SUPPLEMETARY INFORMATION

Simple synthesis of alkyl derivatives of tetrathienoacene and their application in organic field-effect transistors

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1. Experimental section

2.1. Materials

Octanoyl chloride, lithium aluminum hydride and aluminum chloride were obtained from Acros organics and used as received. Thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]thiophene (TTA) was synthesized as described elsewhere [1]. Dichloromethane, diethyl ether, cyclohexane and toluene were dried and purified according to the standard techniques and then used as the solvents.

2.2. Characterization

The ^{1}H NMR spectra were recorded on a Bruker WP250 SY spectrometer (250.13 MHz) using the residual signal of $CDCl_3$ (δ 7.27 ppm) as the internal standard. The ^{13}C NMR spectra were recorded on a Bruker Advance II 300 spectrometer at working frequencies 75 MHz and 60 MHz, respectively. The spectra were then processed on the computer using the ACD Labs software.

Elemental analysis of C, H, N elements was carried out using CHN automatic analyzer CE1106 (Italy). Experimental error is 0.30−0.50%. The burning was done in the Sheninger flask using alkaline solution of hydrogen peroxide as an absorbent.

Thermogravimetric analysis was carried out in dynamic mode in 30-800 °C interval using Mettler Toledo TG50 system equipped with M3 microbalance allowing measuring the weight of the samples in 1-150 mg range with 1 μg precision. Heating/cooling rate was chosen to be 10 °C/min. Every compound was studied twice: in air and under nitrogen flow of 200 mL/min.

GPC analysis was performed on a Shimadzu instrument with a RID10A^{VP} refractometer and a SPD-M10A^{VP} diode matrix as detectors using 7.8 × 300 mm^2 Phenomenex columns (USA) filled with the Phenogel sorbent with pore size of 500 Å and THF as the eluent. In the case of column chromatography, silica gel 60 (“Merck”) was taken. For thin layer chromatography (TLC), “Sorbfil”

(Russia) plates were used. The solvents were removed under vacuum (1 mBar) at 80 °C. All reactions, unless stated otherwise, were carried out in an inert atmosphere using anhydrous solvents.

The absorption spectra were recorded on a Shimadzu UV-2501PC (Japan) spectrophotometer in the standard 10 mm photometric quartz cuvette using THF solutions with the concentrations of 10^{-5} M. The photoluminescence (PL) spectra were measured on an ALS-1M spectrofluorimeter (developed by ISPM RAS) and on a FLUORAN-2 pulsed spectrophotometer-spectrofluorimeter (developed by VNIIOFI) in single photon counting mode at successive time intervals and automatic adjustment of the intensity of the measured emission. Measurements were carried out for several optical densities in the range from 0.06 to 0.12 absorbance units in 10 mm cuvette, measurement geometry – 90°. Measurements of the PL spectra in polystyrene (PS) and polycrystalline thin films were carried out in the integrating sphere. The photoluminescence quantum yield (PLQY) was measured by comparing the integral PL intensity of 10^{-6} M diluted solutions of luminophores in THF with the integral PL intensity of the standard as described elsewhere [2]. As the standards in measuring the PLQY a solution of 1,4-*bis*(5-phenyloxazol-2-*yl*)benzene (POPOP) in cyclohexane (PLQY=1) and a solution of rhodamine 6G in ethanol (PLQY=1) were used.

The electrochemical properties of octyl derivatives of TTA were studied by cyclic voltammetry (CV) both in solution and in a thin film. Electrochemical measurements for the films were carried out in a three-electrode electrochemical cell under inert atmosphere in an acetonitrile solution containing 0.1 M Bu_4NPF_6. For solution, a mixture of acetonitrile and o-dichlorobenzene (4: 1) containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) were used. In each case, a film of investigate compound was applied to a glassy carbon surface used as a working electrode by rubbing. A platinum plate located in the cell served as an auxiliary electrode. The

potentials were measured relative to an aqueous saturated calomel electrode (SCE). Cyclic voltammograms were recorded using an IPC-Pro M potentiostat. The potential sweep rate was 200 mV/s. Based on the CV oxidation potentials, values of the highest occupied molecular orbitals (HOMO) were calculated using the equations E(HOMO)=-e(φ_{ox}+4.40) (eV). Bandgap was estimated from the onset wavelength (λ_{onset}) of the optical absorption: E^{g}_{opt} = 1240/ λ_{onset}.

2.3. XRD

Small-angle and wide-angle diffraction patterns of high resolution were recorded using SAXS- and WAXS camera S3-Micropix, manufactured by Hecus (CuKa, l = 1.542 Å). Two detectors were exploited: two-dimensional Pilatus 100K and linear gas position sensitive detector PSD 50M operating at a pressure of 8 bar Ar/Me, the high-voltage and current at Xenocs Genix generator were 50 kV and 1 mA. For shaping of X-ray beam the Fox 3D vacuum optics were used, the slits in the Kratky collimator were set to 0.1 and 0.2 mm correspondingly. The angular scale was between 0.05 nm^{-1} and 19 nm^{-1}. To calibrate small- and wide-angle diffractograms, silver behenate and lupolen (LDPE) calibrants were used as a reference. To eliminate the influence of air the X-ray optics system and camera was vacuumed to pressure (2÷3) × 10^{-2} mm Hg. The exposition time was 3000 s.

The 2D wide-angle (WAXS) analysis of the samples was performed with a BioMUR station of the Kurchatov synchrotron (National Research Center Kurchatov Institute). A 1.7 T bending magnet operating at an energy of 8 keV (1.445 A), resolution dE/E of 10^{-3}, and a photon flux of 10^{9} was used as a source of radiation. The beam size at a sample was 0.3 × 0.2 mm^2; diffraction patterns were recorded with a Dectris Pilatus 1 M detector. Sample-to-detector distance was approximately 170 mm, silver behenate and NaC(Na2Ca3Al2F14) were used as calibration standards, exposure time was 300 s. Data integration and processing was performed by Fit2D V18.002 software by Andy Hammersly/ESRF.

2.4. Device fabrication

Thin film OFETs were fabricated in top contact bottom gate architecture on highly-doped silicon wafers (highly doped silicon was used as a gate electrode) by vacuum deposition and spin-coating techniques. The thermally grown silica dioxide layer of 200 nm thickness was used as gate dielectric. Evaporated semiconducting layers were fabricated at $5 \cdot 10^{-6}$ mbar at the rate of 1 $A \cdot s^{-1}$ resulting in thickness of 50 nm. Spin-coated layers were obtained by spin processor WS-650Mz-8NPP-UD3 (Laurell Technologies Corporation, USA) at 3000 rpm from toluene solution of 0.4 wt. %. Finally, gold source and drain electrodes were thermally evaporated through shadow mask forming 20 OFETs on the one substrate with channel length and channel width of 30 µm and 1000 µm, correspondingly. Layers morphology was investigated by atomic force microscope Solver Next (NT-MDT, Russia) in tapping mode using HA_FM silicon probes (NT-MDT, Russia) with resonance frequency of 77kHz. All measurements were performed under ambient environment.

OFETs electrical characteristics were measured by Probe Station PS-100 (Printeltech LCC, Russia) using Keithley 2634B source-meter under normal conditions. The time needed for single transfer/output curve measurement was about 15 seconds. Shockley's gradual-channel model in the corresponding voltage range was used for field-effect mobility and threshold voltage values extraction.

2.5. Synthesis

2,6-Dioctylthieno-[3,2-b]thieno[2',3':4,5]thieno[2,3-d]thiophene (C8-TTA-C8)

A flask was charged with thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]thiophene (**TTA**) (195 mg, 0.77 mmol, 1 eq), degassed and dichloromethane (80 mL) was added by a cannula. The reaction mixture was cooled to 0 °C and aluminum chloride (258 mg, 1.9 mmol, 2.5 eq) was added in one portion. After stirring for 30 minutes at this temperature, octanoyl chloride (314 mg, 1.9 mmol,

2.5 eq) was added dropwise. The reaction mixture was stirred for 1 h and the temperature was allowed to rise to the ambient. To quench the reaction mixture, a small amount of water was added, and the formed precipitate was filtered off, washed with water and methanol. Without additional purification, the resulting diketone as a brown solid (220 mg, 0.44 mmol, 1 eq) was dispersed in diethyl ether (100 ml) and lithium aluminum hydride (165 mg, 4.4 mmol, 10 eq) and aluminum chloride (291 mg, 2.2 mmol, 5 eq) were added in one portion. After stirring for 3 h at r.t. 100 mL of diethyl ether and 100 mL of water were added. The organic phase was separated, washed with water, and dried over a sodium sulfate. The solvent was evaporated to give a crude product. Purification by column chromatography on silica gel (eluent cyclohexane) and subsequent recrystallization from hexane yielded pure compound **C8-TTA-C8** (137 mg, 37.2% for two steps) as a colorless solid.

^{1}H NMR (J Hz, $CDCl_3$): δ [ppm] 0.87 (6H, t, J=6.72, -*CH*$_3$), 1.19-1.46 (20H, m, -*CH*$_2$-), 1.72 (4H, m, J=7.63, -*CH*$_2$-), 2.89 (4H, t, J=7.63, *TTA*-*CH*$_2$-), 6.96 (2H, s, *TTA*). ^{13}C NMR ($CDCl_3$): δ [ppm] 14.07, 22.62, 29.00, 29.17, 29.28, 31.13, 31.55, 31.80, 117.41, 129.70, 131.37, 138.75, 146.85. Calcd (%) for $C_{26}H_{36}S_4$: C, 65.49; H, 7.61; S, 26.90. Found: C, 65.70; H, 7.34; S, 26.96.

2-(7-Octanoyl)thieno-[3,2-b]thieno[2',3':4,5]thieno[2,3-d]thiophene (C7-CO-TTA)

A flask was charged with **TTA** (300 mg, 1.2 mmol, 1 eq), degassed and dichloromethane (100 mL) was added by a cannula. The reaction mixture was cooled to -20 °C and aluminum chloride (174 mg, 1.3 mmol, 1.1 eq) was added in one portion. After stirring for 30 minutes at this temperature, octanoyl chloride (213 mg, 1.3 mmol, 1.1 eq) was added dropwise. The reaction mixture was stirred for 1 h and the temperature was allowed to rise to the ambient. To quench the reaction mixture, a small amount of water was added and 100 mL of dichloromethane and 100 mL of water were added. The organic phase was separated, washed with water, and dried over sodium sulfate. The solvent was evaporated to give a crude product. Purification by column

chromatography on silica gel (eluent toluene) yielded pure compound **C7-CO-TTA** (370 mg, 82.2%) as a beige solid.

^{1}H NMR (J Hz, $CDCl_3$): δ [ppm] 0.88 (3H, t, J=7.02, -*CH_3*), 1.19-1.46 (8H, m, -*CH_2*-), 1.78 (2H, m, J=7.02, -*CH_2*-), 2.93 (2H, t, J=7.63, *TTA*-*CH_2*-), 7.34 (1H, m, J=5.18, *TTA*), 7.46 (1H, m, J=5.50, *TTA*), 7.92 (1H, s, *TTA*). ^{13}C NMR ($CDCl_3$): δ [ppm] 13.98, 22.60, 25.07, 29.08, 29.40, 31.71, 39.13, 120.89, 125.27, 127.69, 131.88, 132.74, 136.18, 137.97, 139.81, 142.47, 144.57, 193.25. Calcd (%) for $C_{18}H_{18}OS_4$: C, 57.10; H, 4.79; O, 4.23; S, 33.88. Found: C, 57.56; H, 4.24; S, 33.84.

2-Octylthieno-[3,2-b]thieno[2',3':4,5]thieno[2,3-d]thiophene (C8-TTA)

A flask was charged with **C7-CO-TTA** (340 mg, 0.9 mmol, 1 eq) and dispersed in ether (100 ml). Lithium aluminum hydride (341 mg, 8.98 mmol, 10 eq) and aluminum chloride (599 mg, 4.5 mmol, 5 eq) were added in one portion. After stirring for 3 h at r.t. 100 mL of diethyl ether and 100 mL of water were added. The organic phase was separated, washed with water, and dried over sodium sulfate. The solvent was evaporated to give a crude product. Purification by column chromatography on silica gel (eluent cyclohexane) yielded pure compound **C8-TTA** (281 mg, 82.6%) as a colorless solid.

^{1}H NMR (J Hz, $CDCl_3$): δ [ppm] 0.87 (3H, t, J=6.72, -*CH_3*), 1.17-1.46 (10H, m, -*CH_2*-), 1.73 (2H, m, J=7.63, -*CH_2*-), 2.90 (2H, t, J=7.02, *TTA*-*CH_2*-), 6.98 (1H, s, *TTA*), 7.30 (dd, 2H, J_1=5.19, J_2=10.68, *TTA*). ^{13}C NMR ($CDCl_3$): δ [ppm] 13.85, 22.49, 28.95, 29.05, 29.19, 31.11, 31.41, 31.72, 117.38, 120.58, 125.16, 139.51, 139.66, 147.49. Calcd (%) for $C_{18}H_{20}S_4$: C, 59.29; H, 5.53; S, 35.18. Found: C, 59.11; H, 5.44; S, 35.20.

2-(Octyl)-6-(7-octanoyl)thieno-[3,2-b]thieno[2',3':4,5]thieno[2,3-d]thiophene (C8-TTA-CO-C7).

A flask was charged with **C8-TTA** (289 mg, 0.8 mmol, 1 eq), degassed and dichloromethane (70 mL) was added by a cannula. The reaction mixture was cooled to -20 °C and aluminum chloride

(159 mg, 1.2 mmol, 1.5 eq) was added in one portion. After stirring for 30 minutes at this temperature, octanoyl chloride (193 mg, 1.1 mmol, 1.5 eq) was added dropwise. The reaction mixture was stirred for 1 h and the temperature was allowed to rise to the ambient. To quench the reaction mixture, a small amount of water was added and 100 mL of dichloromethane and 100 mL of water were added. The organic phase was separated, washed with water, and dried over sodium sulfate. The solvent was evaporated to give a crude product. Purification by column chromatography on silica gel (eluent toluene) yielded pure compound **C8-TTA-CO-C7** (94 mg, 24.2%) as a beige solid.

^{1}H NMR (J Hz, $CDCl_3$): δ [ppm] 0.87 (6H, t, J=7.02, -*CH*$_3$), 1.21-1.45 (20H, m, -*CH*$_2$-), 1.76 (4H, m, -*CH*$_2$-), 2.90 (4H, t, J=7.62, *TTA*-*CH*$_2$-), 7.02 (1H, s, *TTA*), 7.90 (1H, s, *TTA*). ^{13}C NMR ($CDCl_3$): δ [ppm] 13.85, 22.49, 24.97, 28.95, 29.05, 29.17, 29.27, 31.20, 31.34, 31.58, 31.71, 38.96, 117.57, 125.22, 129.59, 131.05, 136.53, 138.07, 139.15, 141.84, 143.85, 149.56, 193.08. Calcd (%) for $C_{26}H_{34}OS_4$: C, 63.63; H, 6.98; O, 3.26; S, 26.13. Found: C, 63.39; H, 7.10; S, 26.17.

Diketone **C8-TTA-(CO-C7)2** was also isolated as a by-product (90 mg, 18.4%).

^{1}H NMR (J Hz, $CDCl_3$): δ [ppm] 0.87 (9H, t, J=7.02, -*CH*$_3$), 1.20-1.50 (26H, m, -*CH*$_2$-), 1.78 (6H, m, J=7.63, -*CH*$_2$-), 2.92 (q, 4H, J_1=7.33, J_2=12.82, *TTA*-*CH*$_2$-), 3.25 (2H, t, J=7.94, *TTA*-*CH*$_2$-), 7.91 (1H, s, *TTA*). ^{13}C NMR ($CDCl_3$): δ [ppm] 13.84, 22.48, 23.86, 24.92, 28.94, 29.05, 29.18, 29.21, 29.25, 29.34, 31.57, 31.59, 31.69, 39.02, 42.34, 125.04, 126.68, 131.02, 133.14, 135.43, 137.84, 139.77, 142.67, 144.42, 156.55, 193.06, 194.16. Calcd (%) for $C_{34}H_{48}O_2S_4$: C, 66.18; H, 7.84; O, 5.18; S, 20.79. Found: C, 66.36; H, 7.98; S, 20.63.

C8-TTA-C8 from **C8-TTA-CO-C7**

This compound was obtained according to the procedure for **C8-TTA-C8** described above using compound **C8-TTA-CO-C7** (75 mg, 0.15 mmol, 1 eq), lithium aluminum hydride (58 mg, 1.5 mmol,

10 eq), aluminum chloride (102 mg, 0.76 mmol, 5 eq) and diethyl ether (50 ml). The product was purified by column chromatography on silica gel (eluent cyclohexane) to give pure compound **C8-TTA-C8** (34 mg, 46.5%) as a colorless solid.

2,3,6-Trioctylthieno-[3,2-b]thieno[2',3':4,5]thieno[2,3-d]thiophene (C8-TTA-$(C8)_2$)

This compound was obtained according to procedure for **C8-TTA** as described above using compound **C8-TTA-$(CO\text{-}C7)_2$** (75 mg, 0.12 mmol, 1 eq), lithium aluminum hydride (46 mg, 1.2 mmol, 10 eq), aluminum chloride (81 mg, 0.61 mmol, 5 eq) and diethyl ether (50 ml). The product was purified by column chromatography on silica gel (eluent cyclohexane) to give pure compound **C8-TTA-$(C8)_2$)** (19 mg, 26.2%) as a colorless solid.

^{1}H NMR (J Hz, $CDCl_3$): δ [ppm] 0.87 (9H, t, J=6.71, -*CH_3*), 1.21-1.44 (30H, m, -*CH_2*-), 1.68 (6H, m, J=7.63, -*CH_2*-), 2.65 (2H, t, J=7.93, *TTA*-*CH_2*-), 2.81 (2H, t, J=7.63, *TTA*-*CH_2*-), 2.88 (2H, t, J=7.63, *TTA*-*CH_2*-), 6.96 (1H, s, *TTA*). ^{13}C NMR ($CDCl_3$): δ [ppm] 14.07, 22.66, 27.76, 28.95, 29.07, 29.22, 29.33, 29.39, 29.44, 29.57, 29.70, 31.17, 31.58, 31.87, 31.92, 117.46, 127.57, 129.81, 130.86, 130.92, 131.74, 138.71, 139.90, 140.61, 146.67. Calcd (%) for $C_{34}H_{52}S_4$: C, 69.33; H, 8.90; S, 21.77. Found: C, 69.31; H, 8.84; S, 21.66.

2. Geal permeation chromatography (GPC) data

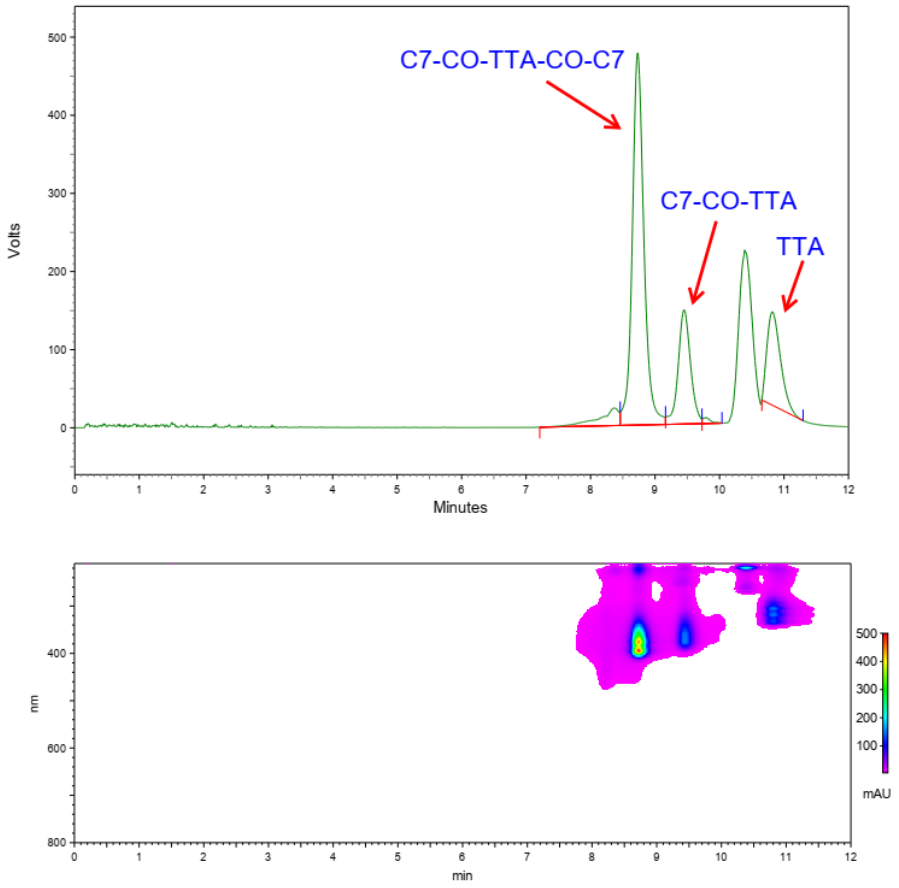


Figure S1. GPC curve of the reaction mixture for the preparation of **C7-CO-TTA-C0-C7**.

