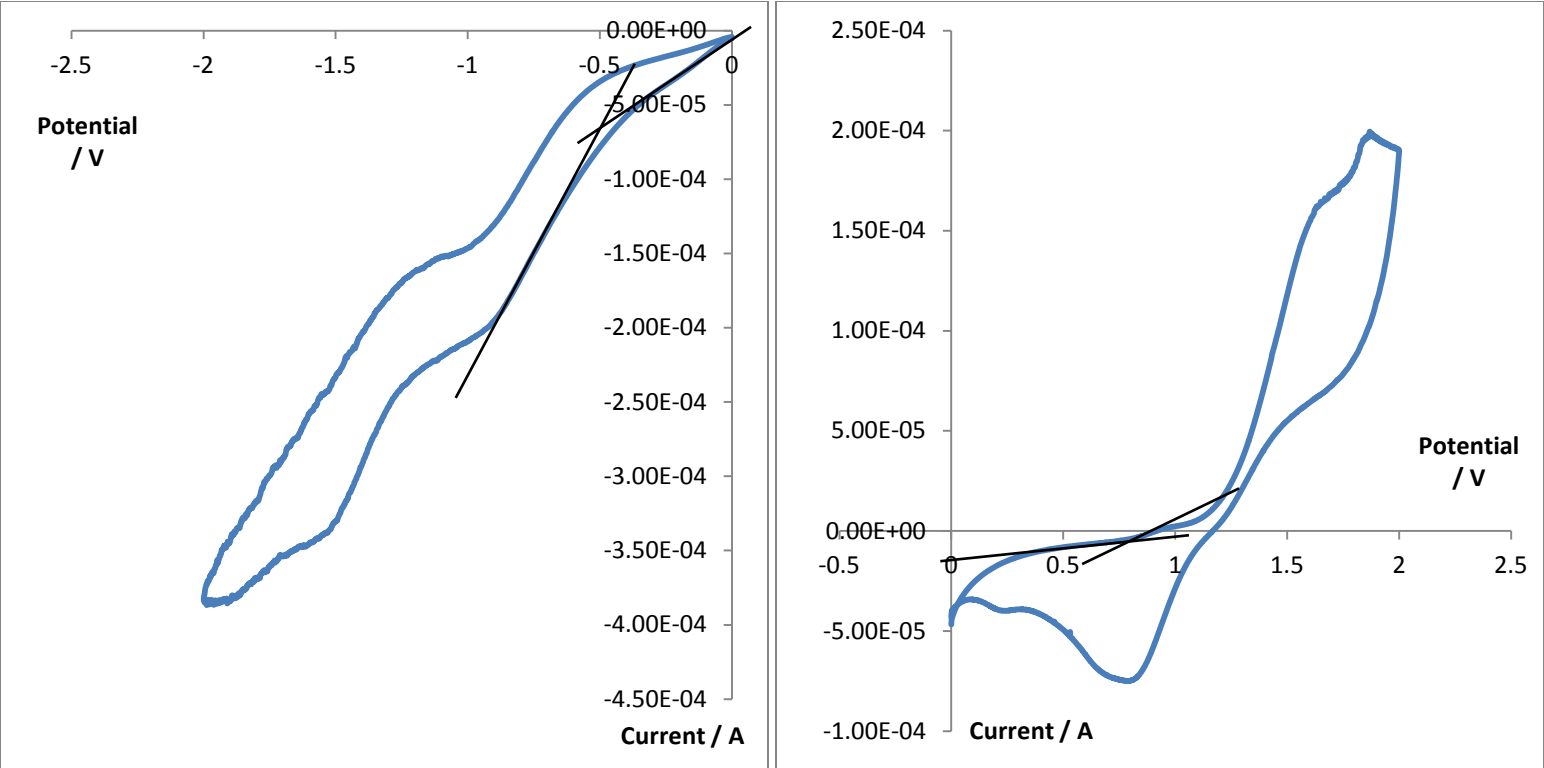
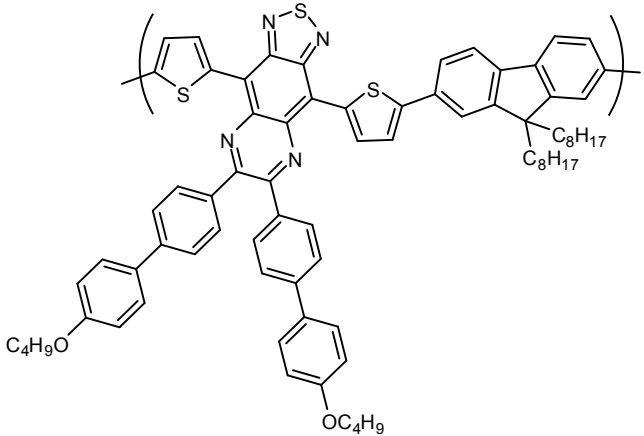


Figure S19. CV of pTQ1F.



