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SUPPORTING INFORMATION

Helical thienothiophene (TT) and benzothieno-benzothiophene (BTBT) derivatives: synthesis, structural characterization and semiconducting properties

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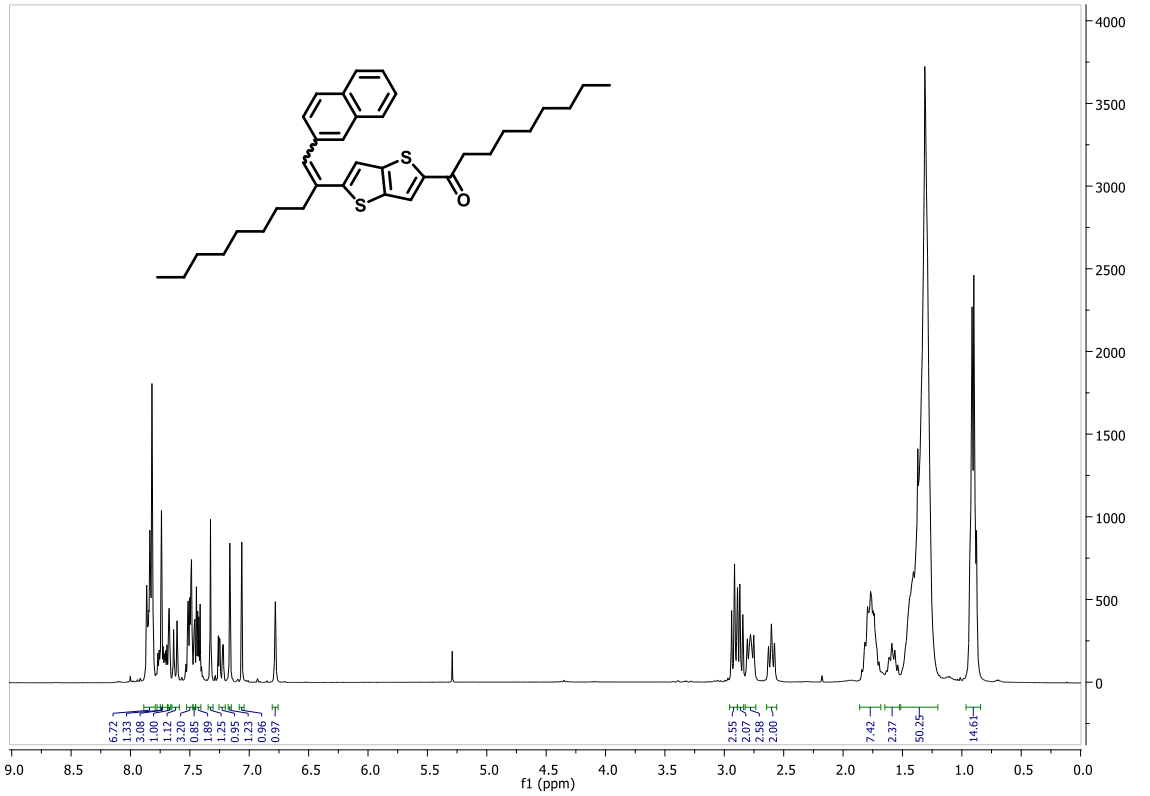
NMR spectra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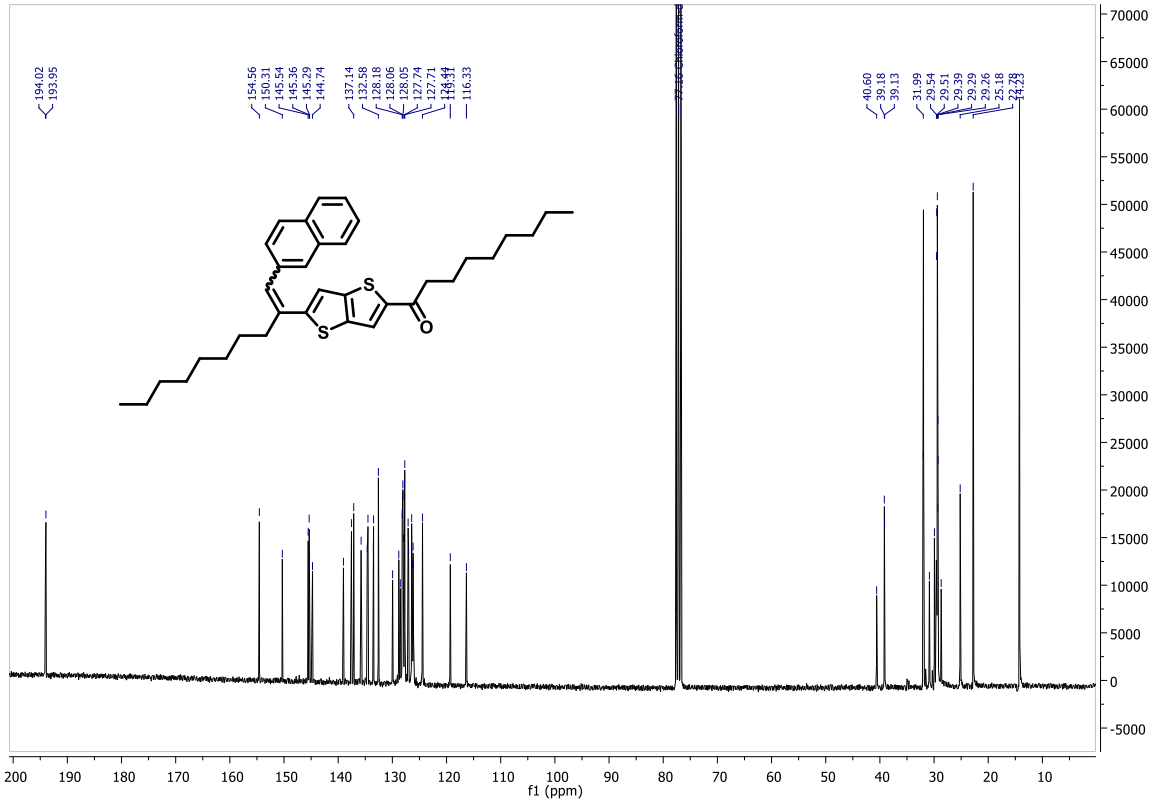
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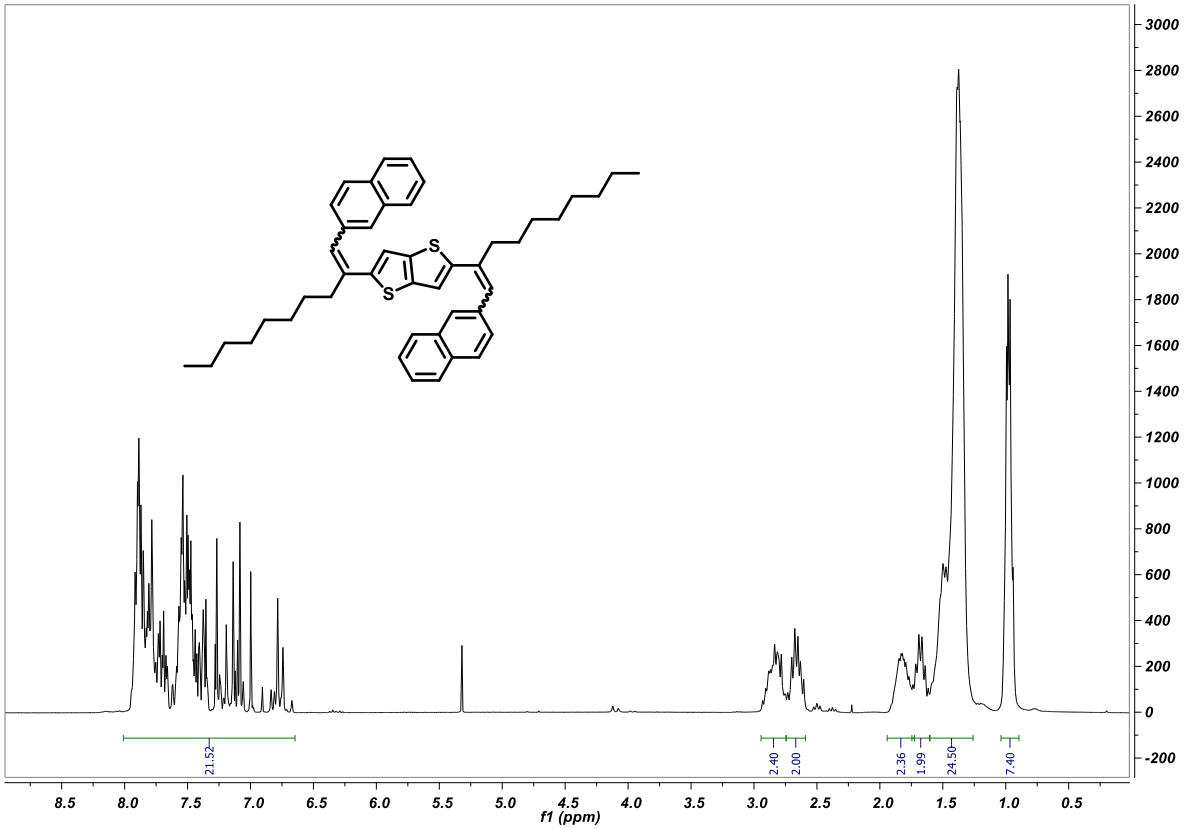