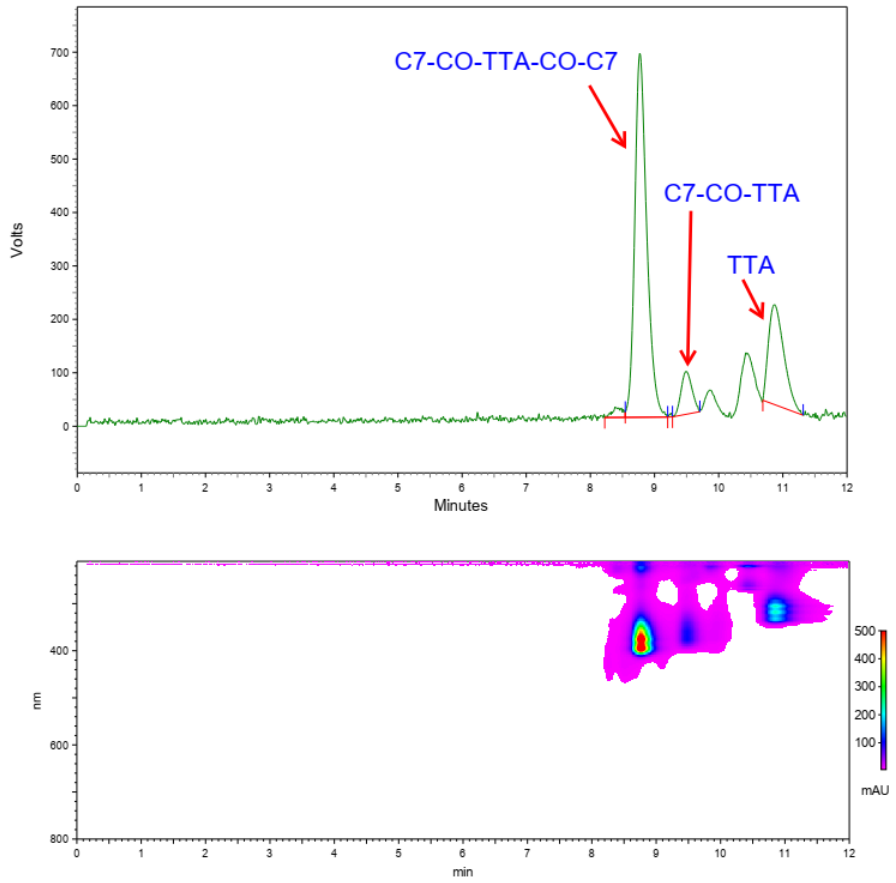


Figure S2. GPC curve of the best reaction mixture for the preparation of **C7-CO-TTA-C0-C7**.

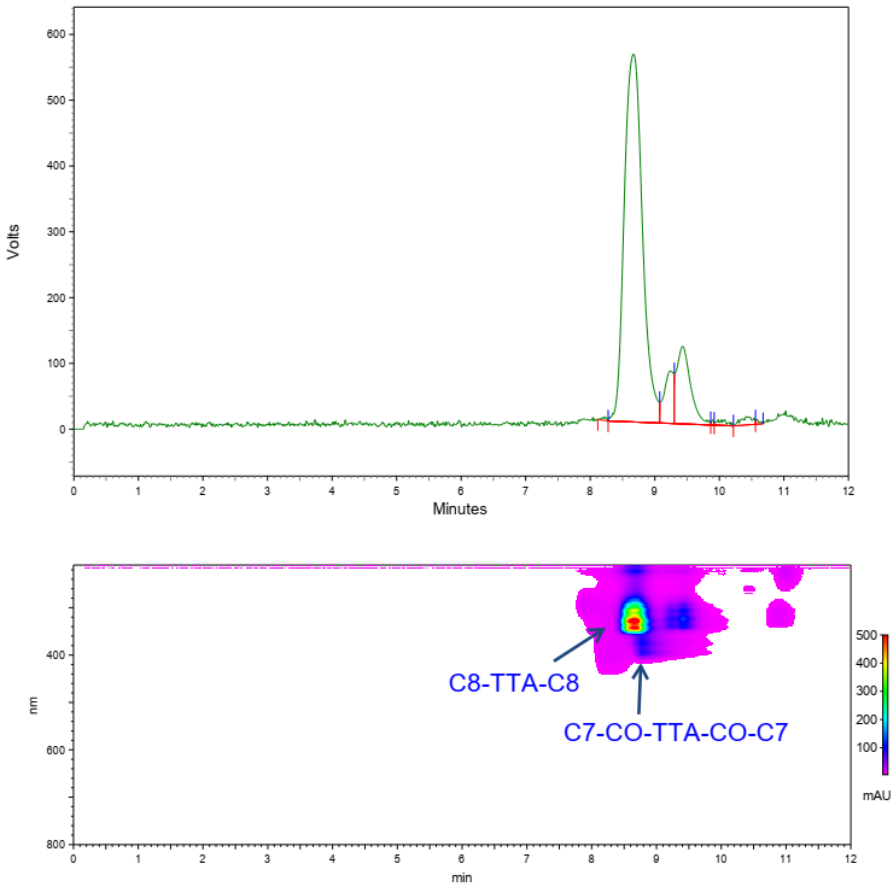


Figure S3. GPC curve of the reaction mixture for the preparation of **C8-TTA-C8**.

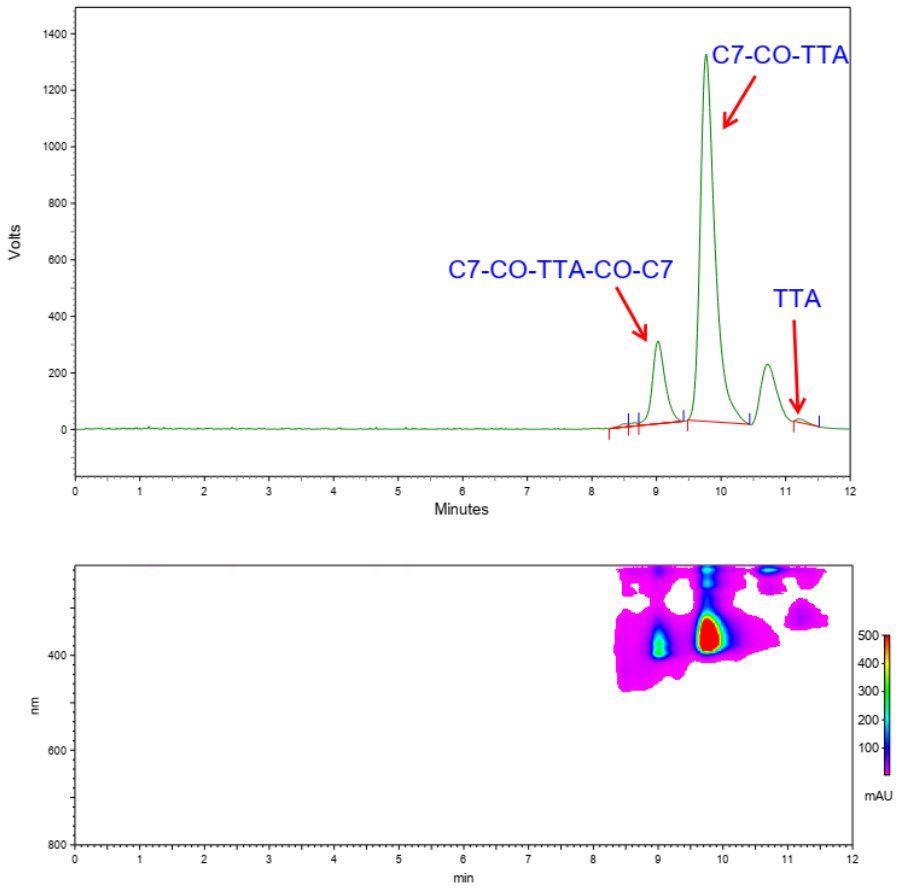


Figure S4. GPC curve of the reaction mixture for the preparation of **C7-CO-TTA**.

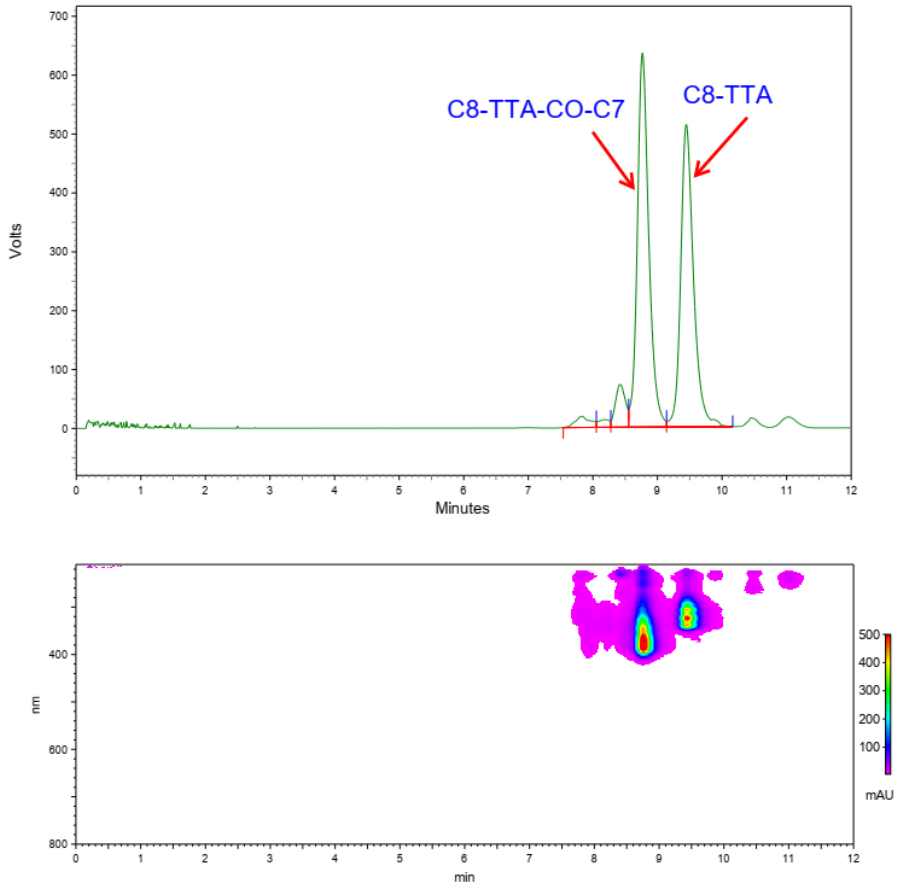


Figure S5. GPC curve of the reaction mixture at -20 °C for the preparation of **C8-TTA-C0-C7**.

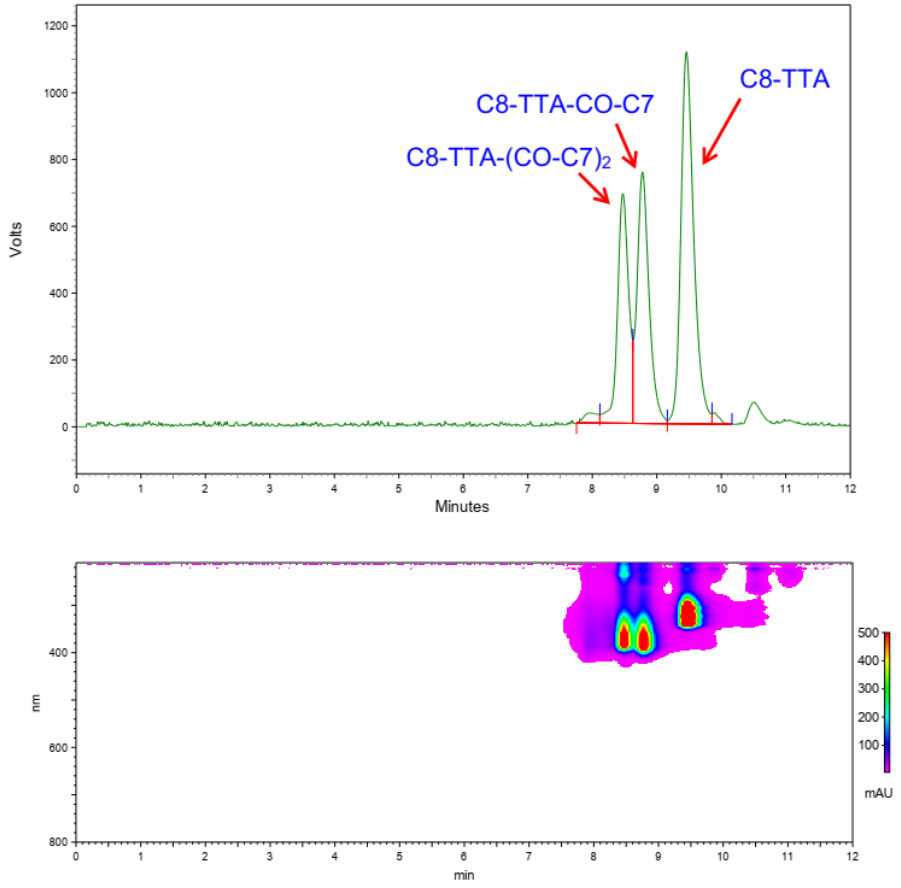
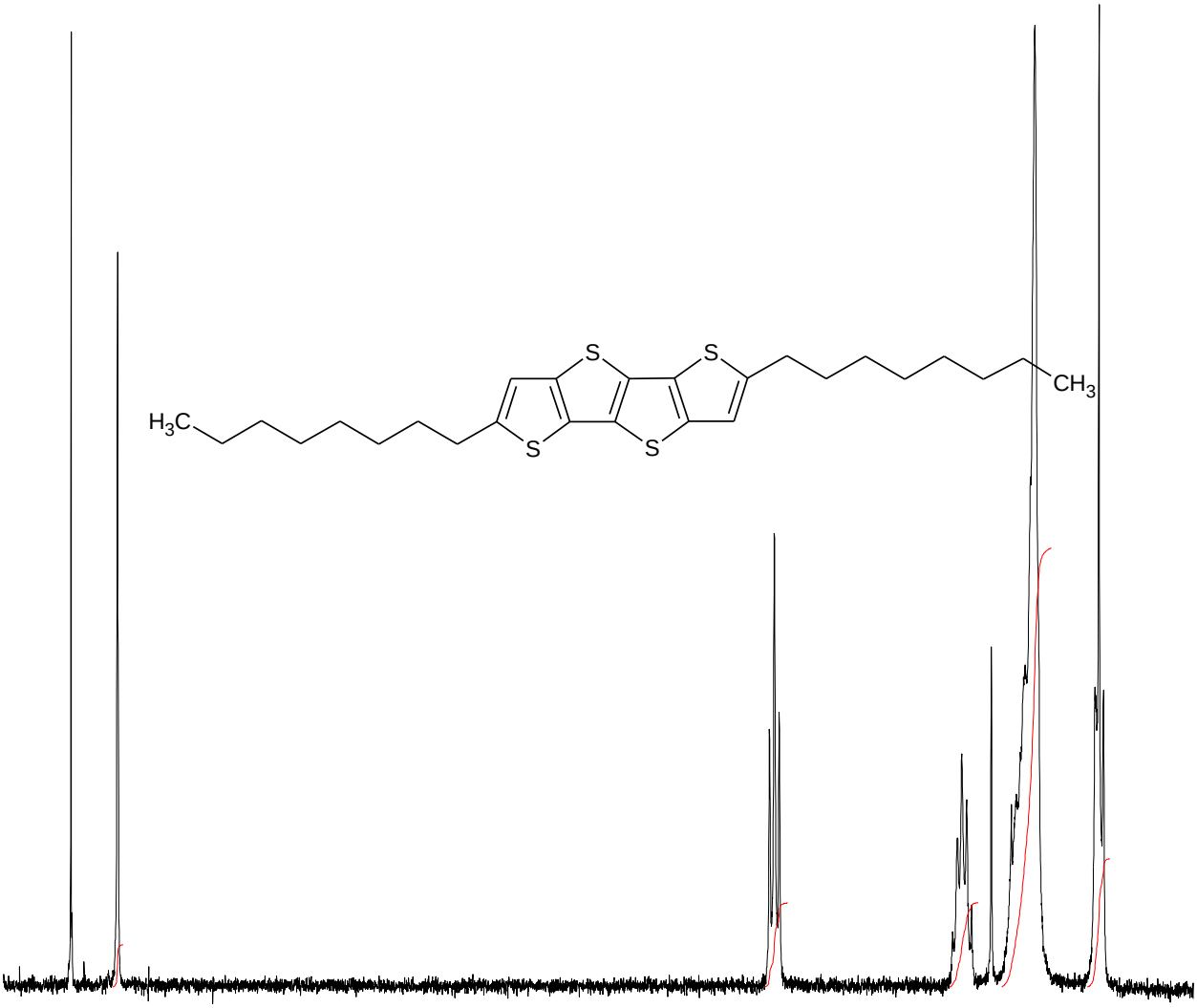


Figure S6. GPC curve of the reaction mixture at r.t. for the preparation of **C8-TTA-C0-C7**.

