

Thiophene-fused bowl-shaped polycyclic aromatics with a dibenzo[a,g]corannulene core for organic field-effect transistors

Ru-Qiang Lu, Yi-Nyu Zhou, Xiao-Yun Yan, Ke Shi, Yu-Qing Zheng, Ming Luo, Xin-Chang Wang, Jian Pei,* Haiping Xia, Laura Zoppi, Kim K. Baldrige,* Jay S. Siegel, and Xiao-Yu Cao*

Supporting information

General. All chemical reagents were purchased and used without further purification unless stated otherwise. ^1H and ^{13}C NMR spectra were recorded on Bruker AVIII-500 spectrometer or Bruker AVIII-400. MS(MALDI-TOF) mass spectra were recorded on Bruker MicroFlex MALDI TOF MS. High-resolution mass spectra (HRMS) were recorded on a Bruker En Apex Ultra 7.0T FTMS mass spectrometer. Elemental analyses were performed using a German Vario EL III elemental analyzer. Thermal gravity analyses (TGA) were carried out on a TA Instrument Q600 analyzer. Absorption spectra were recorded on PerkinElmer Lambda 750 UV-*vis* spectrometer. Cyclic voltammetry (CV) was performed on CHI660D electrochemical workstation in anhydrous tetrahydrofuran solution of Bu_4NPF_6 (0.1 M). A platinum wire was used as a counter electrode and carbon electrode as a working electrode, all potentials were recorded versus Ag/AgCl (saturated) as a reference electrode. The scan rate was $100\text{ mV}\cdot\text{s}^{-1}$.

Computational Methods

The conformational analyses of the molecular systems described in this study were carried out using the B97-D dispersion enabled density functional^{1,2} with an ultrafine grid and in combination with the Def2-TZVPP basis set.³ Full geometry optimizations were performed and uniquely characterized via second derivatives (Hessian) analysis to determine the number of imaginary frequencies (0=minima; 1=transition state), and effects of zero point energy. Ionization potentials were determined with the ΔSCF method, and reduction potentials were calculated using $E_{\text{red}}^\circ = -\Delta G/nF + E_{\text{ref}}$, $n=1$, $F=1\text{ eV}$, corrected to the Ag/AgCl electrode (4.52). Effects of solvation were taken into account using the COSMO method,^{4,5} with the dielectric for THF and solvent radii from Klamt.⁶

For determination of more accurate frontier orbital properties and GW-gap, calculations have also been carried out at a DFT-LDA level with supercell geometries, plane wave basis sets and norm-conserving pseudopotentials using quantum-espresso.⁷ In order to avoid fictitious molecule-molecule interactions occurring in the repeated cell approach, a vacuum thickness of at least 10 angstrom in combination with the Martyna-Tuckerman method⁸ has been used. At the optimized geometries, all the Kohn-Sham eigenvalues and eigenvectors have been calculated at least up to 10 eV above the HOMO energy.

1. Synthesis

Compound 2: Tetrabromocorannulene (400 mg, 0.707 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (30mg, 0.0427mmol) and tributyl(5-hexylthiophen-2-yl)stannane (1.62 g, 3.54 mmol) were stirred at $130\text{ }^\circ\text{C}$ in DMF (new distilled and prior to use, 12 mL) under nitrogen for 48 h. The reaction mixture was cooled and diluted with DCM. The solution was washed with saturated aqueous NaF, saturated aqueous NaCl and water, and the organic layer was separated and dried with Na_2SO_4 . The solvent was removed under reduced pressure. The crude product was purified by column chromatography (PE:DCM = 20:1) to provide the title product (614 mg, 0.671 mmol, 95%). ^1H NMR (400 MHz,

CDCl₃) δ 7.84 – 7.76 (m, 6H), 6.90 (dd, J = 6.5, 3.4 Hz, 4H), 6.74 (dd, J = 4.6, 4.0 Hz, 4H), 2.82 – 2.78 (m, 8H), 1.73 – 1.59 (m, 8H), 1.43 – 1.27 (m, 24H), 0.92 – 0.88 (m, 12H). HRMS(APCI): Calcd for [M]⁺: 915.4120; Found: 915.4138.

