Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supporting Information for

Triphenylene-ethylammonium Tetrachorometallate salts: Multicolumnar Mesophases, Thermochromism and Langmuir films.

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Experimental Section

General Considerations. General procedures are as reported before. Elemental analyses were performed by the "Servicio de análisis elemental, CACTI, Universidad de Vigo". IR spectra were recorded on a Perkin-Elmer Frontier spectrometer coupled to a Pike GladiATR-210 accessory. NMR spectra were recorded on Bruker AV-400 or Varian 500 instruments in $CDCl_3$. UV/Vis spectra were obtained by means of a Shimadzu UV-2550 spectrophotometer, equipped with a diffuse reflectance accessory for the solid samples. Temperature-dependent UV studies in the condensed phases have been performed on a Lambda 35 spectrophotometer.

Microscopy studies were carried out on a Leica DMRB microscope equipped with a Mettler FP82HT hot stage and a Mettler FP90 central processor, at a heating rate of 10 °C min^{-1}. DSC was performed using a DSC Q20 from TA Instruments with samples (2−5 mg) sealed in aluminum pans and a scanning rate of 10 °C/min under a nitrogen atmosphere.

Thermogravimetric analyses (TGA) were carried out with a thermogravimetric analyser model TGA/SDTA 861 or TGA Q500 V6.7 Build 203 instrument. The samples were heated at 10 °C/min under N_2 atmosphere.

Langmuir films were obtained by dispersion of 10^{-5} M solutions of the compounds in HPLC grade chloroform on a water subphase (Wasserlab Ecomatic purifying equip, water resistivity < 0.2 μS/cm, 20 ºC) contained in a KSV 2000 System 2 Langmuir-Blodgett trough. After 15 minutes to evaporate the solvent, the monolayer was compressed symmetrically from both sides at a barrier speed of 10 mm/min and the surface pressure was measured by using the Wilhelmy plate method with a resolution of 4 mN/m. The reciprocal of the compressibility ($1/\beta$) was provided by the program controlling the Langmuir-Blodgett trough. The Langmuir-Blodgett films were built up on glass substrates using the LB technique. Z-type depositions were carried out at speed up = 12 mm/min and speed down = 84 mm/min. Y-type depositions were carried out at speed up = speed down = 12 mm/min. When a hydrophilic substrate was required, it was cleaned by sonication in chloroform and then in sulfochromic acid, followed by treatment with NaOH 1 mM for several hours. In order to hydrophobize the substrates, they were immersed in a solution of hexamethyldisilazane in chloroform and left in for a day. A KSV Nima MicroBAM was used to take images of the floating films by Brewster angle microscopy. X-ray diffractograms of the LB films were carried out on a Bruker D8 Discover A25 diffractometer operating with monochromatic Cu-$K_{\alpha 1}$ radiation (1.5406 Å) at the X-Ray Diffraction Service of University of Valladolid. A parallel optics was mounted (Gobel R0.6mm, 2.7 knife edge, step size 0.02º) and data were collected using a linear Lynxeye detector in mode 1D.

The S/WAXS patterns were obtained by transmission diffraction with a Guinier experimental set-up. A linear focalized monochromatic Cu-$K\alpha_1$ beam (λ = 1.5405 Å) was obtained using a sealed-tube generator (900 W) equipped with a bent quartz monochromator. In all cases, the crude powder was filled in thin Lindemann capillaries of 1 mm diameter and 10 μm wall thickness in air (corrections for air were made), and then heated to produce the mesophase. An initial set of diffraction patterns was recorded with a curved Inel CPS 120 counter gas-filled detector linked to a data acquisition computer; periodicities up to 70 Å can be measured, and the sample temperature controlled to within ± 0.01 ºC from 20 to 200 ºC. Alternatively, patterns were also recorded on an image plate; periodicities up to 120 Å can be measured (scanned by STORM 820 from Molecular Dynamics with 50 μm resolution). In each case, exposure times were varied from 1 to 24 h.

Field dependent magnetization measurements were performed at four different temperatures (277, 300, 350 and 375 K) using a MPMS XL SQUID magnetometer (Quantum Design) with a known mass of the powder samples placed in gelatin capsules.

Synthesis. Literature methods were used for the synthesis of 4-(6-bromohexyloxy)benzaldehyde,[1] 2-(6–(4-formylphenoxy)hexyloxy)-3,6,7,10,11-penta(dodecyloxy) triphenylene.[2]

Only examples are described, as the syntheses were similar for the rest of the complexes. Yields, IR, and analytical data are given for all the complexes.

Synthesis of the triphenylene-ethylammonium chloride salt

Preparation of 2-(6–(4-formylphenoxy)hexyloxy)-3,6,7,10,11-penta(dodecyloxy) triphenylene (1)

To a solution of 2-hydroxy- 3, 6, 7, 10, 11- penta(dodecyloxy)triphenylene (4 g, 3.43 mmol) in dry butanone (100 mL) under nitrogen, 4-(6-bromohexyloxy)benzaldehyde (2.45 g, 8.59 mmol) and K_2CO_3 (1.89 g, 13.7 mmol) were added. The mixture was refluxed for 24 h and then the solvent was evaporated. To the obtained residue, water (100 mL) was added and the mixture was extracted with dichloromethane (3 x 50 mL). The organic layer was separated, dried over $MgSO_4$ and filtered. The solvent was removed on a rotary evaporator, and the residue was chromatographed on silica gel. Elution with dichloromethane/hexane 1:1 afforded a pale-yellow fraction which was recrystallized from dichloromethane/acetone (1:50), yielding compound **2** as a white solid. Yield: 4.08 g; 86.8 %. ^{1}H RMN ($CDCl_3$): δ_1 9.87 (s, 1H, CHO), δ_2 7.84 (s, 6H, TriPh), δ_3 7.82 (d, 2H, ArH, AA' part of AA'XX' spin system, $N_{A,X} = J_{AX} + J_{AX'} = 8.70$ Hz $J_{AA'} \approx J_{XX'}$), δ_4 6.98 (d, 2H, ArH, XX' part of AA'XX' spin system, $N_{A,X} = J_{AX'} + J_{AX} = 8.70$ Hz $J_{AA'} \approx J_{XX'}$), δ_5 4.24 (m, 12H, TriPh-O-CH_2), δ_6 4.07 (t, 2H, Ph-O-CH_2, J = 6.48 Hz), δ_7 2.01-1.87 (m, 14H, O-CH_2-CH_2), δ_8 1.71-1.21 (m, 94H, CH_2), δ_9 0.88 (m, 15H, CH_3). ^{13}C {^{1}H} NMR ($CDCl_3$, 126 MHz): 190.71 (*C*=O), 164.18 (O-*CPh*), 149.07, 149.05, 149.01, 148.98, 148.96, 148.83 (O-*CTriPh*), 131.95 (HA-*CPh*), 129.81 (*CPh*-CHO), 123.73, 123.70, 123.67, 123.58 (*CTriPh*), 114.70 (HX-*CPh*), 107.54, 107.47, 107.42, 107.37, 107.35, 107.22 (H-*CTriPh*), 69.83, 69.76, 69.72, 69.70, 69.59, 69.49 (TriPh-OCH_2), 68.24 (Ph-OCH_2), 31.94, 29.75, 29.72, 29.69, 29.56, 29.54, 29.51, 29.39, 29.10, 26.23, 25.98, 25.86, 22.70 (CH_2), 14.12 (CH_3). IR (cm^{-1}): ν(C=O): 1698. Anal. Calcd. (%) for $C_{91}H_{148}O_8$: C, 79.77; H, 10.89. Found: C, 79.72; H, 10.74.