3. ^{1}H, ^{13}C NMR spectra

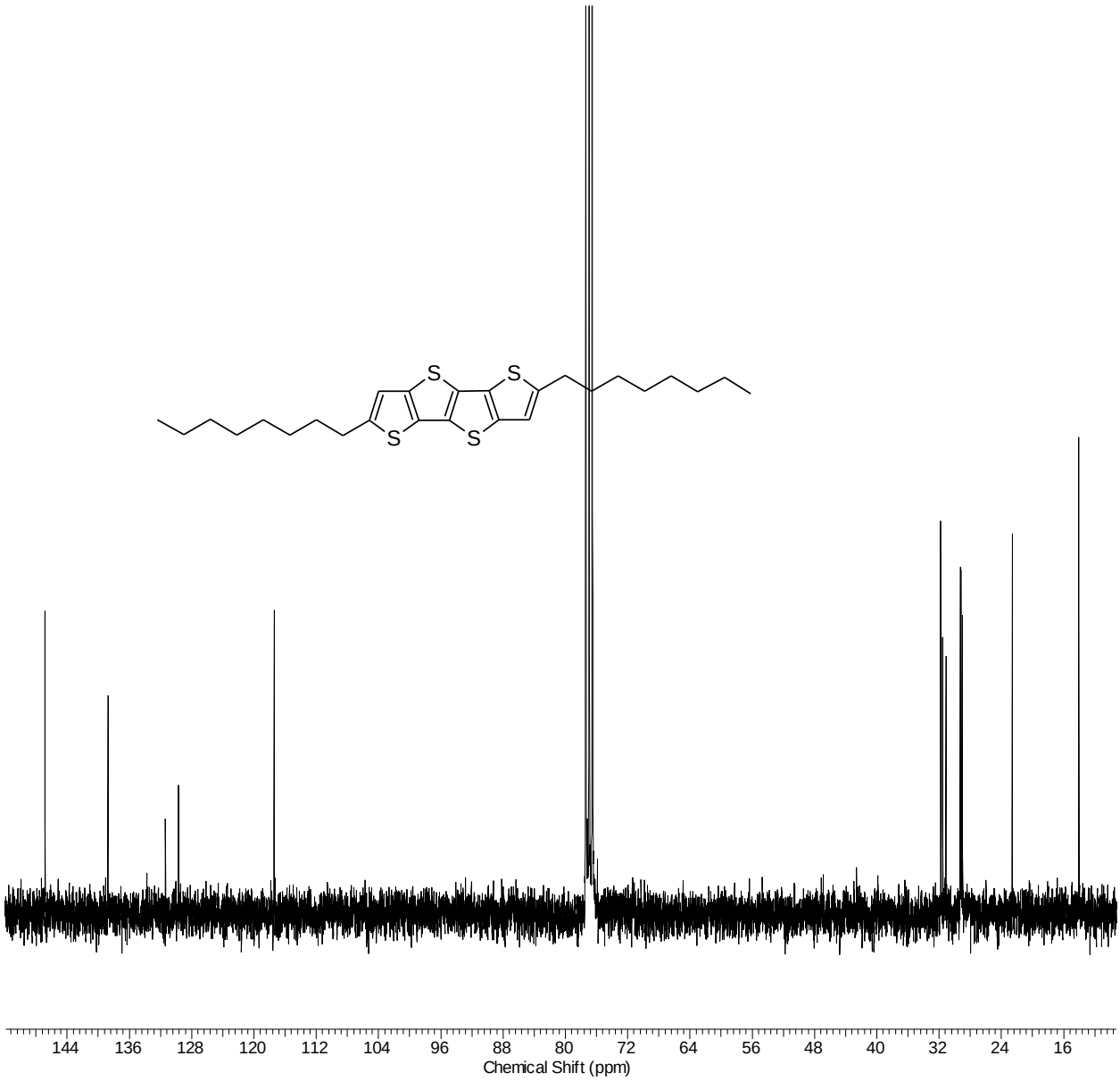


No.	(ppm)	(Hz)	Height
1	0.84	211.2	0.3022
2	0.87	217.9	1.0000
3	0.90	224.3	0.3050
4	1.27	317.7	0.9787
5	1.42	354.0	0.1859
6	1.66	415.6	0.0837
7	1.69	423.6	0.1905
8	1.72	431.2	0.2376
9	2.86	714.4	0.2798
10	2.89	722.1	0.4615
11	2.92	729.7	0.2623
12	6.96	1741.4	0.7479

No.	Annotation	(ppm)
1	Water	1.54
2	Chlorophorm	7.25

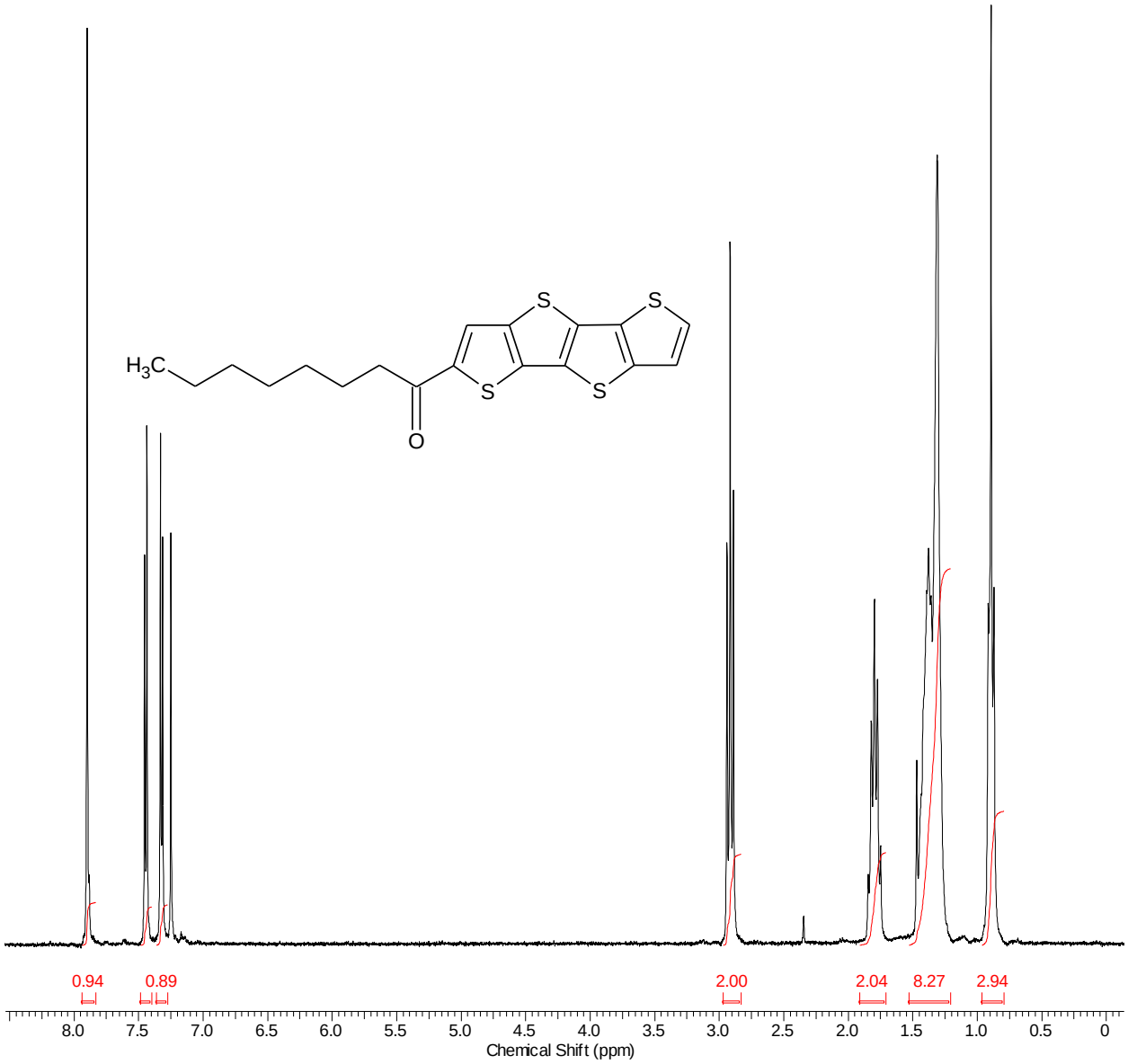
No.	(ppm)	Value	Absolute Value
1	[0.80 .. 0.94]	6.074	4.47087e+7
2	[1.17 .. 1.48]	20.773	1.52900e+8
3	[1.62 .. 1.80]	4.004	2.94715e+7
4	[2.80 .. 2.95]	3.983	2.93202e+7
5	[6.93 .. 7.00]	2.000	1.47208e+7

Figure S7. ^{1}H NMR spectrum **C8-TTA-C8**.



No.	(ppm)	(Hz)	Height
1	14.07	1061.9	0.1627
2	22.62	1707.1	0.1297
3	29.00	2189.2	0.1018
4	29.17	2201.4	0.1175
5	29.28	2210.2	0.1183
6	31.13	2349.5	0.0879
7	31.55	2381.0	0.0943
8	31.80	2400.4	0.1340
9	117.41	8861.8	0.1036
10	129.70	9789.5	0.0438
11	131.37	9915.6	0.0323
12	138.75	10472.9	0.0745
13	146.85	11083.8	0.1032

Figure S8. ^{13}C NMR spectrum of **C8-TTA-C8**.



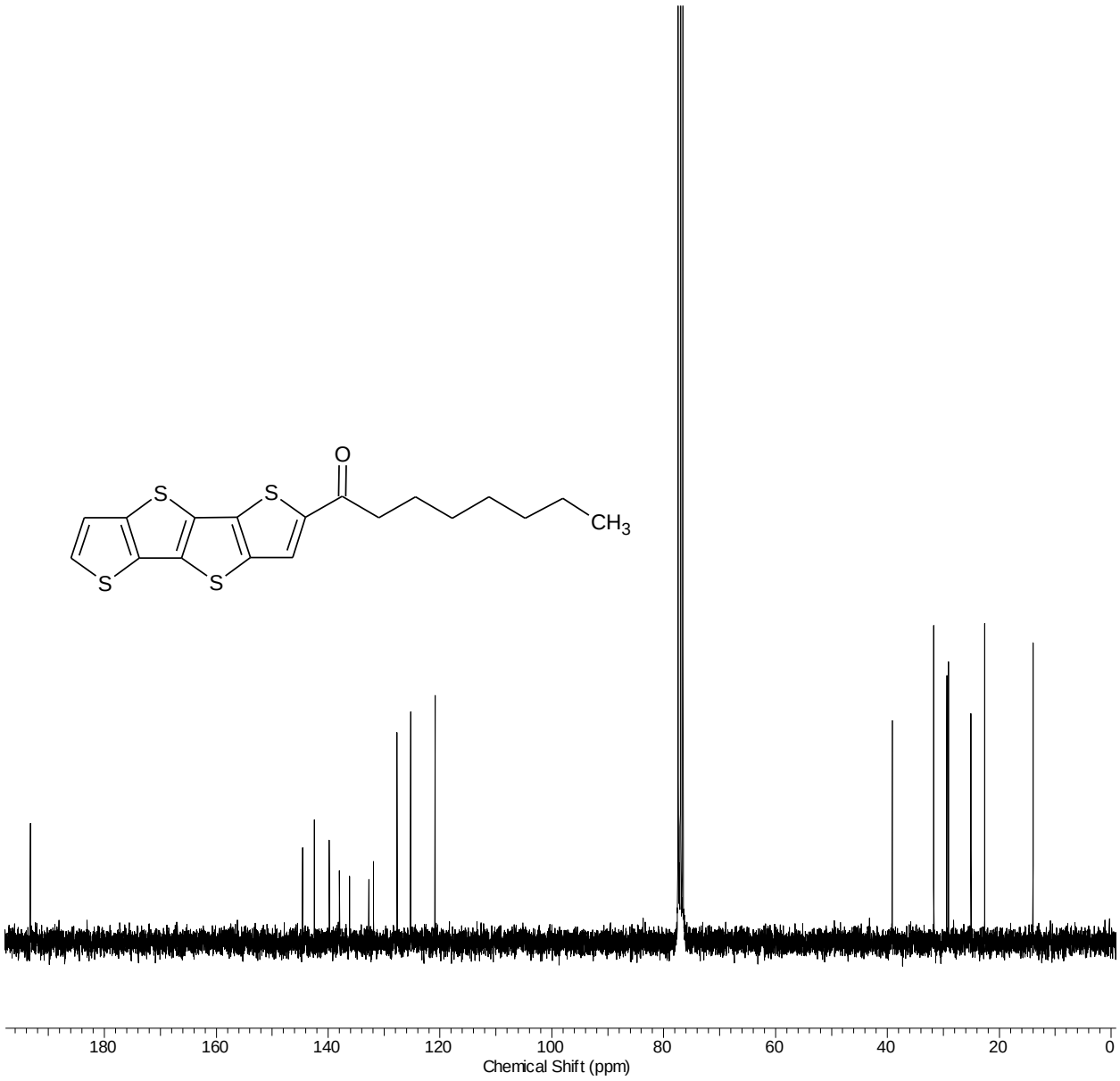
No.	(ppm)	(Hz)	Height
1	0.87	261.1	0.3809
2	0.89	268.1	1.0000
3	0.92	274.7	0.3640
4	1.23	370.4	0.0232
5	1.31	393.2	0.8407
6	1.36	407.9	0.3721
7	1.38	413.4	0.4225
8	1.39	417.8	0.3776
9	1.47	441.2	0.1966
10	1.75	524.9	0.1064
11	1.77	532.2	0.2831

No.	(ppm)	(Hz)	Height
12	1.80	539.5	0.3681
13	1.82	546.9	0.2387
14	1.85	554.2	0.0757
15	2.89	867.5	0.4841
16	2.92	875.2	0.7481
17	2.94	882.5	0.4285
18	7.31	2195.4	0.4343
19	7.33	2200.5	0.5446
20	7.44	2232.1	0.5527
21	7.45	2237.2	0.4153
22	7.90	2371.1	0.9751

No.	Annotation	(ppm)
1	Chloroform	7.25

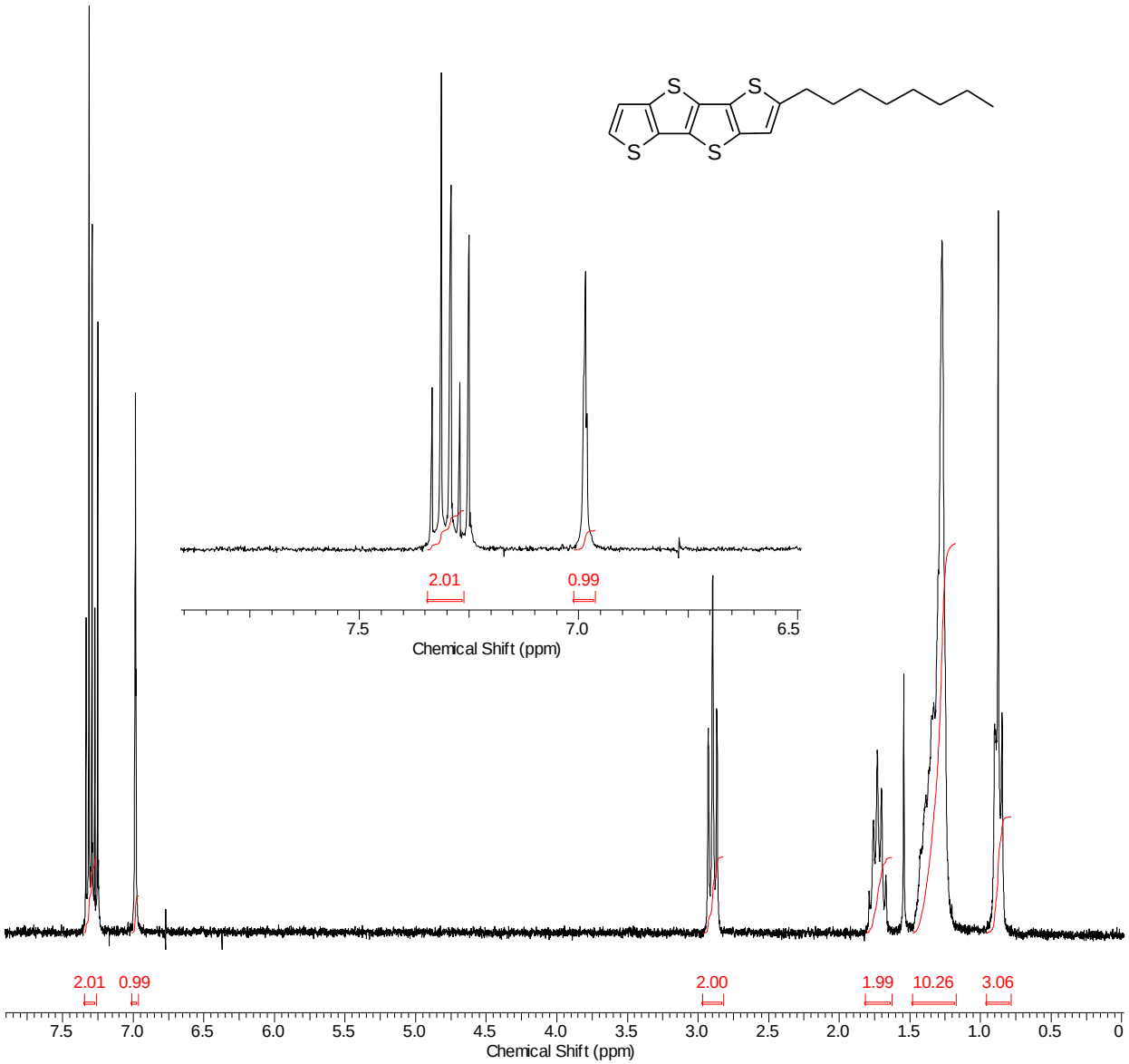
No.	(ppm)	Value	Absolute Value
1	[0.79 .. 0.96]	2.942	8.80944e+9
2	[1.21 .. 1.53]	8.273	2.47713e+10
3	[1.71 .. 1.91]	2.038	6.10105e+9
4	[2.83 .. 2.97]	2.000	5.98835e+9
5	[7.28 .. 7.36]	0.893	2.67255e+9
6	[7.40 .. 7.49]	0.845	2.52961e+9
7	[7.83 .. 7.94]	0.941	2.81709e+9

Figure S9. ^{1}H NMR spectrum **C7-CO-TTA**.



No.	(ppm)	(Hz)	Height
1	13.98	1055.0	0.1228
2	22.60	1705.7	0.1307
3	25.07	1892.0	0.0936
4	29.08	2195.0	0.1150
5	29.40	2219.3	0.1093
6	31.71	2393.5	0.1298
7	39.13	2953.5	0.0909
8	120.89	9124.7	0.1013
9	125.27	9455.3	0.0944
10	127.69	9637.8	0.0859
11	131.88	9954.0	0.0330
12	132.74	10019.2	0.0256
13	136.18	10278.5	0.0270
14	137.97	10413.4	0.0292
15	139.81	10552.2	0.0418
16	142.47	10753.4	0.0502
17	144.57	10911.6	0.0386
18	193.25	14586.0	0.0486

Figure S10. ^{13}C NMR spectrum of **C7-CO-TTA**.