Compound **3**: Under an nitrogen atmosphere, CH₃SO₃H (4 mL) was added to a solution of compound **2** (251 mg, 0.274 mmol) and DDQ (125 mg, 0.550 mmol) in DCM (distilled from anhydrous calcium chloride, 40 mL) at 0 °C. The solution was stirred for 10 min at 0 °C, then quenched with a saturated aqueous solution of NaHCO₃. The organic layer was separated, washed with water and brine solution, and was dried with Na₂SO₄. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (PE:DCM = 10:1) and recrystallization from CH₃OH/CH₂Cl₂ to provide the title product (150 mg, 60%). ¹H NMR (500 MHz, CDCl₃) δ 8.56 (s, 2H), 8.43 (d, J = 8.6 Hz, 2H), 7.69 (d, J = 8.7 Hz, 2H), 7.30 (d, J = 6.4 Hz, 4H), 3.02 – 3.07 (m, 8H), 1.98 – 1.88 (m, 8H), 1.61 – 1.54 (m, 8H), 1.50 – 1.38 (m, 18H), 0.96 – 1.00 (m, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 147.18, 146.82, 134.47, 134.41, 134.39, 134.37, 134.31, 132.44, 131.78, 129.12, 127.27, 126.97, 126.91, 126.70, 126.23, 124.91, 124.89, 118.58, 118.50, 31.76, 31.34, 30.83, 30.80, 29.13, 22.69, 14.17, 14.15. MS (MALDI-TOF): calcd. for C₆₀H₆₂S₄, [M + 1]⁺, 912.4, found 912.2. Anal. Found: C, 79.00; H, 6.61%; Calc. for C₆₀H₆₂S₄: C, 79.07; H, 6.86%.

Compound **4**: Tetrabromocorannulene (254 mg, 0.448 mmol), Pd(PPh₃)₂Cl₂ (32.4 mg, 0.0462 mmol) and tributyl(4-hexylthiophen-2-yl)stannane (1.53 g, 3.34 mmol) in DMF (new distilled and prior to use, 15 mL) were stirred at 130 °C under nitrogen for 48 h. The reaction mixture was cooled and diluted with DCM. The solution was washed with saturated aqueous NaF, saturated aqueous NaCl and water, and the organic layer was separated and dried with Na₂SO₄. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (hexane) to provide the title product (336 mg, 0.368 mmol, 82%). ¹H NMR(400 MHz, CDCl₃) δ 7.83-7.79 (m, 6H), 6.98 (dd, 4H), 6.65-6.64 (m, 4H), 2.85-2.78 (m, 8H), 1.72-1.64 (m, 8H), 1.41-1.35 (m, 24H), 0.99-0.92 (m, 12H). HRMS(APCI): Calcd for [M]⁺: 914.4047; Found: 914.4123.

Compound **5**: A solution of FeCl₃ (1.52 g, 5.25 mmol) in dry ether (50 mL) was added slowly to a solution of compound **4** (962 mg, 1.05 mmol) in DCM (distilled from anhydrous calcium chloride, 125 mL) under nitrogen, and the mixture was stirred overnight at room temperature. The precipitate was filtered, washed with ether for three times, re-dissolved in chloroform, and the solution was then filtered again. The solvent was removed under reduced pressure from the filtrate to provide the title product as a pale yellow solid (255 mg, 0.280 mmol, 27%). ¹H NMR (500 MHz, CS₂/C₆D₆) δ 8.52 (d, J = 9.0 Hz, 2H), 8.50 (s, 2H), 8.30 (d, J = 5.4 Hz, 4H), 7.79 (d, J = 8.7 Hz, 2H), 3.01 (m, 8H), 1.84 (m, 8H), 1.55 – 1.41 (m, 8H), 1.41 – 1.27 (m, 16H), 0.98 – 0.86 (m, 12H). ¹³C NMR (126 MHz, CS₂/C₆D₆) δ 145.41, 137.55, 135.16, 135.05, 134.36, 134.27, 134.21, 130.98, 130.05, 129.72, 127.07, 126.96, 123.38, 123.24, 32.41, 32.21, 32.09, 31.78, 31.75, 29.76, 23.56, 14.87 (Note that some signals are overlapped with residual signals of C₆D₆. The poor solubility of compound **5** made it difficult to obtain any signals from other deuterated solvents.). HRMS(APCI): Calcd for [M]⁺: 910.3734; Found: 910.3686.