Preparation of 2-((6-(4-(ethylamino))phenoxy)hexyloxy)-3,6,7,10,11-penta(dodecyloxy)triphenylene (2).

To a solution of 2-(6–(4-formylfenoxi)hexyloxy)-3,6,7,10,11-penta(dodecyloxy)triphenylene (2.03 g, 1.48 mmol) in dry tetrahydrofuran (30 mL), a solution of ethylamine 2.0 M (2.5 mL, 5 mmol) was added. After stirring for 24 h at room temperature, 30 mL of dry ethanol and solid $NaBH_4$ (0.11 g, 2.90 mmol) were added. The resulting mixture was stirred at room temperature for another 24 h. Then, the solvent was removed on a rotary evaporator, and the product was extracted in dichloromethane (50 mL). The organic solution was washed with water (3 x 50 mL) and dried over $MgSO_4$. The solvent was evaporated to afford a light yellow solid, which was used in the next step without purification. Yield: 1.85 g, 89 %. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (NH, not observed), δ_1 7.83 (s, 6H, TriPh), δ_2 7.21 (d, 2H, ArHA, AA' part of AA'XX' spin system, *NA,X* = *JAX* + *JAX'* = 8.54 Hz, *JAA'* ≈ *JXX'*), δ_3 6.85 (d, 2H, ArHX, XX' part of AA'XX' spin system, *NA,X* = *JAX* + *JAX'* = 8.54 Hz, *JAA'* ≈ *JXX'*), δ_4 4.22 (m, 12H, TriPh-OCH_2), δ_5 3.97 (t, 2H, Ph-OCH_2, *J* = 6.32 Hz), δ_6 3.72 (s, 2H, Ph-CH_2N), δ_7 2.67 (q, 2H, NH-*CH_2*-CH_3, *J* = 7.23 Hz), δ_8 2.05-1.81 (m, 14H, OCH_2-*CH_2*), δ_9 1.70-1.20 (m, 94H, CH_2), δ_{10} 1.12 (t, 3H, NCH_2-*CH_3*, *J* = 7.23 Hz), δ_{11} 0.87 (m, 15H, CH_3). ^{13}C {^{1}H} NMR ($CDCl_3$, 126 MHz): 158.10 (O-*CPh*), 149.01, 148.99, 148.97, 148.90, (O-*CTriPh*), 132.51 (*CPh*), 129.25 (HA-*CPh*), 123.69, 123.65, 123.64, 123.61 (*CTriPh*), 114.35 (HX-*CPh*), 107.46, 107.43, 107.39, 107.31 (H-*CTriPh*), 69.76, 69.74, 69.72, 69.66, 69.57 (TriPh-*OCH_2*), 67.85 (Ph-*OCH_2*), 53.38 (Ph-*CH_2*), 43.54 (NH-*CH_2*-CH_3), 31.94, 29.74, 29.71, 29.69, 29.61, 29.56, 29.54, 29.50, 29.48, 29.46, 29.39, 29.35, 26.22, 26.21, 26.03, 25.99, 22.70 (*CH_2*), 15.26 (NCH_2-*CH_3*), 14.12 (*CH_3*). IR (cm^{-1}): ν(N-H): 1616, ν(O-C): 1260. Anal. Calcd. (%) for $C_{93}H_{155}NO_7$: C, 79.83; H, 11.17; N, 1.00. Found: C, 79.92; H, 11.34; N, 1.01.

Preparation of 2-((6-(4-(ethylaminomethyl))phenoxy)hexyloxy)-3,6,7,10,11-penta(dodecyloxy)triphenylene hydrochloride (3)

To a solution of 2-((6-(4-(ethylamino))phenoxy)hexyloxy)-3,6,7,10,11-penta(dodecyloxy)triphenylene (1.50 g, 1.07 mmol) in dichloromethane (50 mL), hydrochloric acid 37% (4.0 mL, 48.8 mmol) was added dropwise. After stirring for 30 min, water (150 mL) was added and the product was extracted in dichloromethane (3x30 mL). The organic solution was washed with water (3x50 mL), dried over $MgSO_4$, and concentrated to 15 mL. Addition of hexane (25 mL) affords a light yellow solid. Yield: 1.48 g, 96. ^{1}H RMN ($CDCl_3$, 500 MHz): δ_1 9.76 (s, 2H, -NH$_2$-), δ_2 7.83 (s, 6H, TriPh), δ_3 7.47 (d, 2H, ArH, AA' part of AA'XX' spin system, $N = J_{AX} + J_{AX'} = 8.47$ Hz, $J_{AA'} \approx J_{XX'}$), δ_4 6.89 (d, 2H, ArH, XX' part of AA'XX' spin system, $N = J_{AX} + J_{AX'} = 8.47$ Hz, $J_{AA'} \approx J_{XX'}$), δ_5 4.22 (m, 12H, TriPh-O-CH$_2$), δ_6 3.95 (s, 2H, ArH-CH$_2$), δ_7 3.93 (t, 2H, Ph-O-CH$_2$, J = 6.57 Hz), δ_8 2.82 (q, 3H, NH-CH$_2$-CH$_3$, J = 7.24 Hz), δ_9 2.01-1.78 (m, 14H, O-CH$_2$-CH$_2$), δ_{10} 1.70-1.53 (m, 14H, O-CH$_2$-CH$_2$-CH$_2$), δ_{11} 1.48-1.19 (m, 83H, N-CH$_2$-CH$_3$ and -CH$_2$-), δ_{11} 0.88 (m, 15H, -CH$_3$). ^{13}C {^{1}H} NMR ($CDCl_3$, 126 MHz, Me$_4$Si): 159.90 (O-C_{Ph}), 149.01, 149.00, 148.97, 148.96, 148.93, 148.85 (O-C_{TripH}), 131.74 (H$_A$-C_{Ph}), 123.68, 123.64, 123.62, 123.56 (C_{TriPh}), 121.79 (C_{Ph}), 114.92 (H$_X$-C_{Ph}), 107.48, 107.44, 107.39, 107.36, 107.34, 107.25 (H-C_{TriPh}), 69.79, 69.73, 69.71, 69.69, 69.61, 69.54 (TriPh-OCH_2), 67.90 (Ph-OCH_2), 49.50 (Ph-CH_2), 40.61 (NH$_2$-CH_2-CH$_3$), 31.91, 29.73, 29.70, 29.67, 29.65, 29.55, 29.51, 29.50, 29.46, 29.37, 29.36, 29.22, 26.21, 26.18, 26.02, 25.96, 22.68 (CH_2), 14.01 (CH_3). IR (cm^{-1}): ν (N-H): 1616. Anal. calcd (%) for $C_{93}H_{156}ClNO_7$: C, 77.80; H, 10.95; N, 0.98. Found: C, 77.99; H, 11.09; N, 0.98.

Synthesis of the triphenylene-ethylammonium tetrametallate salts

A solution of the appropriate metal salt ($CuCl_2$, $NiCl_2$, $CoCl_2$ or $MnCl_2$) (0.05 mmol) in absolute ethanol (15 mL) was added dropwise to a stirred solution of 2-((6-(4 (ethylaminomethyl))phenoxy)hexyloxy)-3,6,7,10,11-penta(dodecyloxy)triphenylene hydrochloride (0.15 g, 0.10 mmol) in dichloromethane (15 mL). After stirring at room temperature for 16 h, the resulting solution was concentrated to dryness. The product was recrystallized from dichloromethane/ethanol (1:20) at -5°C.