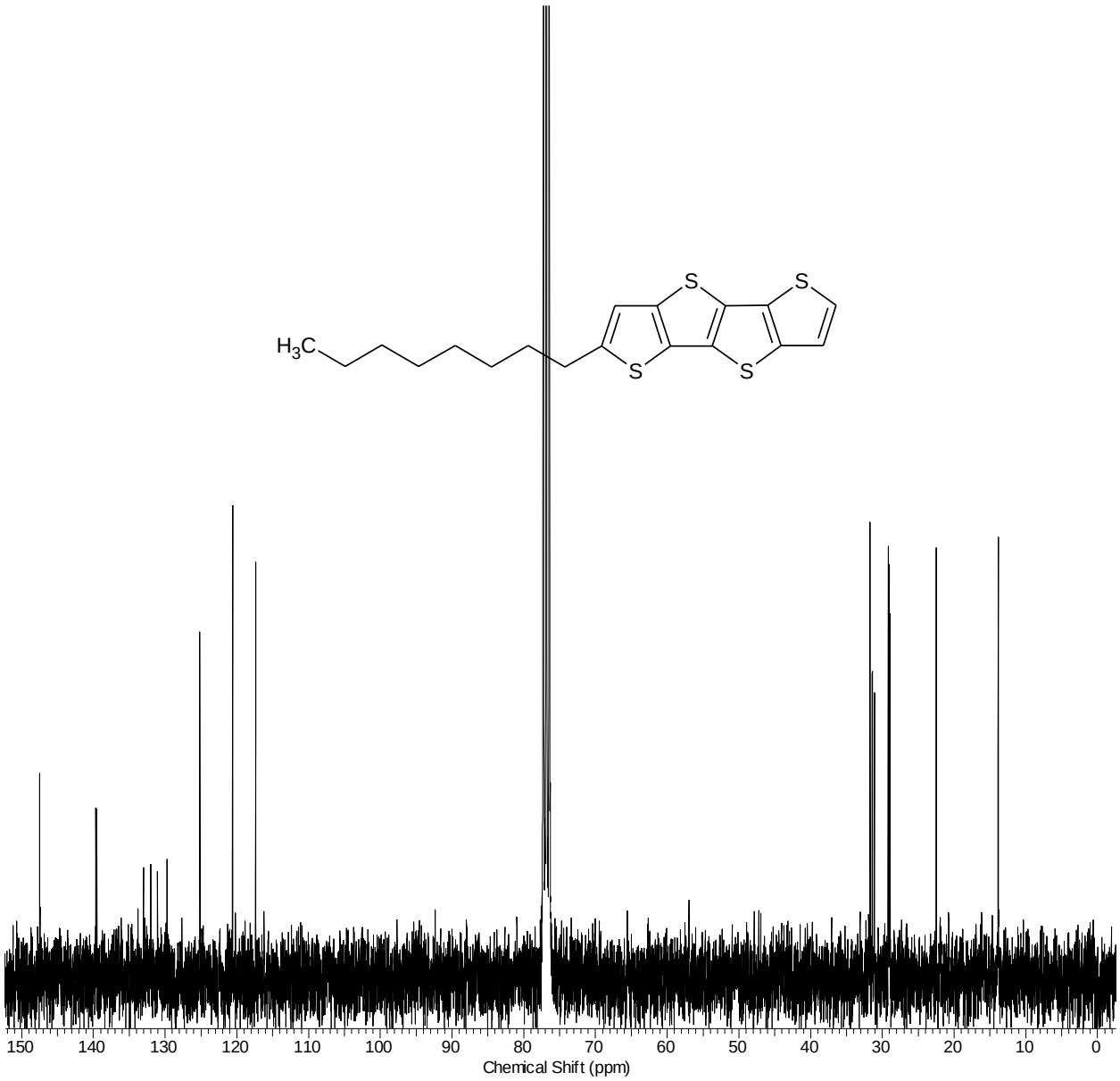


No.	(ppm)	(Hz)	Height
1	0.85	211.8	0.2377
2	0.87	218.5	0.7789
3	0.90	225.2	0.2256
4	1.27	318.3	0.7471
5	1.33	332.6	0.2488
6	1.42	356.4	0.0905
7	1.67	417.8	0.0629
8	1.70	425.4	0.1562
9	1.73	433.0	0.1971
10	1.76	439.8	0.1218
11	1.79	447.4	0.0455
12	2.87	717.5	0.2420
13	2.90	724.5	0.3856
14	2.93	732.4	0.2210
15	6.98	1746.9	0.5829
16	7.27	1818.6	0.3510
17	7.29	1823.8	0.7644
18	7.31	1829.3	1.0000
19	7.33	1834.5	0.3403

No.	Annotation	(ppm)
1	Water	1.54
2	Chloroform	7.25

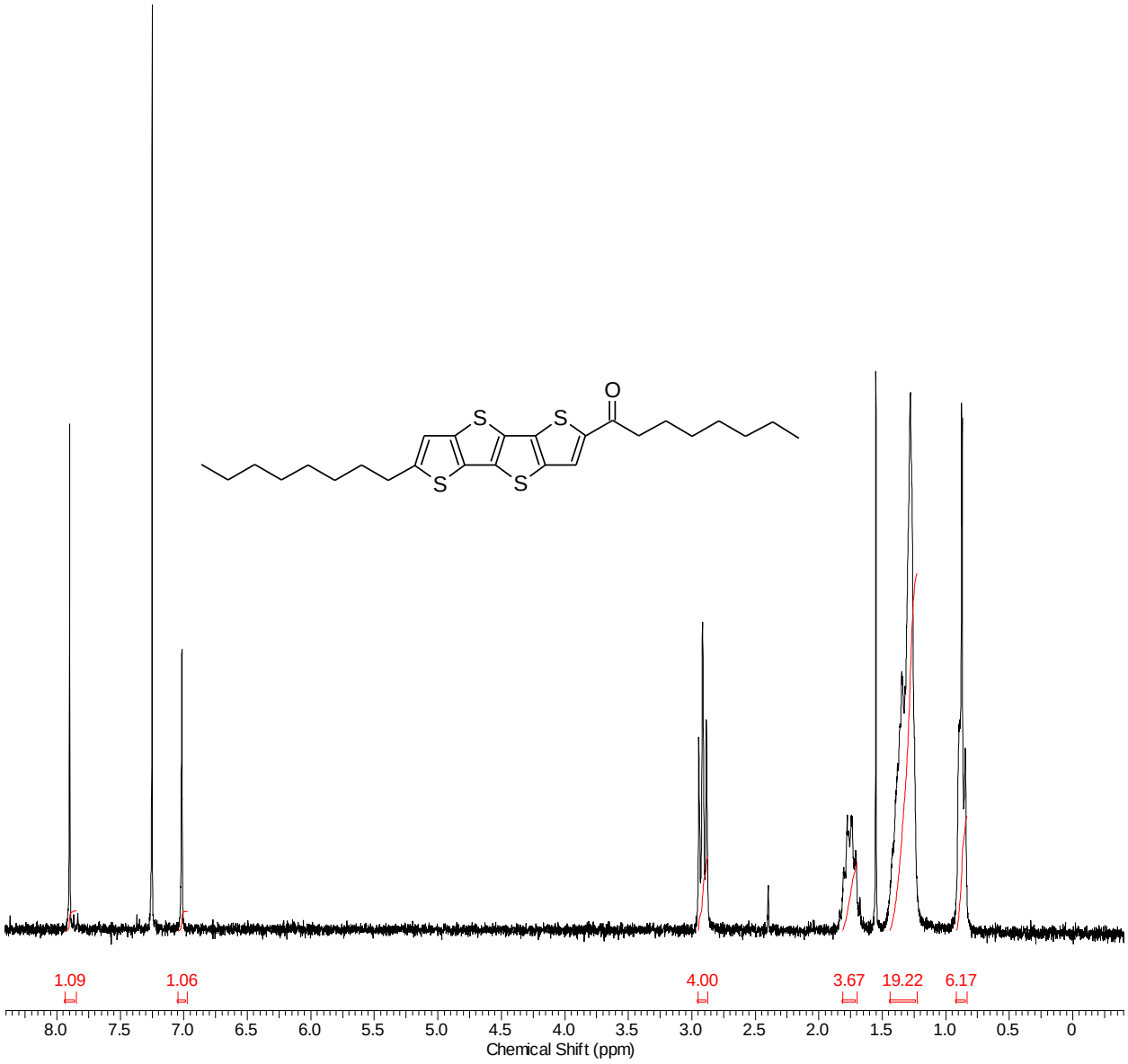
No.	(ppm)	Value	Absolute Value
1	[0.78 .. 0.96]	3.064	3.39054e+7
2	[1.17 .. 1.48]	10.263	1.13554e+8
3	[1.63 .. 1.82]	1.992	2.20454e+7
4	[2.82 .. 2.97]	2.000	2.21296e+7
5	[6.96 .. 7.01]	0.989	1.09405e+7
6	[7.26 .. 7.35]	2.010	2.22374e+7

Figure S11. ^{1}H NMR spectrum of **C8-TTA.**



No.	(ppm)	(Hz)	Height
1	13.85	1045.3	0.0894
2	22.49	1697.7	0.0872
3	28.95	2184.8	0.0738
4	29.05	2192.5	0.0838
5	29.19	2203.0	0.0876
6	31.11	2348.4	0.0578
7	31.41	2370.5	0.0622
8	31.72	2394.3	0.0924
9	117.38	8859.6	0.0843
10	120.58	9101.2	0.0958
11	125.16	9446.7	0.0701
12	139.51	10529.8	0.0344
13	139.66	10541.4	0.0345
14	147.49	11131.9	0.0414

Figure S12. ^{13}C NMR spectrum of **C8-TTA**.

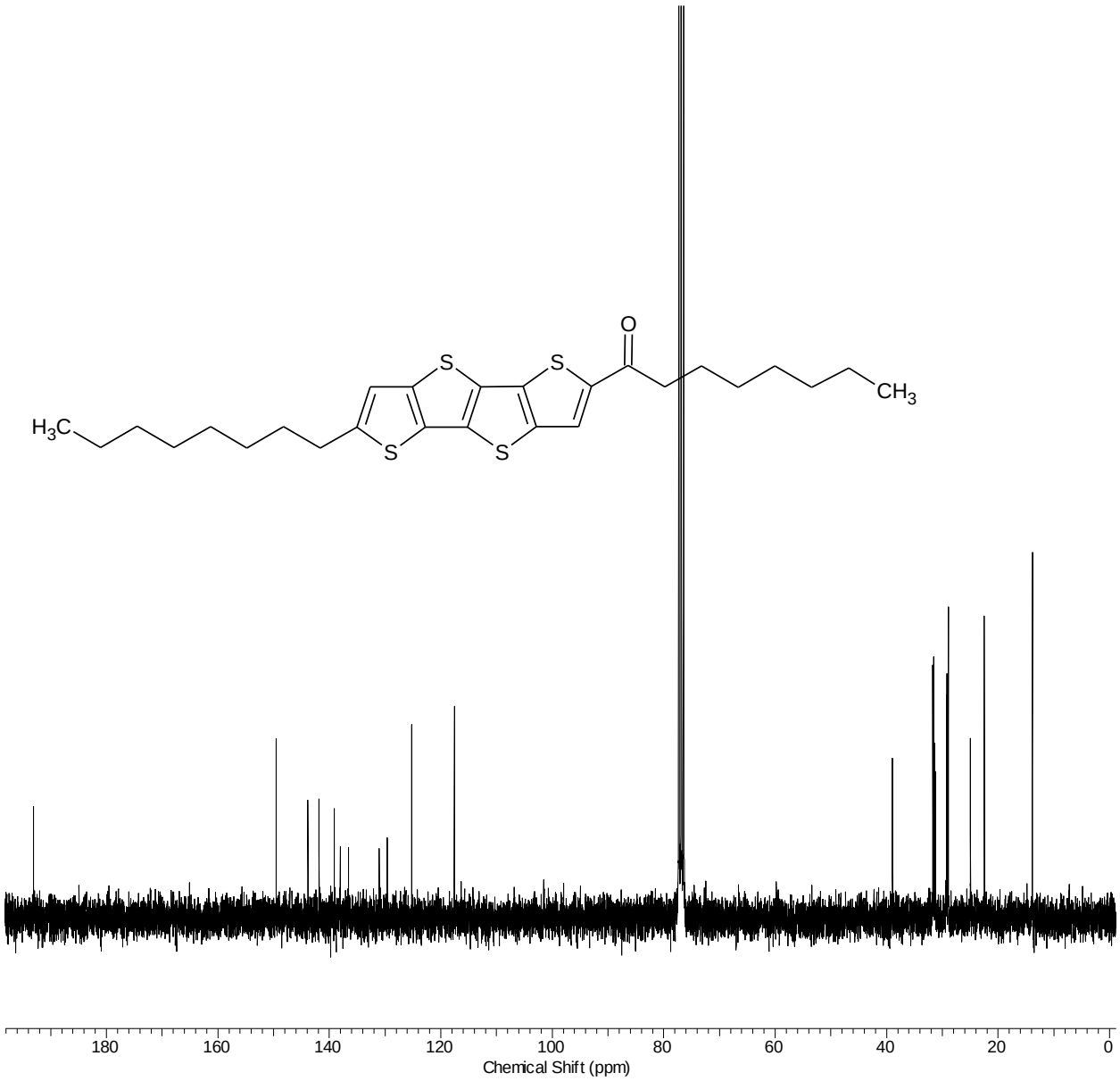


No.	(ppm)	(Hz)	Height
1	0.85	212.1	0.1977
2	0.87	217.9	0.5541
3	0.88	219.1	0.5699
4	0.90	224.3	0.2232
5	1.28	319.8	0.5819
6	1.35	337.2	0.2801
7	1.41	353.7	0.0952
8	1.71	427.5	0.0869
9	1.74	436.1	0.1254
10	1.78	444.0	0.1253
11	1.80	449.2	0.0640
12	2.89	721.8	0.2284
13	2.92	729.4	0.3333
14	2.95	736.7	0.2094
15	7.02	1754.8	0.3039
16	7.90	1975.8	0.5472

No.	Annotation	(ppm)
1	Water	1.55
2	Chloroform	7.25

No.	(ppm)	Value	Absolute Value
1	[0.83 .. 0.92]	6.167	4.80034e+7
2	[1.23 .. 1.44]	19.220	1.49609e+8
3	[1.70 .. 1.81]	3.671	2.85758e+7
4	[2.87 .. 2.95]	4.000	3.11355e+7
5	[6.97 .. 7.04]	1.065	8.28866e+6
6	[7.85 .. 7.94]	1.091	8.48954e+6

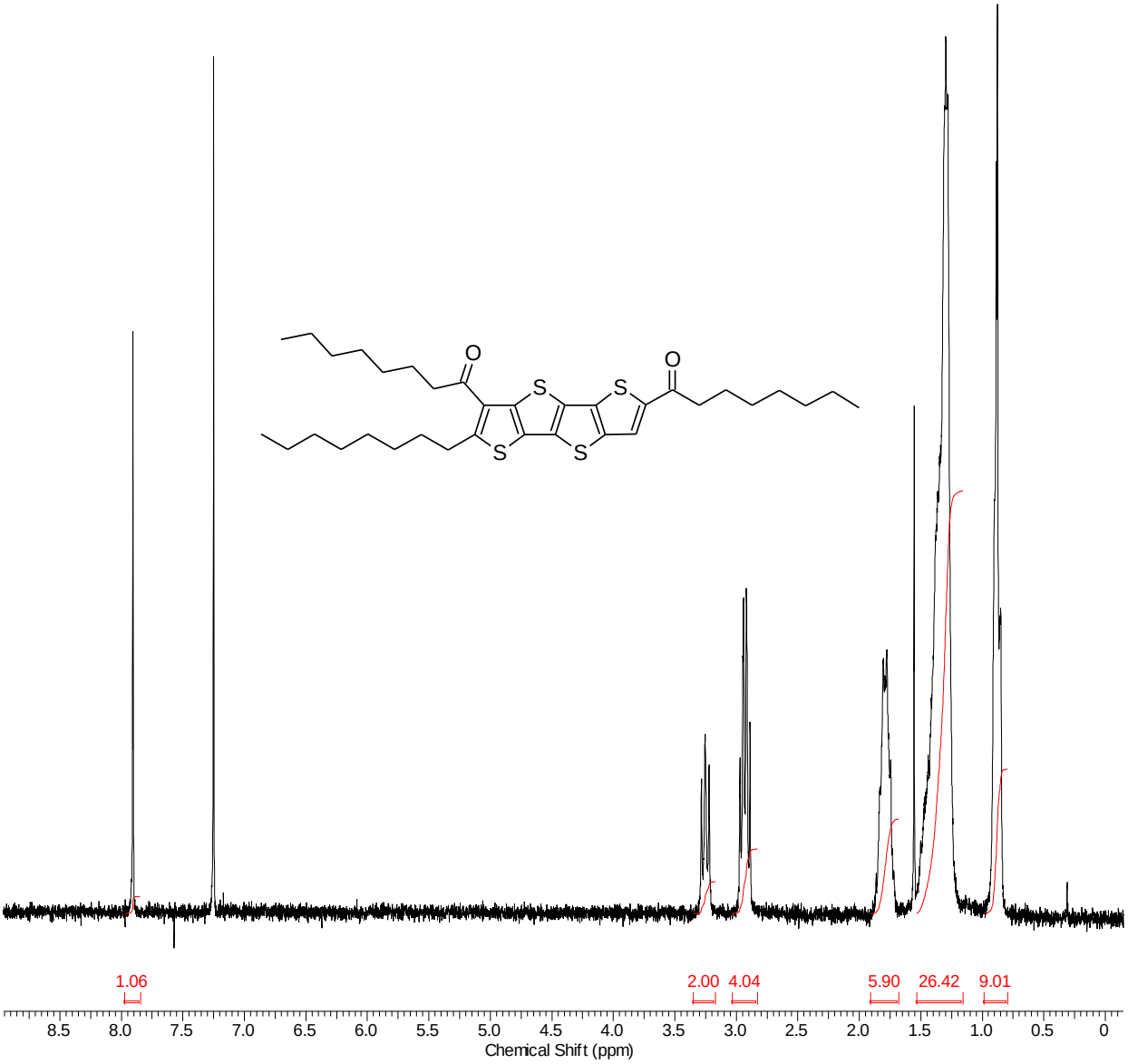
Figure S13. ^{1}H NMR spectrum of **C8-TTA-CO-C7**.



No.	(ppm)	(Hz)	Height
1	13.85	1045.3	0.1306
2	22.49	1697.1	0.1079
3	24.97	1884.6	0.0641
4	28.95	2184.8	0.1111
5	29.03	2191.4	0.0856
6	29.17	2201.4	0.0873
7	29.27	2209.1	0.0794
8	31.20	2355.1	0.0522
9	31.34	2365.6	0.0624
10	31.58	2383.3	0.0932
11	31.71	2393.8	0.0904
12	38.96	2940.5	0.0570

No.	(ppm)	(Hz)	Height
13	117.57	8874.0	0.0757
14	125.22	9451.2	0.0691
15	129.59	9781.2	0.0285
16	131.05	9891.3	0.0247
17	136.53	10305.4	0.0251
18	138.07	10420.9	0.0255
19	139.15	10502.7	0.0391
20	141.84	10705.6	0.0425
21	143.85	10857.1	0.0421
22	149.56	11288.4	0.0639
23	193.08	14573.0	0.0397

Figure S14. ^{13}C NMR spectrum of **C8-TTA-CO-C7**.

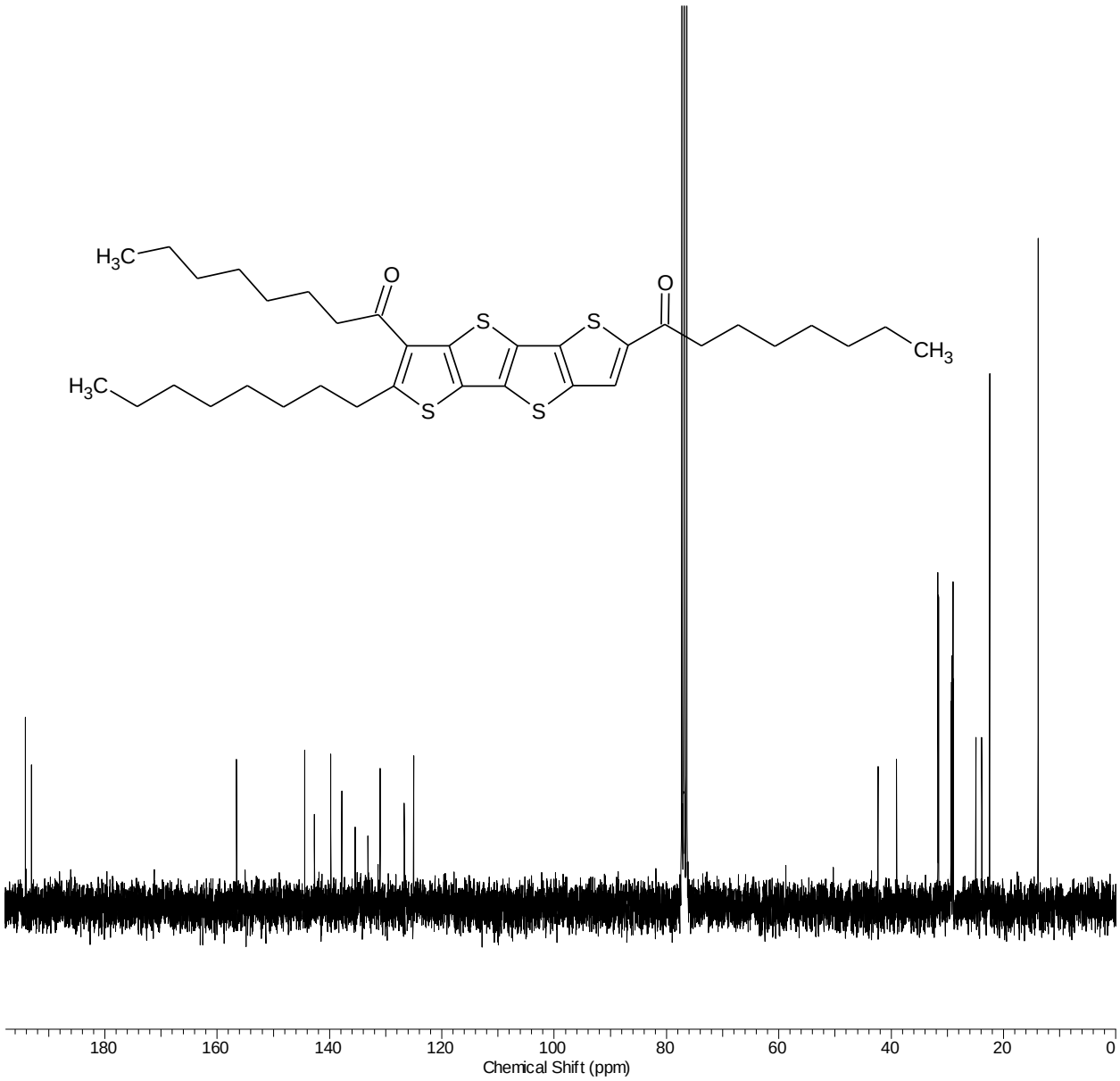


No.	(ppm)	(Hz)	Height
1	0.85	212.7	0.3358
2	0.88	219.7	1.0000
3	0.89	221.5	0.8271
4	1.28	320.4	0.9012
5	1.30	324.4	0.9643
6	1.47	368.0	0.1279
7	1.75	436.7	0.1687
8	1.78	444.3	0.2904
9	1.81	451.7	0.2808
10	1.83	457.8	0.1393
11	2.89	722.7	0.2107
12	2.92	730.3	0.3578
13	2.94	735.8	0.3471
14	2.97	743.1	0.1716
15	3.22	805.7	0.1639
16	3.25	813.6	0.1968
17	3.28	821.2	0.1480
18	7.91	1977.6	0.6403