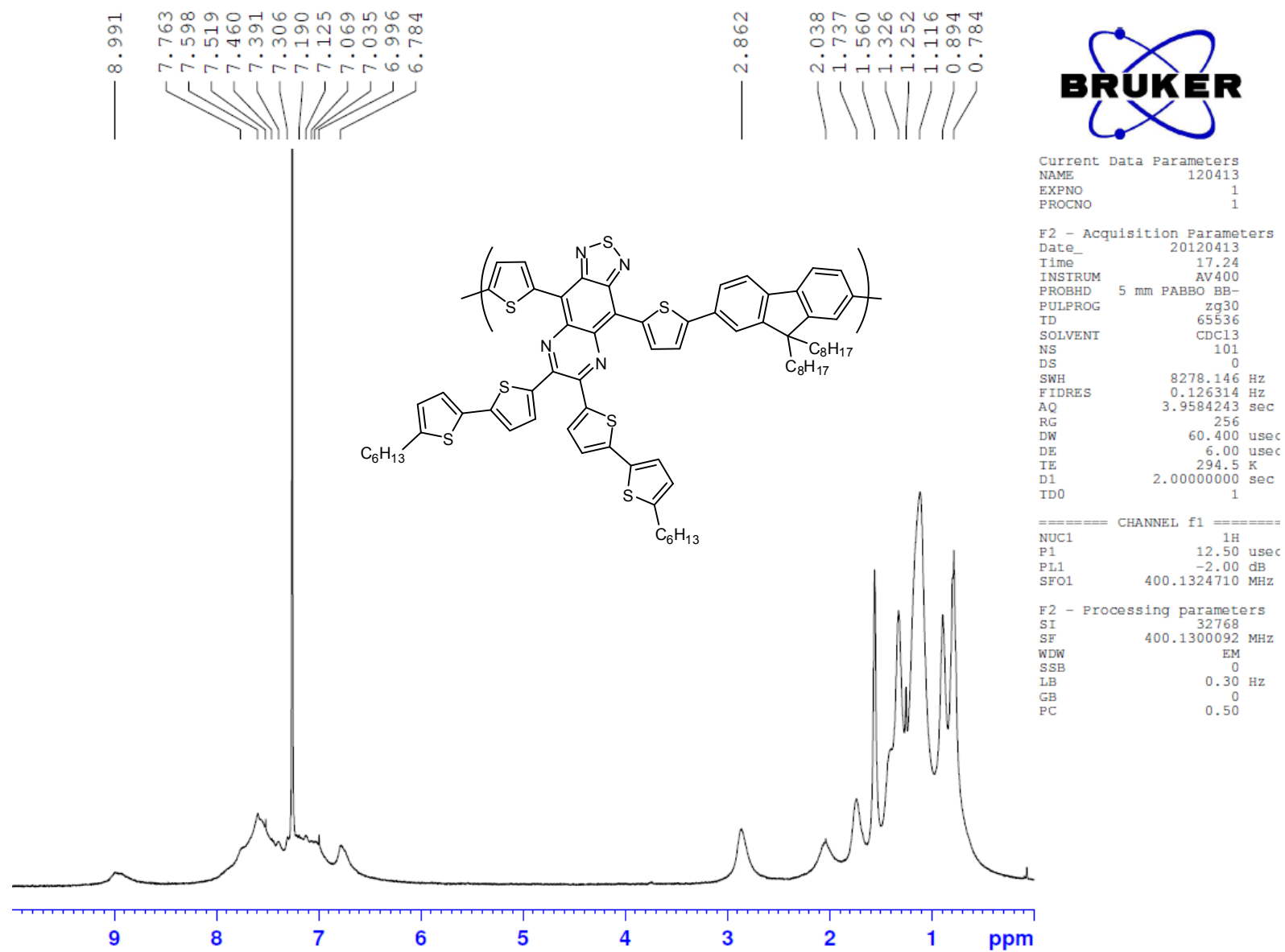


Figure S20. ¹H NMR of pTQ2F.

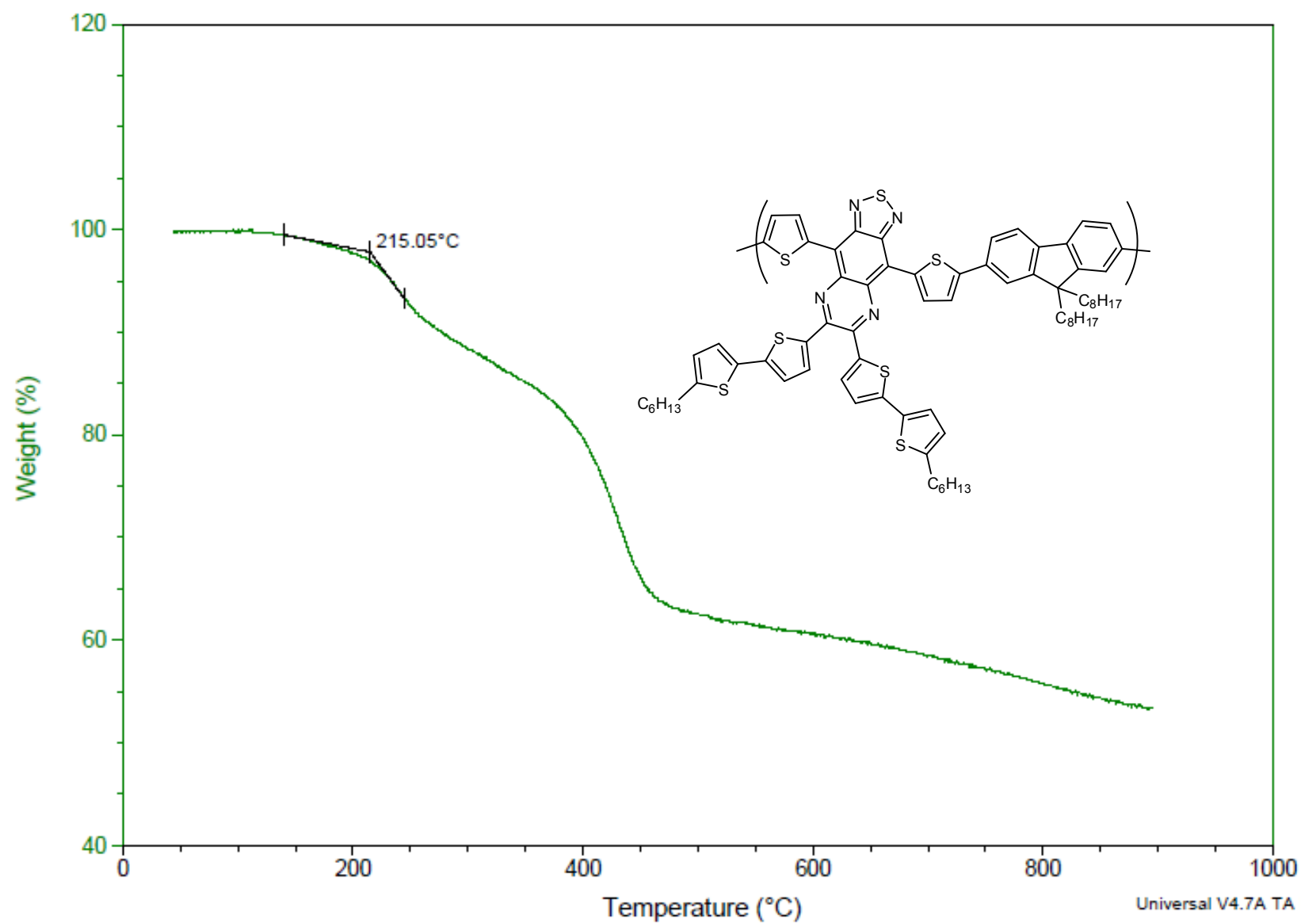


Figure S21. TGA of **pTQ2F**.