[TriPh-NH$_2$Et][CuCl$_4$] (4). Dark-green solid. Yield: 0.15 g, 95 %. IR (cm^{-1}): δ(NH$_2$): 1615; ν(Cu-Cl): 226. Anal. calcd (%) for $C_{186}H_{312}Cl_4CuN_2O_{14}$: C, 74.32; H, 10.46; N, 0.93. Found: C, 74.06; H, 10.69; N, 0.91.

[TriPh-NH$_2$Et][NiCl$_4$] (5). Light-green solid. Yield: 0.13 g, 88 %. IR (cm^{-1}): δ(NH$_2$): 1616; ν(Ni-Cl): 223. Anal. calcd (%) for $C_{186}H_{312}Cl_4N_2NiO_{14}$: C, 74.44; H, 10.48; N, 0.93. Found: C, 74.32; H, 10.69; N, 0.91.

[TriPh-NH$_2$Et][CoCl$_4$] (6). Blue solid. Yield: 0.20 g, 96 %, starting from 0.070 mmol of $CoCl_2 \cdot 6H_2O$. IR (cm^{-1}): ν(N-H): 1615; ν(Co-Cl): 280. Anal. calcd (%) for $C_{186}H_{312}Cl_4CoN_2O_{14}$: C, 74.44; H, 10.48; N, 0.93. Found: C, 74.28; H, 10.57; N, 0.98.

[TriPh-NH$_2$Et][MnCl$_4$] (7). Brown solid. Yield: 0.20 g, 98.5%, starting from 0.070 mmol of $MnCl_2 \cdot 10H_2O$. IR (cm^{-1}): δ(NH$_2$): 1615; ν(Mn-Cl): 227. Anal. calcd (%) for $C_{186}H_{312}Cl_4MnN_2O_{14}$: C, 74.54; H, 10.49; N, 0.93. Found: C, 74.64; H, 10.48; N, 0.91.

^{1}H NMR spectra (Agilent 500 in $CDCl_3$)