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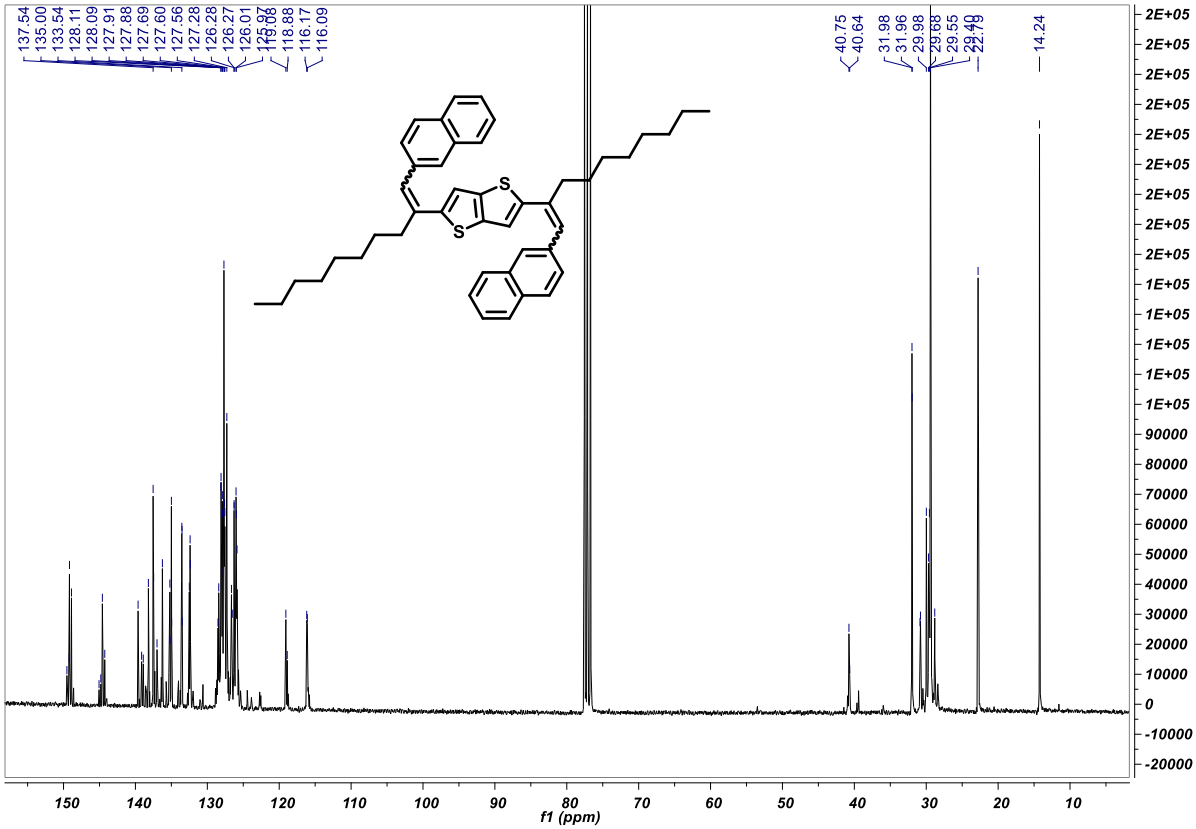
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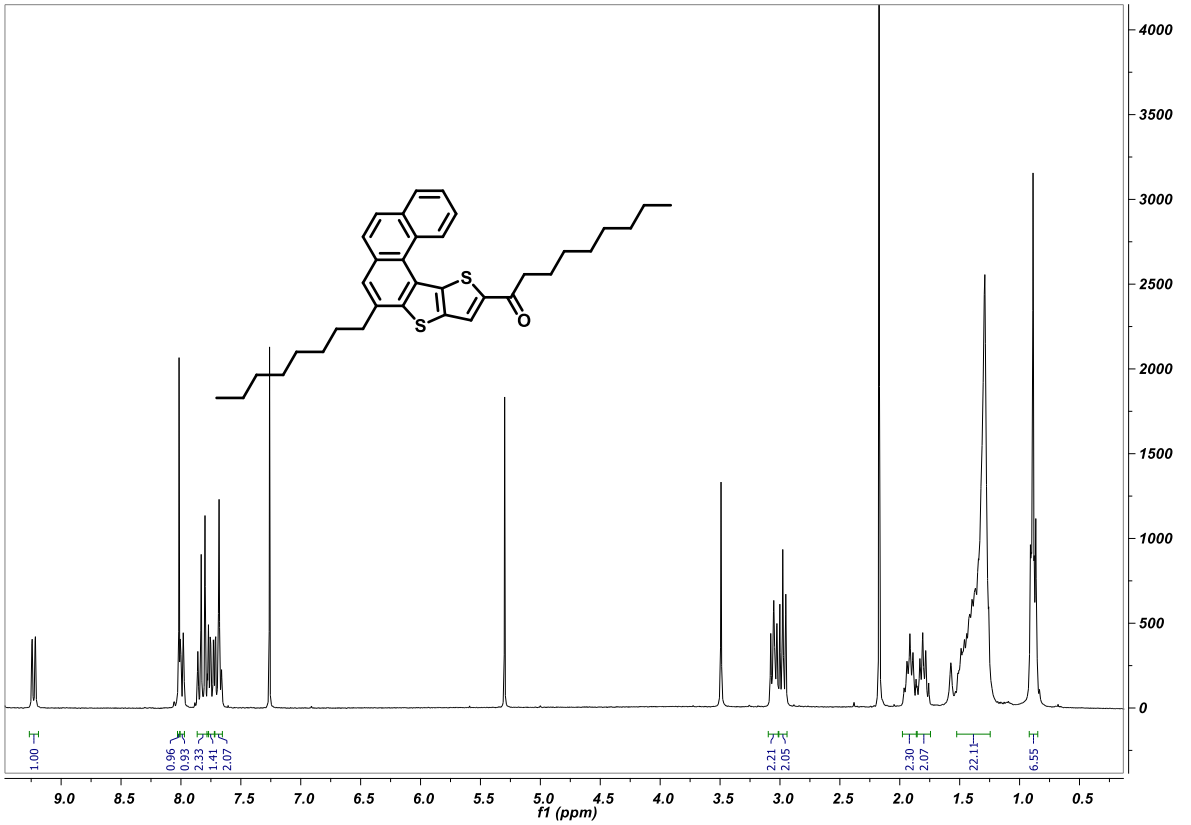
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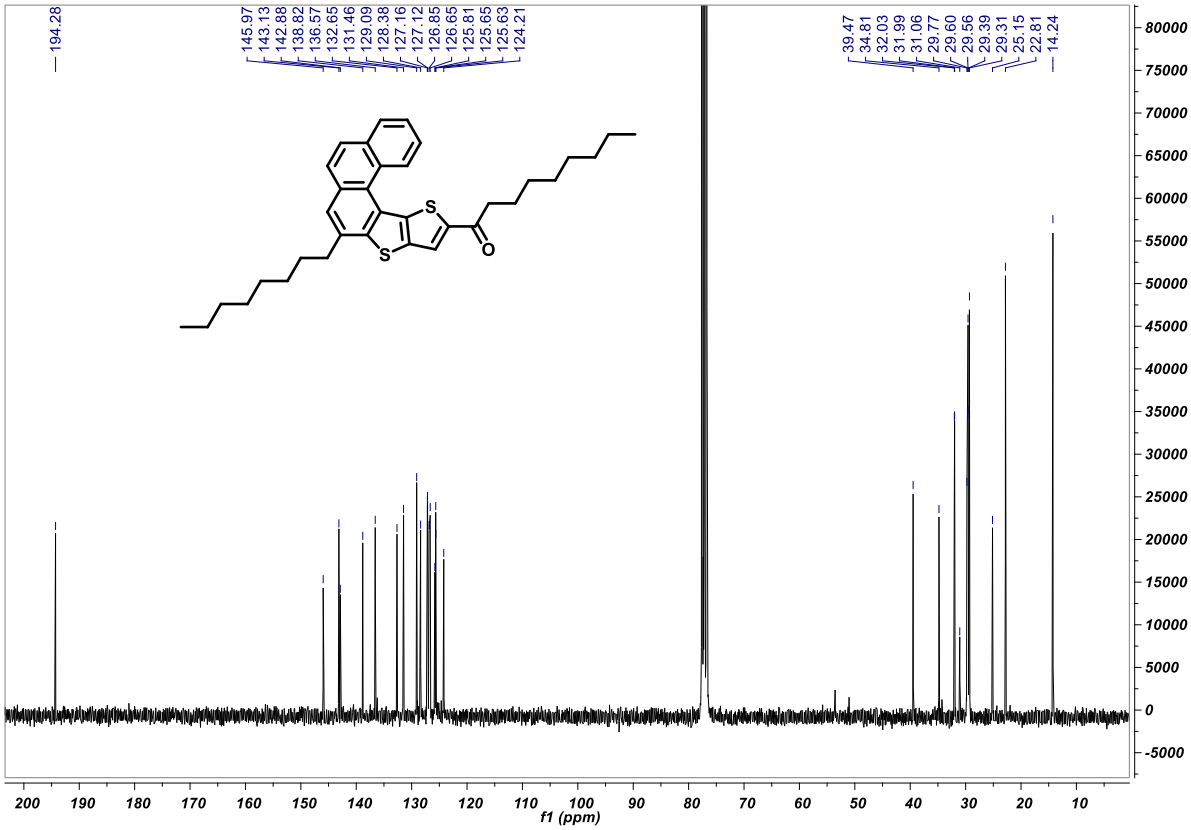
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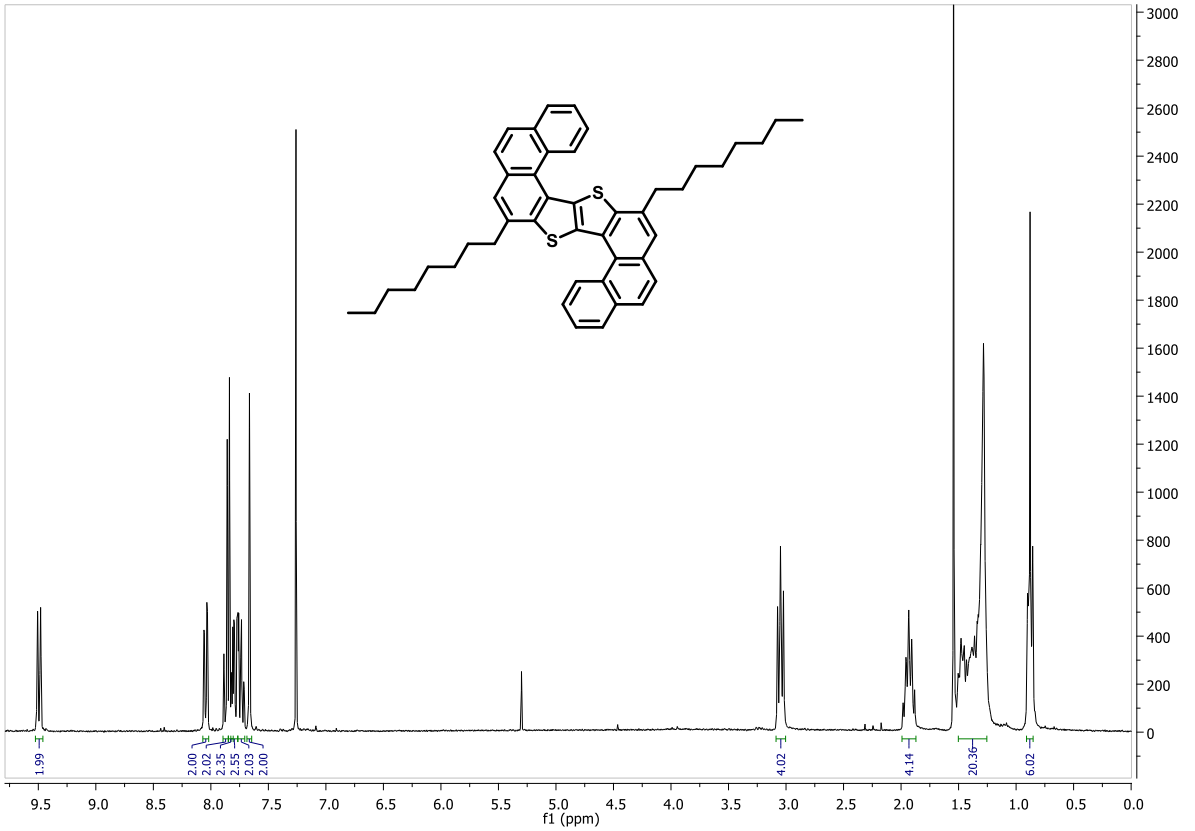
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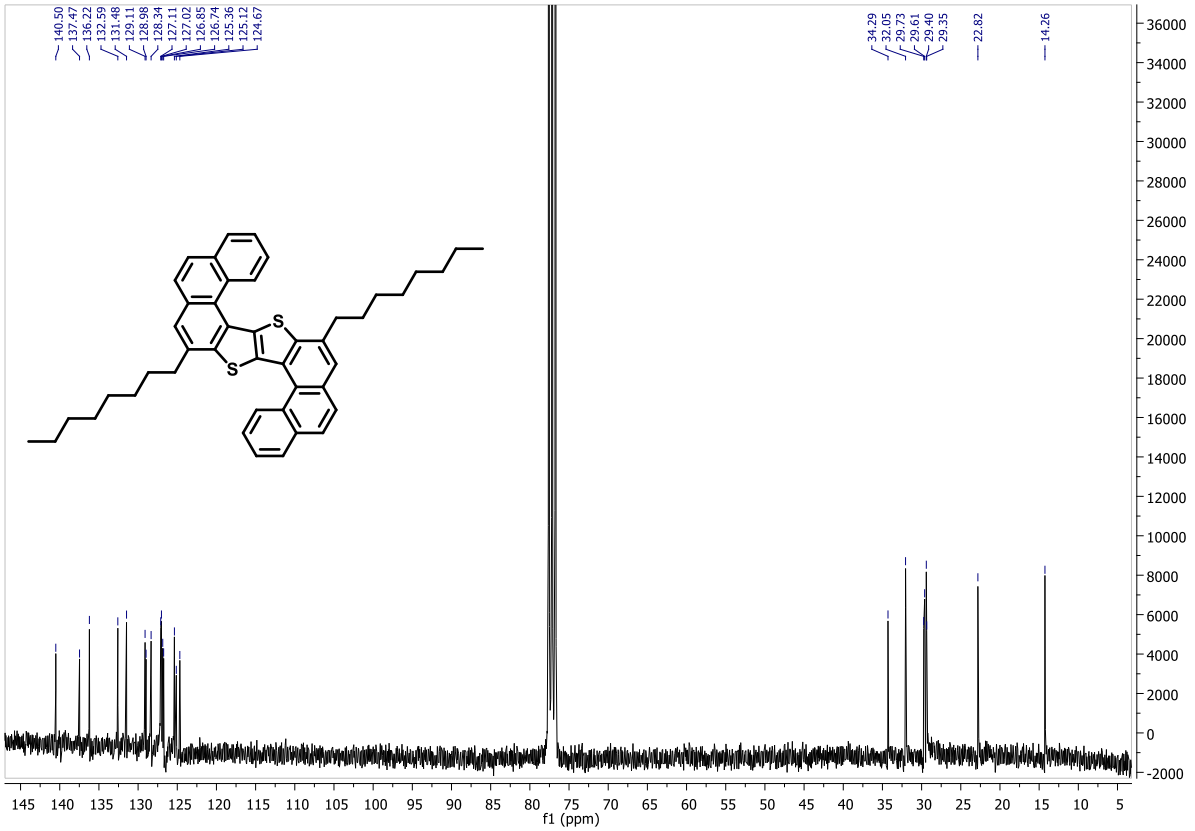
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f1 (ppm)

