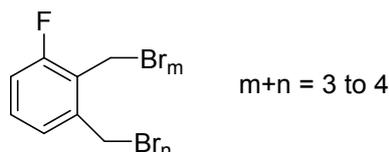


Supplementary Information for Towards Solution Processable Air Stable P-type Organic Semiconductors: Synthesis and Evaluation of Mono and Di-Fluorinated Pentacene Derivatives:

Jaroslav M. Wasikiewicz, Laila Abu-Sen, Andrew Horn, Jacobus M. Koelewijn, Adam V. S. Parry John J. Morrison, and Stephen G. Yeates.

Synthetic routes for molecules **10** and **11**.

Tri/tetrabromo-3-fluoro-*o*-xylene (**10**)

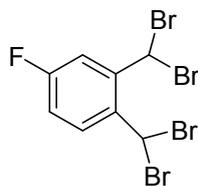


A 1 L round-bottom flask was charged with 23.08 g (186 mmol) of 3-fluoro-*o*-xylene and 166 g (930 mmol) of N-bromosuccinamide (NBS) and 600 ml of carbon tetrachloride and a magnetic stirrer. The flask was flushed with N₂. Next a 200 W UV lamp was placed at a distance of 2cm with the beam focused at the centre of the flask. The reaction progress was monitored by GS-MS measurements. After 6.5h 100% of substrate was converted to tribromo-3-fluoro-*o*-xylene. Extended reaction time resulted in production of mixture of tri and tetrabromo-3-fluoro-*o*-xylene at the maximum ratio of 47 to 53% after 24 h. The resulting yellow liquid was washed with sodium thiosulphate, water and saturated NaCl solutions. Next it was dried with MgSO₄, filtered off and concentrated in vacuum giving 64.0 g of the mixture as a pale yellow waxy solid. CAUTION - this product was found to be a potent lachrymator.

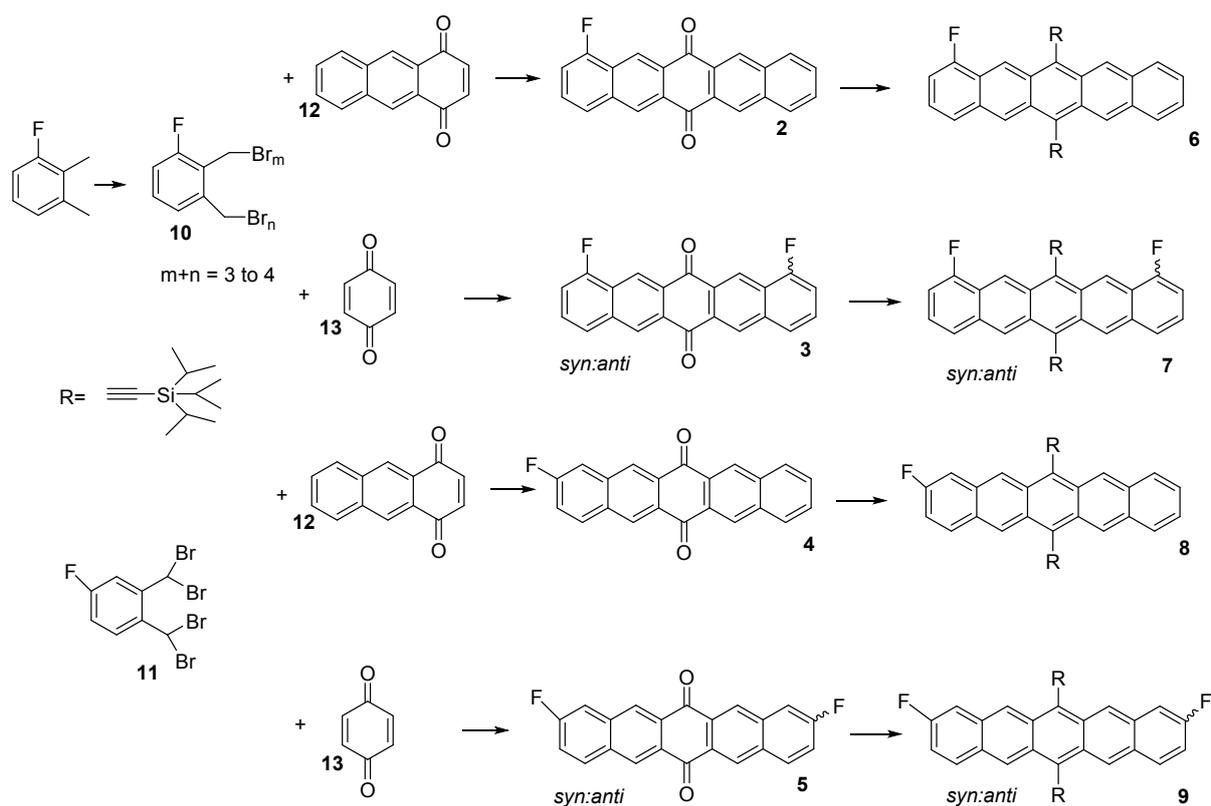
Alternatively this material may be accessed by the Green Chemistry route below.

To methyl acetate (75 mL) was added 3-fluoro-*o*-xylene (1 g, 8.05 mmol), NBS(3.2 g, 17.98 mmol) and a few drops of hydrobromic acid with stirring. A condenser was attached and the reaction mixture was irradiated with a 60 W lightbulb for 48 h. The reaction was monitored by GC-MS until the degree of bromination stopped increasing. Workup as above gave a mixture of tri and tetrabromo-3-fluoro-*o*-xylene **10** (4.69 g, 66.18%) as a pale orange liquid which crystallised upon cooling. CAUTION - this product was found to be a potent lachrymator.

1,2-bis(dibromomethyl)-4-fluorobenzene (**11**)



Using the above method a 500ml round-bottom flask was charged with 3g (24.4 mmol) of 4-fluoro-*o*-xylene and 21.5 g (120.8 mmol) of NBS and 300 ml of carbon tetrachloride and a magnetic stirrer. After 6.5 h 100% of substrate was converted to 21.5g of the title material (19.8 mmol, 82%). Analysis showed this was identical to the commercial material from Acros Organics. Mpt 92-97 °C.

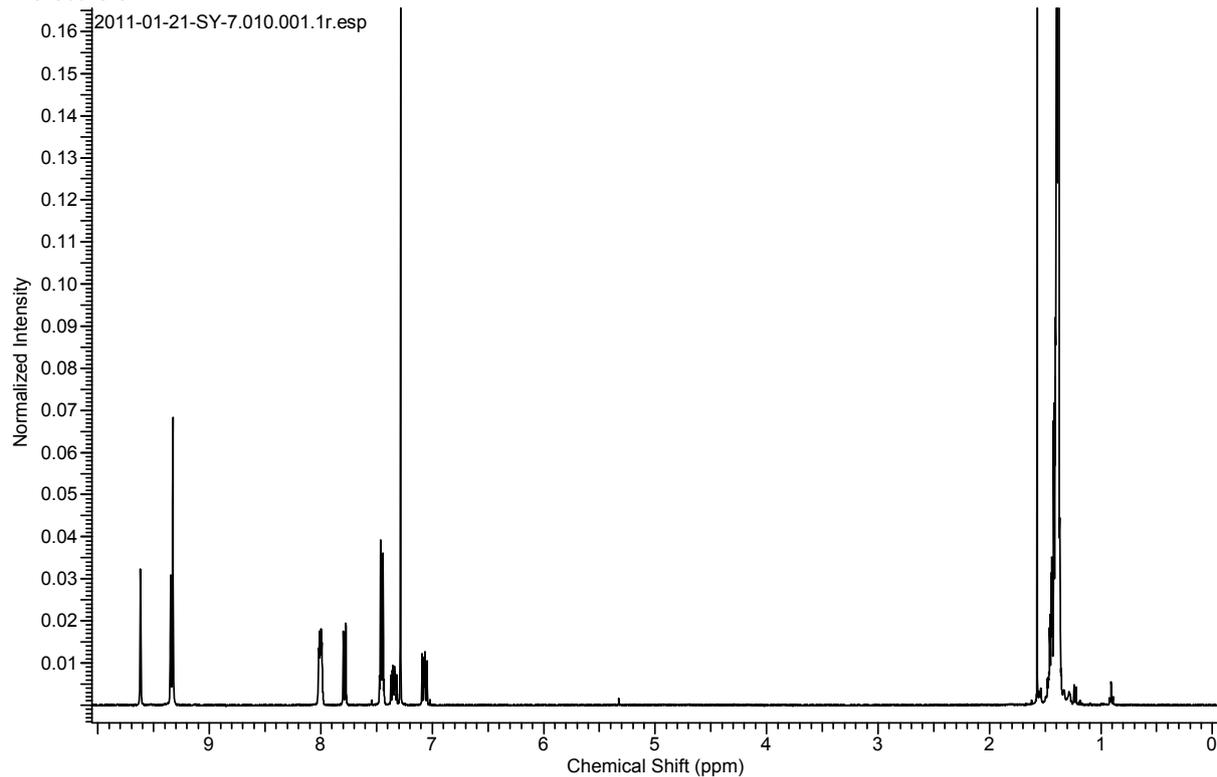


Scheme S1. Synthetic route to fluorinated TIPS pentacenes.