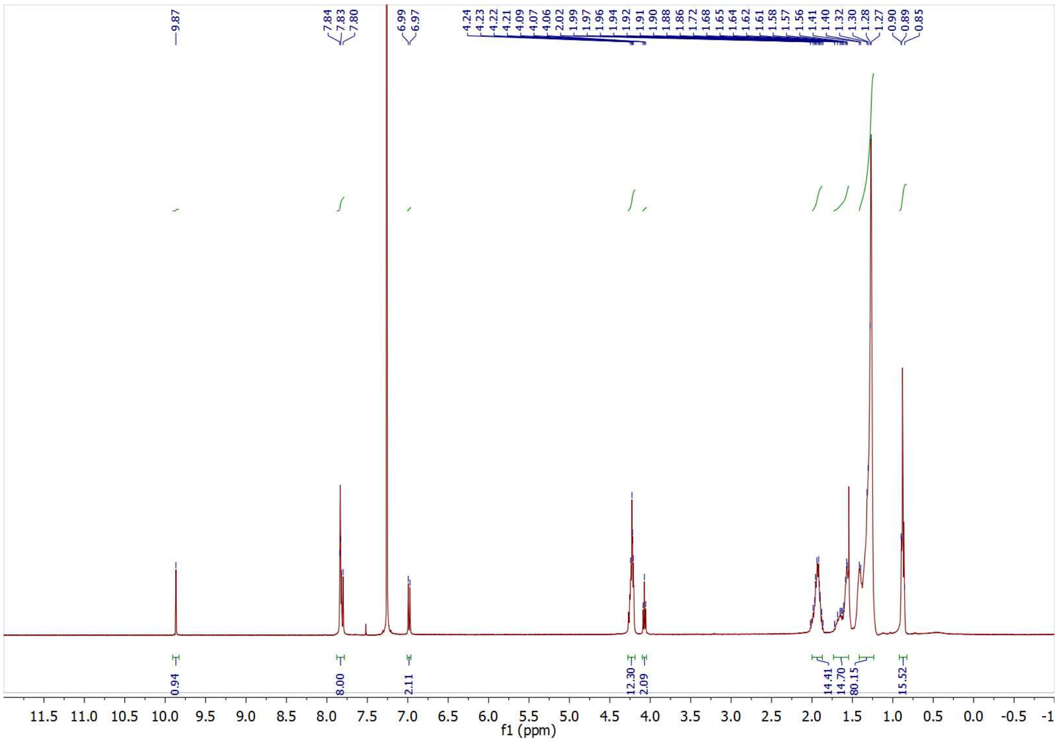


Figure S1: ^{1}H NMR spectrum of **1.**

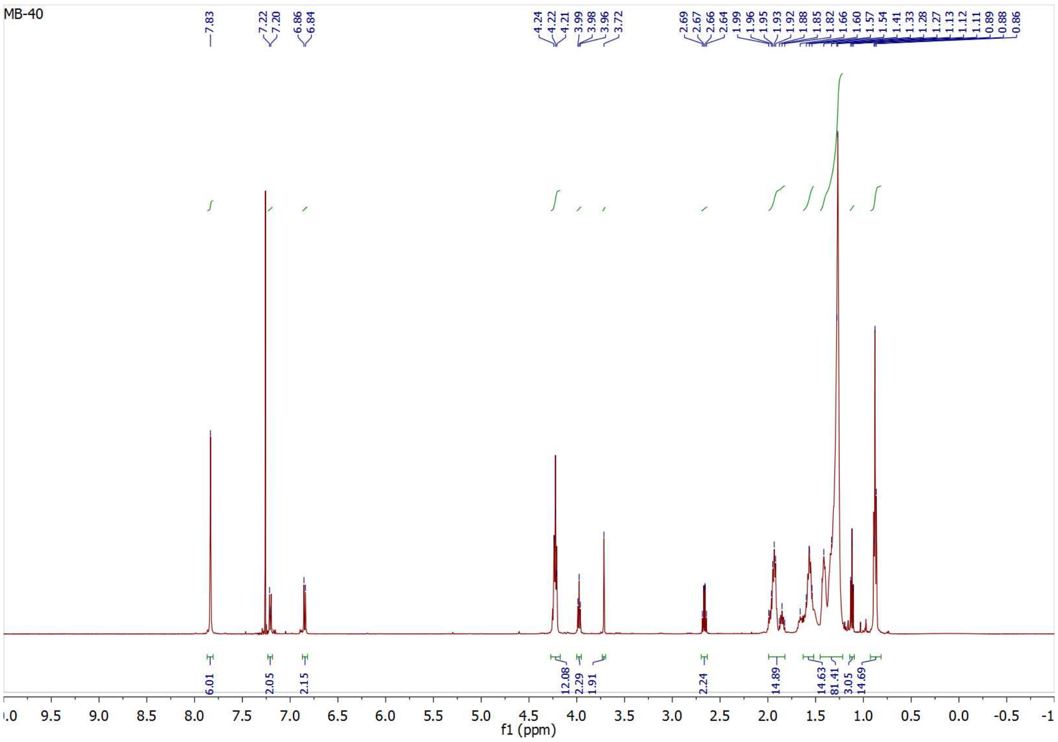


Figure S2: ^{1}H NMR spectrum of **2.**

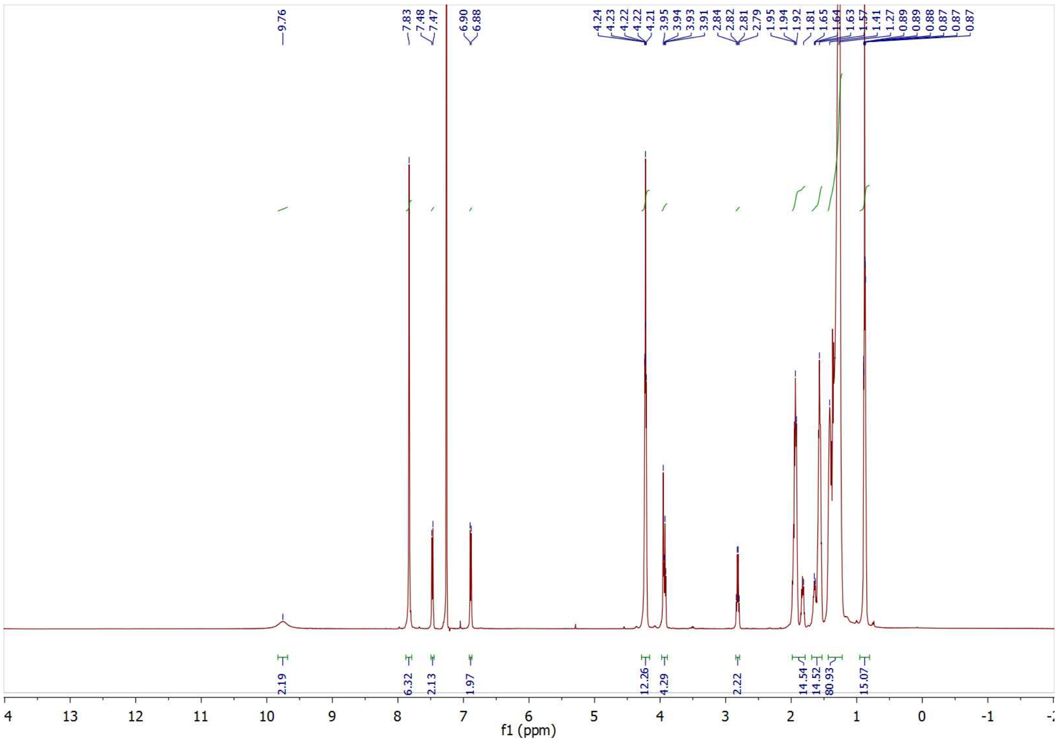


Figure S3: ^{1}H NMR spectrum of [TPh-NH$_2$Et]Cl **(3)**.