X-ray structure determinations

Compound **4**

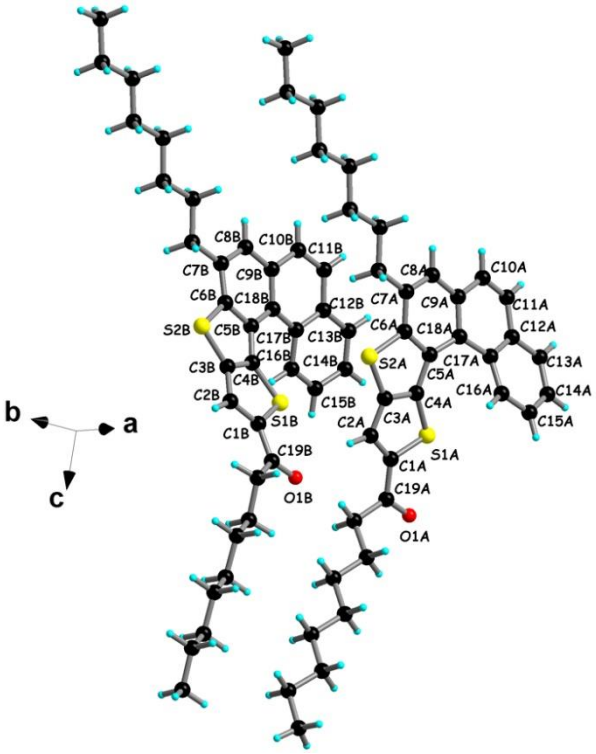

Fig. S1 The two independent molecules of compound **4** in the crystal phase, with partial numbering of the atoms (excluding those of the alkyl chains for clarity purpose).