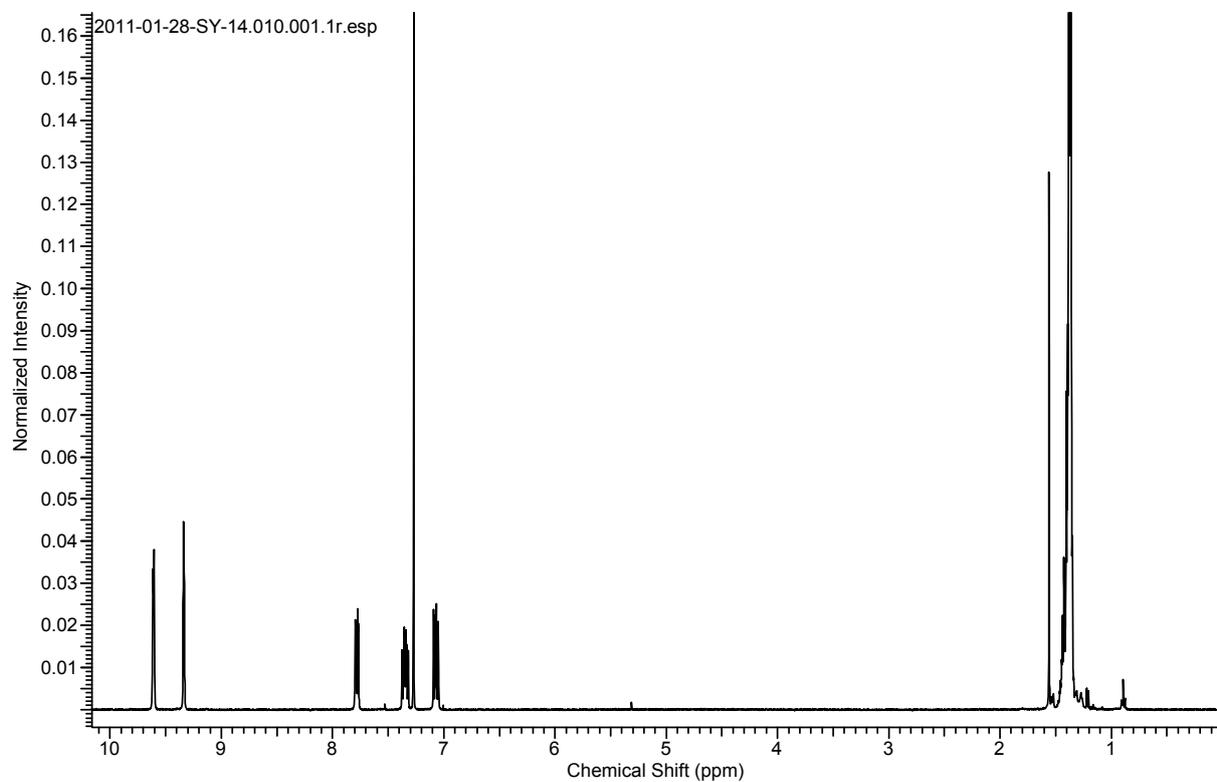
Figures S1 below. ^1H NMR 400MHz spectra of target compounds 1-fluoro-6,13-bis[triisopropylsilyl-ethynyl]pentacene (**6**); 1,(8:11)-difluoro-6,13-bis[triisopropylsilyl-ethynyl]pentacene (**7**); 2-fluoro-6,13-bis[triisopropylsilyl-ethynyl]pentacene (**8**); 2,(9:10)-difluoro-6,13-bis[triisopropylsilyl-ethynyl]pentacene (**9**) followed by APCI mass spectrographs.

Supplementary Information for Towards Solution Processable Air Stable P-type Organic Semiconductors: Synthesis and Evaluation of Mono and Di-Fluorinated Pentacene Derivatives.