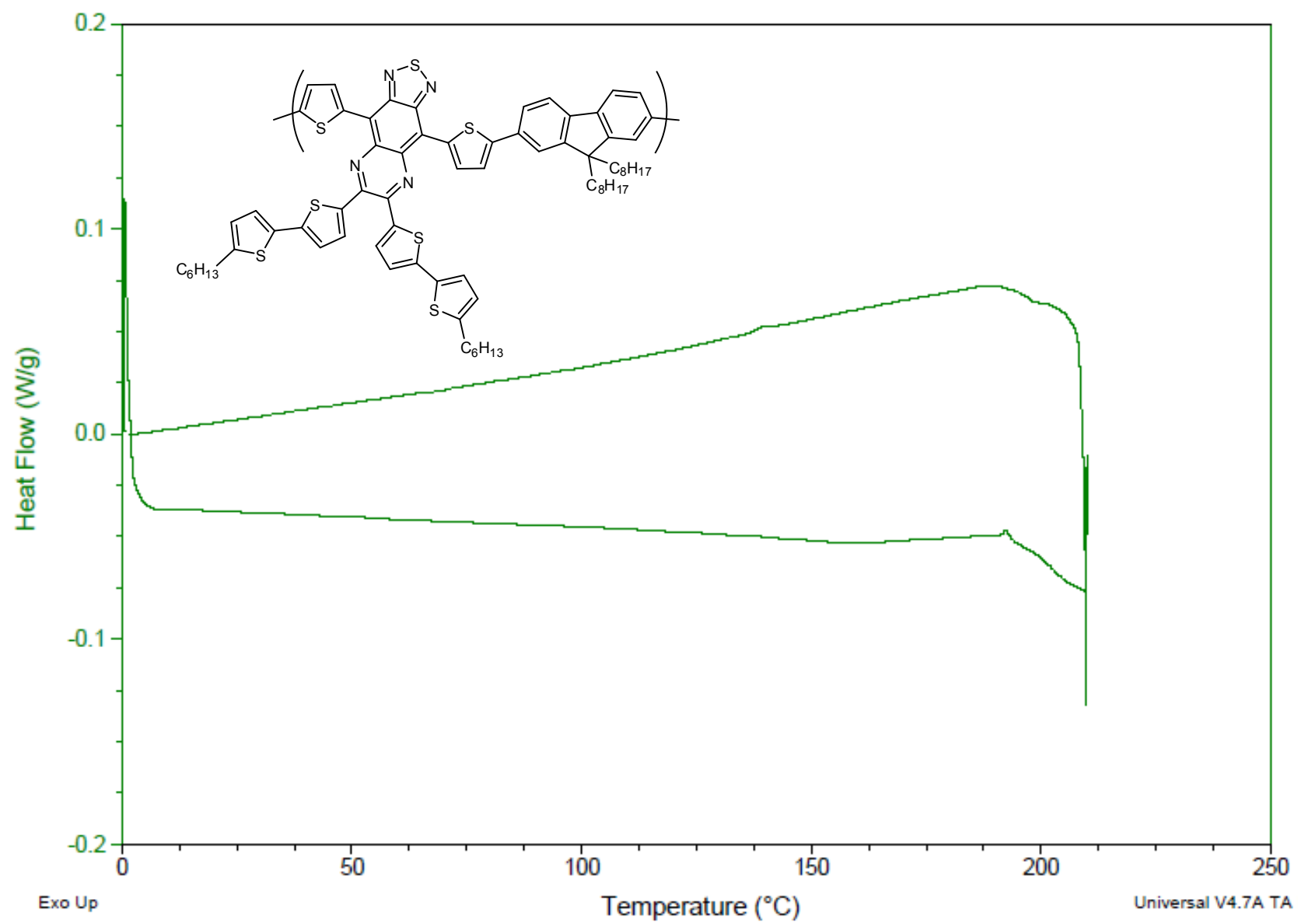


Figure S22. 2nd cycle DSC of **pTQ2F**.

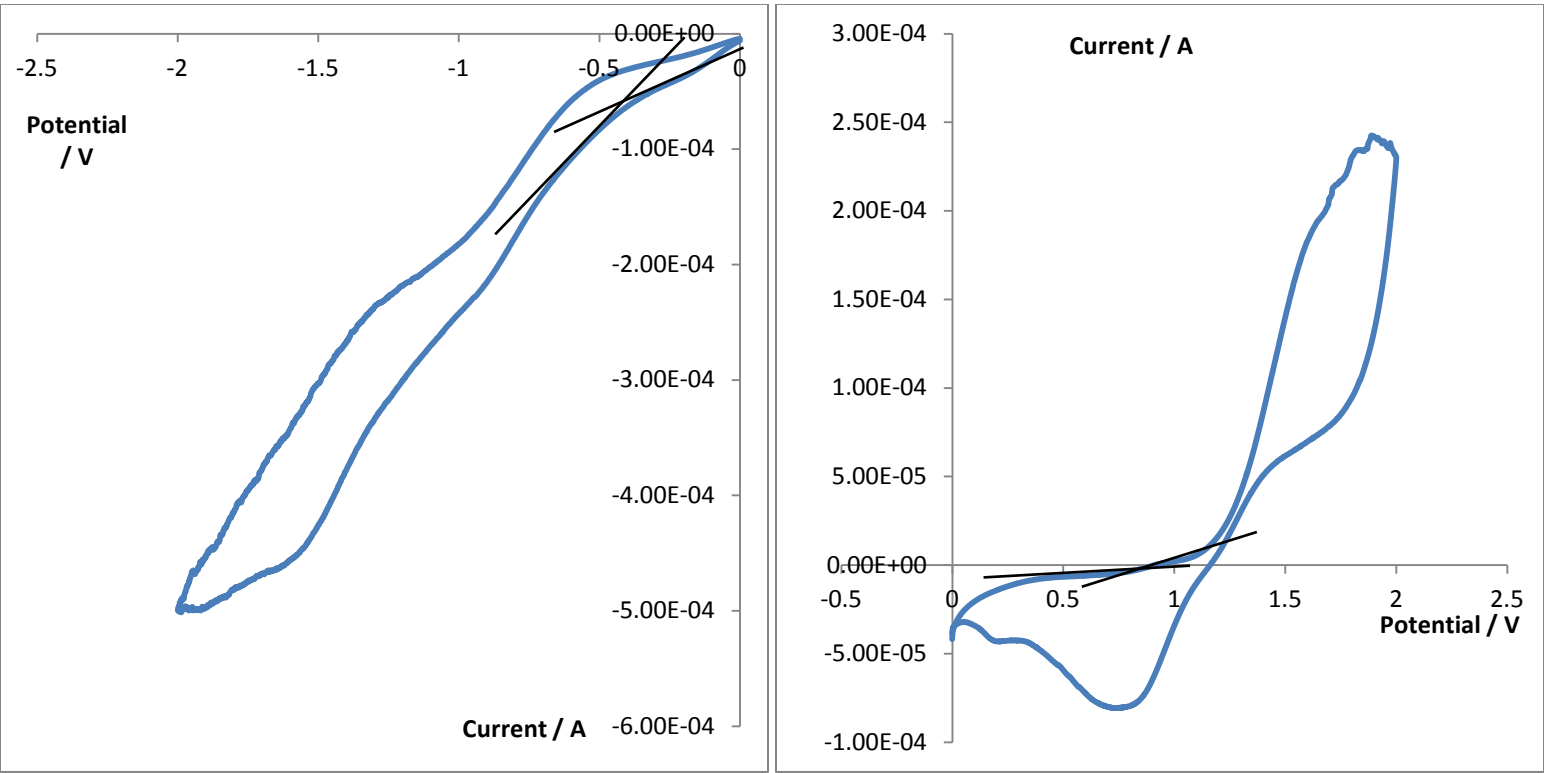
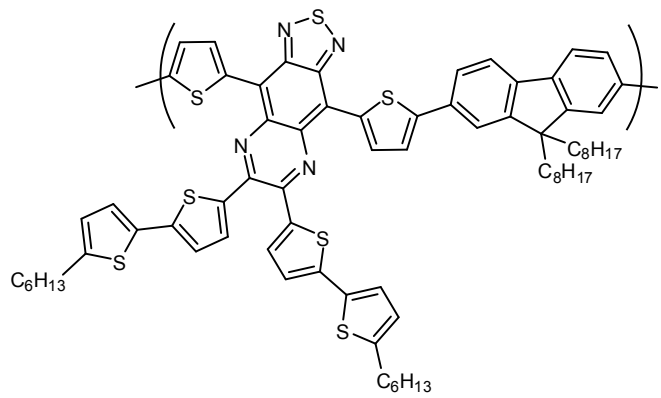


Figure S23. CV of pTQ2F.