2. Device fabrication and characterization

Top-gate/bottom-contact FET devices were fabricated using n⁺⁺-Si/SiO₂ (300 nm) substrates. The substrates were cleaned by acetone, detergent, deionized water (twice) and iso-propanol for 10 min respectively and then dried in vacuum oven at 80 °C for 1 h. The substrates were modified with polystyrene solution (6 mg.mL⁻¹ in toluene). The thickness of PS layer was measured to be 20 nm. The micro-ribbons suspension of **3** and **5** in hexane was spin-coated on substrates and annealed at 60 °C in vacuum oven overnight. The shadow mask were made as reported.⁹ Gold was deposited as drain and source electrodes with a thickness of 400 Å. All devices were measured by a Keithley 4200 parameter analyzer on a probe stage under ambient condition. The mobility was estimated in the saturated regime.

3. Single crystal structure

Single crystal of **3** was obtained from CHCl₃/Hexane.

Identification code	6
Empirical formula	C ₁₂₁ H ₁₁₃ S ₈ Cl ₃
Formula weight	1929.94
Temperature/K	173 (2)
Crystal system	triclinic
Space group	P-1
a/Å	11.7098(8)
b/Å	12.2432(8)
c/Å	19.7420(12)
α/°	75.9530(10)
β/°	72.973(2)
γ/°	75.614(2)
Volume/Å ³	2576.9(3)
Z	1
ρ _{calc} /mg/mm ³	1.244
m/mm ⁻¹	0.301
F(000)	1018.0
Crystal size/mm ³	0.4 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2θ range for data collection	6.078 to 50°
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 13, -23 ≤ l ≤ 23
Reflections collected	20566
Independent reflections	9064 [R _{int} = 0.1008, R _{sigma} = 0.1367]
Data/restraints/parameters	9064/0/614
Goodness-of-fit on F ²	1.122
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.1076, wR ₂ = 0.3038
Final R indexes [all data]	R ₁ = 0.1896, wR ₂ = 0.3679
Largest diff. peak/hole / e Å ⁻³	2.00/-0.80

4. Figure S1-S4

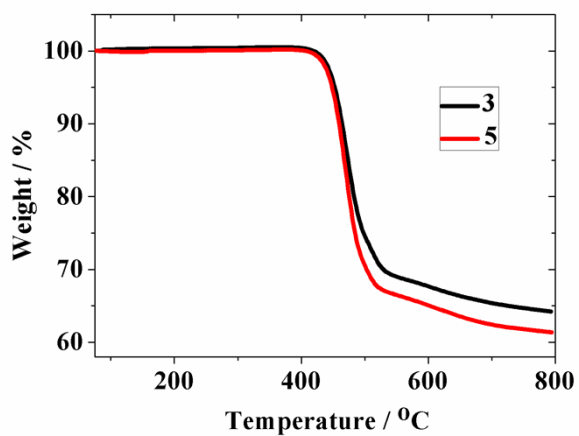


Figure S1. a) Thermal gravity analyses (TGA) of **3** (5% loss, 451 °C) and **5** (5% loss, 447 °C).

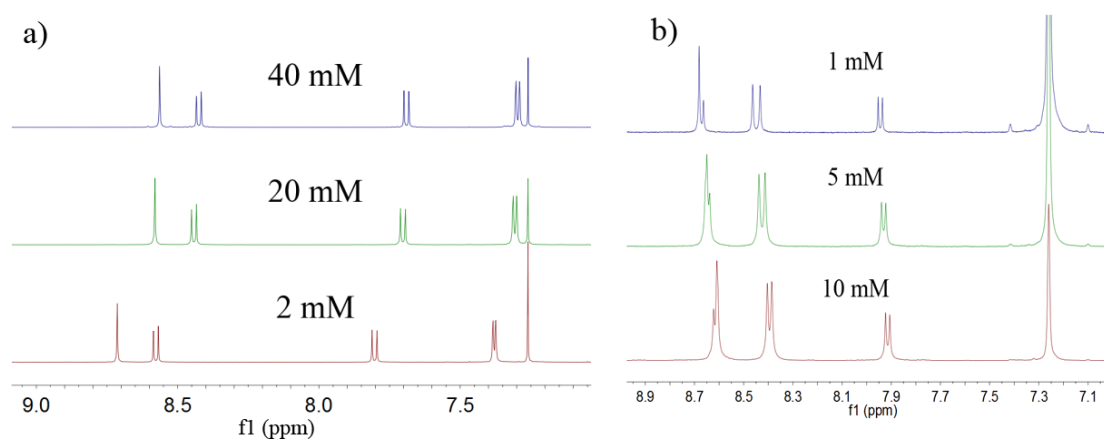


Figure S2. Concentration-dependent ¹H NMR spectra of a) **3** in CDCl₃ and b) **5** in DCM-C₆D₆.