No.	Annotation	(ppm)
1	Water	1.55
2	Chloform	7.25

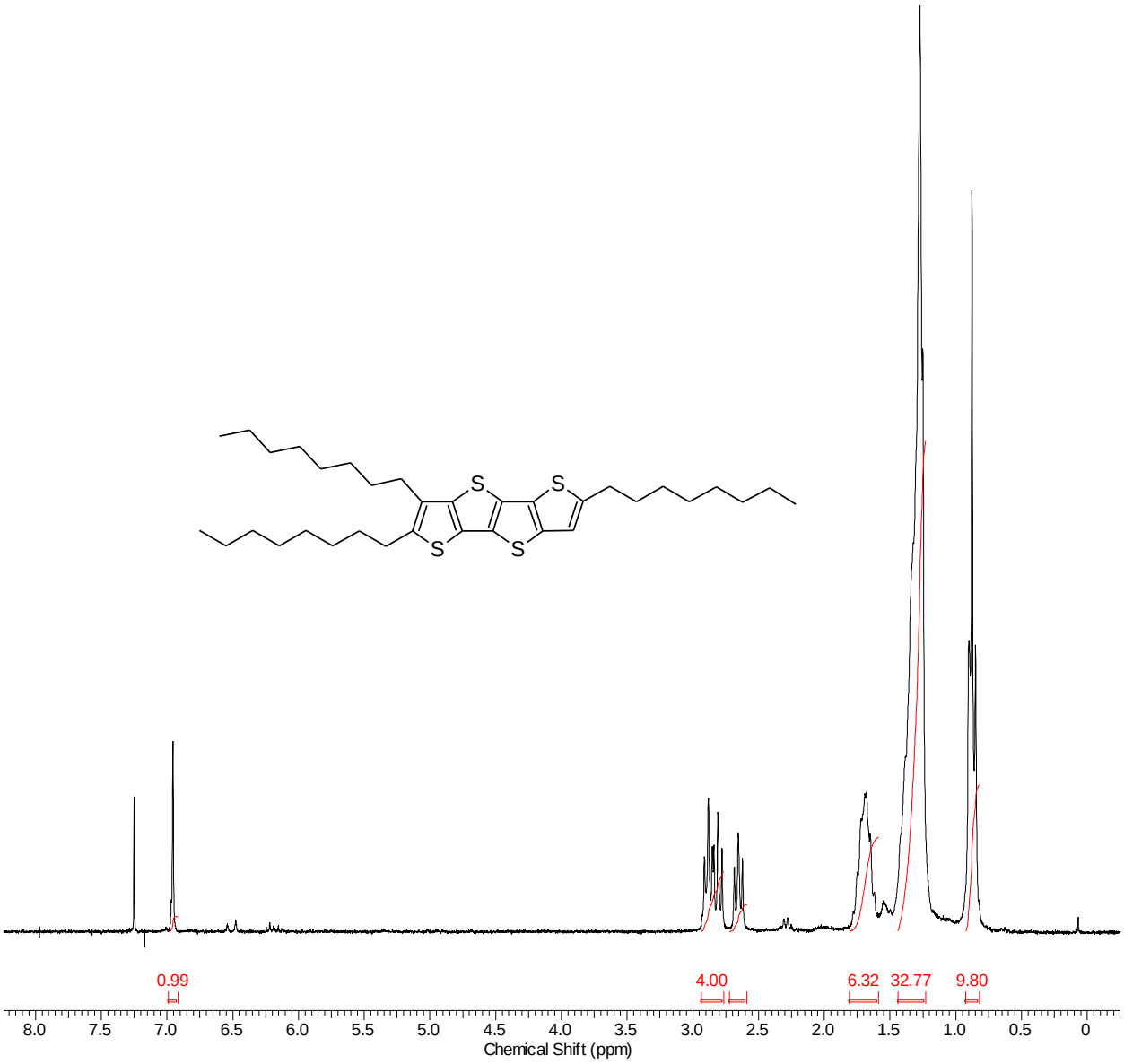
No.	(ppm)	Value	Absolute Value
1	[0.79 .. 0.99]	9.008	7.99432e+7
2	[1.16 .. 1.53]	26.425	2.34507e+8
3	[1.68 .. 1.91]	5.901	5.23662e+7
4	[2.83 .. 3.03]	4.037	3.58279e+7
5	[3.17 .. 3.35]	2.000	1.77491e+7
6	[7.85 .. 7.97]	1.057	9.38478e+6

Figure S15. ^{1}H NMR spectrum of **C8-TTA-(CO-C7)$_2$**.



No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	13.84	1044.8	0.2072	14	42.34	3195.4	0.0433
2	22.48	1696.6	0.1652	15	125.04	9437.9	0.0465
3	23.86	1801.1	0.0523	16	126.68	9561.7	0.0319
4	24.92	1881.2	0.0523	17	131.02	9889.0	0.0426
5	28.94	2184.2	0.0705	18	133.14	10048.8	0.0218
6	29.03	2190.9	0.1006	19	135.43	10221.9	0.0244
7	29.18	2202.5	0.0763	20	137.84	10403.8	0.0356
8	29.21	2204.7	0.0776	21	139.77	10549.7	0.0471
9	29.25	2208.0	0.0695	22	142.67	10768.7	0.0284
10	29.34	2214.6	0.0633	23	144.42	10900.8	0.0483
11	31.59	2384.4	0.0964	24	156.55	11816.3	0.0454
12	31.69	2392.1	0.1034	25	193.06	14571.9	0.0438
13	39.02	2945.0	0.0456	26	194.16	14654.8	0.0584

Figure S16. ^{13}C NMR spectrum of **C8-TTA-(CO-C7)$_2$**.



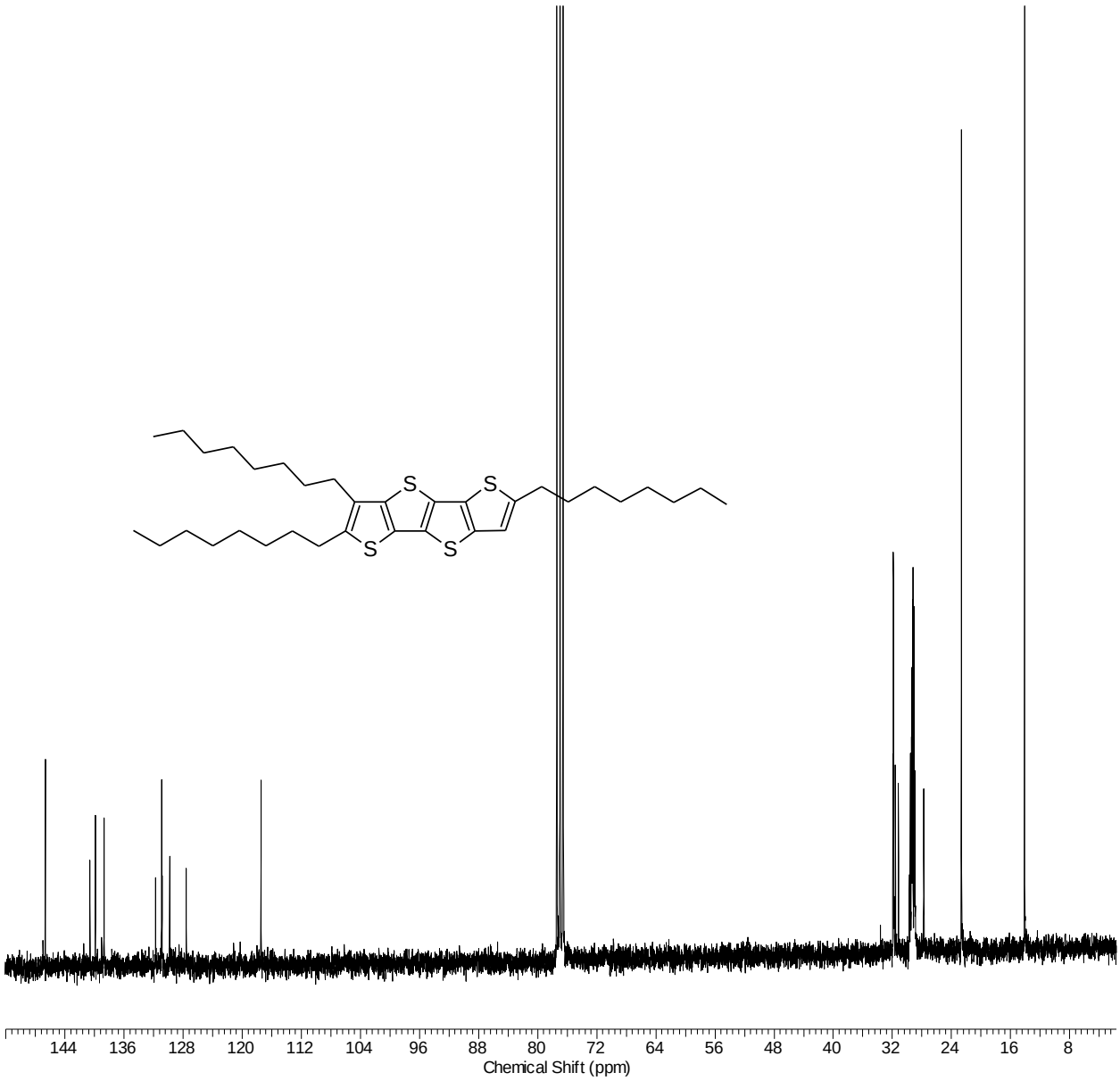
No.	(ppm)	(Hz)	Height
1	0.85	212.7	0.3095
2	0.88	219.4	0.8007
3	0.90	224.9	0.3145
4	1.25	312.8	0.6296
5	1.27	318.6	1.0000
6	1.32	331.1	0.4200
7	1.42	355.2	0.1037
8	1.62	405.0	0.0424
9	1.65	413.2	0.1060
10	1.68	420.2	0.1504
11	1.72	430.3	0.1217

No.	(ppm)	(Hz)	Height
12	1.75	437.9	0.0643
13	2.62	656.1	0.0792
14	2.65	664.1	0.1070
15	2.68	671.4	0.0696
16	2.78	695.2	0.0903
17	2.81	702.8	0.1291
18	2.84	710.5	0.0935
19	2.85	713.2	0.0920
20	2.88	720.8	0.1441
21	2.91	728.5	0.0807
22	6.96	1739.9	0.2056

No.	Annotation	(ppm)
1	9	0.88
2	30	1.27
3	Chloroform	7.25

No.	(ppm)	Value	Absolute Value
1	[0.82 .. 0.92]	9.795	6.00002e+7
2	[1.23 .. 1.44]	32.773	2.00748e+8
3	[1.59 .. 1.81]	6.318	3.86995e+7
4	[2.59 .. 2.72]	1.797	1.10077e+7
5	[2.76 .. 2.93]	4.000	2.45018e+7
6	[6.91 .. 6.99]	0.992	6.07821e+6

Figure S17. ^{1}H NMR spectrum of **C8-TTA-(C8)$_2$**.



No.	(ppm)	(Hz)	Height
1	14.11	1065.2	0.5961
2	22.66	1710.4	0.4984
3	27.76	2095.2	0.0825
4	28.95	2185.3	0.0940
5	29.06	2193.0	0.1976
6	29.22	2205.2	0.2223
7	29.33	2213.5	0.1591
8	29.39	2218.5	0.1152
9	29.44	2221.8	0.1042
10	29.57	2231.7	0.1050
11	29.70	2241.7	0.0283
12	31.17	2352.8	0.0859
13	31.58	2383.8	0.0978

No.	(ppm)	(Hz)	Height
14	31.87	2405.3	0.2320
15	31.92	2409.2	0.1044
16	117.46	8865.6	0.0881
17	127.57	9628.6	0.0324
18	129.81	9797.8	0.0400
19	130.86	9877.4	0.0277
20	130.92	9881.8	0.0884
21	131.74	9943.7	0.0266
22	138.71	10469.5	0.0643
23	139.90	10559.6	0.0656
24	140.61	10613.3	0.0374
25	146.67	11070.5	0.1013

Figure S18. ^{13}C NMR spectrum of **C8-TTA-(C8)$_2$**.

4. Differential scanning calorimetry (DSC) data

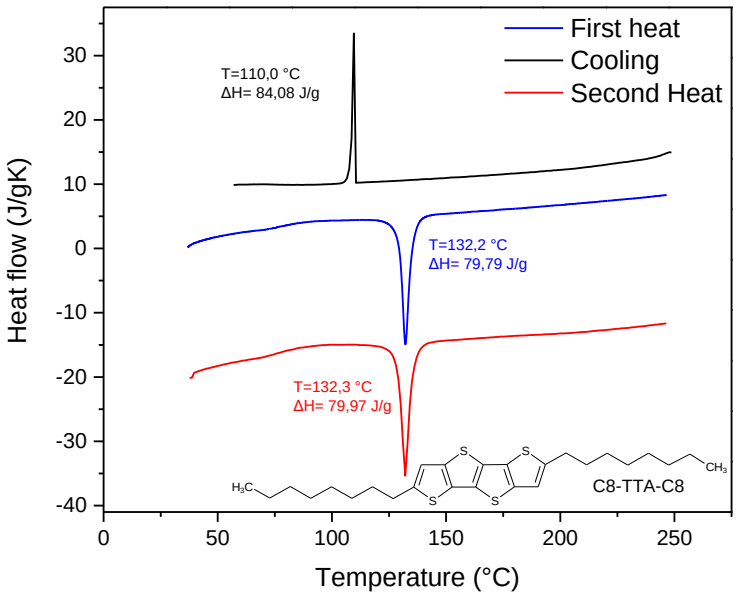


Figure S19. The DSC curves of **C8-TTA-C8** - first heating (blue), subsequent cooling (black) and second heating scans (red).

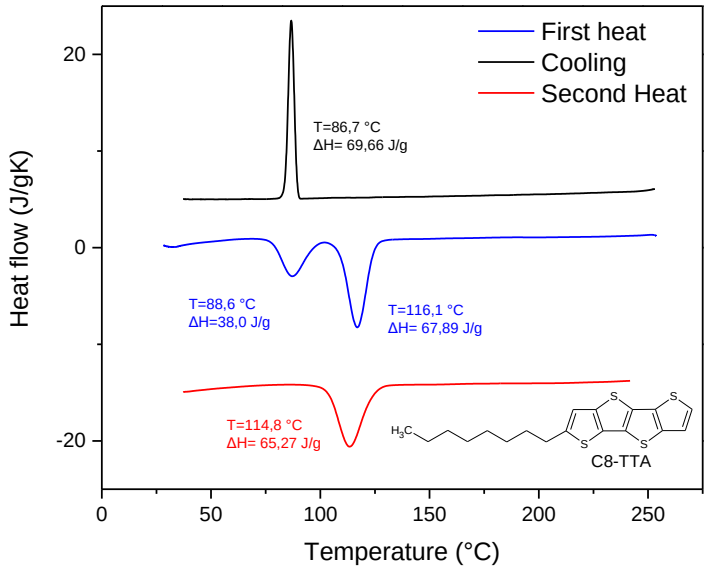


Figure S20. The DSC curves of **C8-TTA** - first heating (blue), subsequent cooling (black) and second heating scans (red).

5. Thermogravimetric analysis (TGA) data

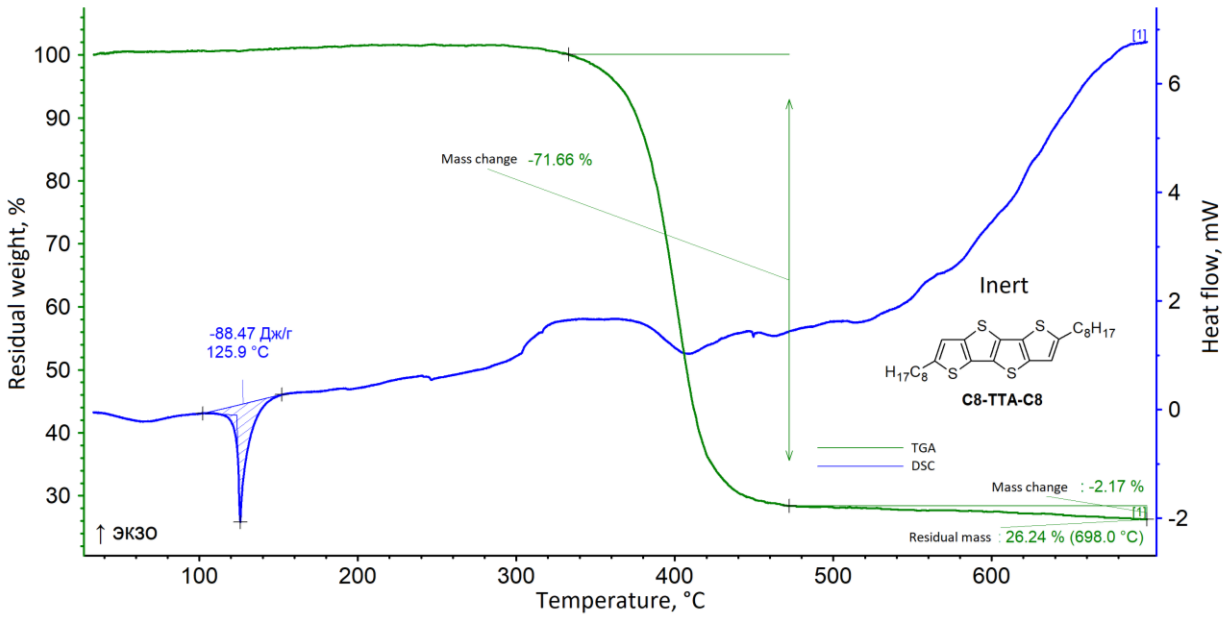


Figure S21. Thermogravimetric analysis (TGA) curves of **C8-TTA-C8** in inert.

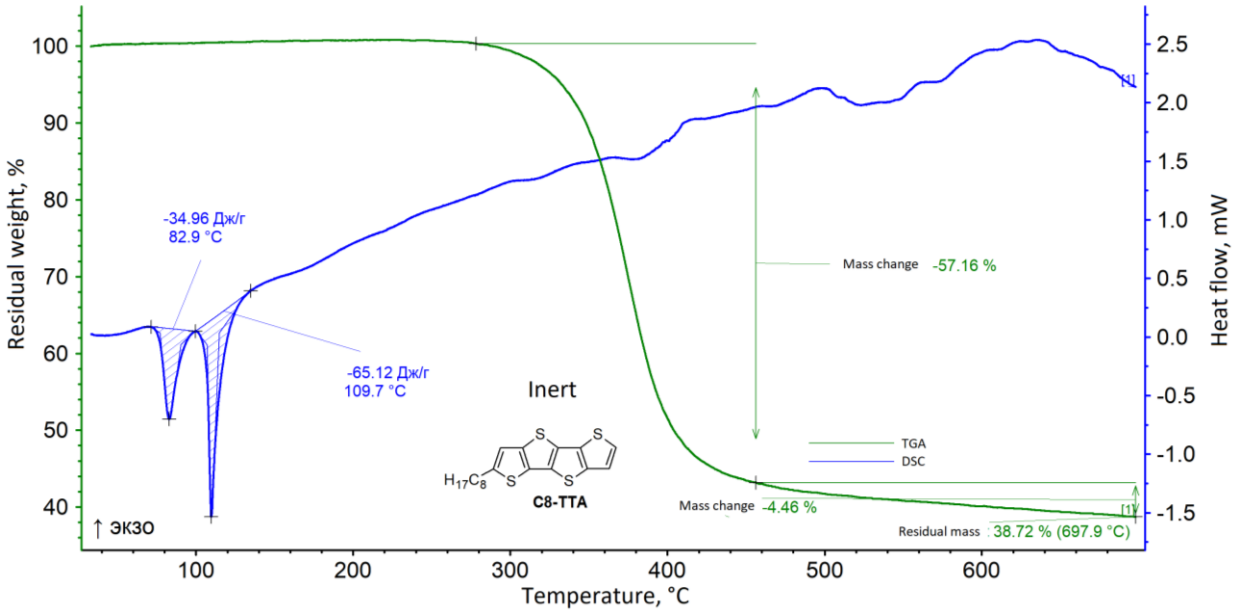


Figure S22. Thermogravimetric analysis (TGA) curves of **C8-TTA** in inert.