$^{13}C\{^{1}H\}$ NMR spectra (Agilent 500 (126 MHz MHz) in $CDCl_3$

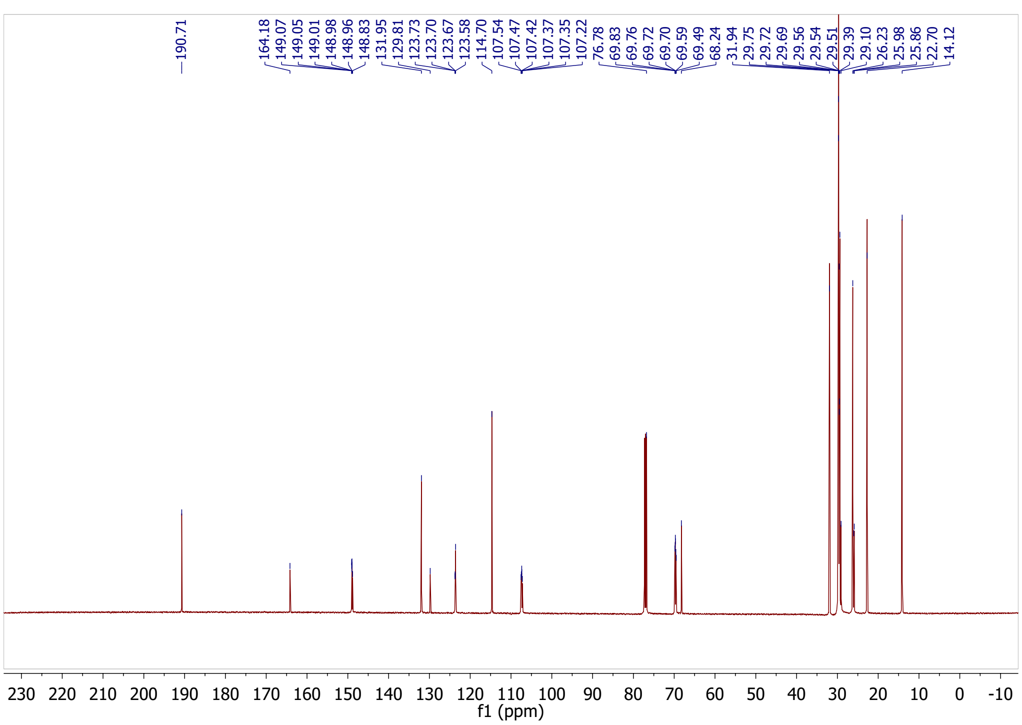


Figure S4: $^{13}C\{^{1}H\}$ NMR spectrum of **1**

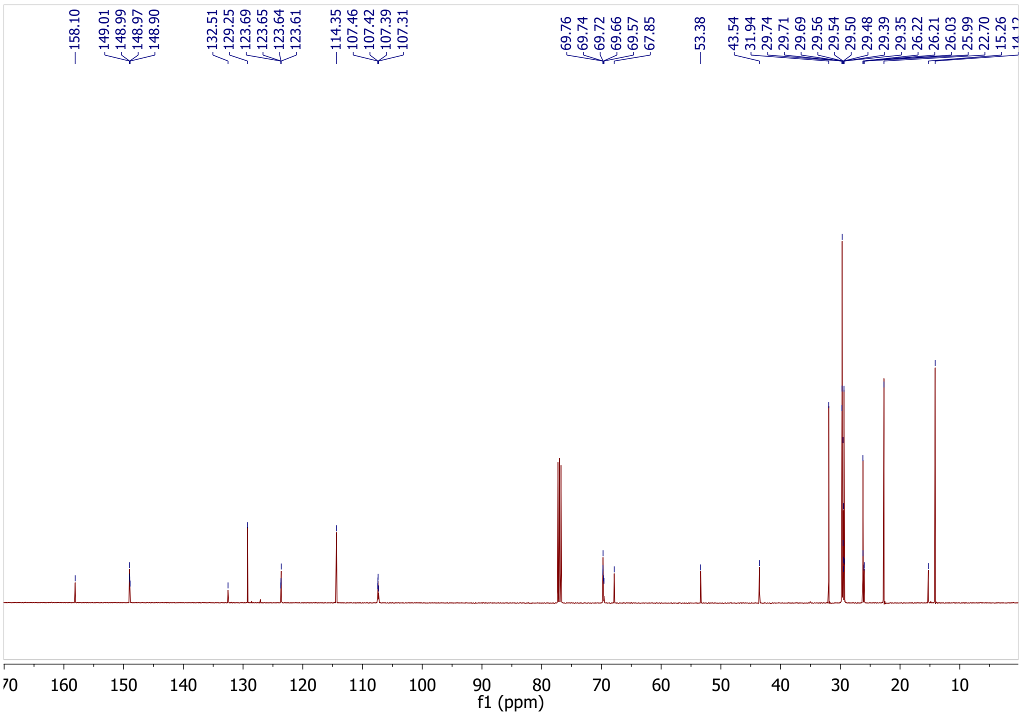


Figure S5: $^{13}C\{^{1}H\}$ NMR spectrum of **2**

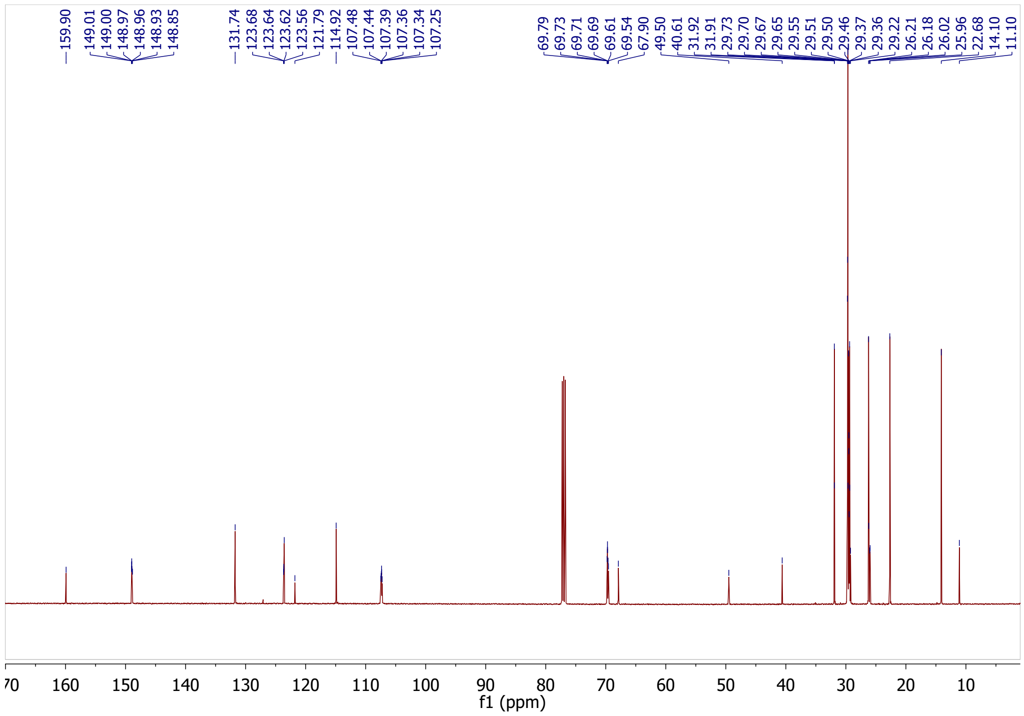


Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum of **3**

DSC scans: a) first heating, b) first cooling, c) second heating.