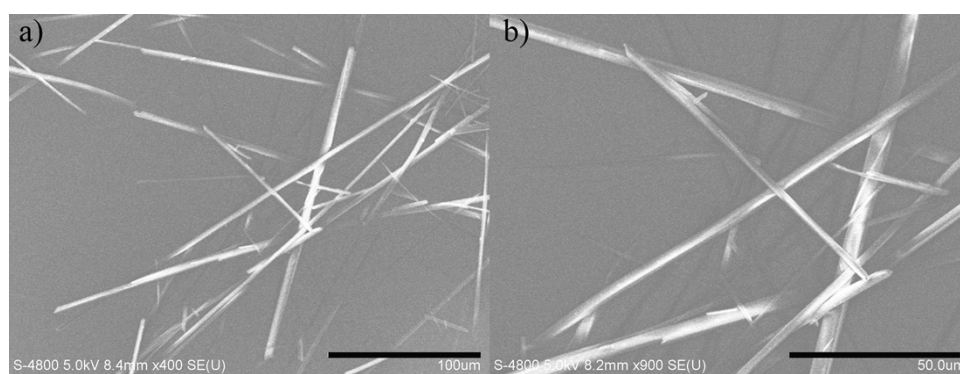
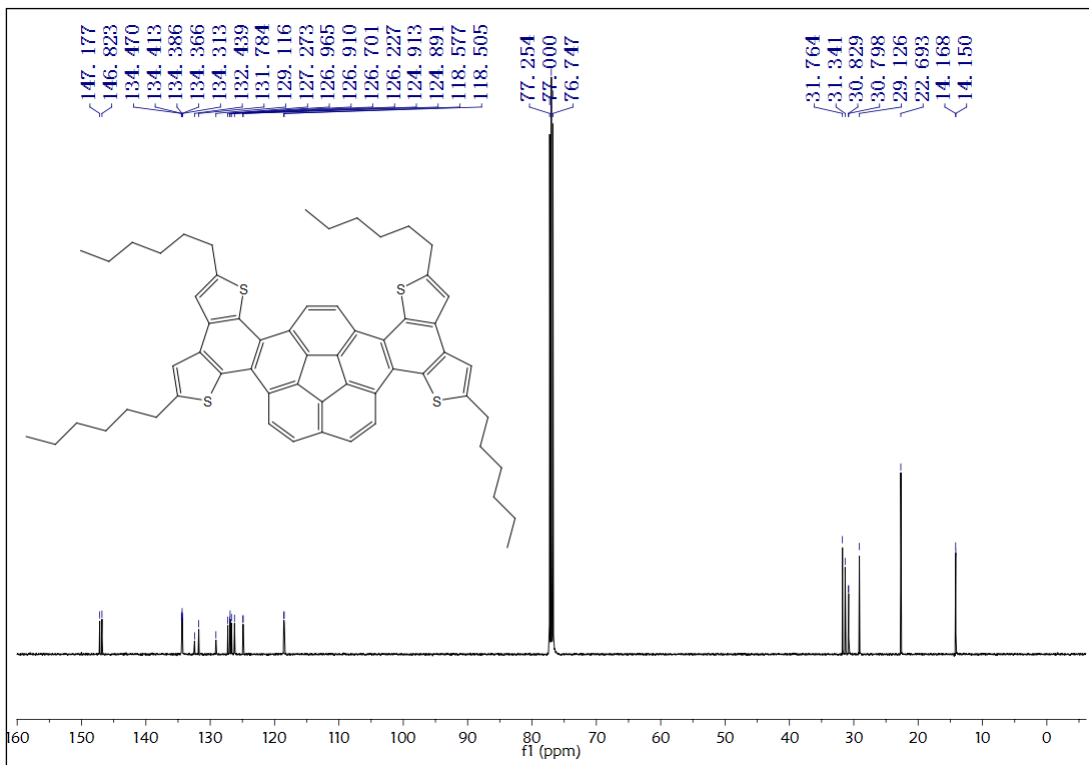