Table S1 Bond Lengths for compound **4** in the crystal phase.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S2A	C3A	1.721(5)	C25B	C26B	1.514(9)
S2A	C6A	1.733(5)	C29B	C30B	1.524(7)
S1B	C1B	1.734(5)	C29B	C28B	1.525(7)
S1B	C4B	1.723(5)	C5B	C6B	1.419(7)
S2B	C3B	1.716(5)	C5B	C18B	1.442(7)
S2B	C6B	1.735(5)	C32A	C31A	1.522(8)
S1A	C4A	1.732(5)	C6B	C7B	1.412(7)
S1A	C1A	1.727(5)	C28A	C29A	1.526(7)
O1A	C19A	1.233(6)	C28A	C7A	1.502(7)
O1B	C19B	1.228(7)	C29A	C30A	1.527(7)
C35B	C34B	1.529(8)	C12A	C13A	1.417(8)
C33B	C32B	1.510(8)	C12A	C17A	1.420(7)
C33B	C34B	1.519(9)	C13A	C14A	1.362(8)
C10A	C11A	1.348(8)	C3A	C4A	1.392(7)
C10A	C9A	1.436(7)	C3A	C2A	1.407(7)
C11B	C10B	1.351(8)	C4A	C5A	1.438(7)
C11B	C12B	1.422(8)	C30A	C31A	1.520(7)
C3B	C4B	1.401(7)	C5A	C6A	1.421(7)
C3B	C2B	1.404(8)	C5A	C18A	1.438(6)

C23B	C24B	1.512(8)		C26B	C27B	1.511(10)	
C23B	C22B	1.510(8)		C14A	C15A	1.392(8)	
C20A	C21A	1.519(8)		C1A	C19A	1.450(8)	
C20A	C19A	1.506(7)		C1A	C2A	1.384(7)	
C31B	C32B	1.521(8)		C23A	C22A	1.512(8)	
C31B	C30B	1.516(8)		C23A	C24A	1.523(7)	
C11A	C12A	1.419(8)		C28B	C7B	1.499(7)	
C26A	C27A	1.506(9)		C19B	C20B	1.501(8)	
C26A	C25A	1.518(8)		C9B	C18B	1.405(8)	
C33A	C34A	1.519(9)		C9B	C8B	1.419(8)	
C33A	C32A	1.516(8)		C6A	C7A	1.406(7)	
C35A	C34A	1.538(8)		C17A	C18A	1.450(7)	
C1B	C2B	1.372(7)		C17A	C16A	1.409(8)	
C1B	C19B	1.465(8)		C15A	C16A	1.388(7)	
C10B	C9B	1.441(7)		C7B	C8B	1.378(7)	
C4B	C5B	1.434(7)		C12B	C17B	1.416(7)	
C21B	C22B	1.509(8)		C8A	C9A	1.421(8)	
C21B	C20B	1.520(8)		C8A	C7A	1.368(7)	
C25A	C24A	1.518(8)		C9A	C18A	1.411(8)	
C13B	C12B	1.416(8)		C14B	C15B	1.412(8)	
C13B	C14B	1.356(9)		C18B	C17B	1.449(7)	
C21A	C22A	1.524(7)		C15B	C16B	1.368(7)	
C24B	C25B	1.509(8)		C17B	C16B	1.411(8)	

Table S2 Bond Angles for compound **4** in the crystal phase.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C3A	S2A	C6A	91.1(2)	C31B	C30B	C29B	114.2(5)
C4B	S1B	C1B	92.1(2)	C27B	C26B	C25B	114.1(6)
C3B	S2B	C6B	90.8(2)	C13A	C14A	C15A	121.0(5)
C1A	S1A	C4A	92.2(2)	C19A	C1A	S1A	118.2(4)
C32B	C33B	C34B	113.5(5)	C2A	C1A	S1A	112.2(4)
C11A	C10A	C9A	121.5(5)	C2A	C1A	C19A	129.6(5)
C10B	C11B	C12B	120.8(5)	C22A	C23A	C24A	113.3(5)
C4B	C3B	S2B	112.5(4)	C7B	C28B	C29B	116.8(4)
C4B	C3B	C2B	114.4(5)	O1B	C19B	C1B	119.2(5)
C2B	C3B	S2B	132.8(4)	O1B	C19B	C20B	121.7(5)
C22B	C23B	C24B	113.7(5)	C1B	C19B	C20B	119.1(5)
C19A	C20A	C21A	113.7(5)	C18B	C9B	C10B	119.4(5)
C30B	C31B	C32B	112.9(5)	C18B	C9B	C8B	121.6(4)
C10A	C11A	C12A	120.7(5)	C8B	C9B	C10B	119.0(5)
C27A	C26A	C25A	113.0(6)	C5A	C6A	S2A	113.8(4)
C32A	C33A	C34A	112.9(5)	C7A	C6A	S2A	122.6(4)
C2B	C1B	S1B	112.2(4)	C7A	C6A	C5A	123.5(4)
C2B	C1B	C19B	130.1(5)	O1A	C19A	C20A	120.4(5)
C19B	C1B	S1B	117.7(4)	O1A	C19A	C1A	119.3(5)
C11B	C10B	C9B	121.1(5)	C1A	C19A	C20A	120.3(5)

C3B	C4B	S1B	109.7(4)	C21B	C22B	C23B	114.9(5)
C3B	C4B	C5B	113.7(5)	C1A	C2A	C3A	111.2(4)
C5B	C4B	S1B	136.1(4)	C12A	C17A	C18A	119.0(5)
C22B	C21B	C20B	112.1(5)	C16A	C17A	C12A	117.6(5)
C24A	C25A	C26A	113.2(5)	C16A	C17A	C18A	123.3(4)
C14B	C13B	C12B	121.2(5)	C16A	C15A	C14A	119.0(6)
C33B	C32B	C31B	114.2(5)	C6B	C7B	C28B	119.0(4)
C20A	C21A	C22A	112.0(5)	C8B	C7B	C6B	116.5(5)
C25B	C24B	C23B	114.9(5)	C8B	C7B	C28B	124.4(5)
C24B	C25B	C26B	113.5(6)	C13B	C12B	C11B	121.0(5)
C30B	C29B	C28B	110.6(4)	C13B	C12B	C17B	119.4(5)
C4B	C5B	C18B	133.0(5)	C17B	C12B	C11B	119.4(5)
C6B	C5B	C4B	108.9(4)	C7A	C8A	C9A	122.1(5)
C6B	C5B	C18B	117.8(5)	C8A	C9A	C10A	119.6(5)
C33A	C34A	C35A	112.6(6)	C18A	C9A	C10A	119.2(5)
C33A	C32A	C31A	114.1(5)	C18A	C9A	C8A	121.3(4)
C5B	C6B	S2B	113.9(4)	C30A	C31A	C32A	112.4(5)
C7B	C6B	S2B	122.0(4)	C6A	C7A	C28A	118.2(4)
C7B	C6B	C5B	123.9(5)	C8A	C7A	C28A	124.9(5)
C7A	C28A	C29A	116.6(4)	C8A	C7A	C6A	116.8(5)
C28A	C29A	C30A	111.3(4)	C13B	C14B	C15B	119.9(5)
C11A	C12A	C17A	119.5(5)	C23A	C22A	C21A	113.8(5)
C13A	C12A	C11A	121.3(5)	C5B	C18B	C17B	124.3(5)
C13A	C12A	C17A	119.1(5)	C9B	C18B	C5B	117.2(5)
C14A	C13A	C12A	120.8(5)	C9B	C18B	C17B	118.4(4)
C4A	C3A	S2A	112.1(4)	C5A	C18A	C17A	124.8(5)
C4A	C3A	C2A	114.9(5)	C9A	C18A	C5A	116.9(5)
C2A	C3A	S2A	132.8(4)	C9A	C18A	C17A	118.3(4)
C33B	C34B	C35B	113.8(6)	C16B	C15B	C14B	119.2(6)
C1B	C2B	C3B	111.6(4)	C12B	C17B	C18B	119.3(5)
C3A	C4A	S1A	109.6(4)	C16B	C17B	C12B	116.9(5)
C3A	C4A	C5A	114.3(5)	C16B	C17B	C18B	123.7(5)
C5A	C4A	S1A	135.9(4)	C19B	C20B	C21B	114.0(5)
C31A	C30A	C29A	114.8(4)	C25A	C24A	C23A	114.2(5)
C4A	C5A	C18A	132.7(5)	C15B	C16B	C17B	122.6(5)
C6A	C5A	C4A	108.6(4)	C7B	C8B	C9B	121.8(5)
C6A	C5A	C18A	118.4(5)	C15A	C16A	C17A	121.8(5)

contact	type	distance (Å)	Sum of VdW radii (Å)
d_1	S-S	3,54	3,60
d_2	S-S	3,89	
d_3	S-H	2,87	3,00
d_4	S-H	2,86	
d_5	O-H	2,67	2,72
d_6	O-H	2,58	
d_7	O-H	2,73	