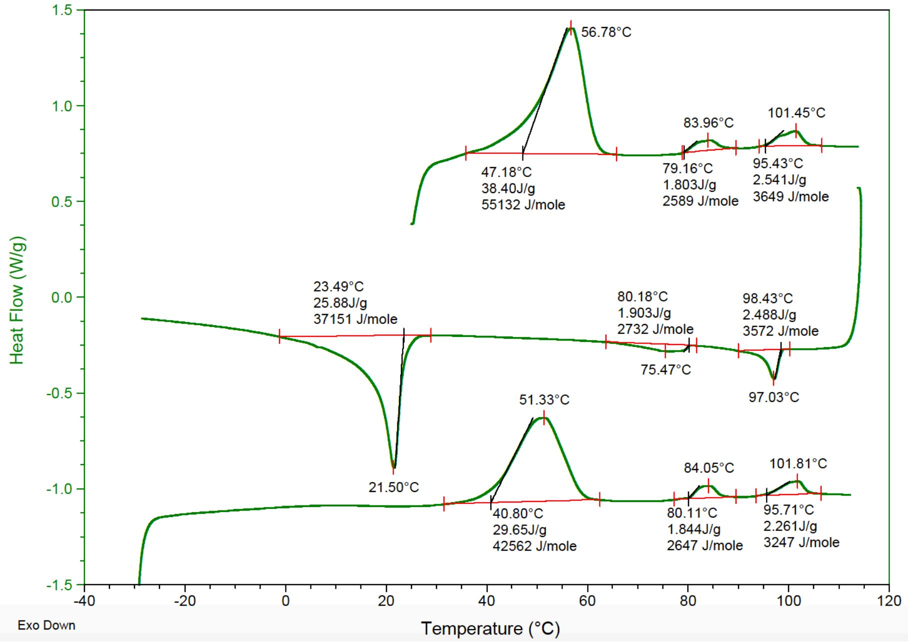


Figure S7: DSC scans of of [TPh-NH_2Et]Cl **(3)**

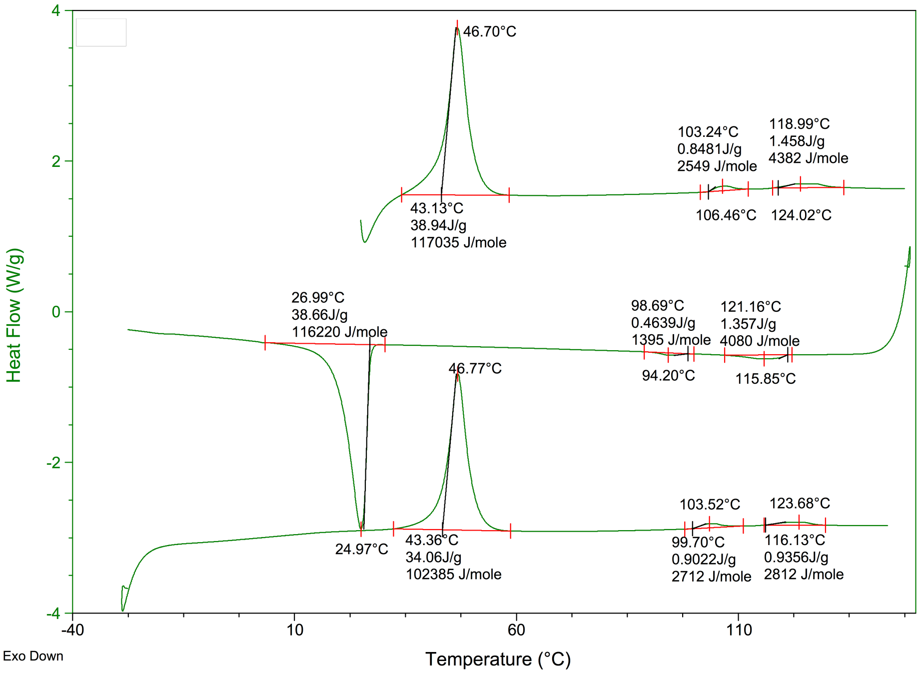


Figure S8: DSC scans of [TPh-NH_2Et]$_2$[$CuCl_4$] **(4)**

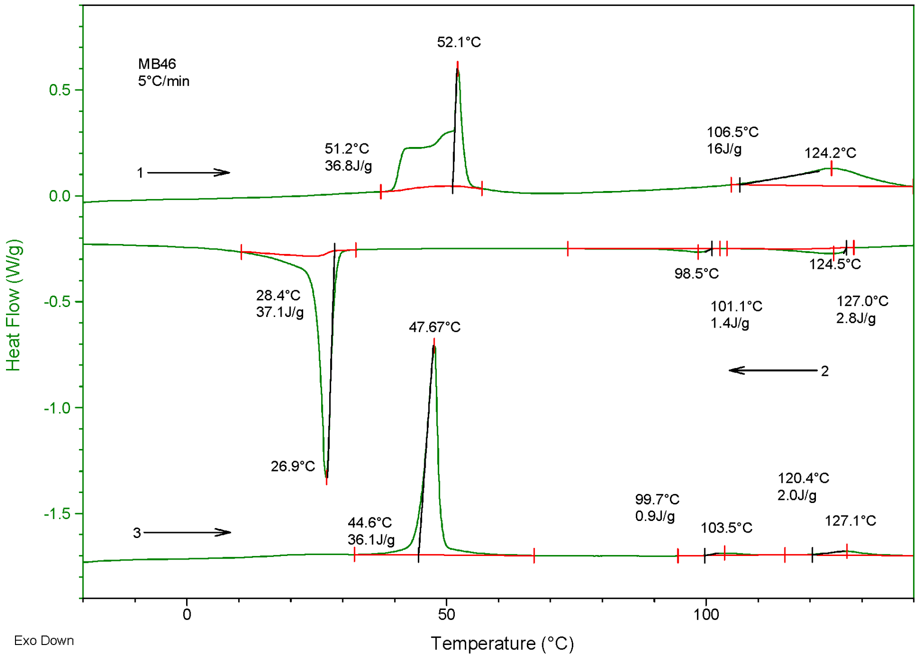


Figure S9: DSC scans of [TPh-NH_2Et]$_2$[$NiCl_4$] **(5)**

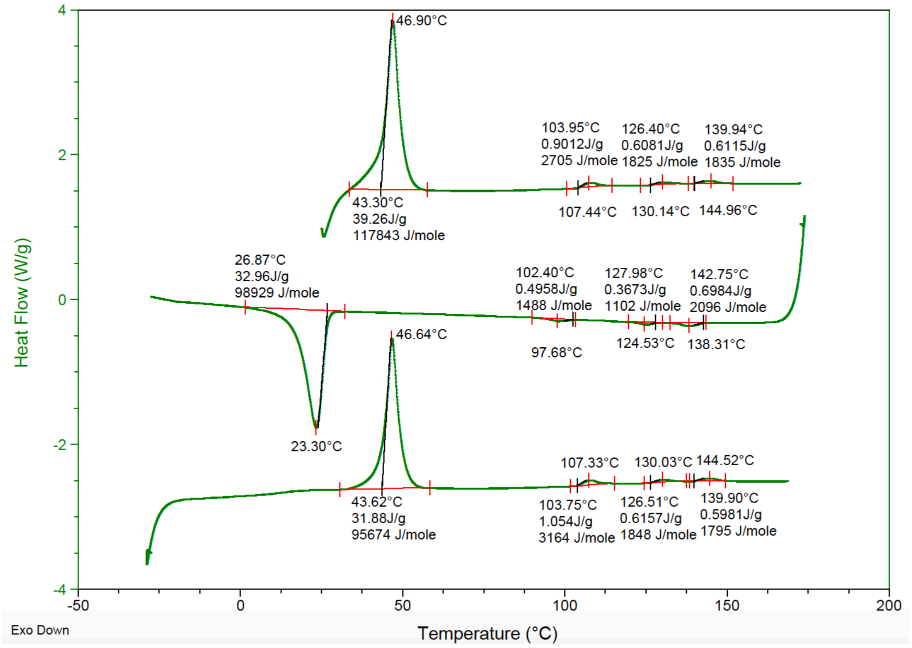


Figure S10: DSC scans of [TPh-NH_2Et]$_2$[$CoCl_4$] **(6)**

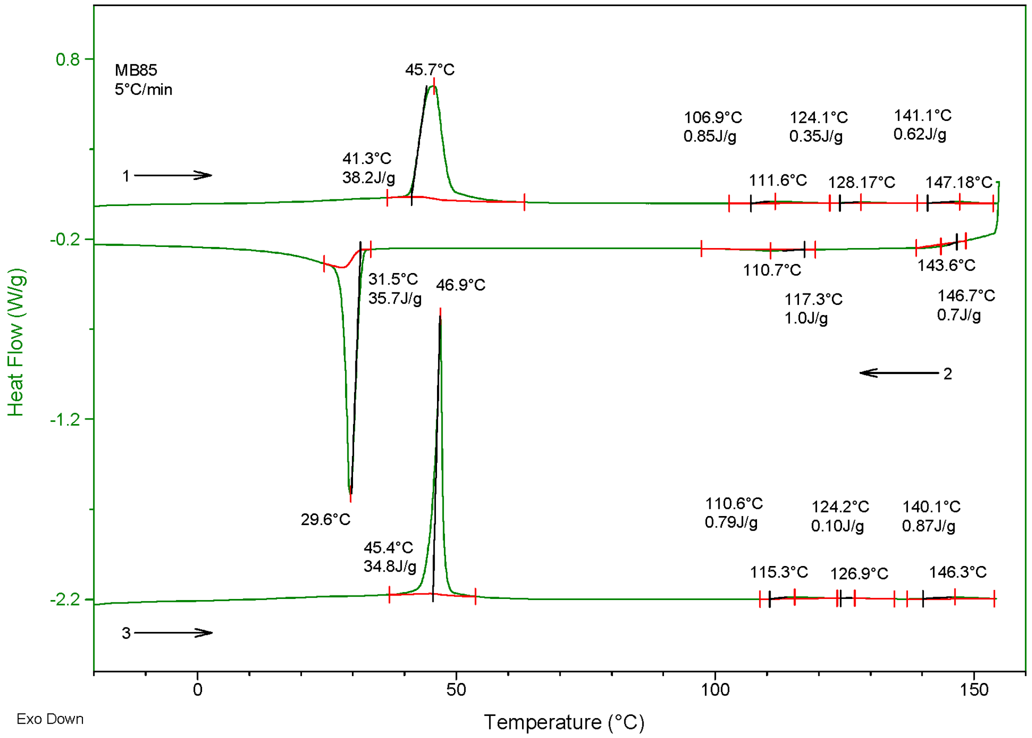


Figure S11: DSC scans of [TPh-NH$_2$Et]$_2$[MnCl$_4$] **(7)**

Thermogravimetric analysis

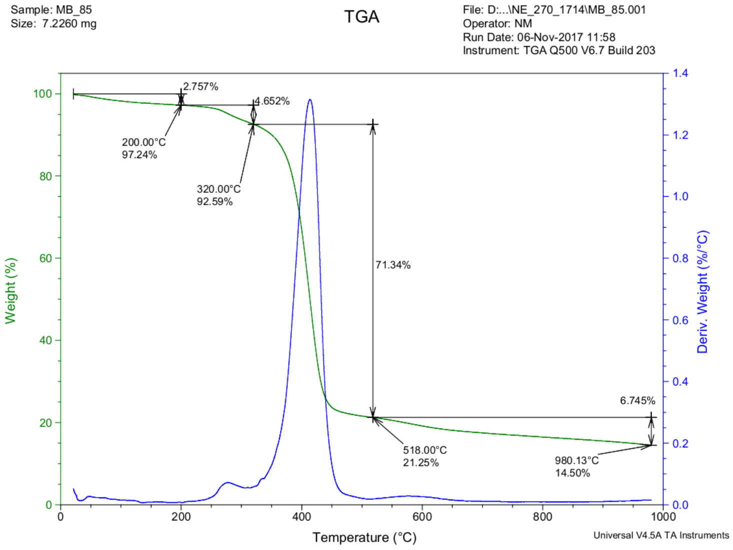
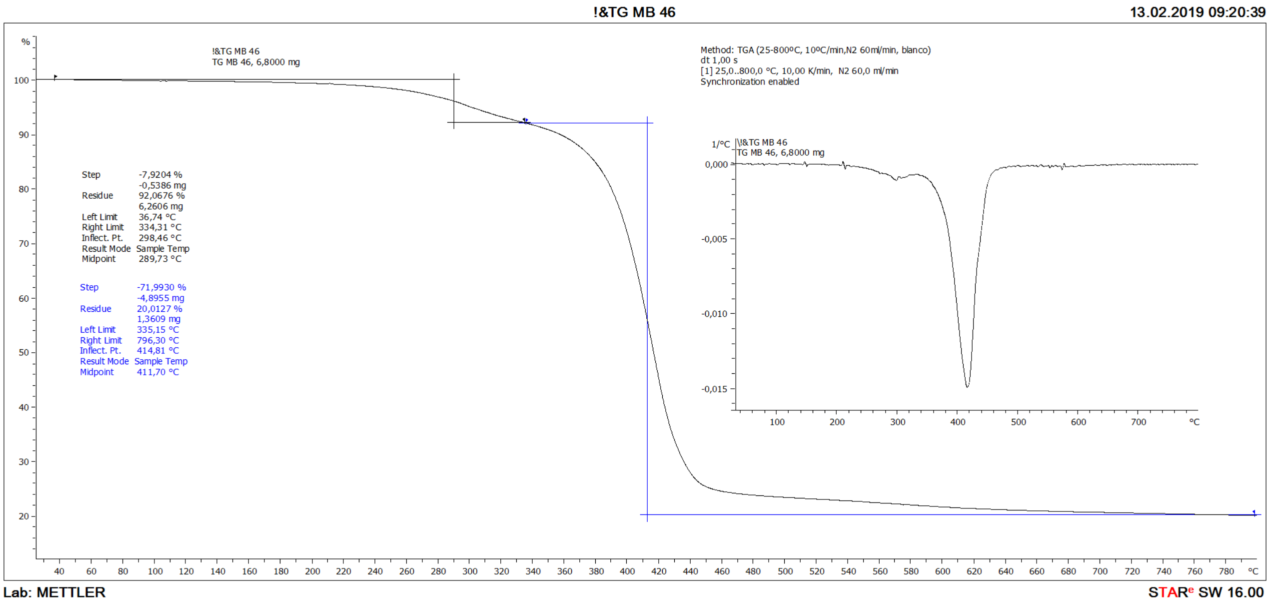