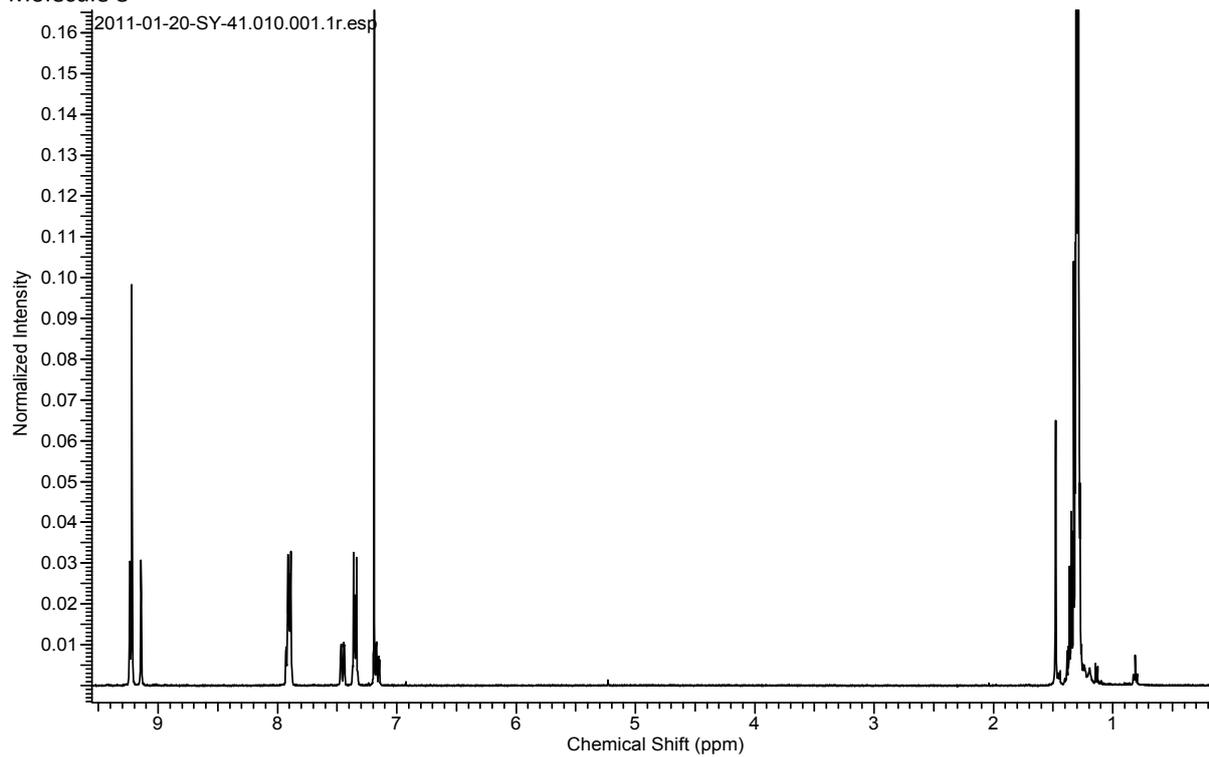
Molecule 6



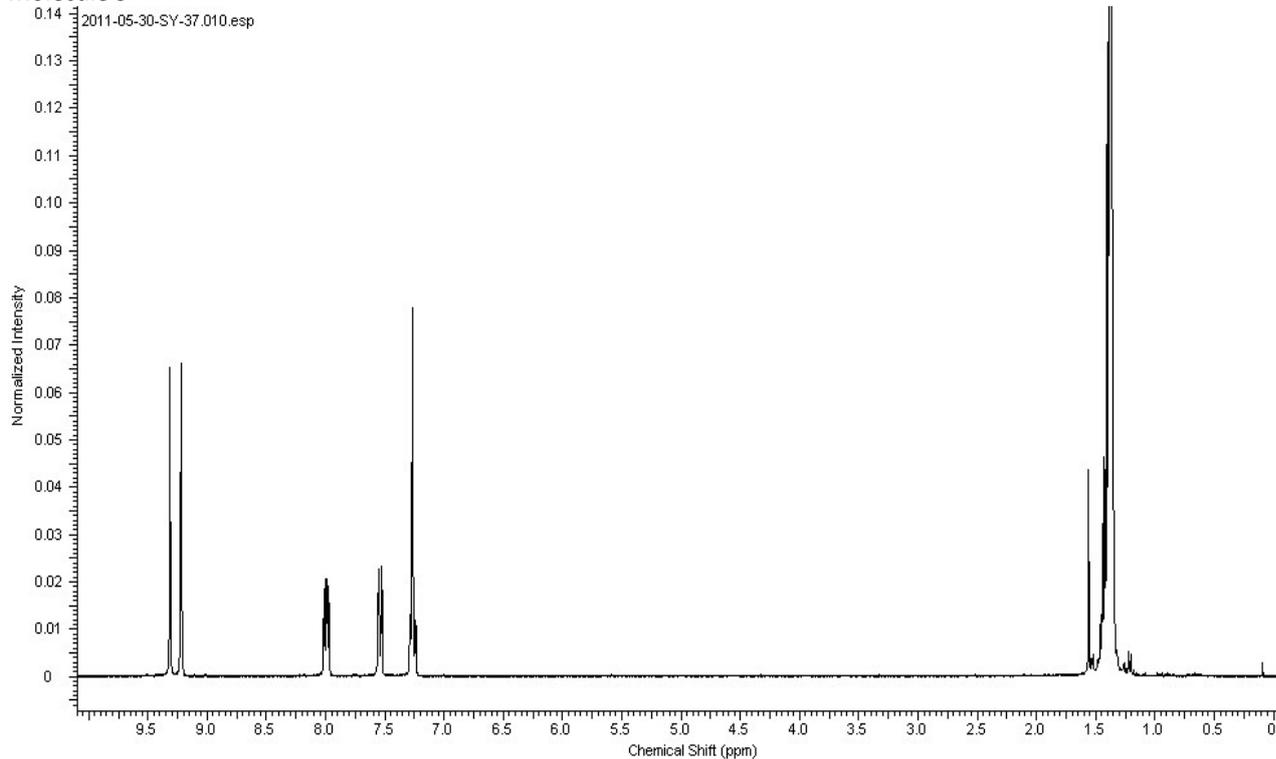
Molecule 7



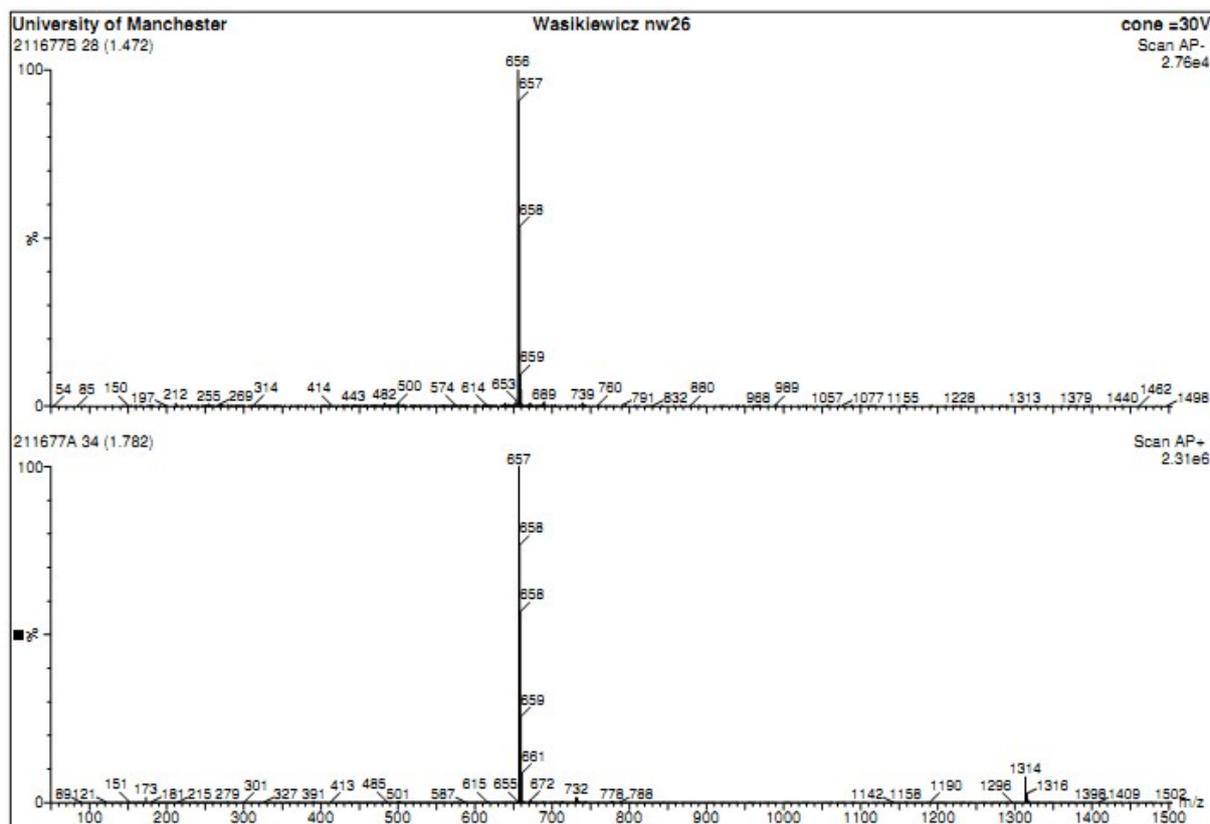
Molecule 8



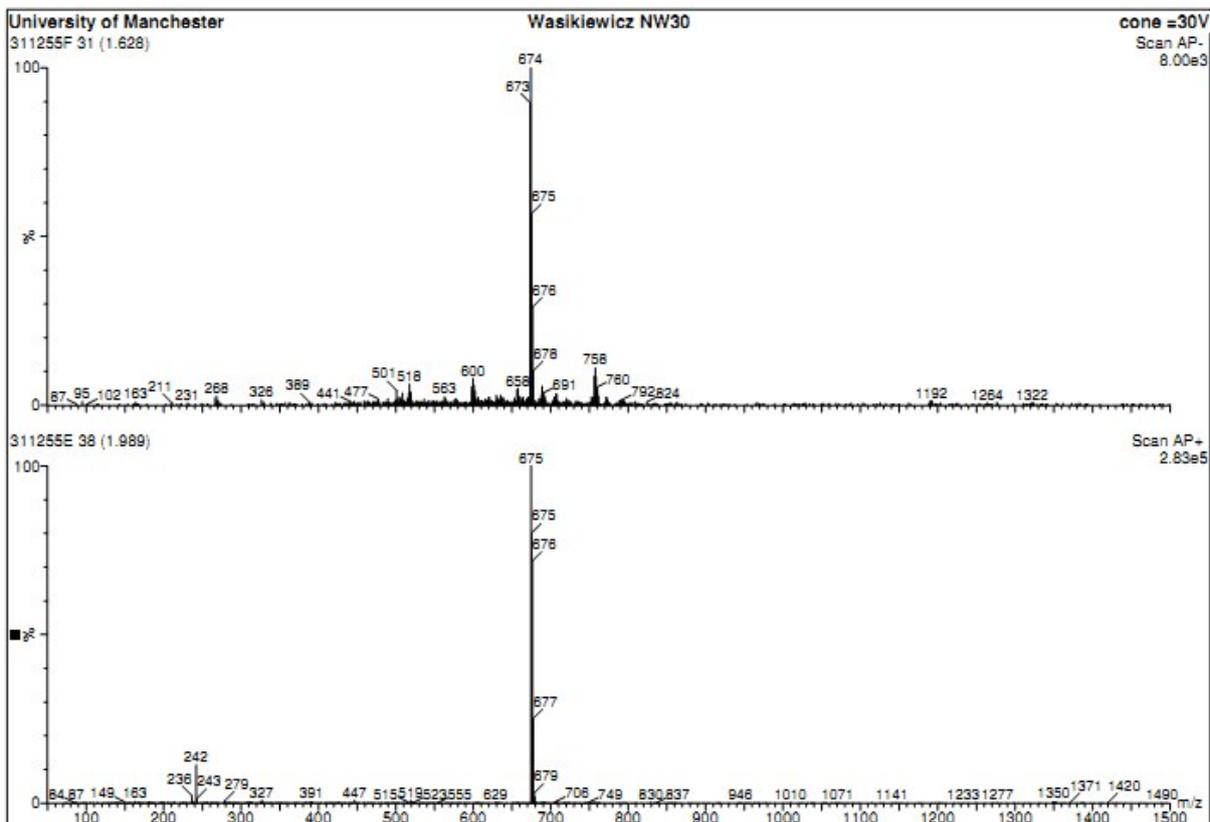
Molecule 9



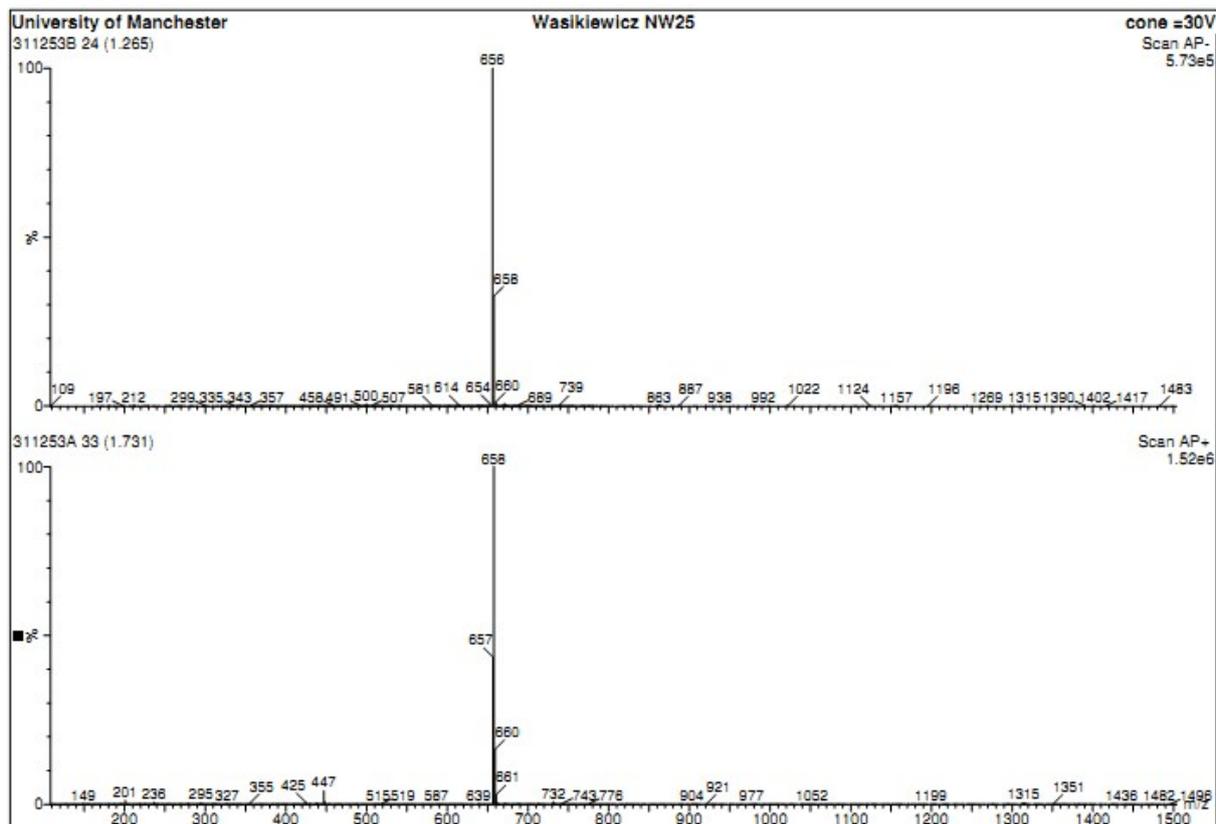
Molecule 6



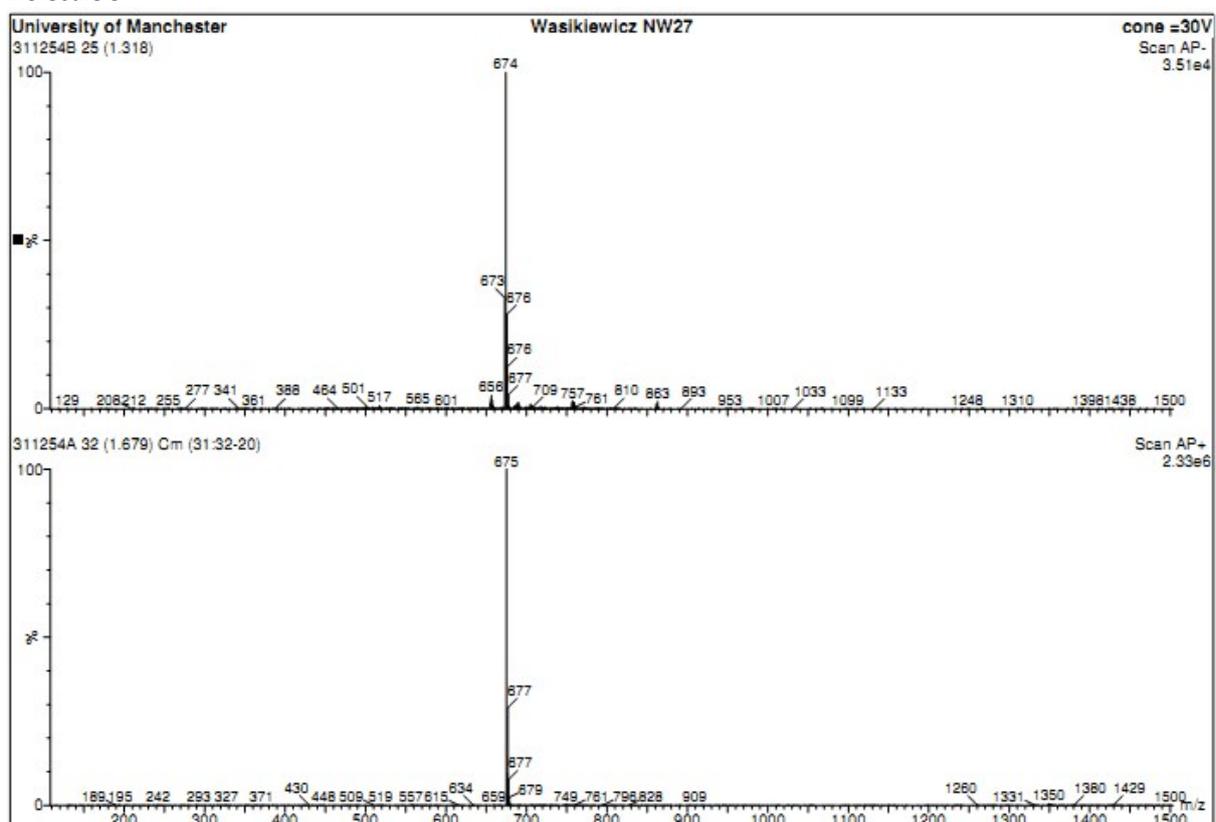
Molecule 7



Molecule 8



Molecule 9



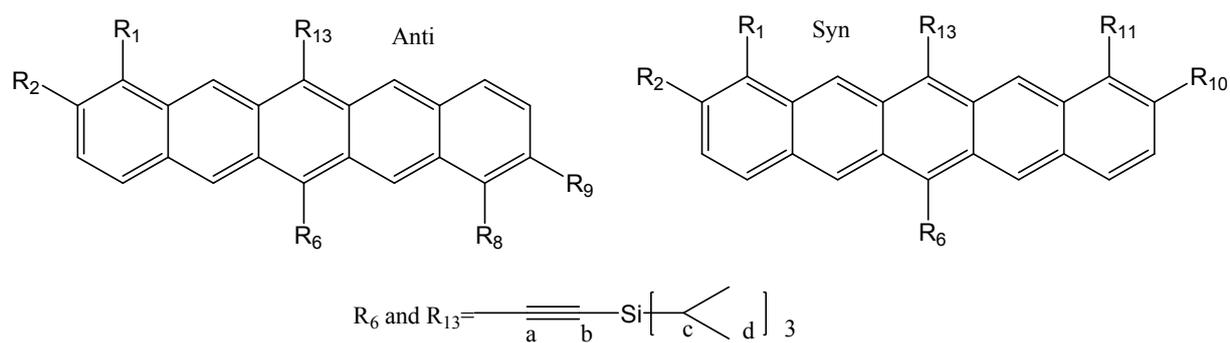


Fig. S2. Structural key for NMR assignments of compounds **6-9**.

Tables S1 below. NMR assignments of fluorinated TIPS-pentacenes. Where not entered assignment uncertain.

Compound 6

	δ H ppm	3J (H,H)	3J (H,F)	4J (H,F)	δ C ppm	1J (C,F)	2J (C,F)	3J (C,F)	4J (C,F)
1					158.96	256.6			
2	7.06	7.31	10.48		107.62		19.4		
3	7.38	8.51, 7.38		5.55	125.12			7.38	
4	7.78	8.58			124.59				4.6
4a					132.41			7.4	
5	9.34				126.25				3.7
5a, 6a, 7a, 11a, 12a, 13a					130.29, 130.31, 130.65, 130.75, 130.84, 132.98,				
6,13					119.15, 118.40				Both 1.9 long range
7,12	9.32				126.45, 126.34,				
8, 11	7.95-8.04				128.70, 128.65				