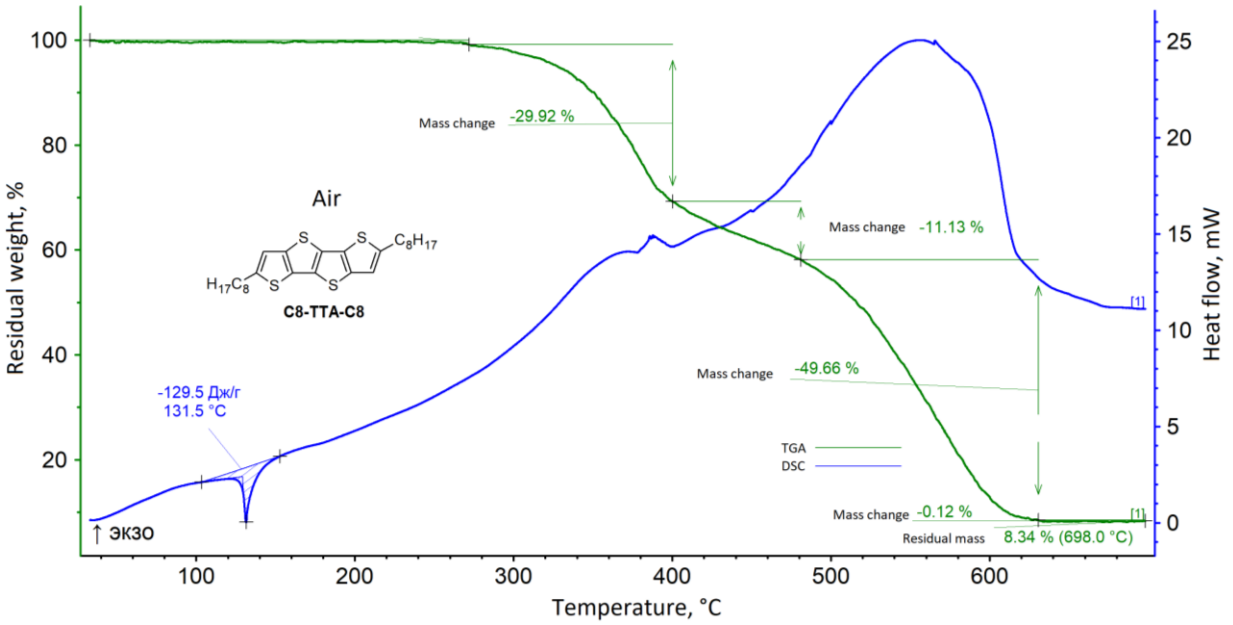


Figure S23. Thermogravimetric analysis (TGA) curves of **C8-TTA-C8** in air.

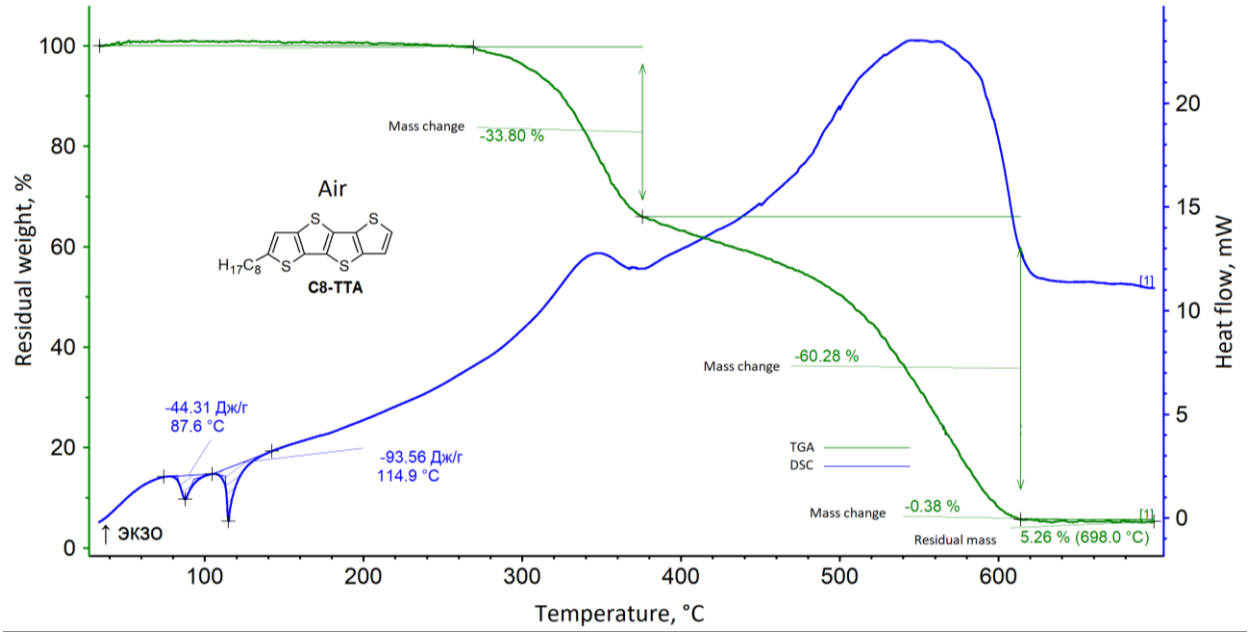


Figure 24. Thermogravimetric analysis (TGA) curves of **C8-TTA** in air.

6. XRD data and discussion

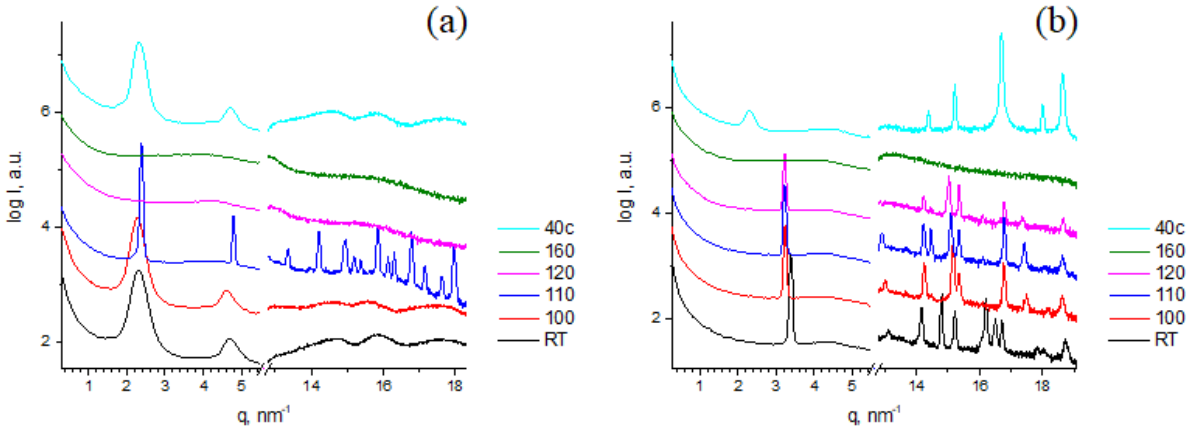


Figure S25. Small- and wide-angle diffraction patterns for **C8-TTA** (a), and **C8-TTA-C8** (b) at different temperatures: room temperature, 100°C, 110°C, 120°C, 160°C and cooling down to 40°C. Curves shifted for clarity.

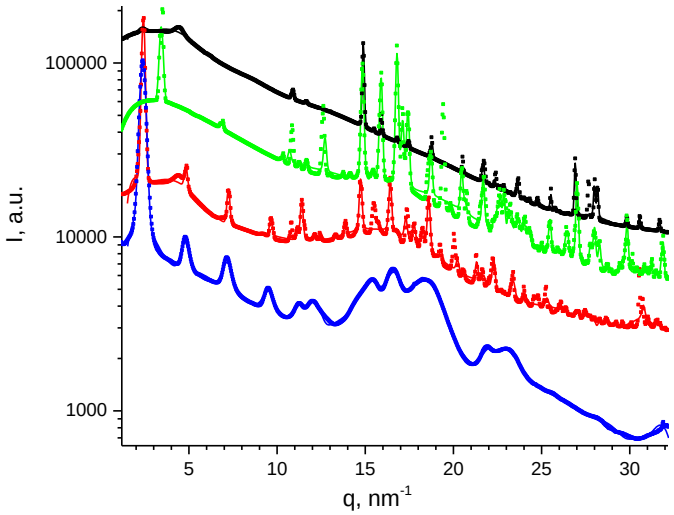


Figure S26. WAXS patterns for as-received and annealed **C8-TTA** (blue, red), and **C8-TTA-C8** (green, black). Dots are the experimental values; lines represent Pawley refined patterns for each crystal cell. Cell parameters given in Table S1.

Table S1. Crystal cell parameters of **C8-TTA-C8**, and **C8-TTA** in compere to **C8-BTBT-C8** and **C8-BTBT**. Data on BTBT derivatives were described earlier [3].

Compound	System	c	a	b	b	Extinction Class
C8-TTA-C8	Monoclinic	18.3	5.9	5.7	91.7	P2
C8-BTBT-C8	Monoclinic	29.2	5.9	7.88	92.4	P21/a
C8-TTA	Orthorhombic	26.2	5.6	4.8	90	Pmma
C8-BTBT	Monoclinic	40.6	5.8	8.3	90.6	P21/a

7. Polarization optical microscopy (POM)

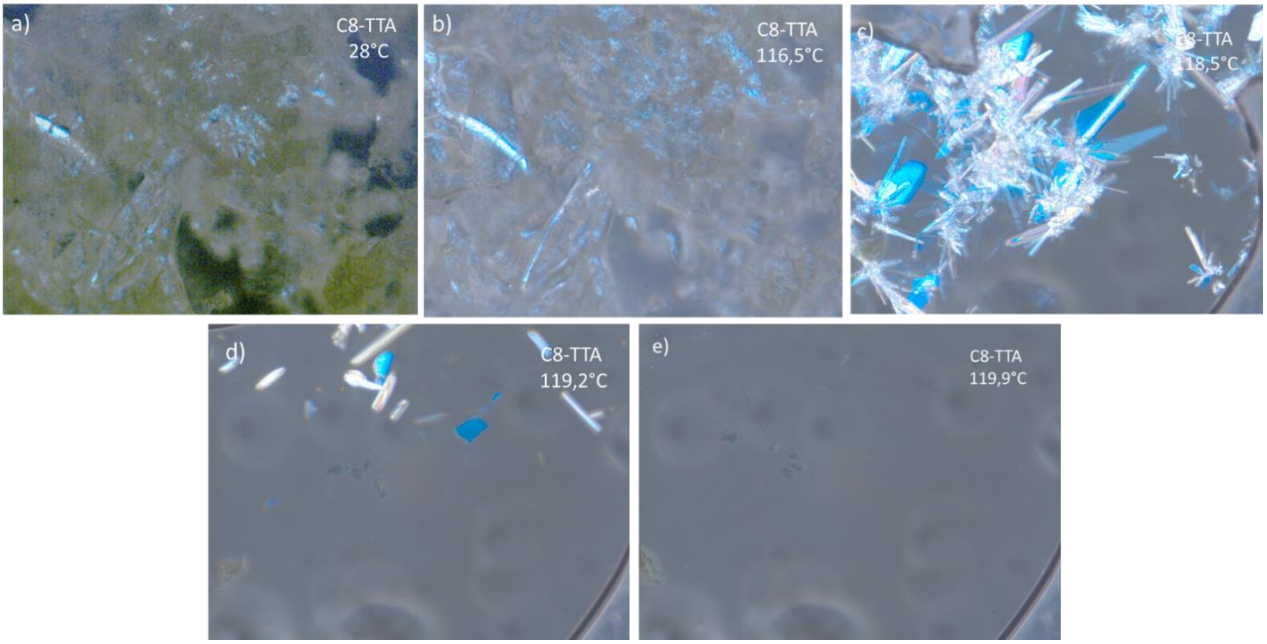


Figure S27. Microphotos of **C8-TTA** made in optical microscope in cross-polarizers at different temperatures.

8. Spectral-luminescence properties

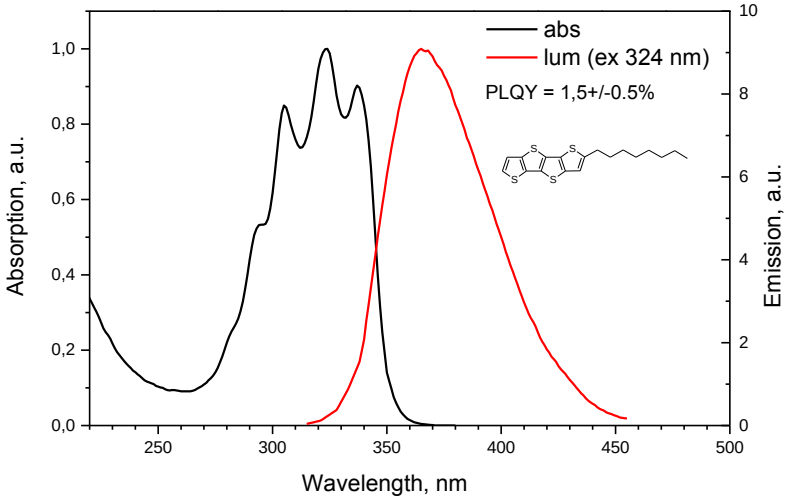


Fig. S28. Absorption (black) and photoluminescence (red) spectra of the C8-TTA in diluted THF solutions.

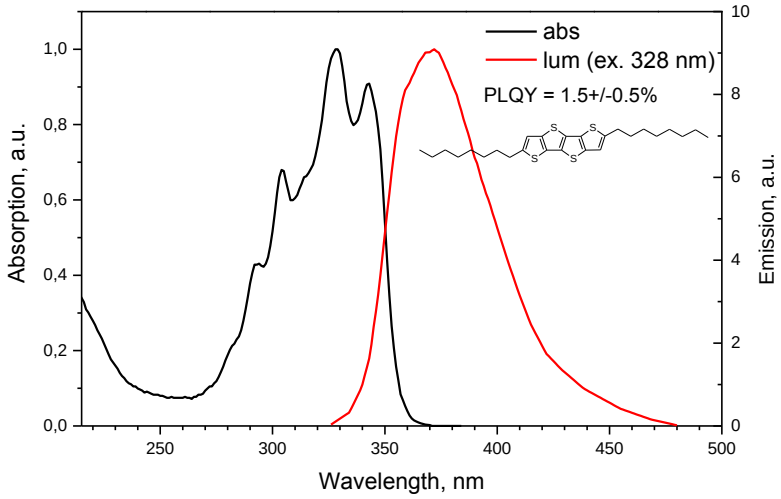


Fig. S29. Absorption (black) and photoluminescence (red) spectra of the C8-TTA in diluted THF solutions.

9. Cyclic voltammetry (CV) data

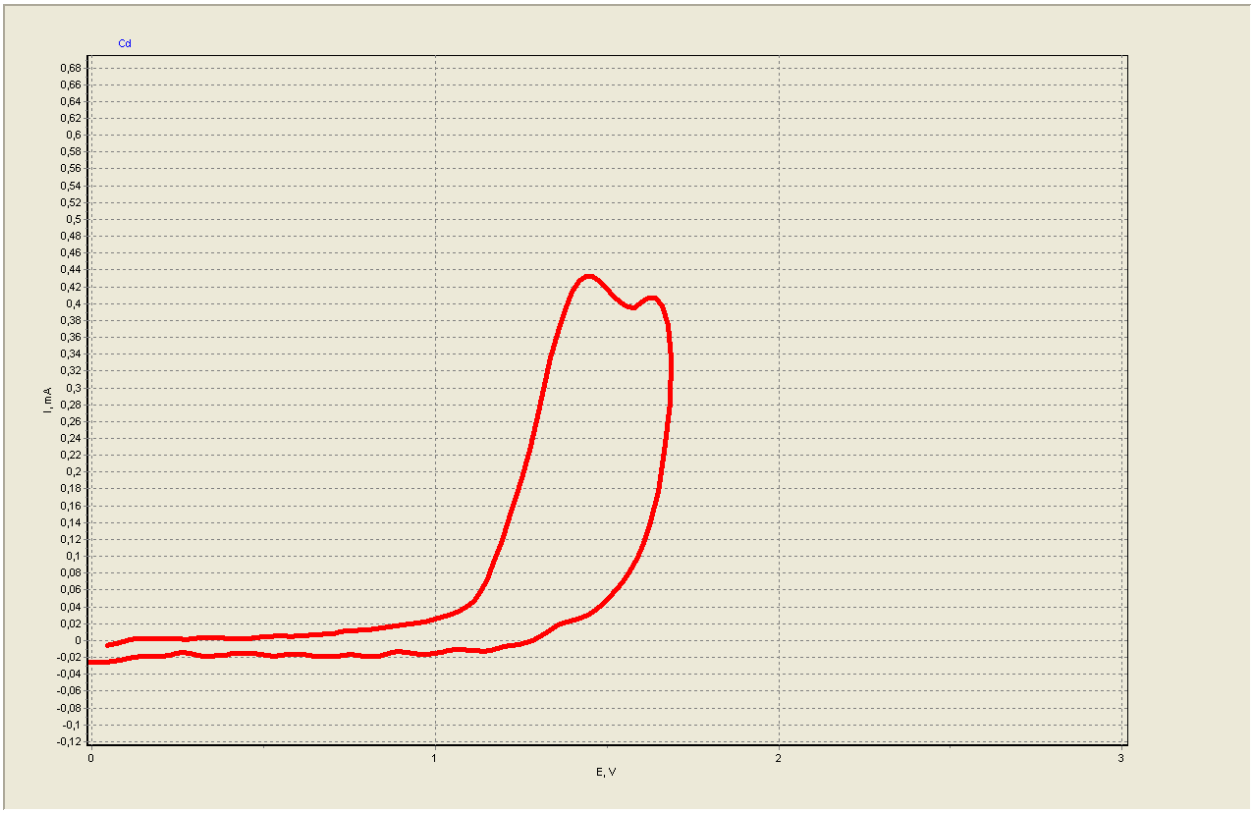


Figure S30. Electrochemical oxidation curve of **C8-TTA-C8** in thin film.