Figure S12: TGA scan of [TPh-NH_2Et]$_2$[$CuCl_4$] **(4)**



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Synchronization enabled
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Residue       92,0676 %
              6,2606 mg
Left Limit    36,74 °C
Right Limit   334,31 °C
Inflect. Pt.  298,46 °C
Result Mode   Sample Temp
Midpoint      289,73 °C

Step          -71,9930 %
              -4,8955 mg
Residue       20,0127 %
              1,3609 mg
Left Limit    335,15 °C
Right Limit   796,30 °C
Inflect. Pt.  414,81 °C
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Figure S13: TGA scan of [TPh-NH_2Et]$_2$[$NiCl_4$] **(5)**

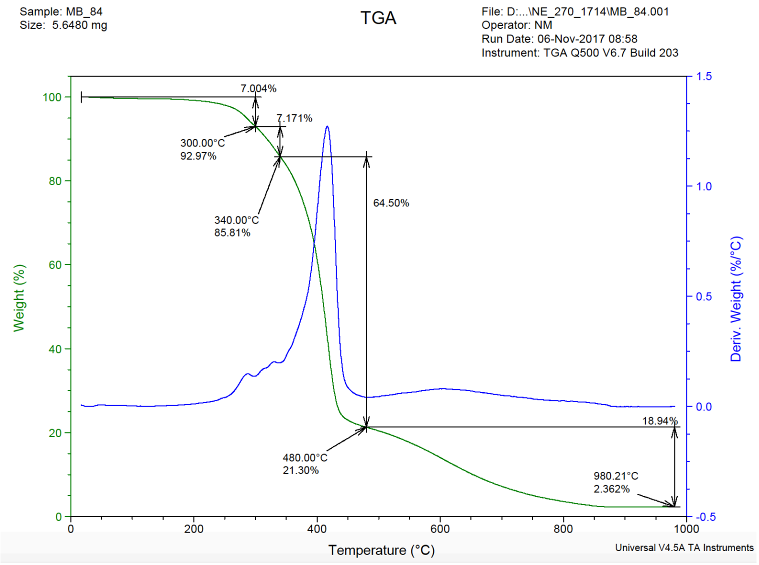

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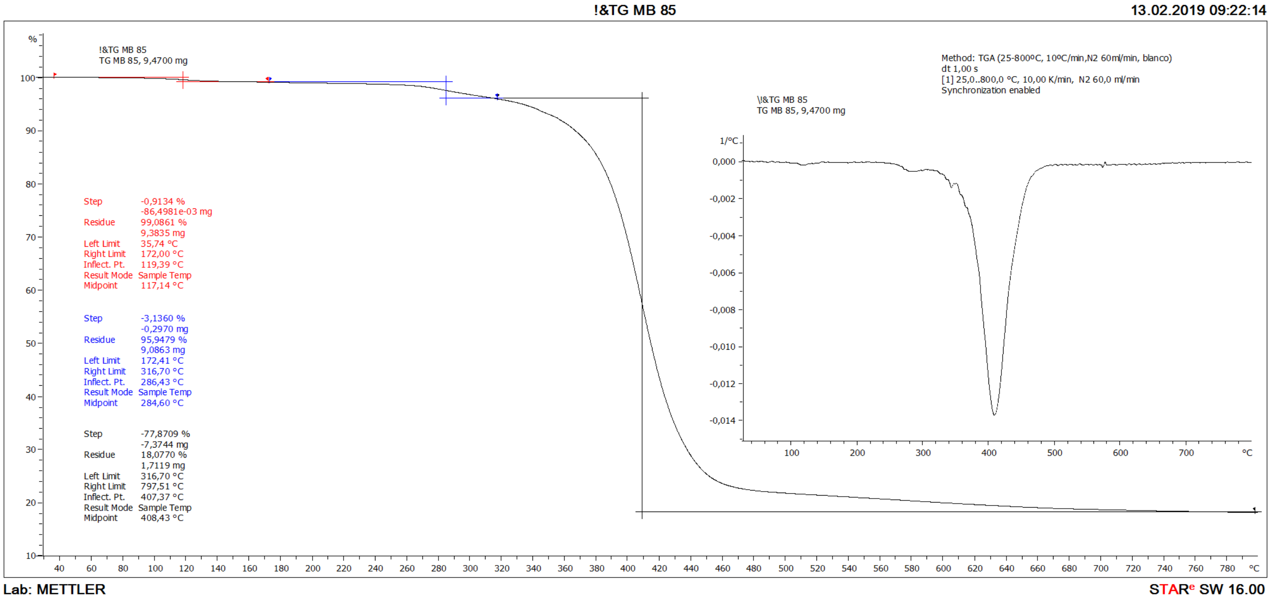
Figure S14: TGA scan of [TPh-NH_2Et]$_2$[$CoCl_4$] **(6)**



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TG MB 85, 9,4700 mg

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Right Limit  172,00 °C
Inflect. Pt. 119,39 °C
Result Mode  Sample Temp
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Result Mode  Sample Temp
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             1,7119 mg
Left Limit   316,70 °C
Right Limit  797,51 °C
Inflect. Pt. 407,37 °C
Result Mode  Sample Temp
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[1] 25,0..800,0 °C, 10,00 K/min,  N2 60,0 ml/min
Synchronization enabled

\!&TG MB 85
TG MB 85, 9,4700 mg

Lab: METTLER                                  STARe SW 16.00
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Figure S15: TGA scan of [TPh-NH_2Et]$_2$[$MnCl_4$] **(7)**