9,10	7.40-7.48				126.21, 126.17				
14	9.61				120.18			3.7	
14a					123.98		18.5		
a					107.49, 107.82				
b					104.26, 104.41				
c	1.34 - 1.43				18.93, 18.97				
d	1.34 - 1.43				11.60, 11.63				

Compound 7

	δ H ppm	3J (H,H)	3J (H,F)	4J (H,F)	δ C ppm	1J (C,F)	2J (C,F)	3J (C,F)	4J (C,F)
1 (8, 11)					158.95	255.3			
2 (9,10)	7.07	7.31	10.59		107.86 107.91		20.5 19.1		
3 (9,10)	7.38	8.51, 7.38		5.30	125.31 125.37			7.3 7.3	
4 (8, 11)	7.78	8.77			124.58 124.64				4.4 4.4
4a (7a,11a)					133.20 133.22			8.8 7.3	
5 (7,12)	9.34				126.31 126.43				4.4 4.4
5a, 6a,12a,13a					130.40 130.59 130.86 131.05				
6.13 (anti)					119.26				
6,13 (syn)					118.51 120.03				
14 (7,12 for ¹ H)	9.61 9.62				120.27 120.39			2.9 3.7	
14a (8a, 12a)					124.18 124.25		18.3 19.1		
a (anti)					108.23				
a(syn)					107.89 108.56				
b (anti)					104.08				
b (syn)					103.93 104.23				
c (anti)	1.34 - 1.40				18.92				
c (syn)	1.34 - 1.40				18.87 18.98				
d (anti)	1.34 - 1.40				11.62				
d (syn)	1.34 - 1.40				11.60 11.65				