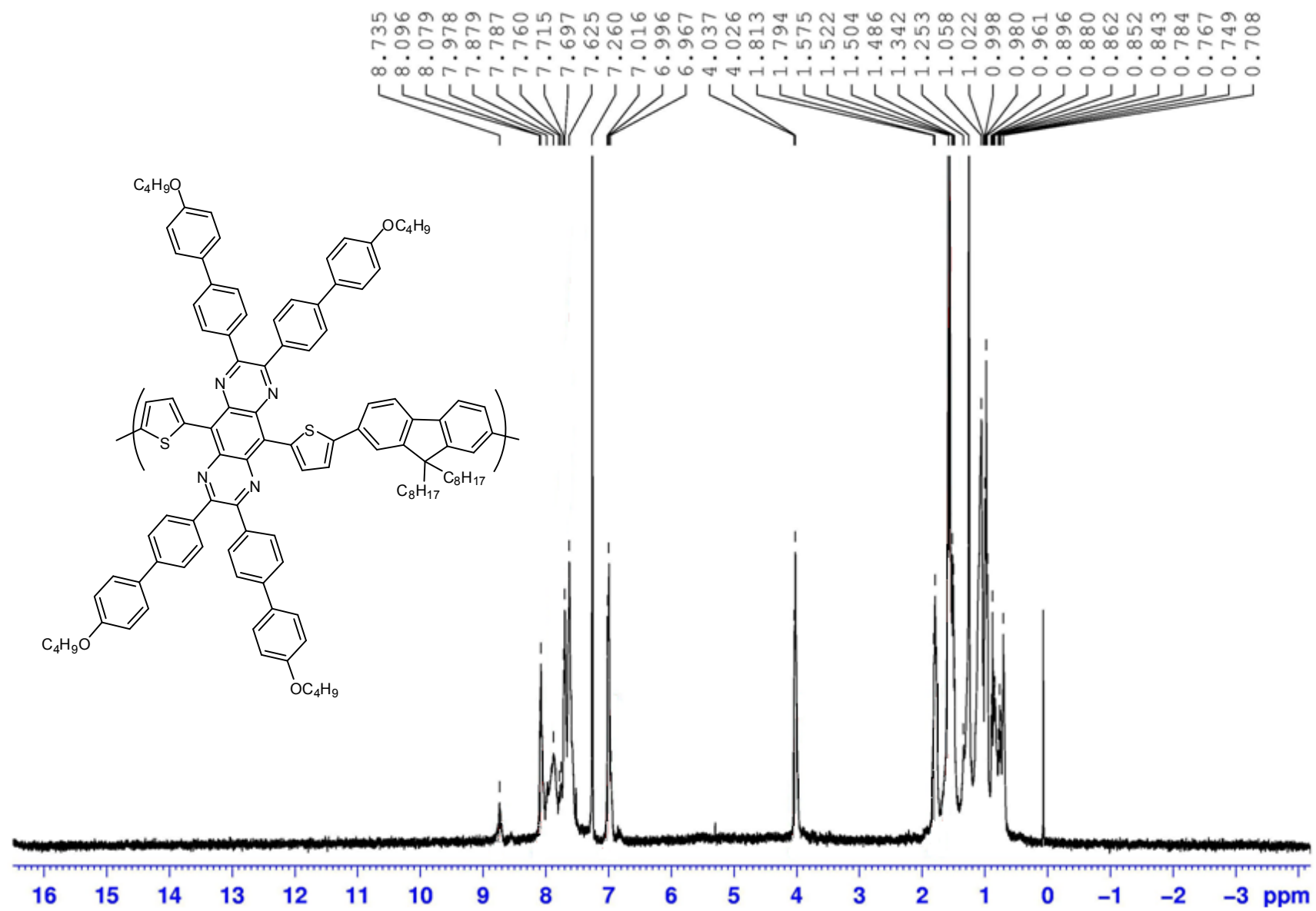


Figure S24. ¹H NMR of pPQ1F.

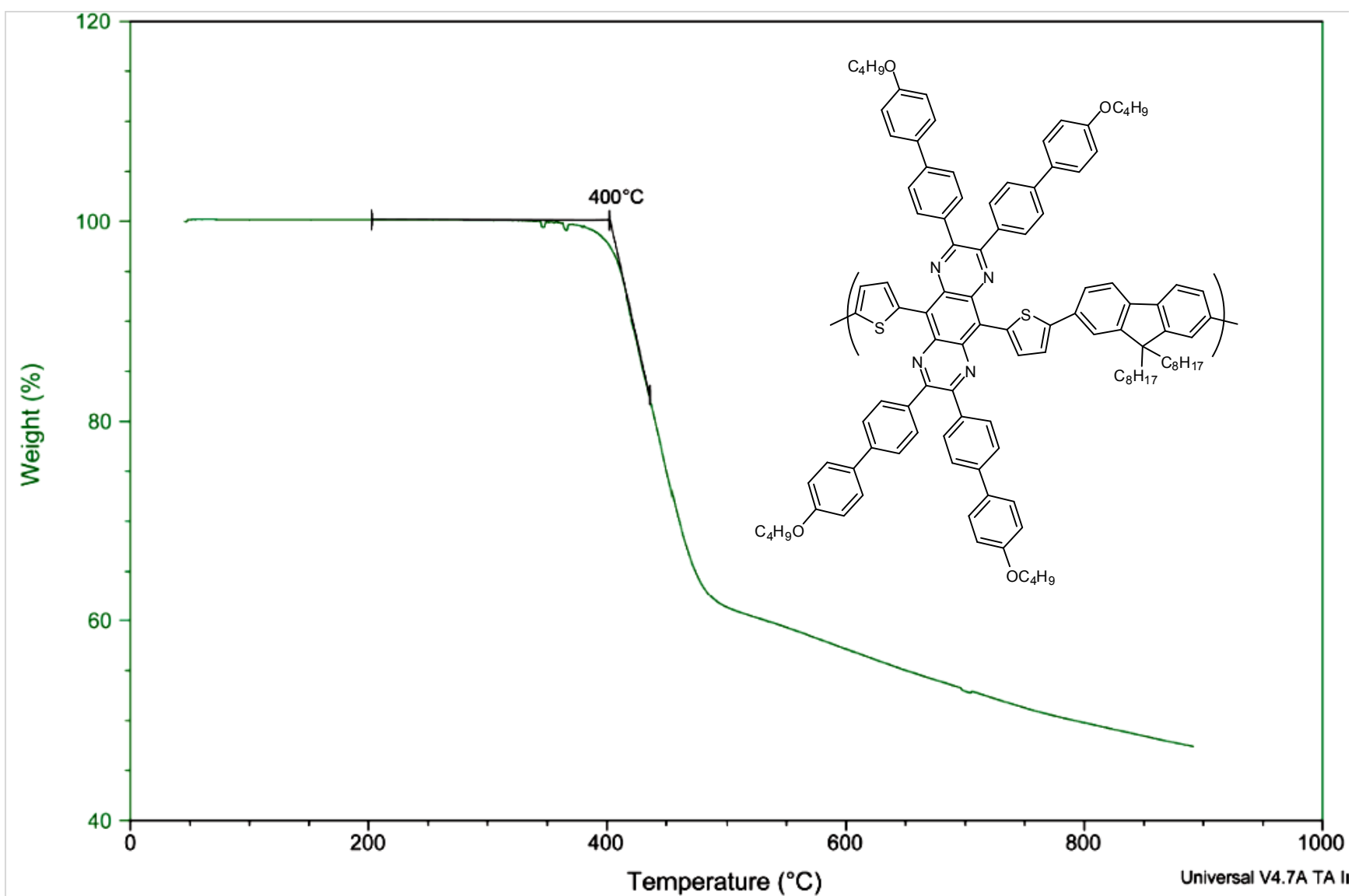


Figure S25. TGA of pPQ1F.