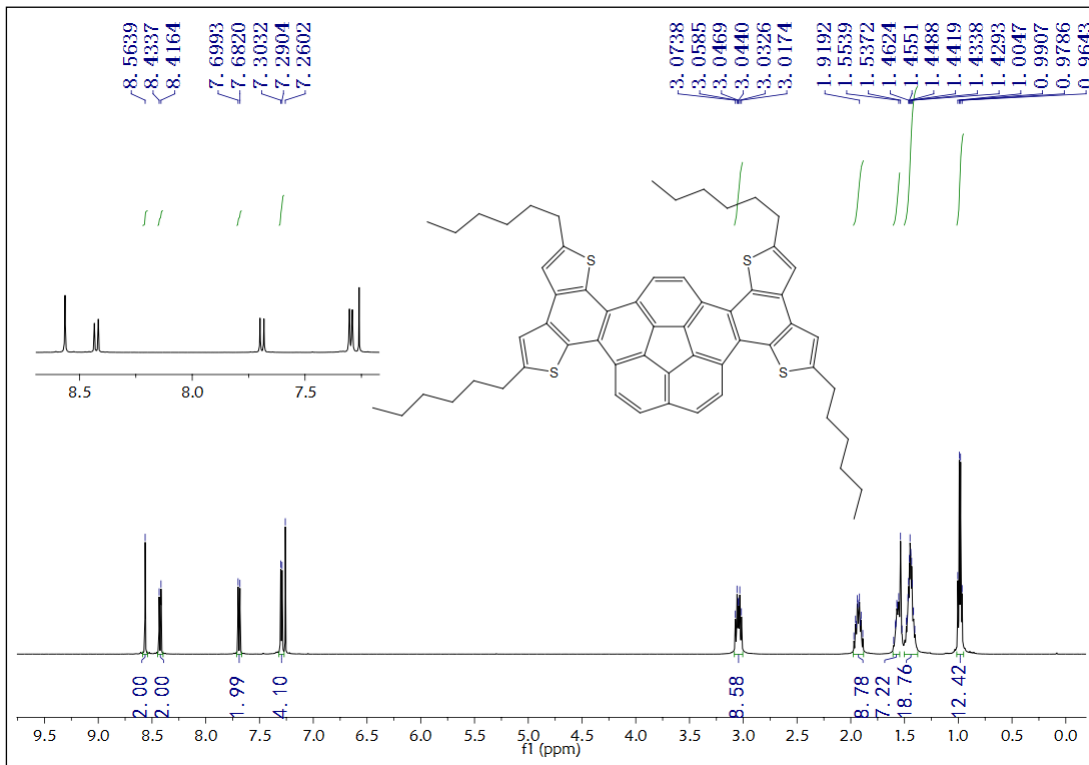