Compound 8

	δ H ppm	3J (H,H)	3J (H,F)	4J (H,F)	δ C ppm	1J (C,F)	2J (C,F)	3J (C,F)	4J (C,F)
1	7.55		10.01	2.02 (4J H,H)	109.61		21.2		
2					160.40	250.1			
3	7.23-7.29				118.61		29.3		
4	7.96-8.03				131.69			8.8	
4a					130.09				1.8
5	9.23				126.96				2.9 (5J)
5a, 6a, 7a, 11a, 12a, 13a					129.78, 130.49, 130.81, 132.11, 132.25, 132.41.				
6,13					117.83, 118.70				2.7 long range
7,12	9.31				126.28, 126.36				1.7 long range
8, 11	7.96-8.03				128.65, 128.66				
9,10	7.41-7.46				126.07, 126.16				
14	9.33				126.95				2.7
14a					132.09			9.2	
a					107.32, 107.41				
b					104.42, 104.48				
c	1.35-1.41				18.98				
d	1.35-1.41				11.63				

Compound 9

	δ H ppm	3J (H,H)	3J (H,F)	4J (H,F)	δ C ppm	1J (C,F)	2J (C,F)	3J (C,F)	4J (C,F)
1 (8,11)	7.54		9.84	1.77 (4J H,H)	109.67		20.5		
2 (9, 10)					160.40, 160.50	251.0, 251.0			
3 (9, 10)	7.23-7.29				118.75, 118.68		29.5, 29.5		
4 (8, 11)	7.99	9.33		5.80	131.67, 131.68			8.3, 9.2	
4a (7a,11a)					130.28, 130.30				2.2, 1.9
5 (7,12)	9.22				126.92, 127.01				2.9, 2.2 (5J)
5a, 6a,12a,13a and 4a					129.78, 129.95, 130.30, 130.70, 131.00, 131.02,				
6,13 (anti)					118.19				
6,13 (syn)					118.16, 118.21				
14 (7,12) (anti)	9.31				125.36,				2.2
14 (7.12) (syn)	9.31				125.28 125.46				1.5
14a (7a,11a)					132.11, 132.29			10.1, 8.3	
a (anti)					107.58				
a (syn)					107.49, 107.67				
b (anti)					104.23				
b (syn)					104.18, 104.30				
c	1.35-1.39				18.96				
d	1.35-1.39				11.61				

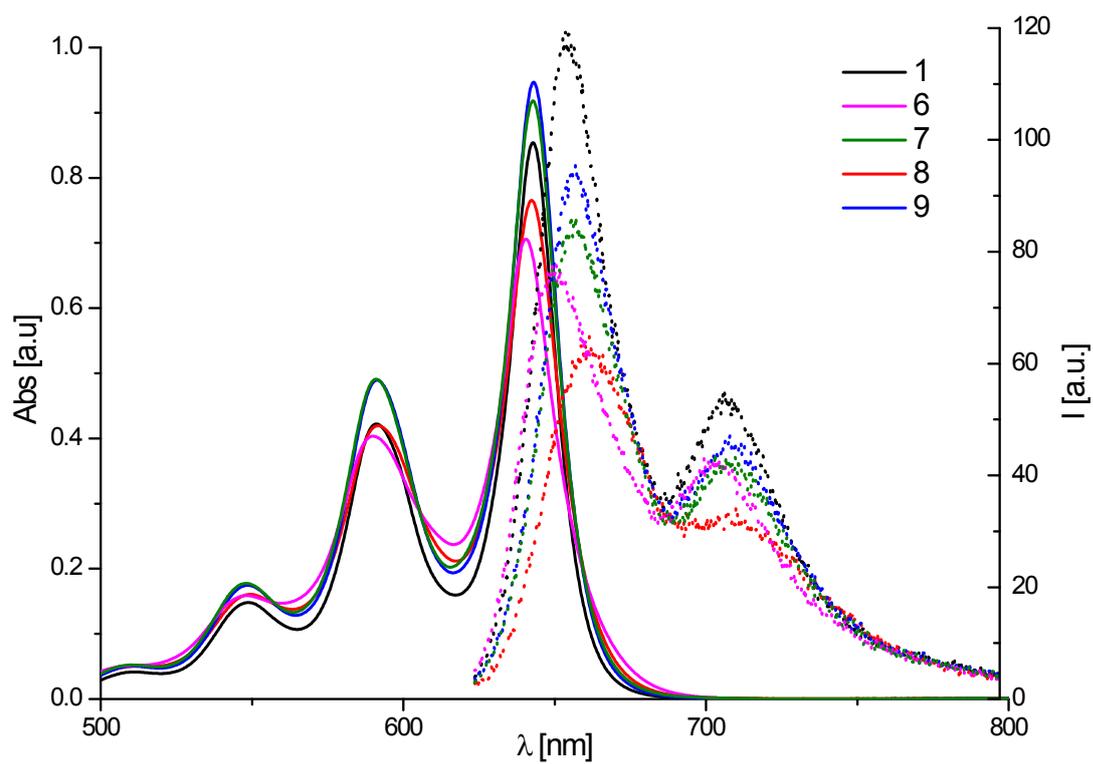


Fig. S3 UV-VIS fluorescence spectra of **6**, **7**, **8**, **9**, **10** compounds in toluene. Solvent spectrum was used as a baseline and subtracted from compound spectra. Absorbance and fluorescence intensity were normalised against maximum peaks.

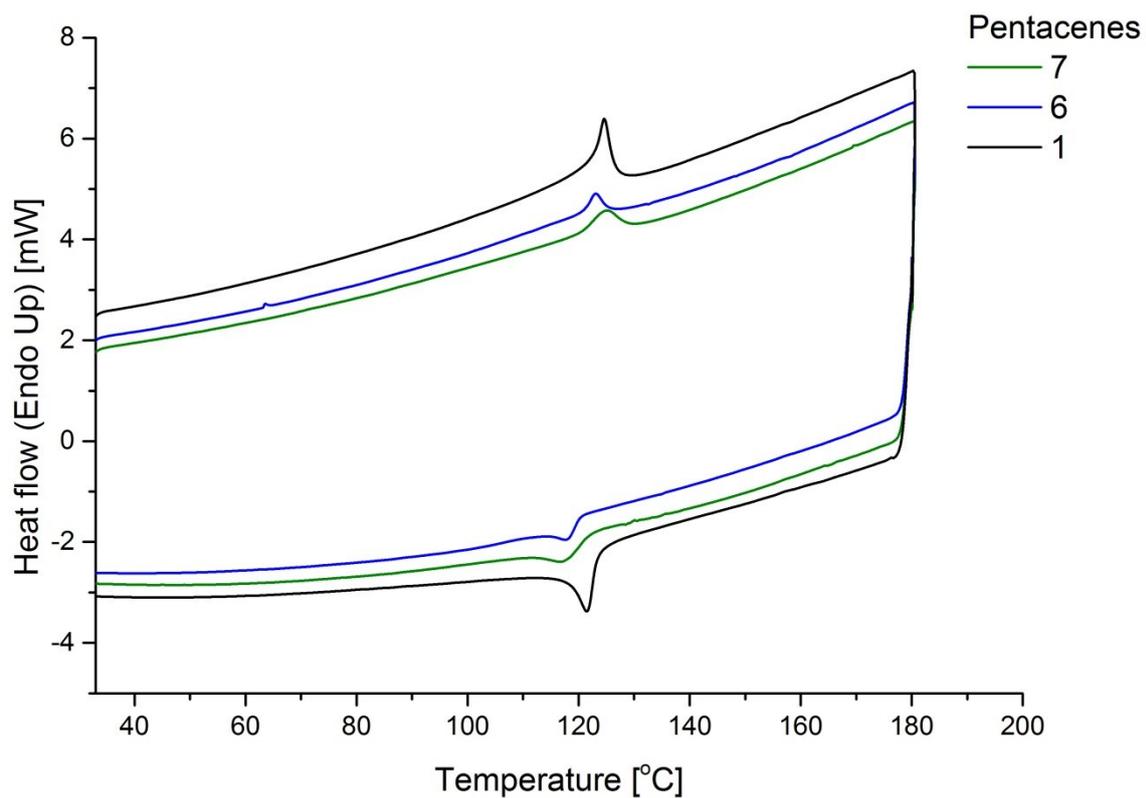


Fig. S4 DSC of pentacene derivatives. Fully reversible transitions of compounds **1** (black), **6** (blue) and **7** (green) shown. For compounds **8** and **9** transition was not detected.