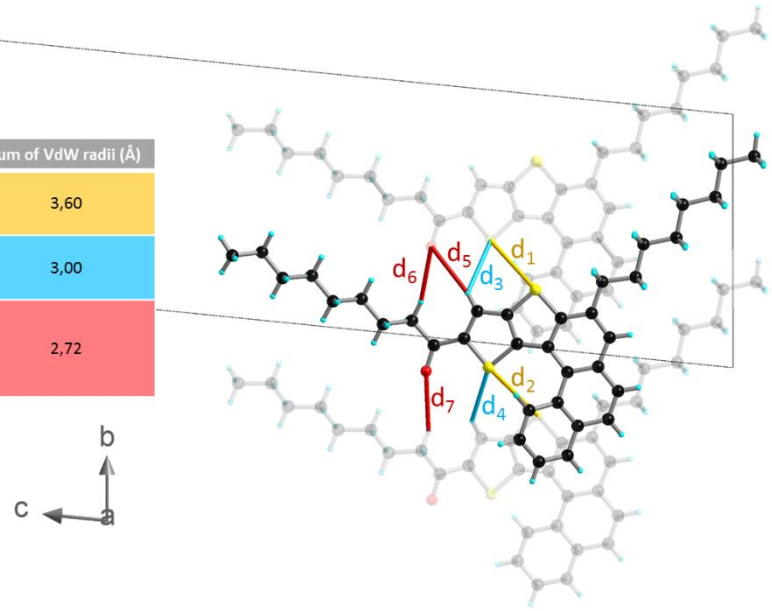

Fig. S2 Crystal packing of compound **4** with short intermolecular contacts highlighted. The corresponding distances and the related sums of Van der Waals radii[1] are listed in the inset table.

Compound **5**

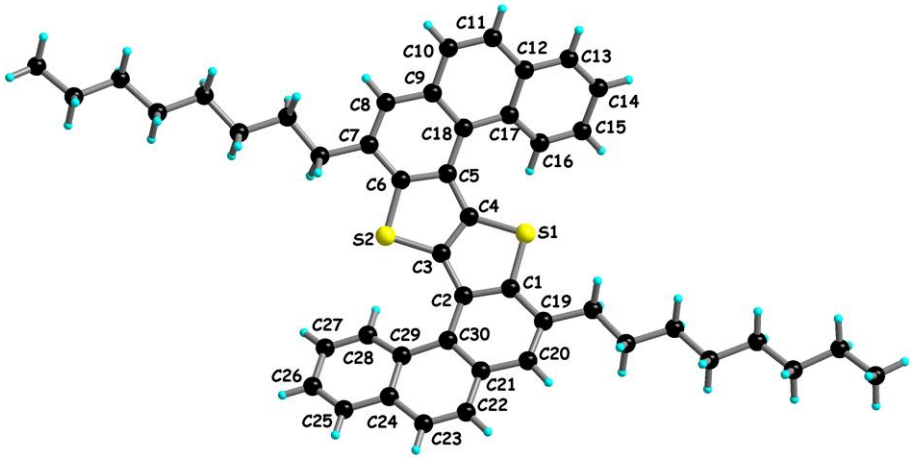

Fig. S3 Independent molecule of compound **5** in the crystal phase, with partial numbering of the atoms (excluding those of the alkyl chains for clarity purpose).

Table S3 Bond Lengths for compound **5** in the crystal phase.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C4	1.739(3)	C17	C16	1.418(4)
S1	C1	1.735(3)	C43	C44	1.517(4)
S2	C3	1.737(3)	C29	C28	1.414(4)
S2	C6	1.732(3)	C29	C30	1.447(4)
C21	C20	1.425(4)	C29	C24	1.423(5)
C21	C30	1.423(4)	C44	C45	1.516(4)
C21	C22	1.425(5)	C9	C18	1.425(4)
C2	C3	1.444(4)	C9	C8	1.418(4)
C2	C1	1.402(4)	C9	C10	1.429(4)
C2	C30	1.442(4)	C12	C11	1.415(5)
C4	C5	1.441(4)	C12	C13	1.376(5)
C4	C3	1.387(4)	C33	C34	1.516(4)
C5	C6	1.411(4)	C28	C27	1.317(4)
C5	C18	1.440(4)	C34	C35	1.517(4)
C6	C7	1.421(4)	C10	C11	1.347(5)
C1	C19	1.425(4)	C35	C36	1.508(5)
C40	C41	1.515(4)	C13	C14	1.368(6)
C40	C39	1.524(4)	C16	C15	1.325(4)
C19	C39	1.505(4)	C36	C37	1.541(5)
C19	C20	1.338(4)	C27	C26	1.431(6)
C42	C41	1.523(4)	C45	C46	1.517(5)
C42	C43	1.518(4)	C15	C14	1.425(6)
C7	C8	1.350(4)	C24	C23	1.431(5)
C7	C31	1.511(4)	C24	C25	1.398(5)
C32	C33	1.521(4)	C22	C23	1.310(5)
C32	C31	1.514(4)	C26	C25	1.340(6)

C17	C18	1.451(4)	C37	C38	1.458(6)
C17	C12	1.439(4)			

Table S4 Bond Angles for compound **5** in the crystal phase.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	S1	C4	91.64(13)	C24	C29	C30	119.6(3)
C6	S2	C3	91.52(12)	C45	C44	C43	113.4(3)
C30	C21	C20	121.3(3)	C18	C9	C10	119.6(3)
C30	C21	C22	118.6(3)	C8	C9	C18	120.7(3)
C22	C21	C20	120.1(3)	C8	C9	C10	119.6(3)
C1	C2	C3	108.5(2)	C5	C18	C17	125.7(3)
C1	C2	C30	117.7(2)	C9	C18	C5	117.0(2)
C30	C2	C3	133.6(3)	C9	C18	C17	117.2(3)
C5	C4	S1	133.5(2)	C19	C39	C40	116.8(2)
C3	C4	S1	110.3(2)	C11	C12	C17	118.7(3)
C3	C4	C5	115.6(2)	C13	C12	C17	119.0(3)
C6	C5	C4	108.3(2)	C13	C12	C11	122.1(3)
C6	C5	C18	117.8(2)	C34	C33	C32	114.2(2)
C18	C5	C4	133.5(2)	C27	C28	C29	124.9(3)
C2	C3	S2	133.2(2)	C7	C8	C9	123.1(3)
C4	C3	S2	110.6(2)	C7	C31	C32	116.8(2)
C4	C3	C2	115.7(2)	C33	C34	C35	111.7(3)
C5	C6	S2	113.93(19)	C11	C10	C9	121.8(3)
C5	C6	C7	124.4(2)	C10	C11	C12	121.2(3)
C7	C6	S2	121.5(2)	C19	C20	C21	122.6(3)
C2	C1	S1	113.86(19)	C21	C30	C2	116.4(3)
C2	C1	C19	124.8(3)	C21	C30	C29	117.8(3)
C19	C1	S1	121.1(2)	C2	C30	C29	125.8(3)
C41	C40	C39	112.3(2)	C36	C35	C34	114.4(3)
C1	C19	C39	119.6(3)	C14	C13	C12	122.6(4)
C20	C19	C1	116.1(3)	C15	C16	C17	122.5(3)
C20	C19	C39	124.3(3)	C35	C36	C37	112.3(3)
C43	C42	C41	112.0(2)	C28	C27	C26	118.0(4)
C6	C7	C31	119.2(2)	C44	C45	C46	113.5(3)
C8	C7	C6	116.1(2)	C16	C15	C14	120.8(3)
C8	C7	C31	124.6(2)	C29	C24	C23	118.8(3)
C31	C32	C33	112.0(2)	C25	C24	C29	119.0(4)
C40	C41	C42	114.5(2)	C25	C24	C23	122.2(4)
C12	C17	C18	119.8(3)	C23	C22	C21	123.4(4)
C16	C17	C18	123.6(3)	C22	C23	C24	120.7(3)
C16	C17	C12	116.5(3)	C25	C26	C27	120.0(4)
C44	C43	C42	114.9(2)	C13	C14	C15	118.0(3)
C28	C29	C30	124.5(3)	C26	C25	C24	121.8(4)
C28	C29	C24	115.7(3)	C38	C37	C36	113.9(5)

Cyclic voltammetry

Cyclic voltammograms were recorded in 1mM dichloromethane solutions in the presence of tetrabutylammonium hexafluorophosphate ($TBAPF_6$ 0.1 M) as supporting electrolyte and at a scan rate of 100 mV/s. Platinum electrodes were used as the working electrode (Pt disk, Ø=2mm) and counter electrode (Pt wire), while an Ag/AgCl electrode was used as the reference. The potentials were calibrated against ferrocene/ferrocenium ($E_{1/2}$ = +0.475 V vs. SCE)[2] under identical conditions.