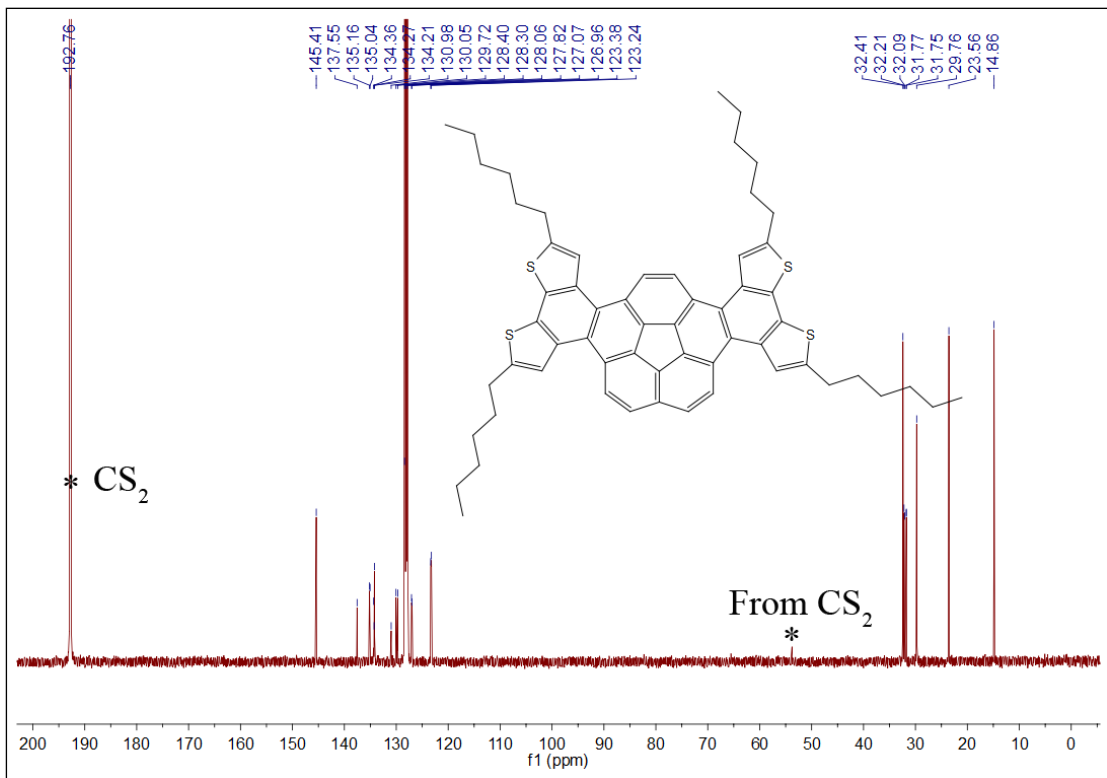
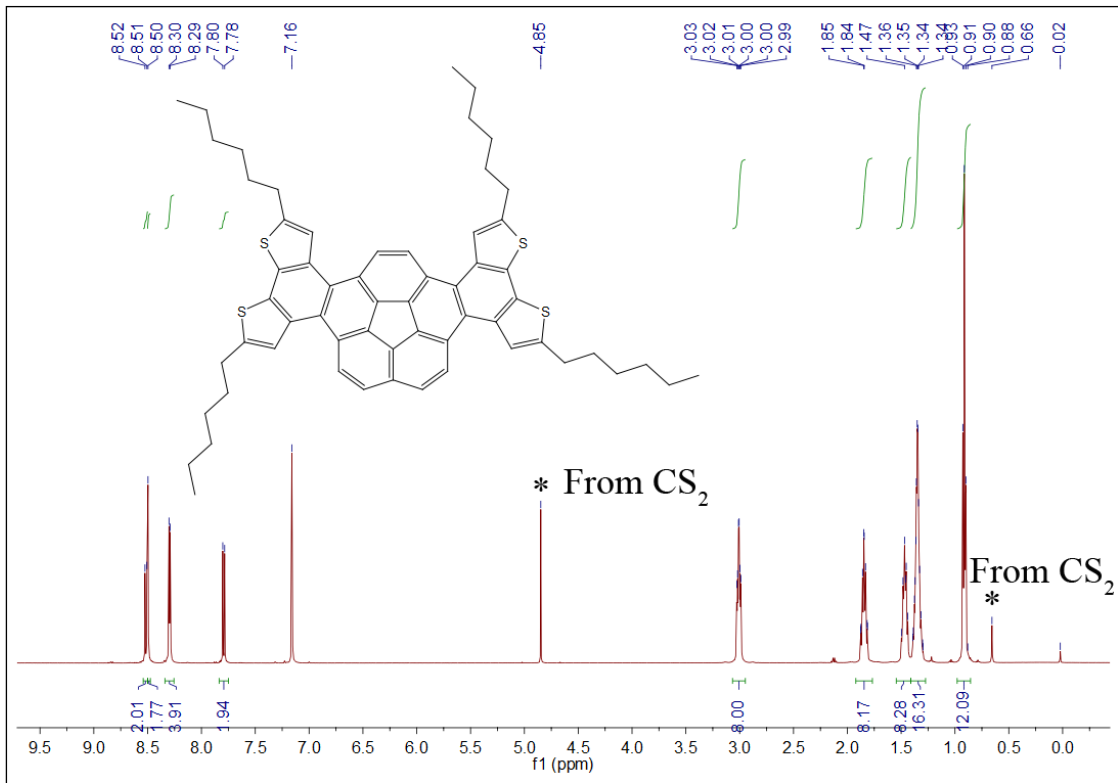