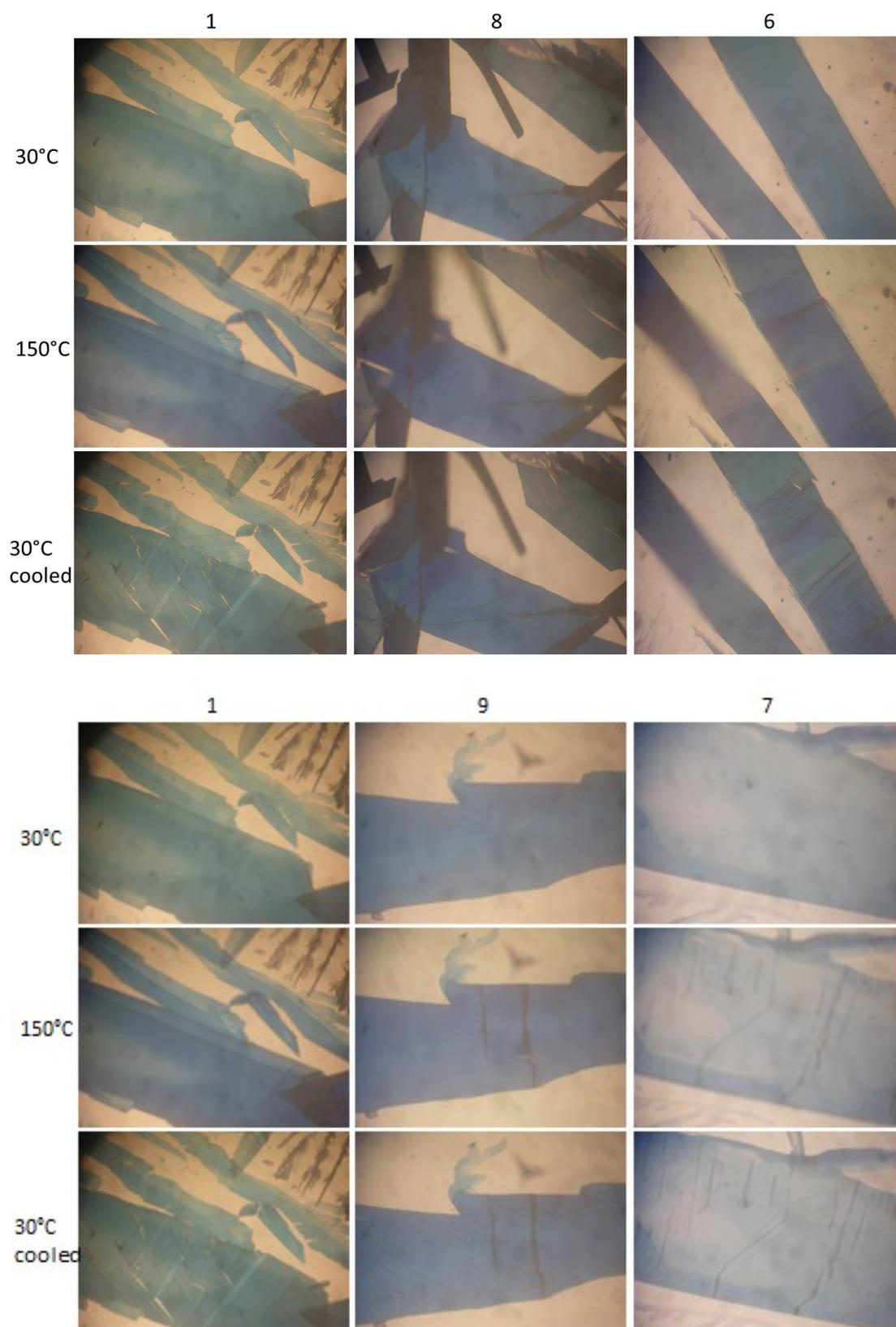
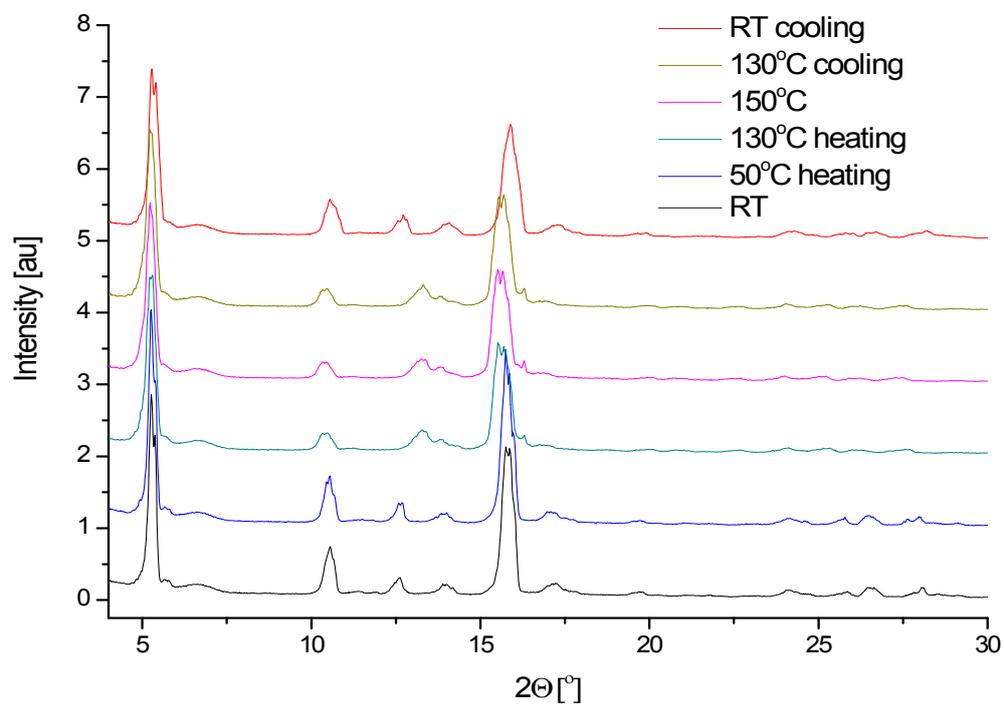


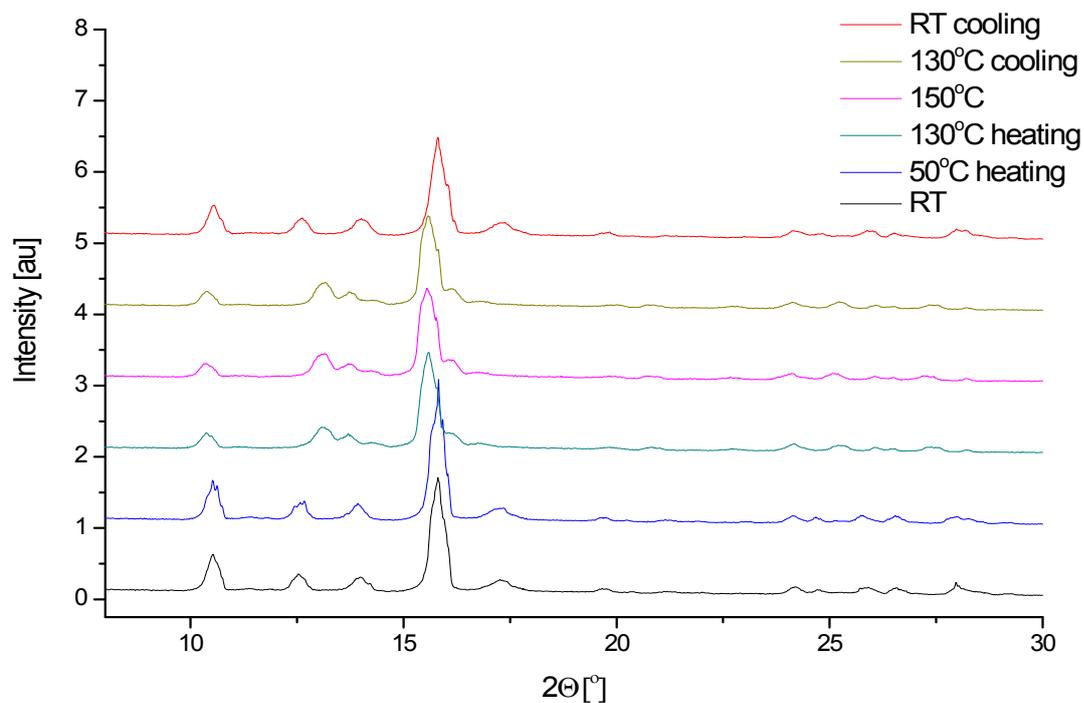
Fig. S5 Optical microscope images of crystals of **1**, **6**, **7**, **8**, and **9** exposed to heating and cooling cycle. Heating to 150 °C at 10 °C/min; holding for 5min at 150 °C; cooling down to room temperature.

Fig. S6 below. Powder XRD of compounds **6**, **7**, **8** and **9**. Samples were exposed to thermal treatment at the heat/cooling rates 10 °C/min and XRD patters taken at the indicated temperatures.