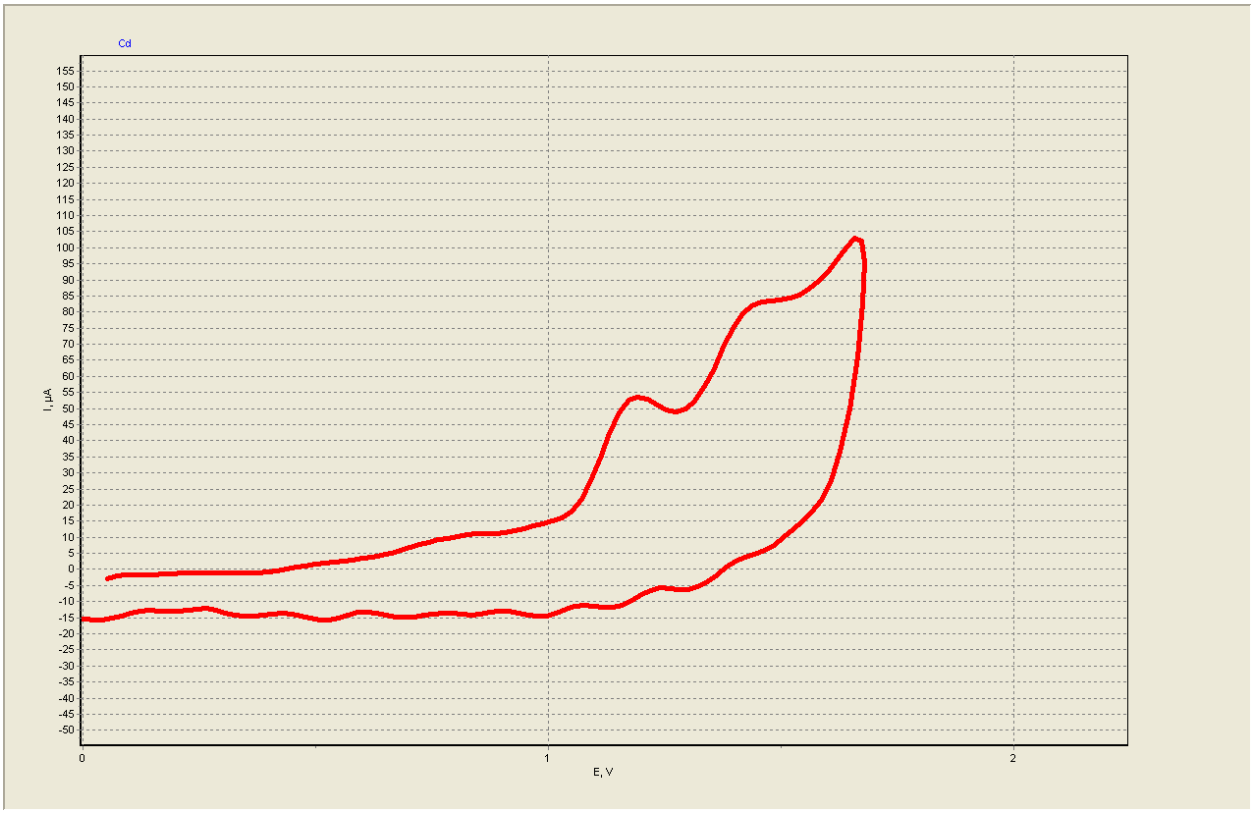


Figure S31. Electrochemical oxidation curve of **C8-TTA-C8** in solution.

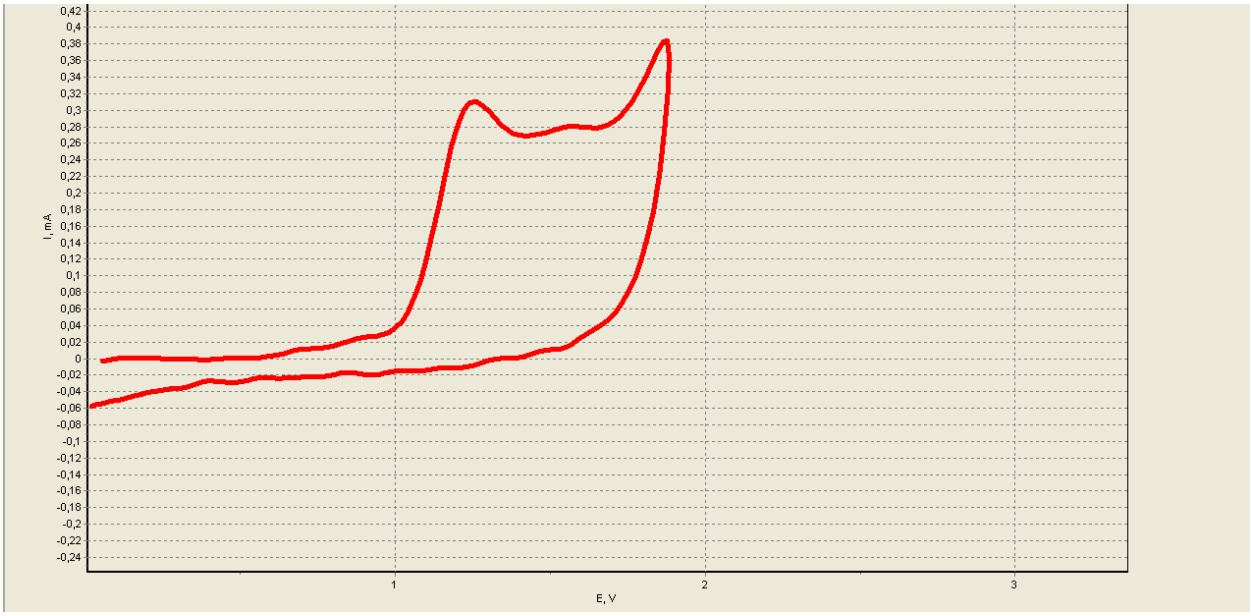


Figure S32. Electrochemical oxidation curve of **C8-TTA** in thin film.

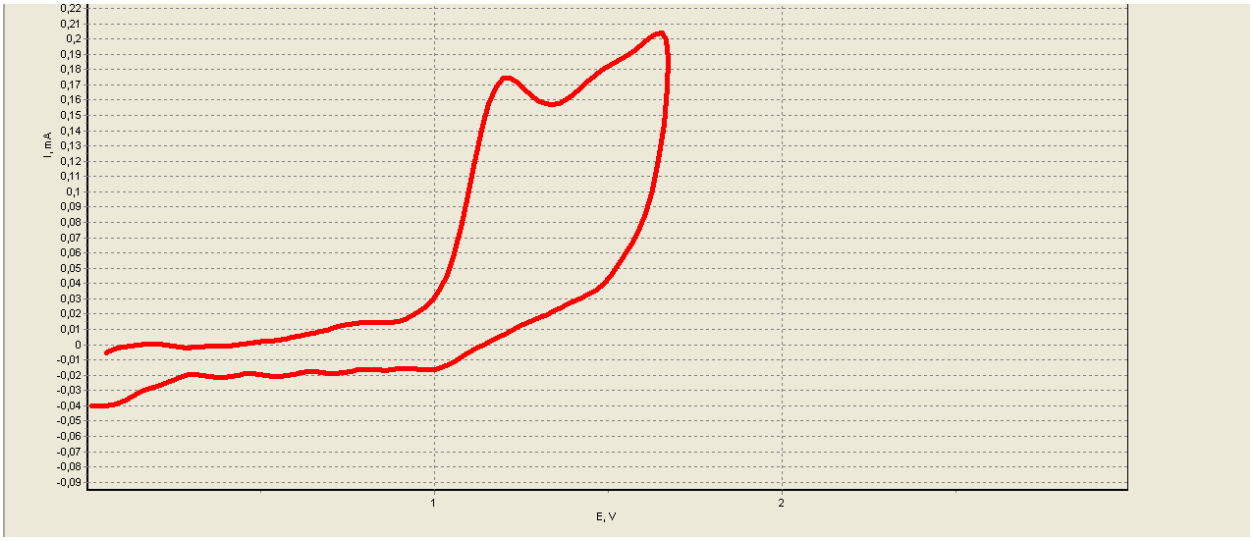


Figure S33. Electrochemical oxidation curve of **C8-TTA** in solution.

Table S2. The study of electrochemical properties of **C8-TTA** and **C8-TTA-C8** (CV – cyclic voltammetry data, φ_{ox} – standard oxidation potential in solution and film).

	CV	
	φ_{ox}^{sol} (HOMO) (V)/(eV)	φ_{ox}^{film} (HOMO) (V)/(eV)
C8-TTA-C8	1.10/-5.50	1.36/-5.76
C8-TTA	1.13/-5.53	1.17/-5.57

10. Morphology and electrical characteristics of the OFETs

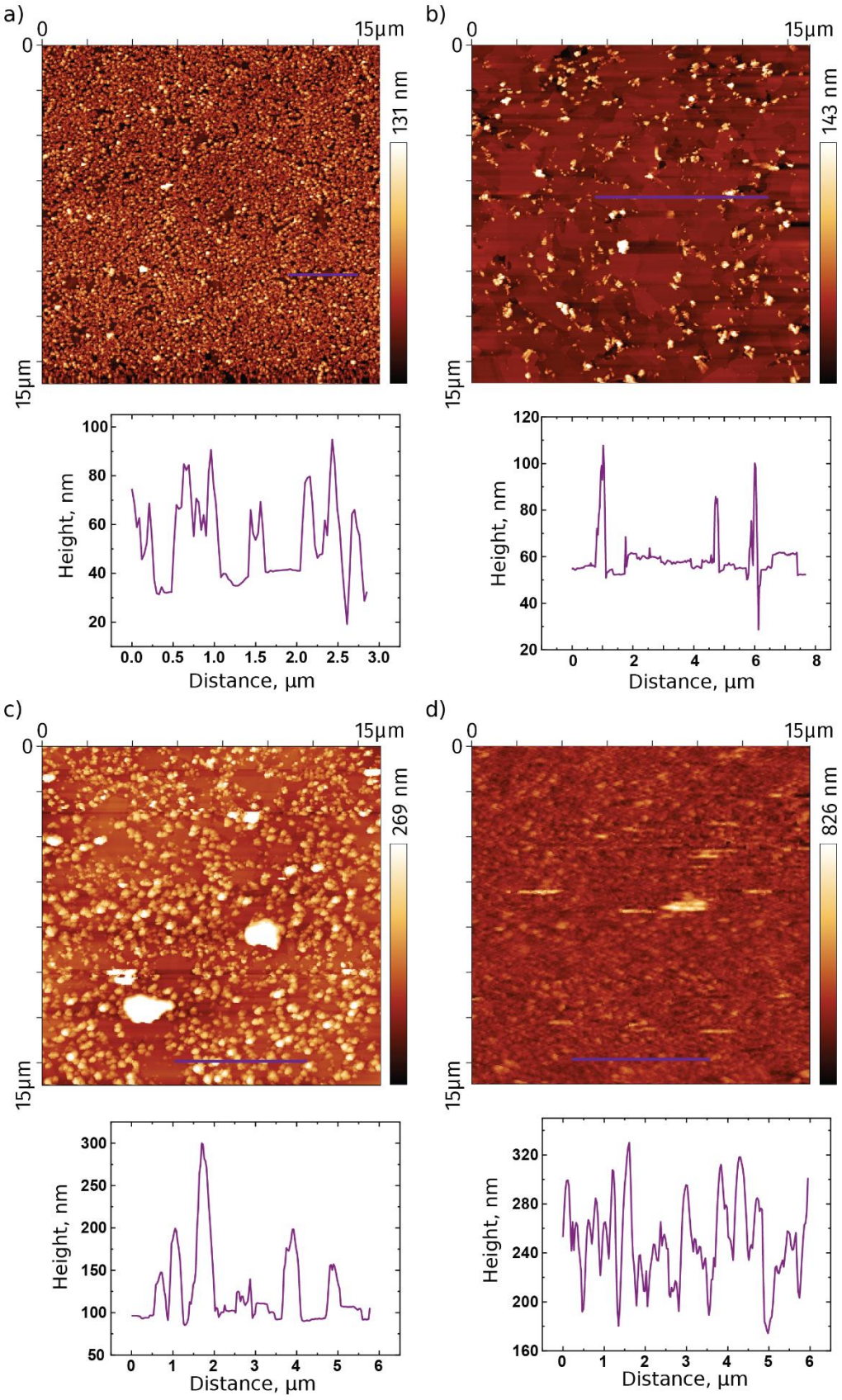


Figure S34. Typical AFM images and corresponding cross-sections of **C8-TTA** layers vacuum deposited on (a) untreated, (b) ODMS-treated, (c) PMMA-coated and (d) PS-coated silicon substrates.

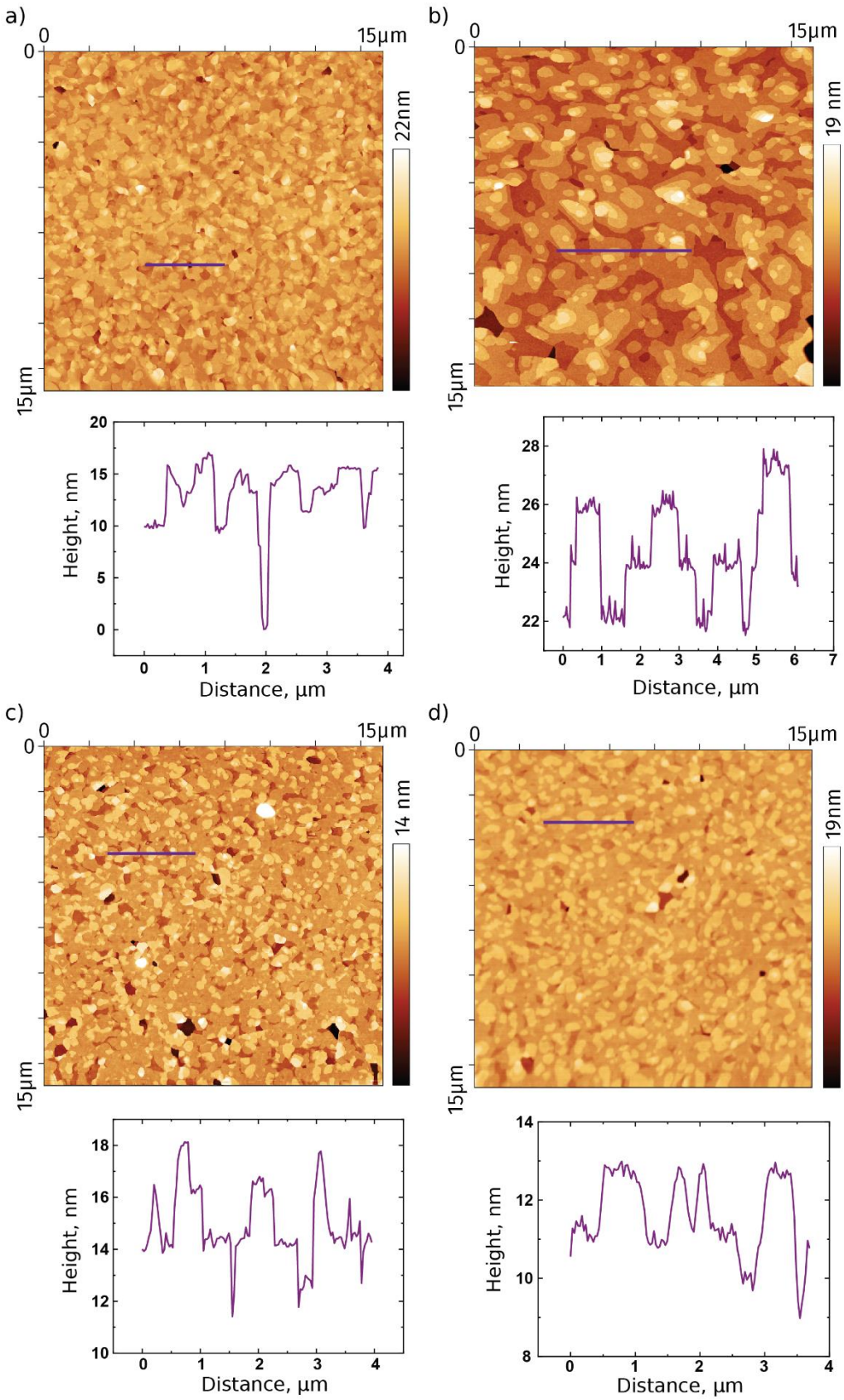


Figure S35. Typical AFM images and corresponding cross-sections of **C8-TTA-C8** layers vacuum deposited on (a) untreated, (b) ODMS-treated, (c) PMMA-coated and (d) PS-coated silicon substrates.

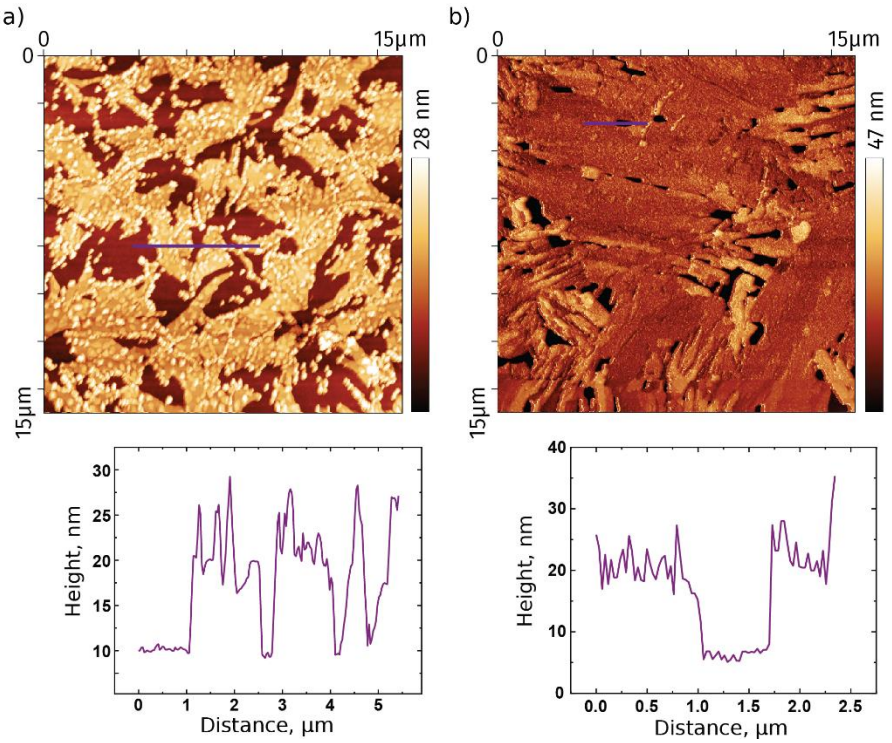


Figure S36. Typical AFM images and corresponding cross-sections of (a) **C8-TTA** and (b) **C8-TTA-C8** layers obtained by spin-coating on untreated silicon substrates.