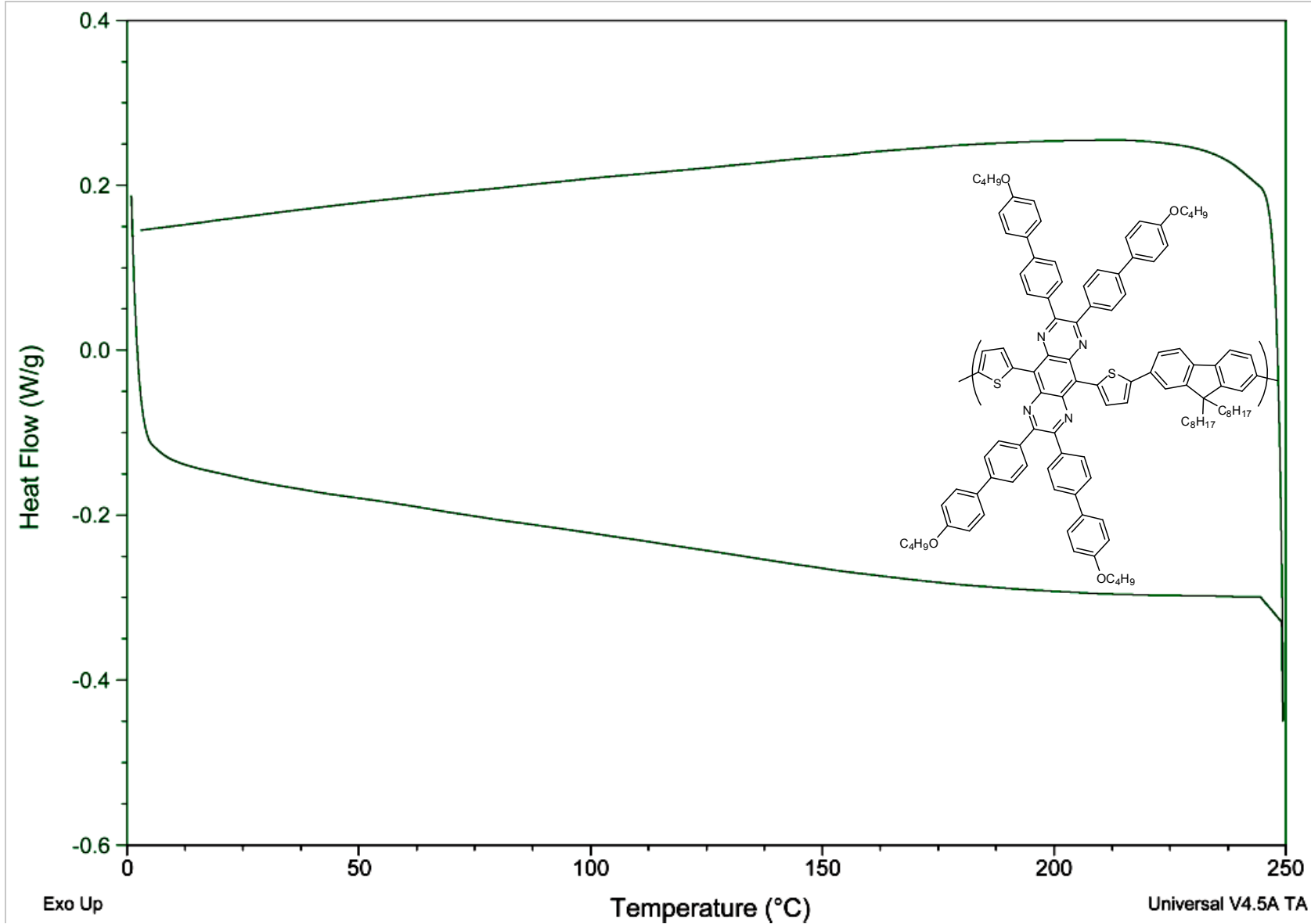


Figure S26. 2nd cycle DSC of pPQ1F.

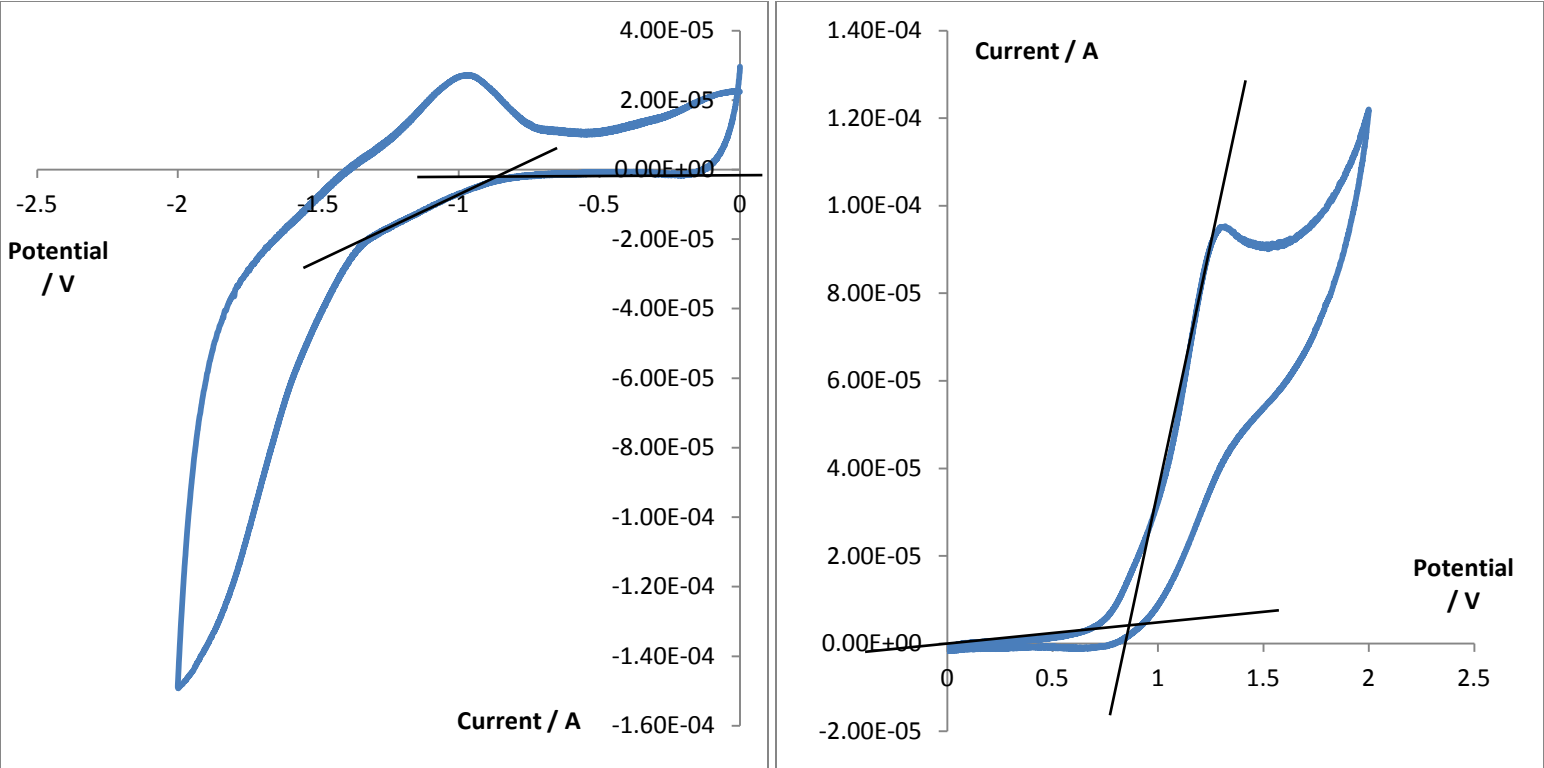
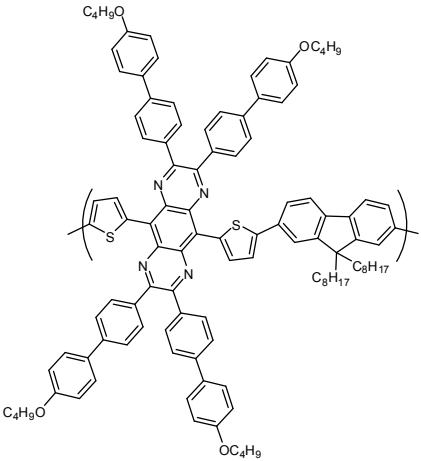