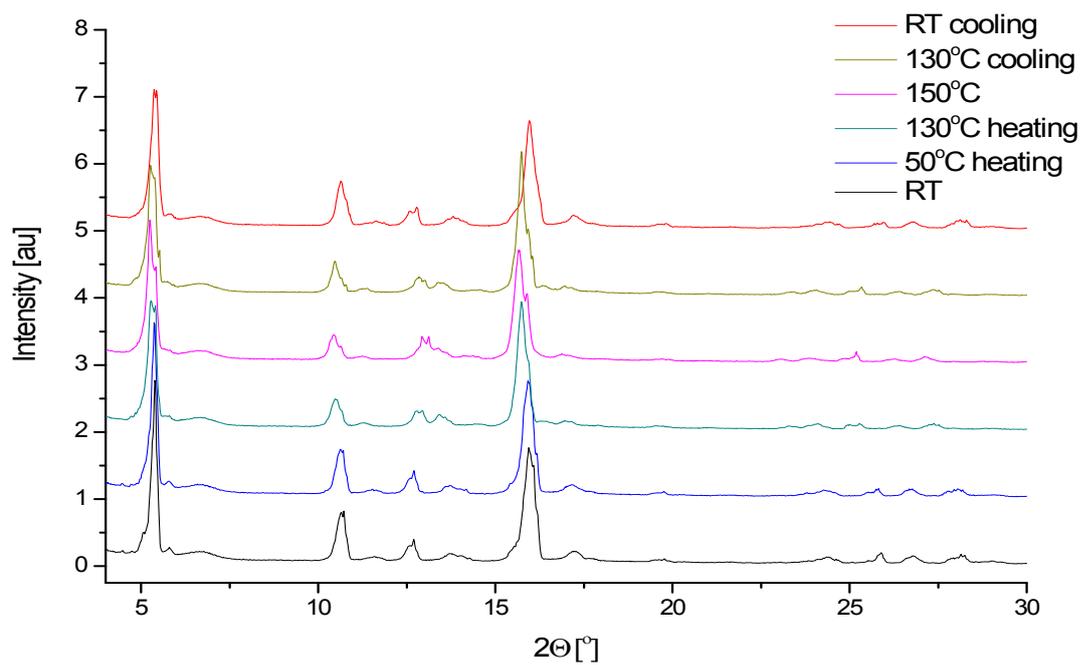
Molecule 6



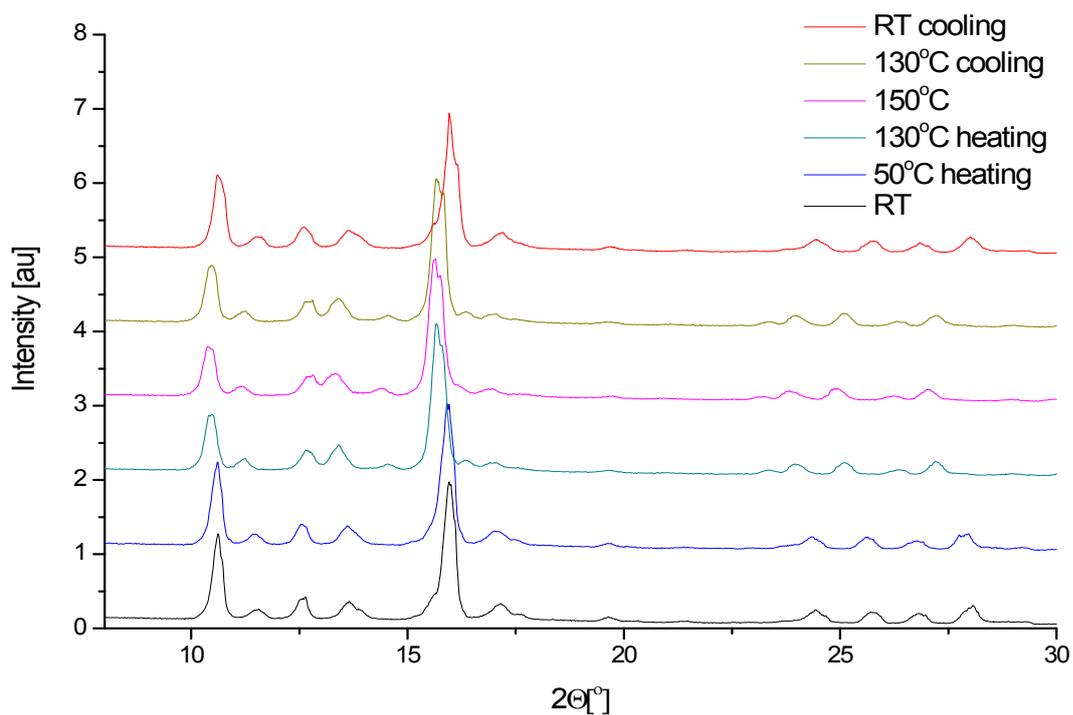
Molecule 7



Molecule 8



Molecule 9



Thin Film Transistors

Field effect transistors were created for the compounds **6**, **7**, **8**, **9** and tips-Pentacene (**1**). Thin films were characterised by X-ray diffraction and atomic force microscopy and transistors were created and analysed using conventional thin film transistor techniques.

All materials and devices were prepared on heavily doped silicon (n++) substrates with 290 nm of thermally grown silicon dioxide. The substrates were cleaned by washing and sonication in acetone, propan-2-ol and methanol followed by UV-Ozone treatment. The surfaces of the substrates were then treated with octadecyltrichlorosilane (OTS) monolayers to reduce the surface energy, passivate traps and improve thin film growth. OTS treatment was done by spin coating of an OTS solution from chloroform, 3 times in ambient conditions. Unreacted OTS was removed by sonication in chloroform and dried at 105 °C. OTS treated substrates were all washed with organic solvents and dried with nitrogen before being transferred to the vacuum chamber for thin film deposition.

Evaporation of the organic semiconductors was performed in a modified Edwards Auto306 vacuum evaporator with a base pressure of 5×10^{-7} mbar. Nominally, 50 nm of compounds **1,6,7,8** and **9** was deposited onto substrates held at 40 °C at a rate of 0.5 \AA s^{-1}

To create thin film transistors the as prepared substrates were transferred to a separate Edwards Auto500 vacuum evaporator (base pressure 3×10^{-7} mbar) for gold evaporation. Nominally, 50 nm of gold was deposited on top of the organic layers at a rate of 1 \AA s^{-1} through a shadow mask.

The thin films were characterised using a Park XE100 atomic force microscope in tapping mode and a Bruker D8 discover X-ray diffractometer for out-of-plane X-ray diffraction. Transfer and output curves were obtained and device performance was analysed in the saturation regime using the standard equation.

$$I_D = C_i \frac{W}{2L} \mu_{\text{sat}} (V_G - V_T)^2$$

Where, I_D is the source-drain current, C_i is the capacitance, W the channel width, L the channel length, μ_{sat} is the saturation mobility, V_G is the swept gate voltage and V_T is the threshold voltage. The transistors had a channel width of 2000 μm and a channel length of 60 μm , the 290 nm silicon dioxide with OTS monolayer was calculated to have a capacitance of approximately 11.7 nFcm^{-2} .

Out-of plane X-ray diffraction, **Figure S7**, shows reflections from the (00n) plane.. All compounds show very similar crystal structure with d-spacing between 16.1-16.6 Å. Compounds **6** and **7** diffraction peaks are slightly shifted to slightly lower angles than the others. Interestingly the atomic force microscopy images, **Figure S8**, show that compounds **6** and **7** thin film morphology is strikingly different than for tips-Pentacene (**1**) whereas compounds **8** and **9** show very similar structure in crystallite size and shape.

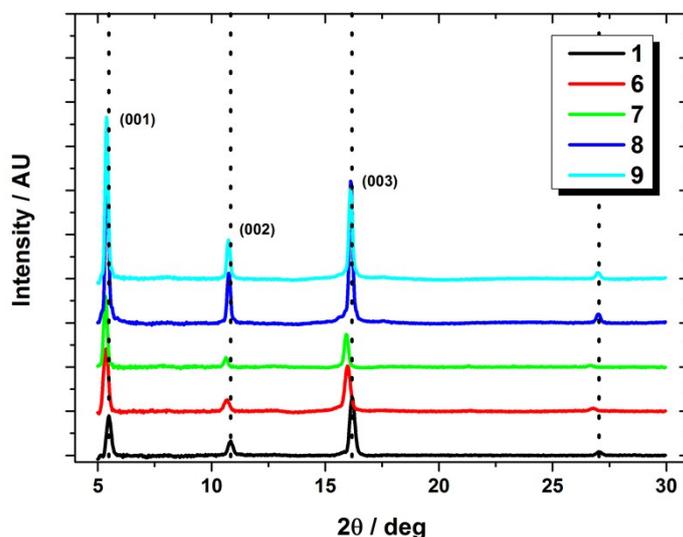


Figure S7. Out-of-plane, x-ray diffraction for compounds **1**, **6**, **7**, **8** and **9**.