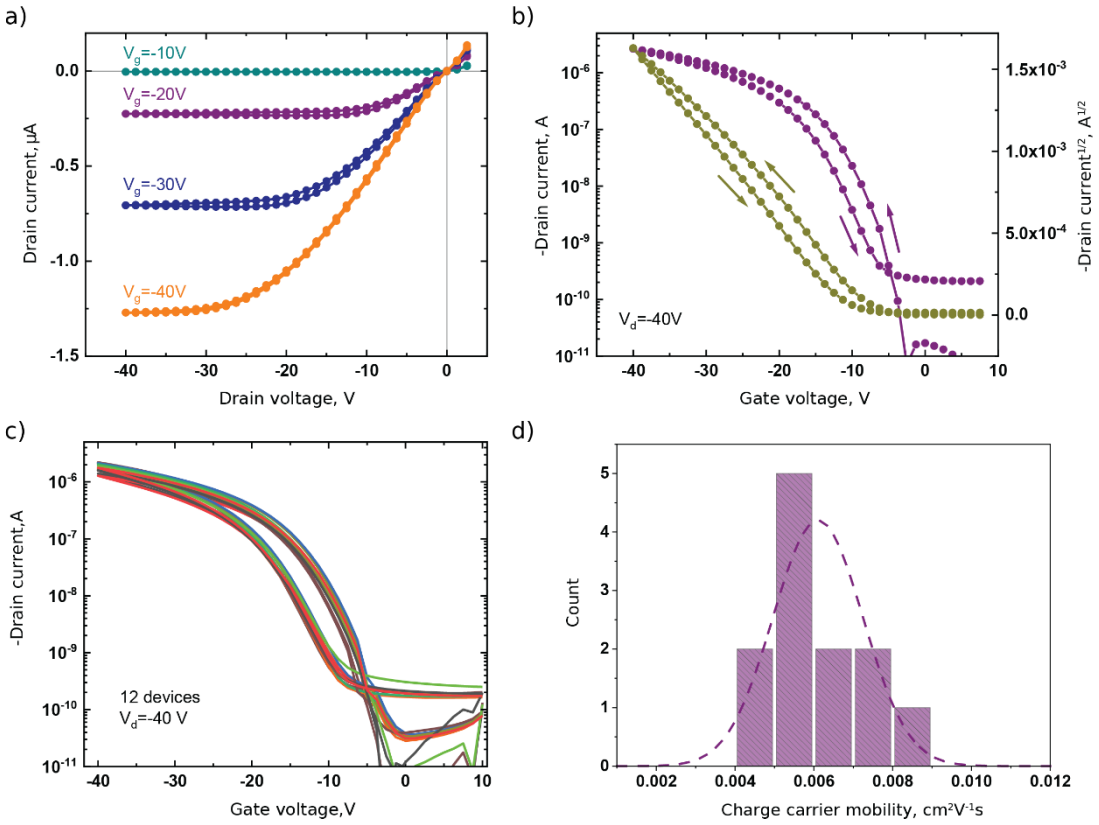


Figure S37. Typical output (a) and transfer (b) characteristics, set of the transfer curves for one substrate (c) and charge carrier distribution (d) for OFETs based on vacuum deposited **C8-TTA** fabricated on untreated silicon substrate. The substrate has 20 pairs of source and drain electrodes

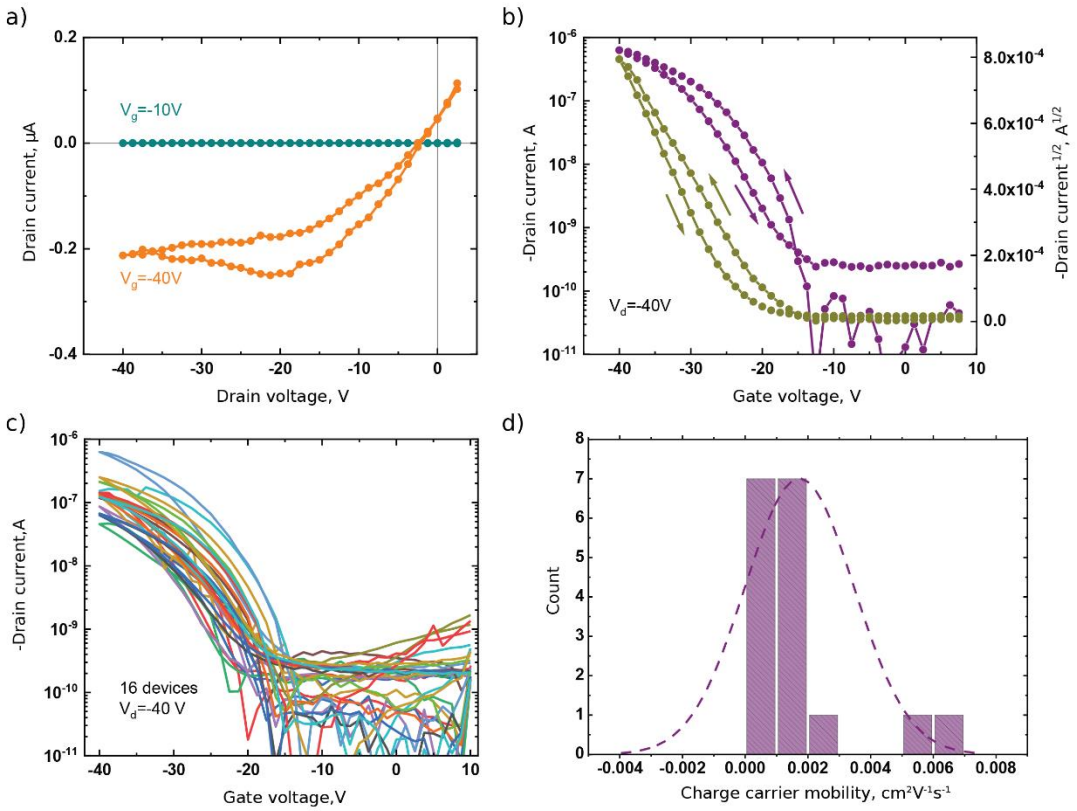


Figure S38. Typical output (a) and transfer (b) characteristics, set of the transfer curves for one substrate (c) and charge carrier distribution (d) for OFETs based on vacuum deposited **C8-TTA** fabricated on PMMA-covered silicon substrate. The substrate has 20 pairs of source and drain electrodes

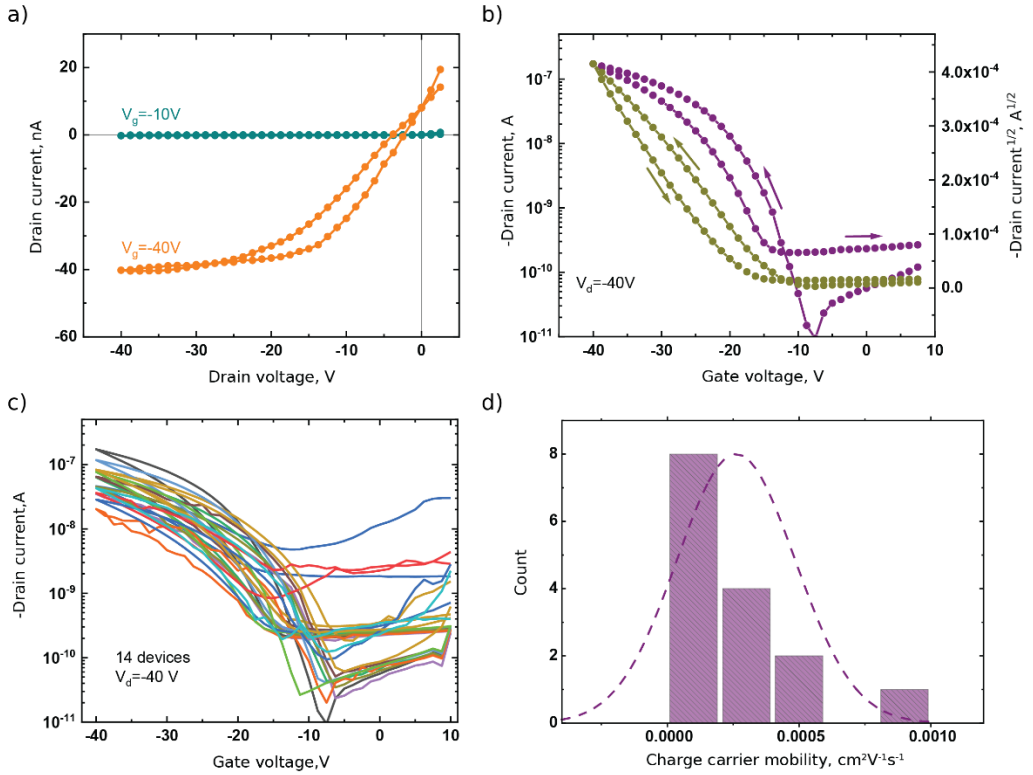


Figure S39. Typical output (a) and transfer (b) characteristics, set of the transfer curves for one substrate (c) and charge carrier distribution (d) for OFETs based on vacuum deposited **C8-TTA** fabricated on PS-covered silicon substrate. The substrate has 20 pairs of source and drain electrodes

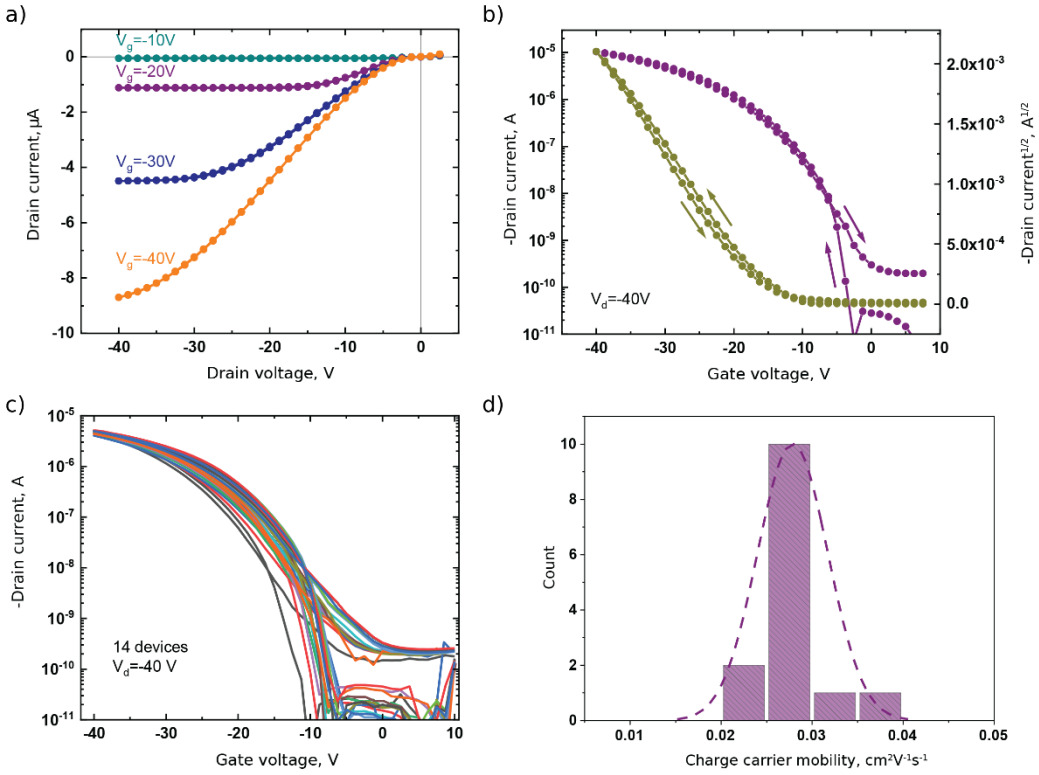


Figure S40. Typical output (a) and transfer (b) characteristics, set of the transfer curves for one substrate (c) and charge carrier distribution (d) for OFETs based on vacuum deposited **C8-TTA-C8** fabricated on untreated silicon substrate. The substrate has 20 pairs of source and drain electrodes

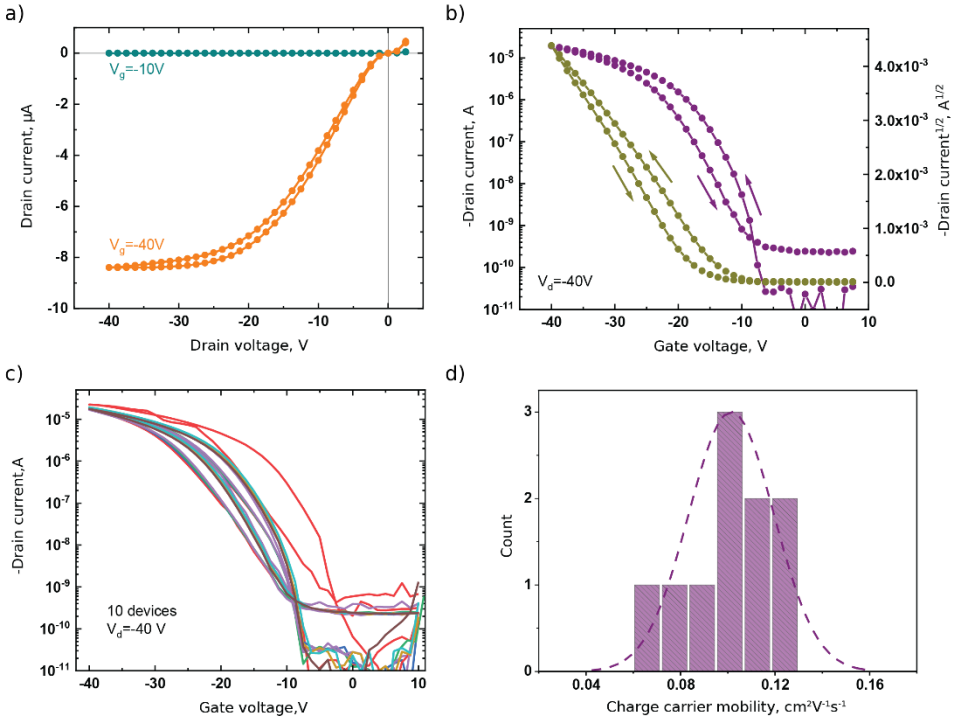


Figure S41. Typical output (a) and transfer (b) characteristics, set of the transfer curves for one substrate (c) and charge carrier distribution (d) for OFETs based on vacuum deposited **C8-TTA-C8** fabricated on ODMS-treated silicon substrate. The substrate has 20 pairs of source and drain electrodes

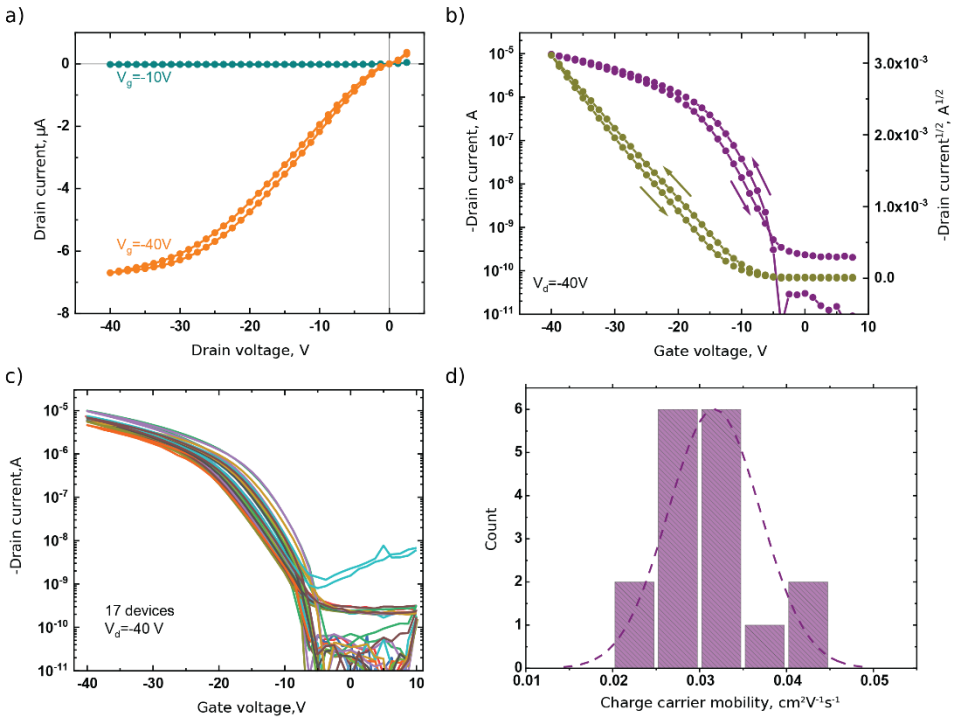


Figure S42. Typical output (a) and transfer (b) characteristics, set of the transfer curves for one substrate (c) and charge carrier distribution (d) for OFETs based on vacuum deposited **C8-TTA-C8** fabricated on PMMA-covered silicon substrate. The substrate has 20 pairs of source and drain electrodes

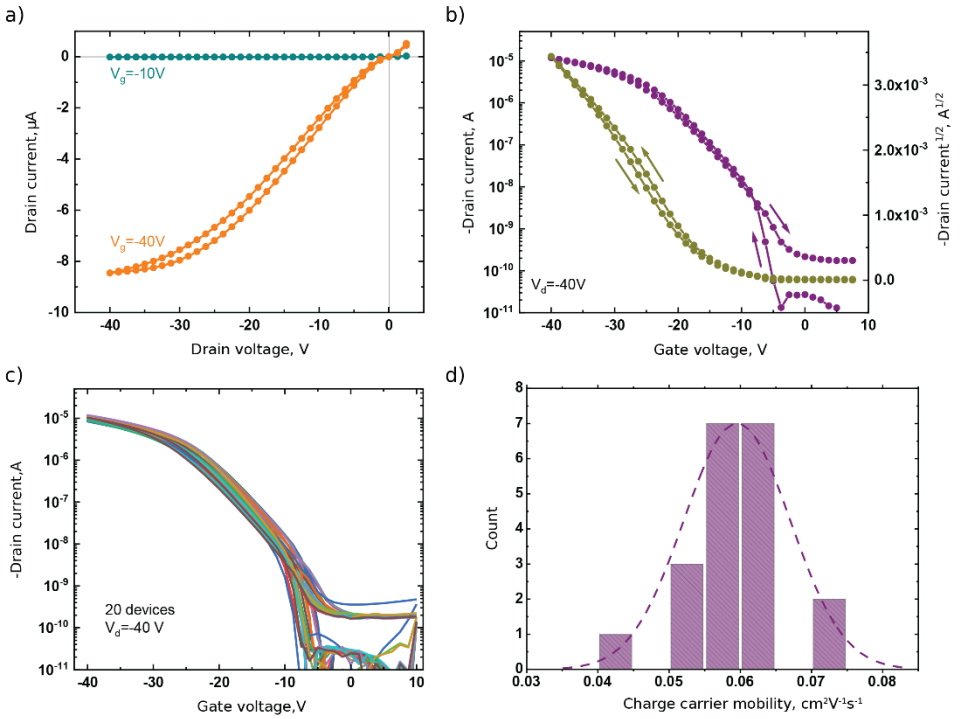


Figure S43. Typical output (a) and transfer (b) characteristics, set of the transfer curves for one substrate (c) and charge carrier distribution (d) for OFETs based on vacuum deposited **C8-TTA-C8** fabricated on PS-covered silicon substrate. The substrate has 20 pairs of source and drain electrodes

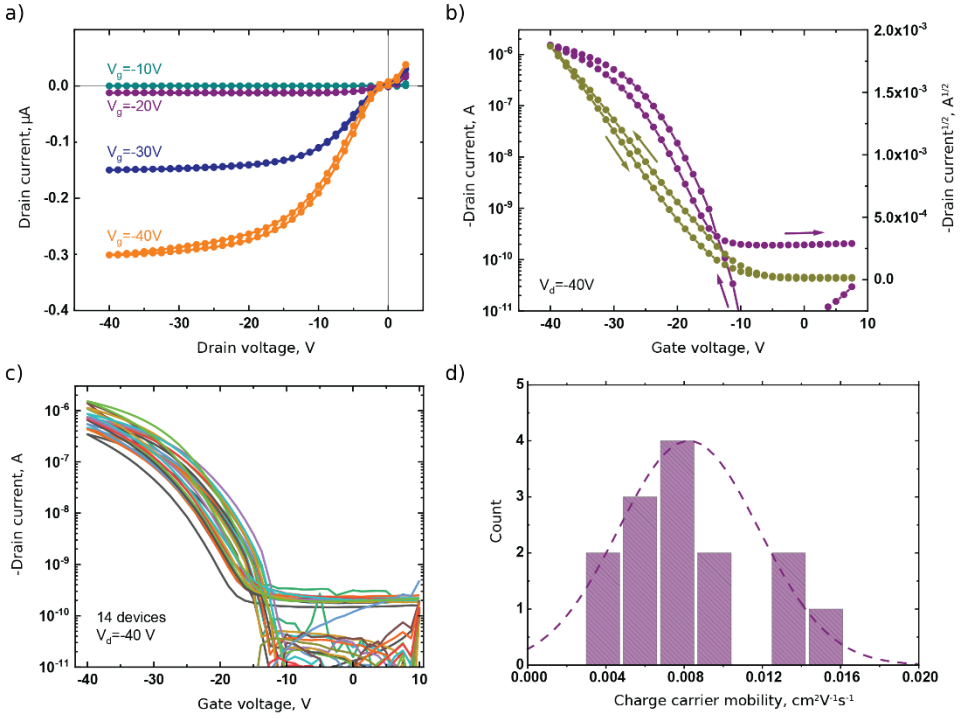


Figure S44. Typical output (a) and transfer (b) characteristics, set of the transfer curves for one substrate (c) and charge carrier distribution (d) for OFETs based on spin-coated **C8-TTA-C8** fabricated on untreated silicon substrate. The substrate has 20 pairs of source and drain electrodes

11. References

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2. G.A. Crosby, J.N. Demas. Measurement of photoluminescence quantum yields. Review. *J Phys Chem* 1971, **75**, 991–1024.
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