Figure S27. CV of pPQ1F.



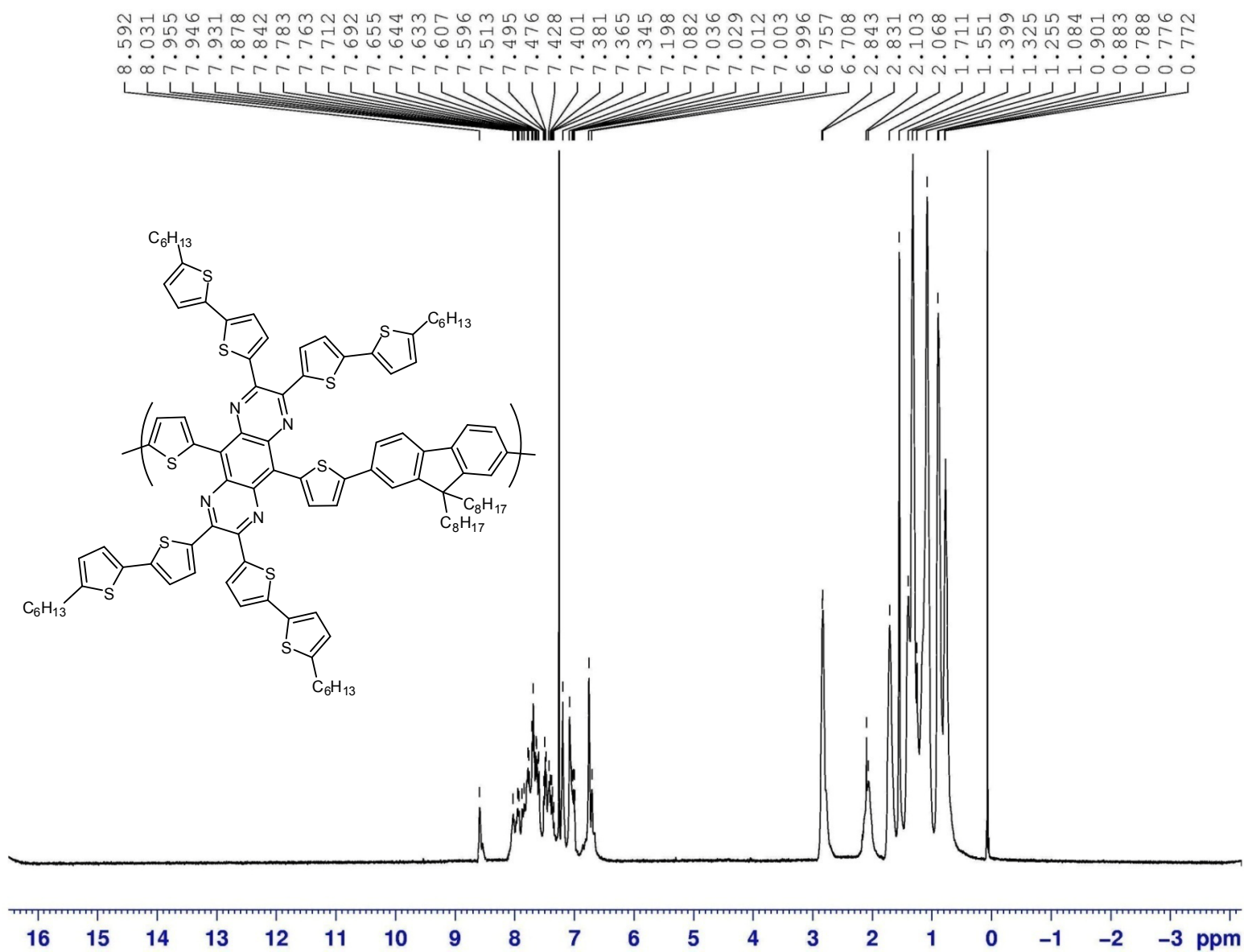


Figure S28. ^1H NMR of pPQ2F.