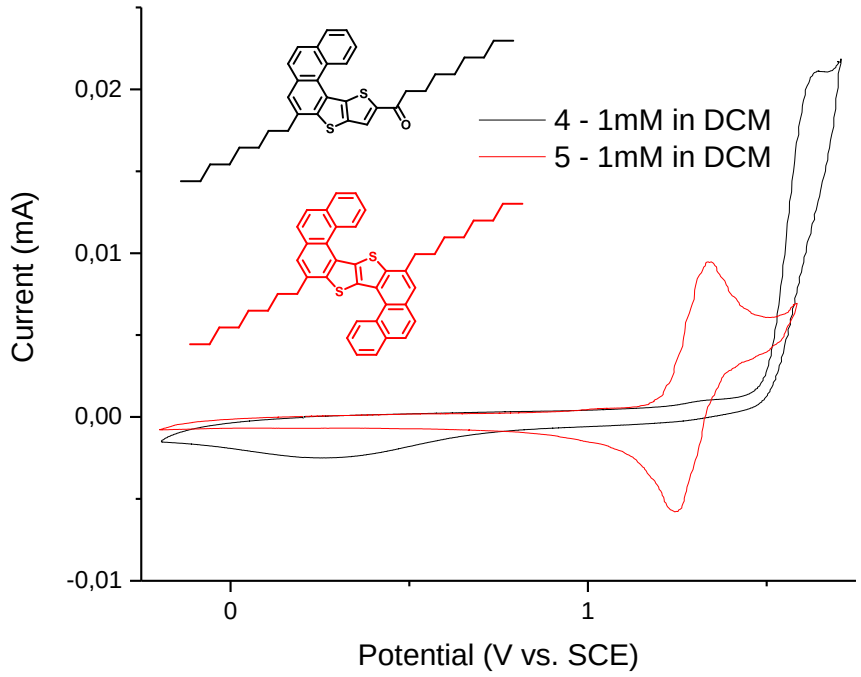

Fig. S4 Cyclic voltammograms of the molecules **4** and **5** in 1mM DCM solutions.

Micrographs of the devices under polarised light

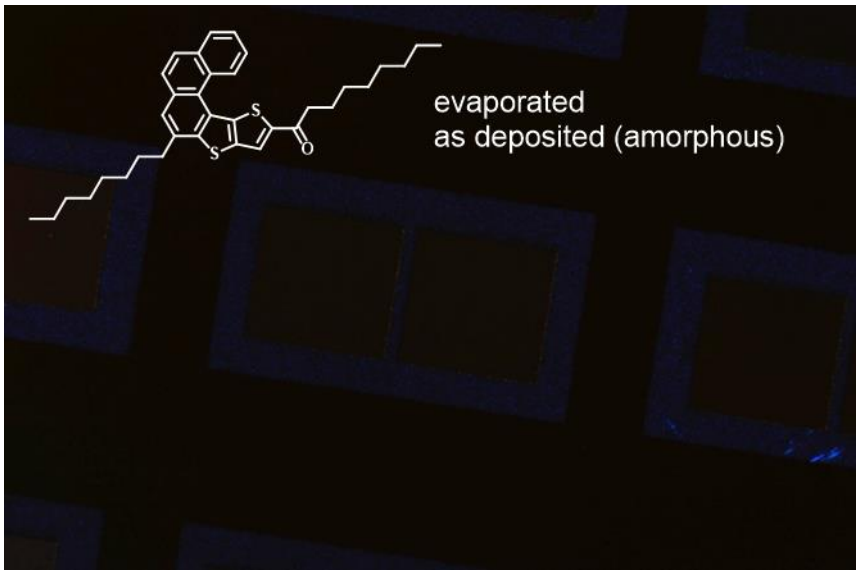

Fig. S5 Micrographs under cross-polarized light of the OFET devices based on evaporated layer of molecule **4**, as deposited.

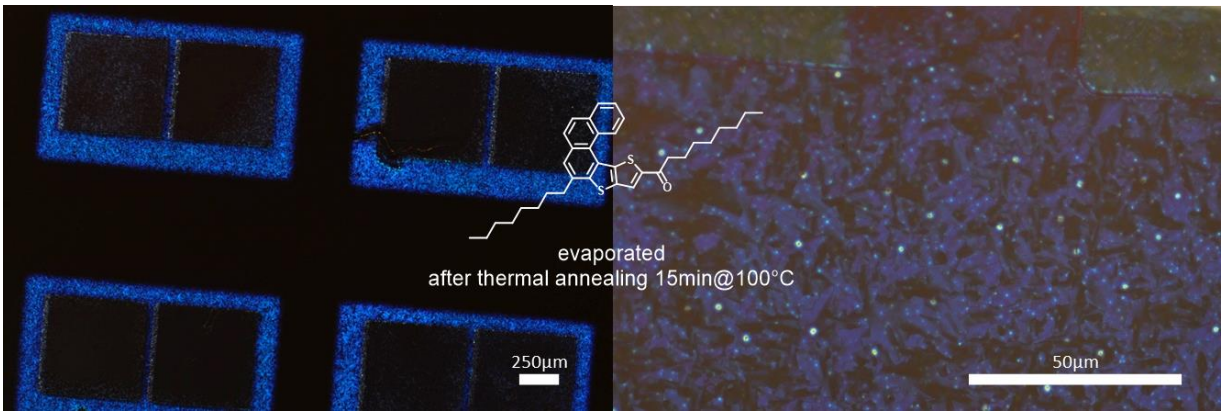

Fig. S6 Micrographs under cross-polarized light of the OFET devices based on evaporated layer of molecule **4**, thermally annealed at 100°C for 15 min.

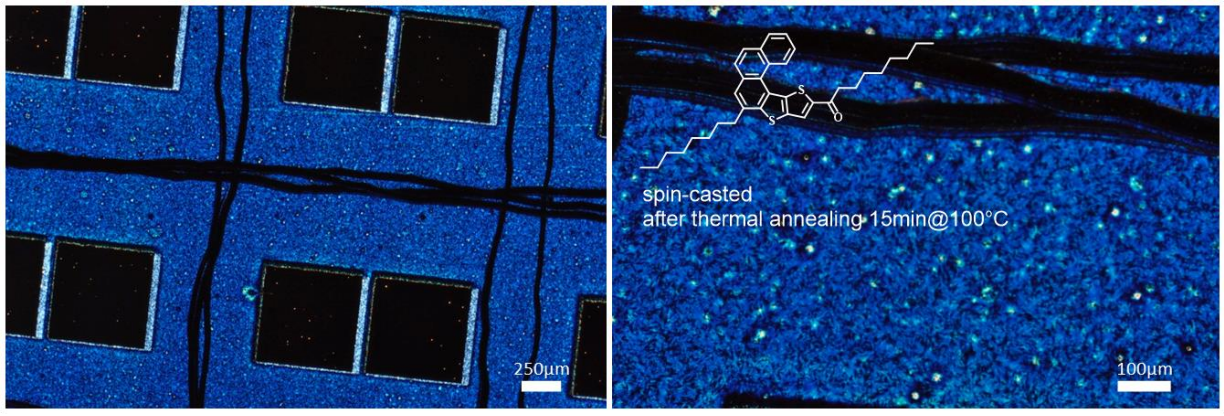

Fig. S7 Micrographs under cross-polarized light of the OFET devices based on spin-casted layer of molecule **4**, thermally annealed at 100°C for 15 min.