Figure S3. a) and b) different scale bar SEM images of microwires of **5**.





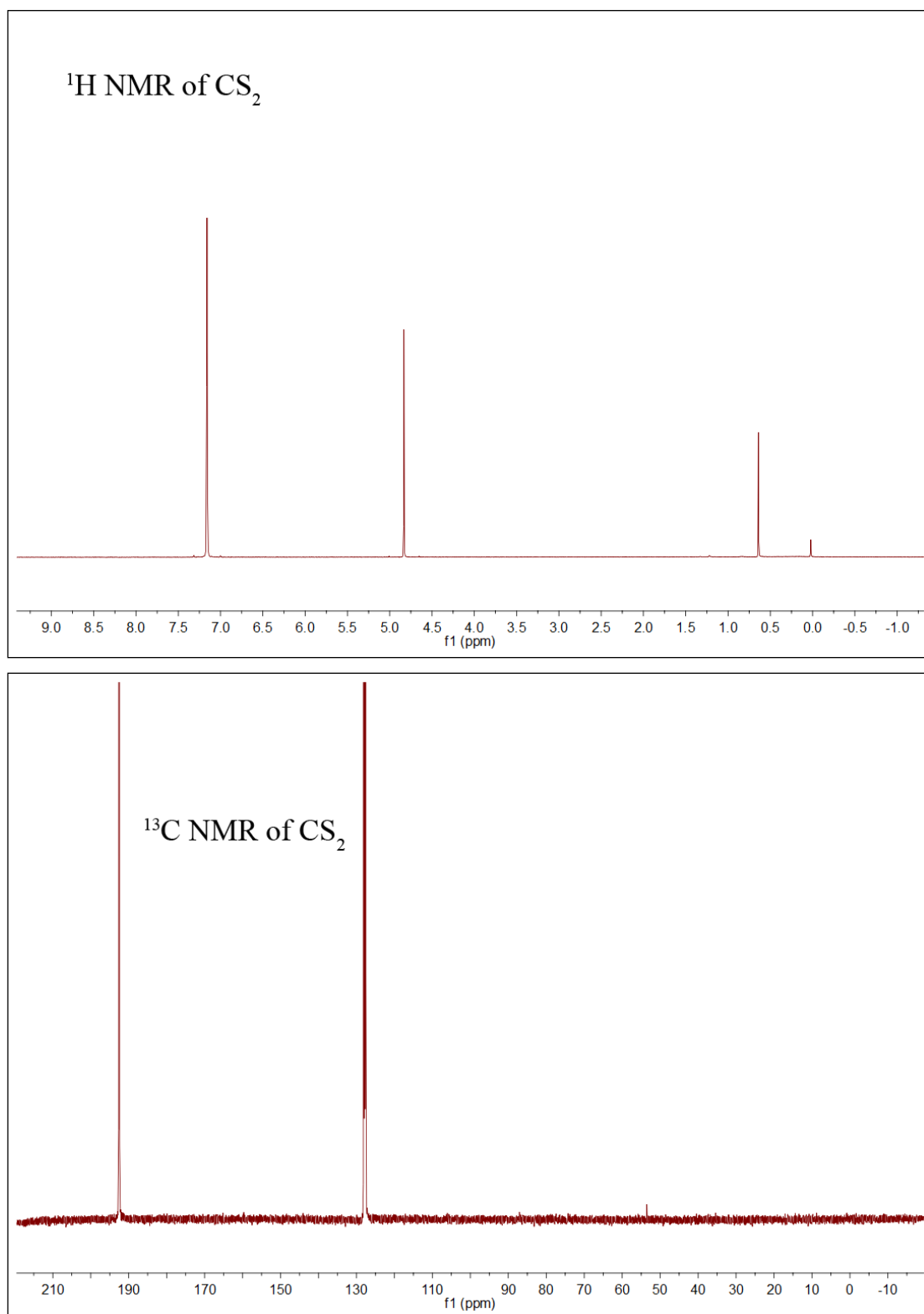


Figure S4. NMR spectra

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