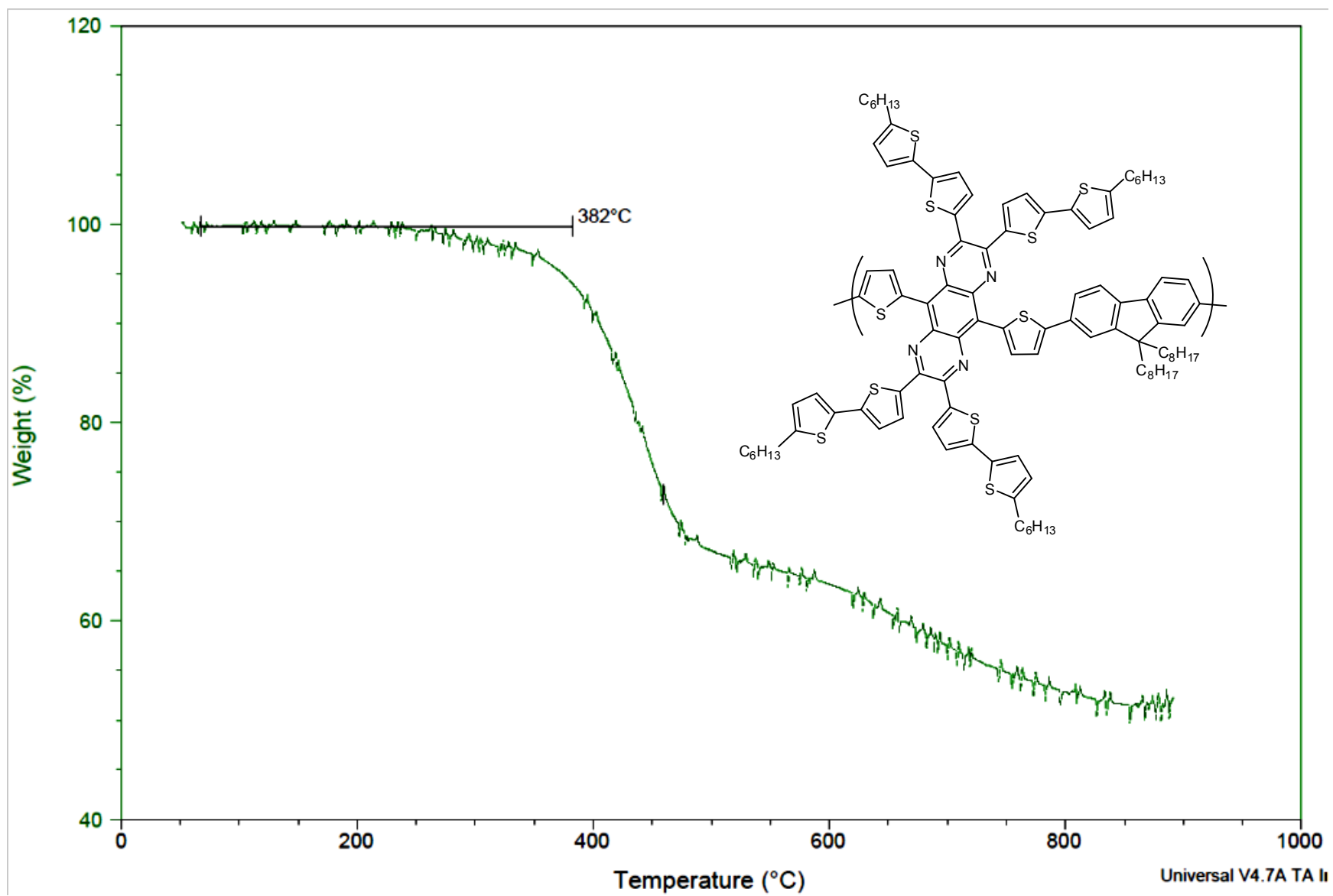


Figure S29. TGA of pPQ2F.

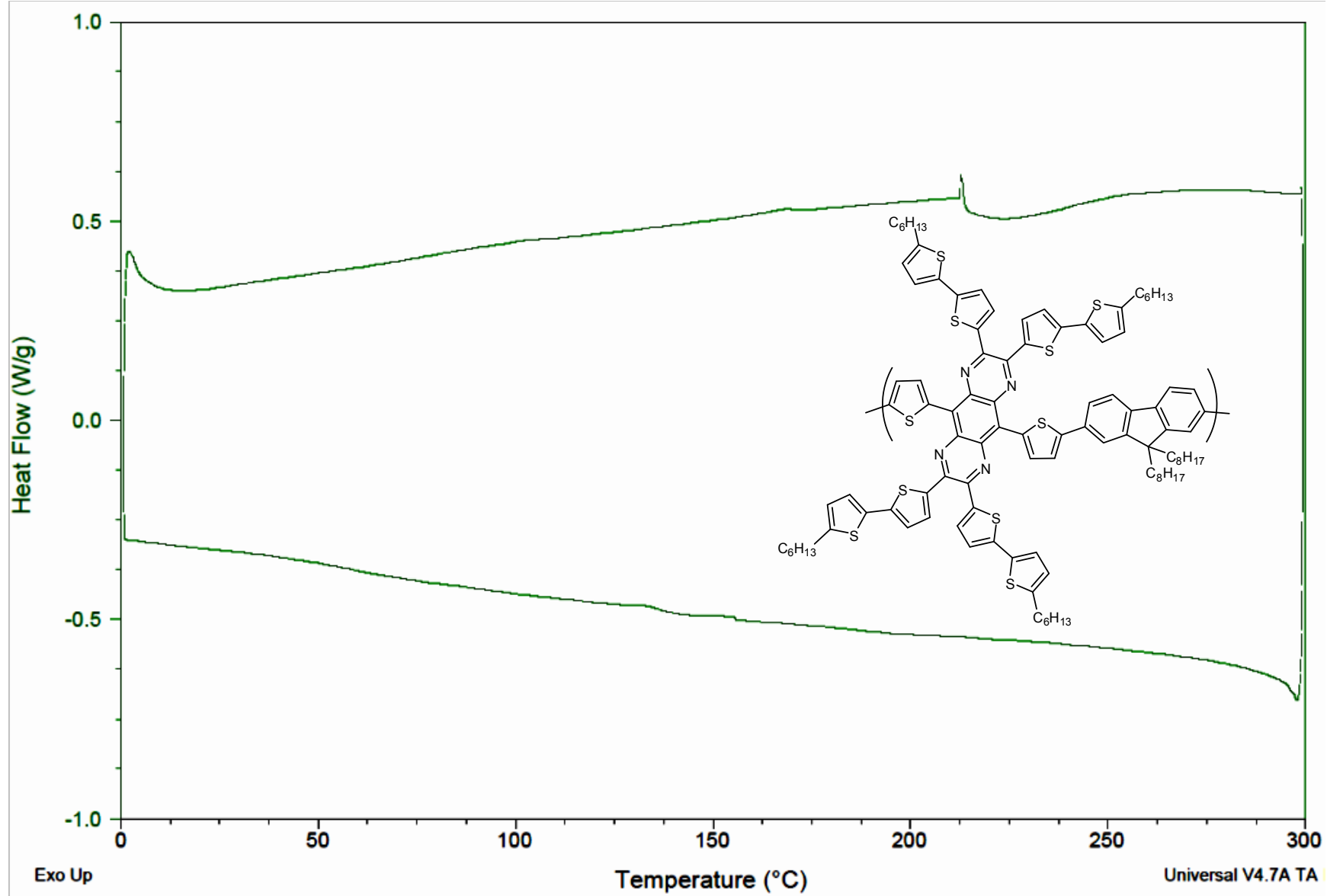


Figure S30. 2nd cycle DSC of pPQ2F.