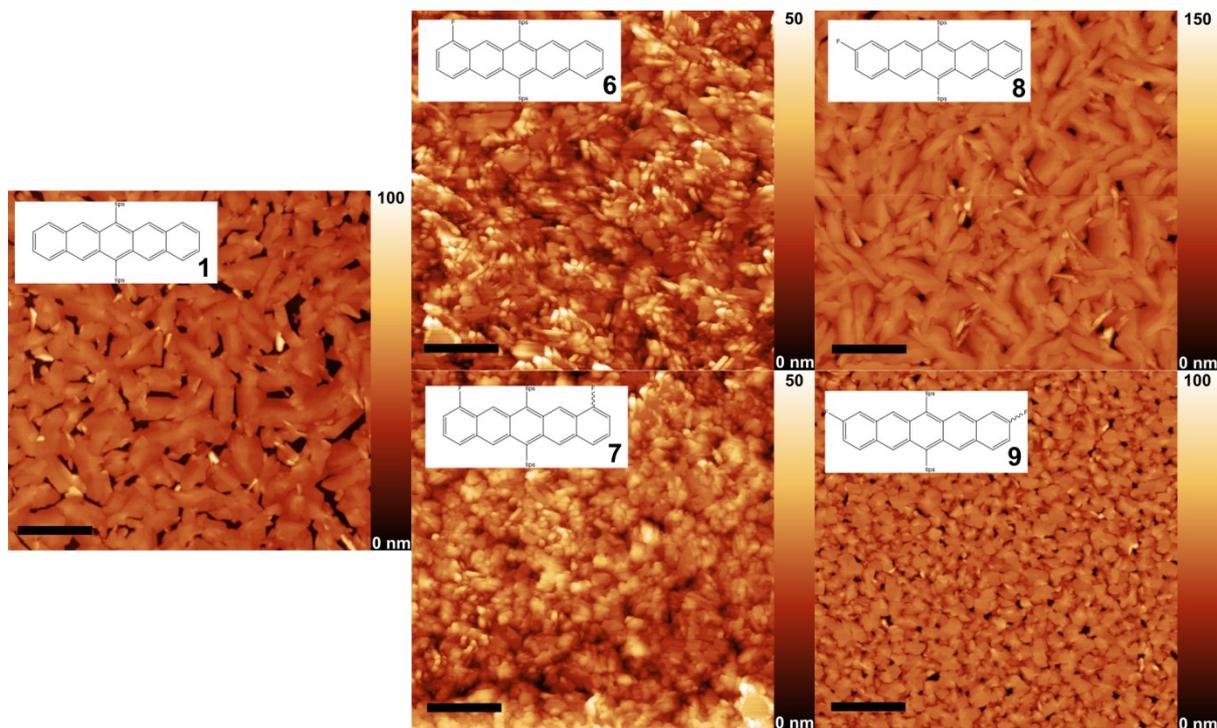


Figure S8. Atomic force microscopy for compounds **1**, **6**, **7**, **8** and **9**. Scale bar is 2 μm .

All devices fabricated were tested in an inert nitrogen glovebox. A probe station connected to an Agilent E5270b parameter analyser was used to obtain output and transfer curves, **Figure S9**. All devices showed similar mobility on the order of $10^{-2} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ (summarised in **Table 2**), consistent with previous findings for this class of material. Further, all devices exhibited a threshold voltage close to zero, high on/off current ratio, currents of approximately $10 \mu\text{A}$, less than $1 \text{ V} \cdot \text{dec}^{-1}$ sub-threshold swing and only small hysteresis.

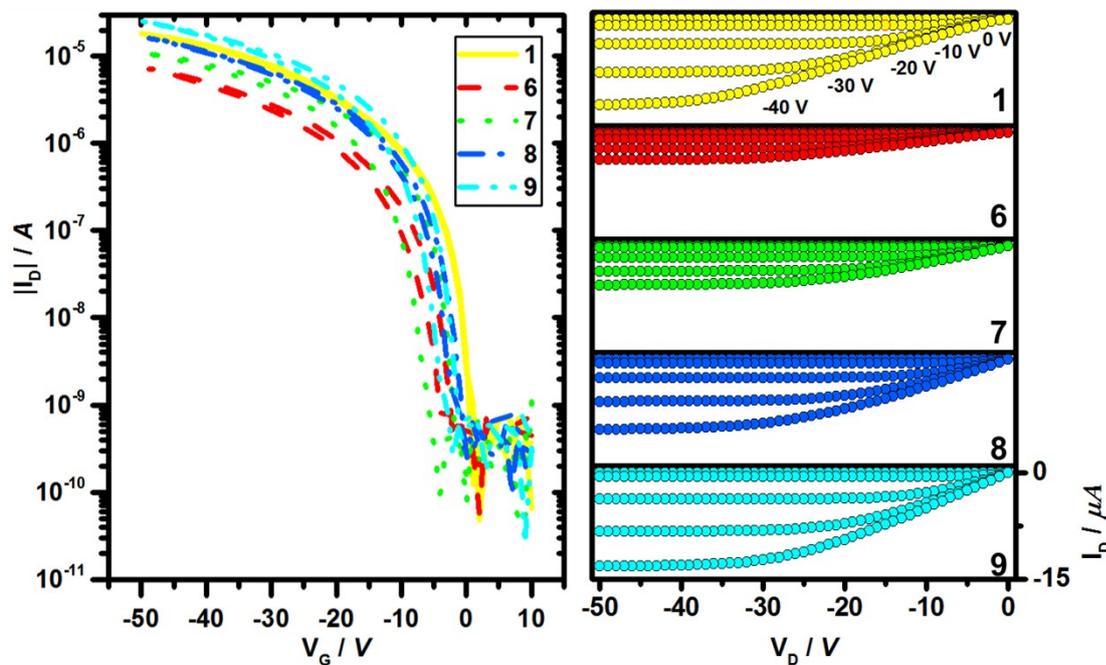


Figure S9. Transfer and output curves for compounds **1**, **6**, **7**, **8** and **9**

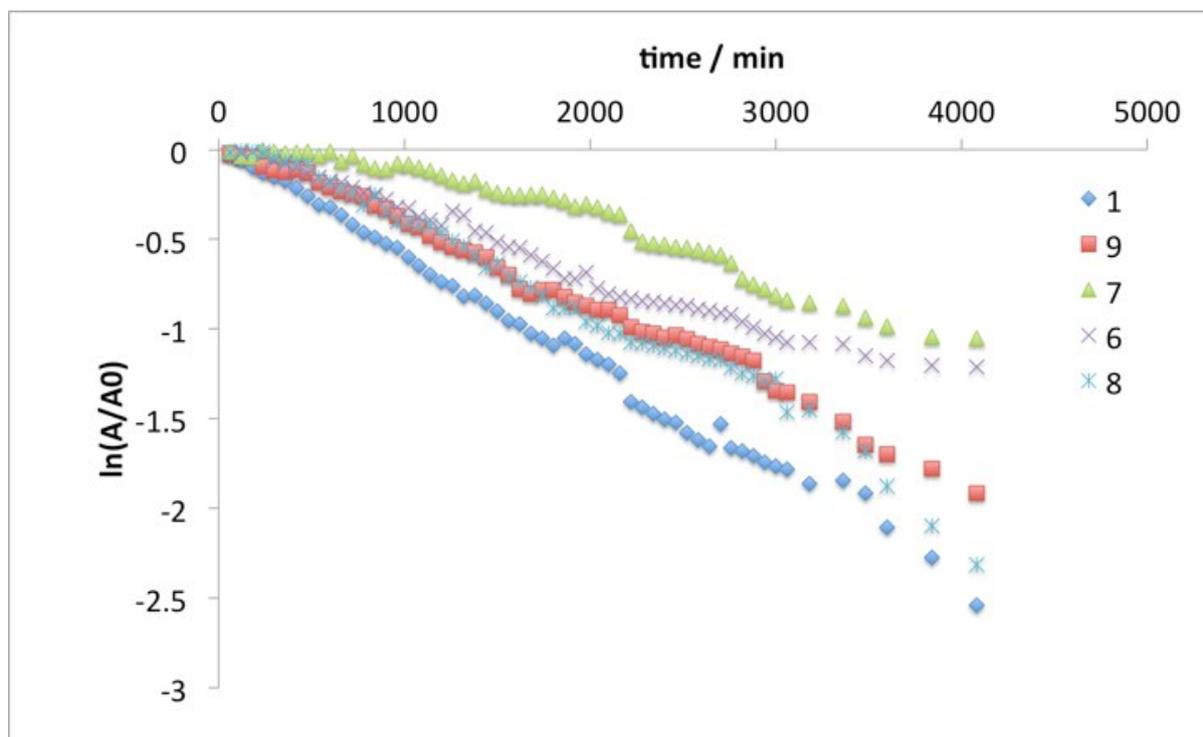


Figure S10: Plots of $\ln(A_t/A_0)$ versus time t at 1×10^{-5} M in toluene at room temperature of compounds 1, 6, 7, 8, and 9