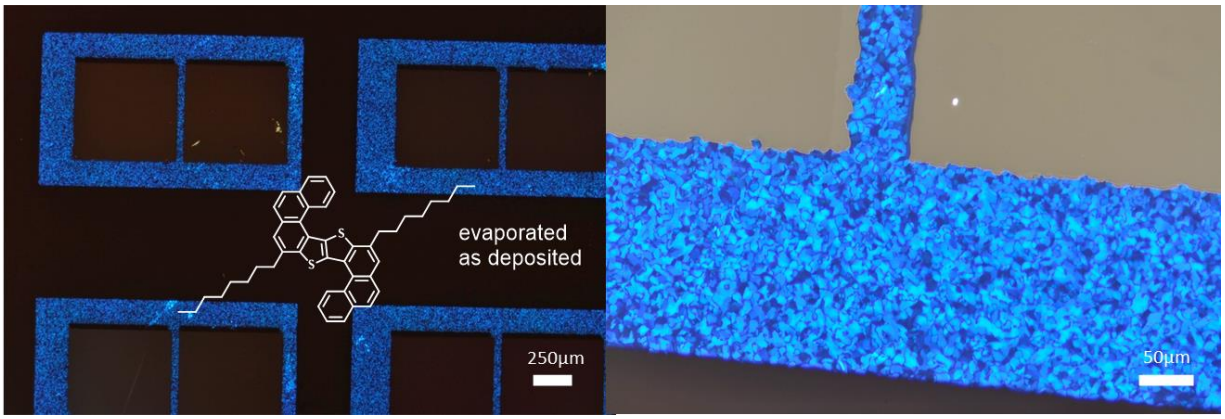

Fig. S8 Micrographs under cross-polarized light of the OFET devices based on evaporated layer of molecule **5**, as deposited.

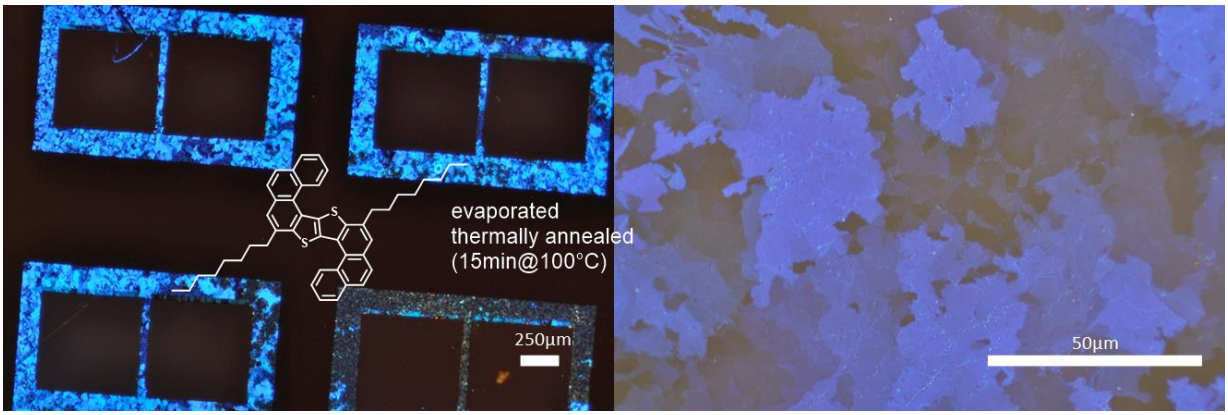

Fig. S9 Micrographs under cross-polarized light of the OFET devices based on evaporated layer of molecule **5**, thermally annealed at 100°C for 15 min.

Crystallographic characterization of the thin films of 4 and 5

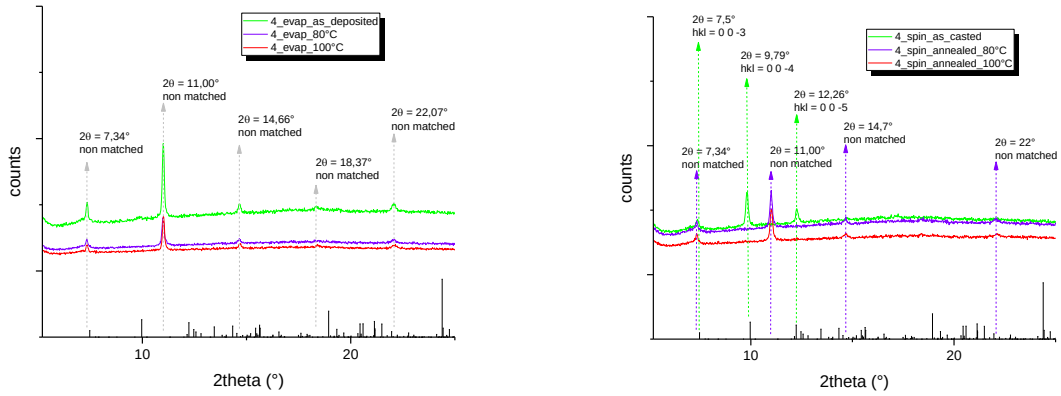

Fig. S10 X-ray diffraction patterns from vapour deposited (left) and spin-casted (right) films of compound **4**: as deposited (green line), after 10 min at 80 °C (violet line), after 10 min at 100 °C (red line), and theoretical isotropic powder diffraction (black histogram).

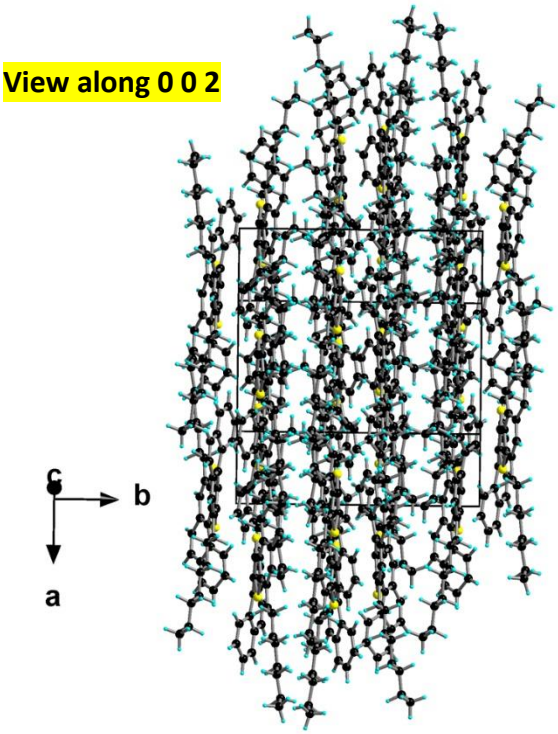

Fig. S11 Crystal packing along the (0 0 2) direction for compound **5**.

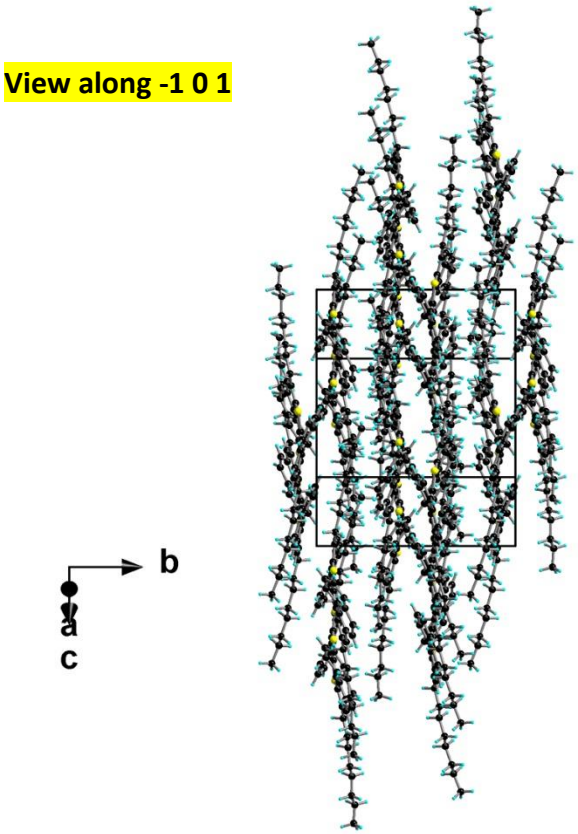

Fig. S12 Crystal packing along the (-1 0 1) direction for compound **5**.

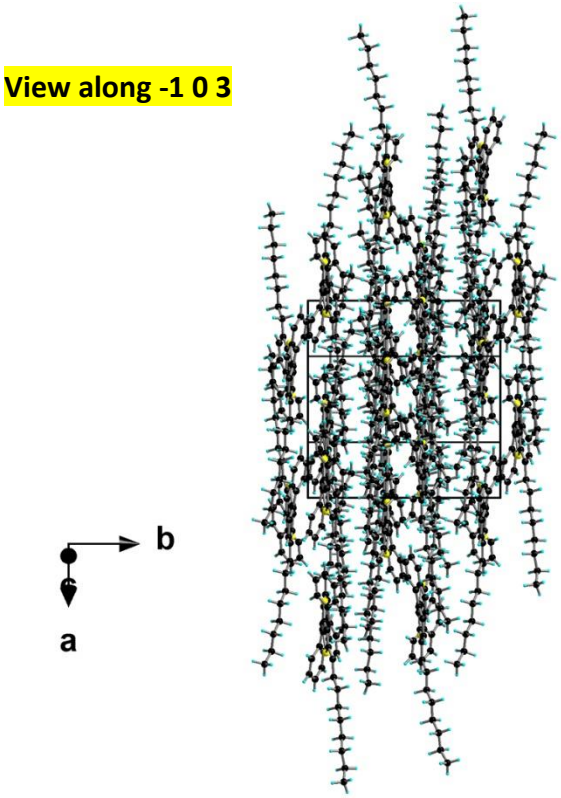

Fig. S13 Crystal packing along the (-1 0 3) direction for compound **5**.