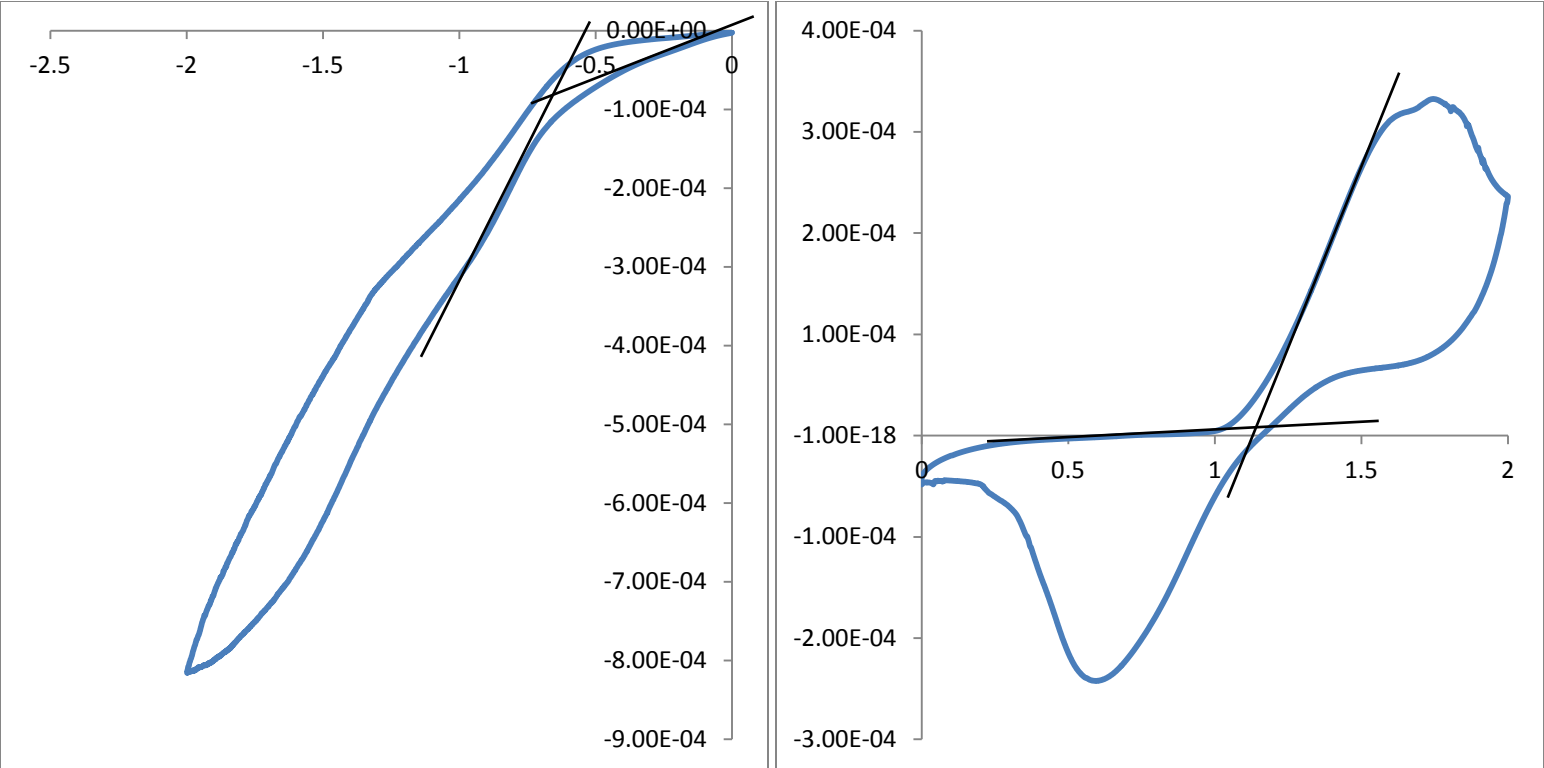
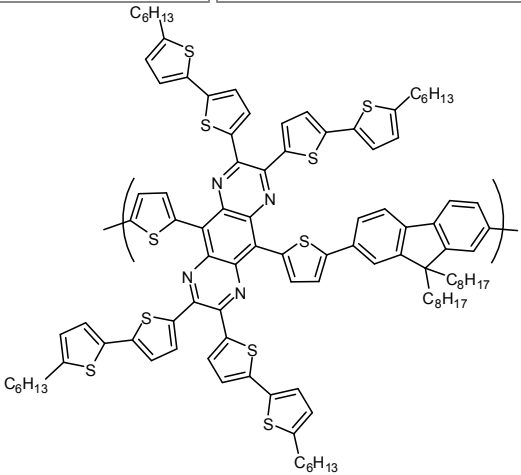


Figure S31. CV of pPQ2F.



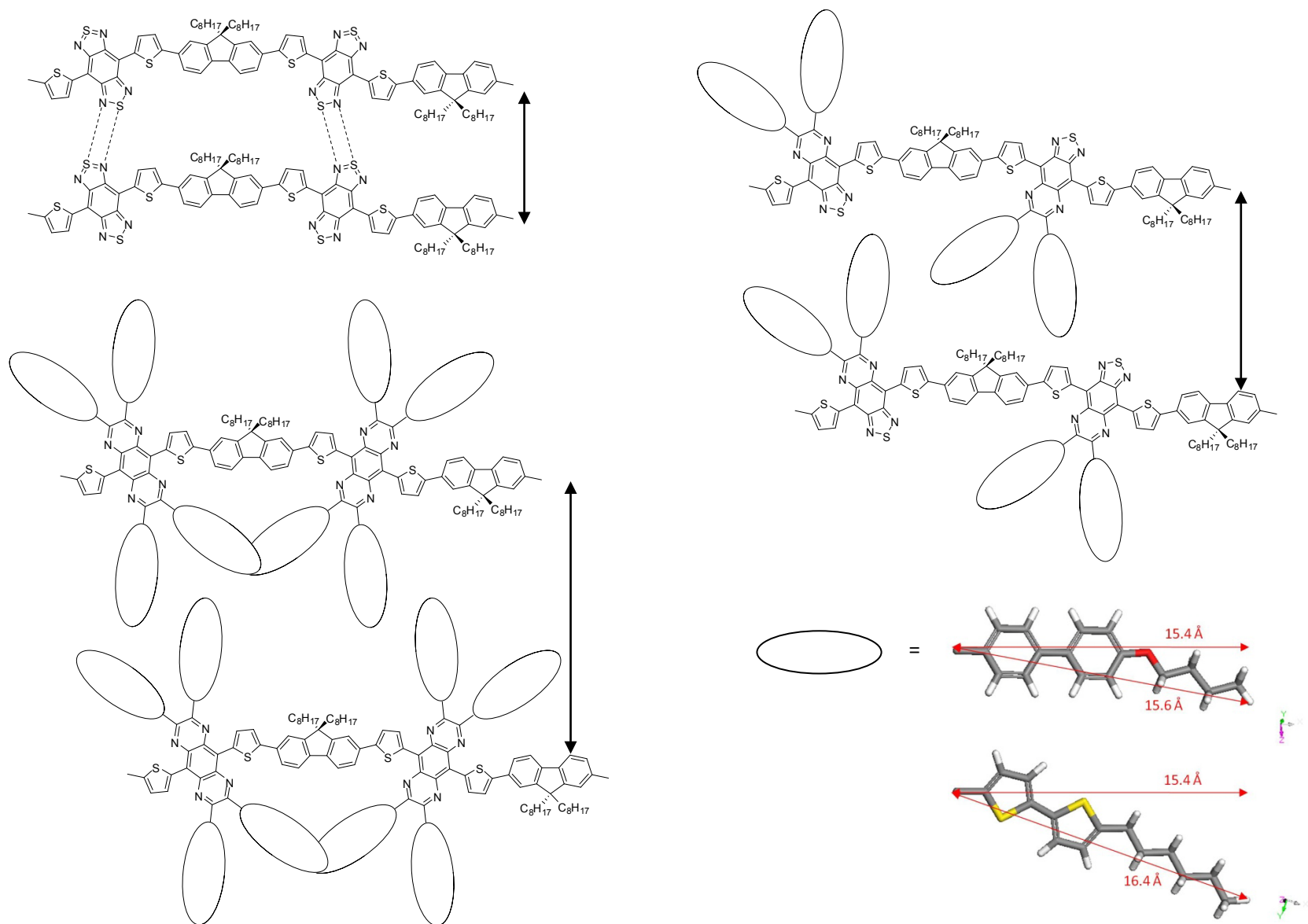


Figure S32. Schematics of the interchain distance for the BBT, TQ and PQ polymers, and the dimensions of the aromatic substituents.

Reference:

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