Thermal measurements

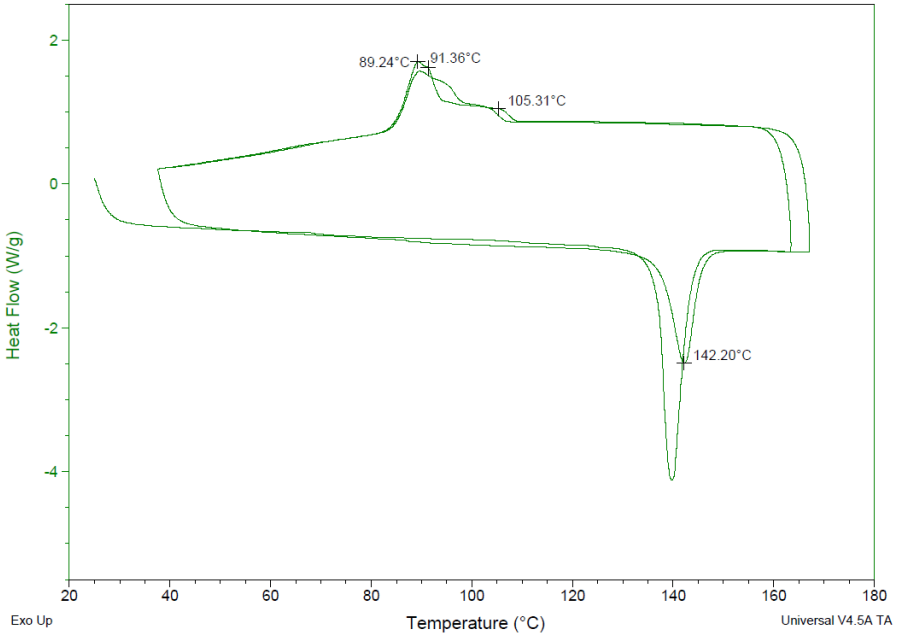

Fig. S14 Differential scanning calorimetry of compound **5**, with a ramp of 10 °C/min, showing an endothermal process (fusion) between 140 °C and 142 °C, and two exothermic processes in the intervals 92-105 °C and 89-91 °C.

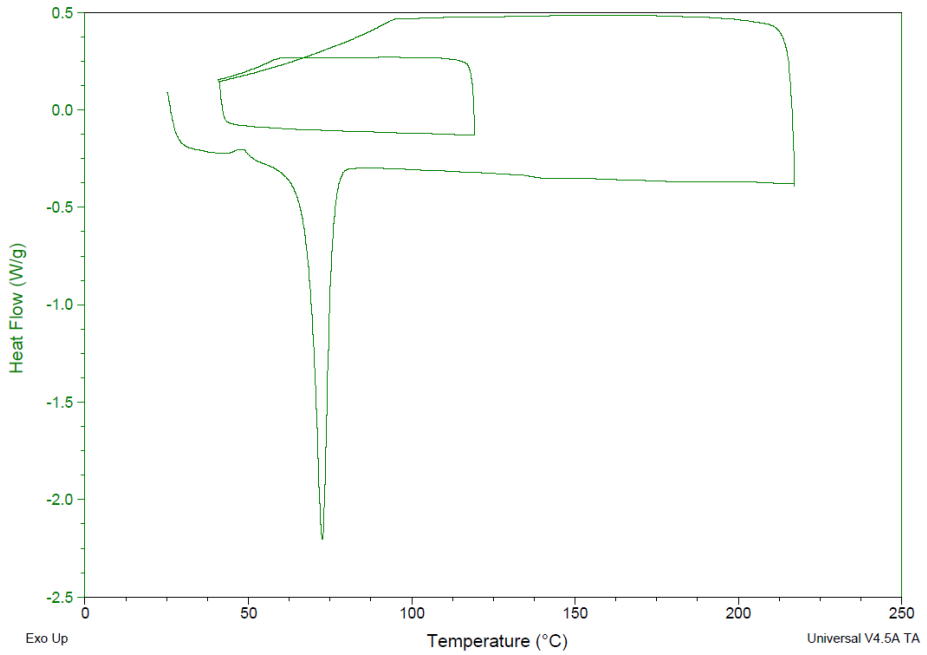

Fig. S15 Differential scanning calorimetry of compound **4**, with a ramp of 10 °C/min (5 °C/min for the last inner cycle), showing an endothermal process (fusion) around 73 °C. The exothermal process was not visible under the experimental conditions, probably due to the formation of a metastable glass state. The same sample cycled again, after resting 2 hours at room temperature, reproduced the same calorimetric profile.

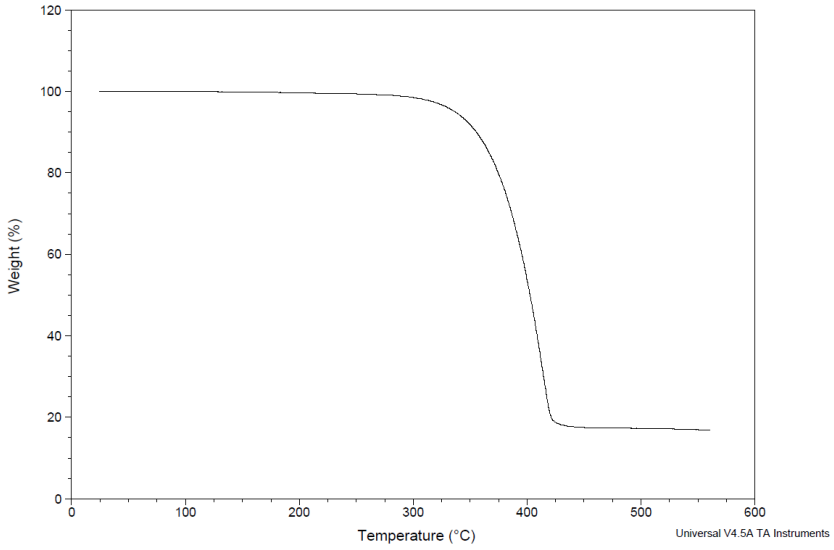

Fig. S16 Thermogravimetric analysis of compound **4** showing thermal decomposition above 320 °C.

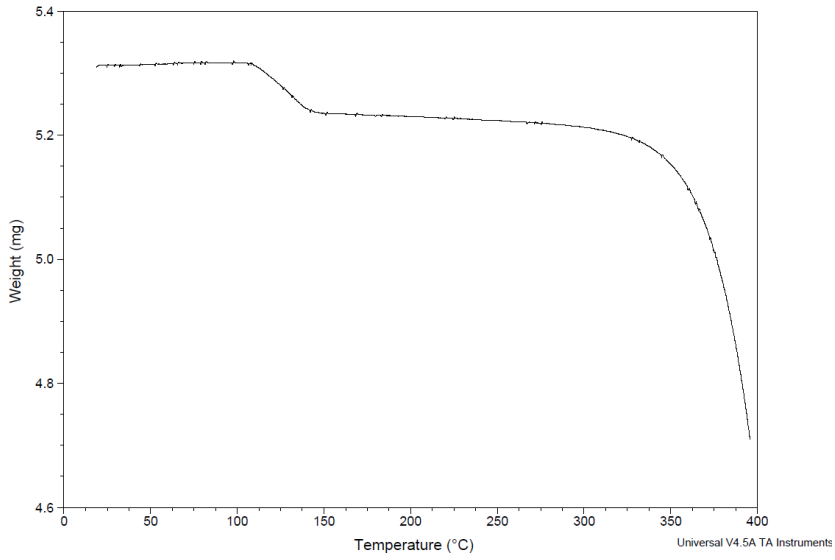

Fig. S17 Thermogravimetric analysis of compound **5** showing a 3% weight loss (residual solvent evaporation) between 110 °C and 140 °C, and thermal decomposition above 320 °C.

DFT results

Electronic Coupling (meV)	Centroid-Centroid Distance (Å)
22.5	6.4
0.5	6.3
9.9	7.8
14.5	8.4

Table S5 DFT-predicted electronic couplings for hole transfer between unique molecular pairs taken from the crystal structure of compound **4**.

Electronic Coupling (meV)	Centroid-Centroid Distance (Å)
7.8	8.1
9.3	11.5
0.6	14.7
1.5	13.6
5.6	12.9

Table S6 DFT-predicted electronic couplings for hole transfer between unique molecular pairs taken from the crystal structure of compound **5**.

Bibliography

1. A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441-451.
2. J. R. Aranzaes, M.-C. Daniel and D. Astruc, *Can. J. Chem.*, 2006, **84**, 288-299.