S/WAXS patterns of the precursor 3 and complexes 4-7

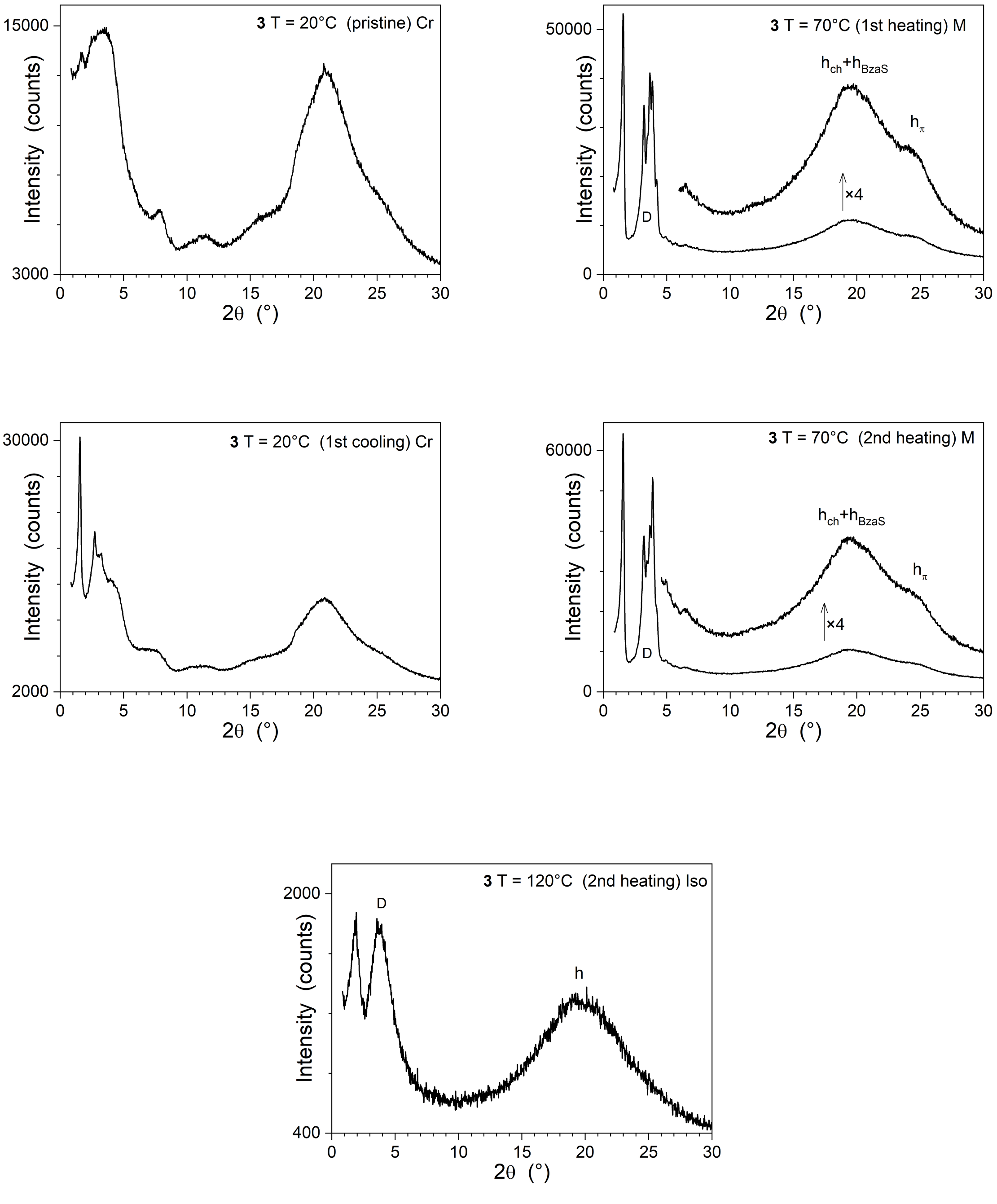


Figure S16. S/WAXS patterns of **3** at various temperatures.

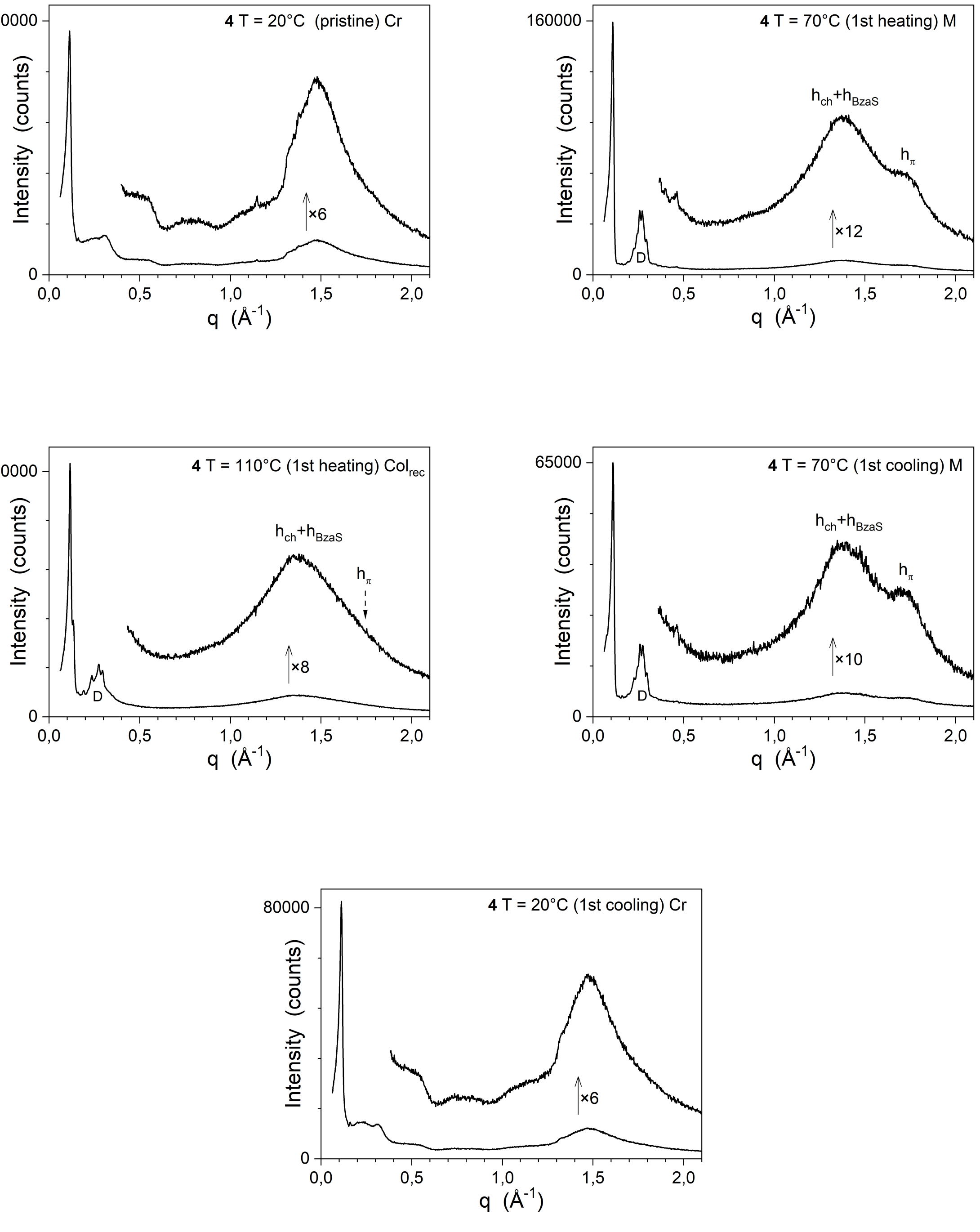


Figure S17. S/WAXS patterns of **4** at various temperatures ($q = 2\pi/d = 4\pi\sin\theta/\lambda$).

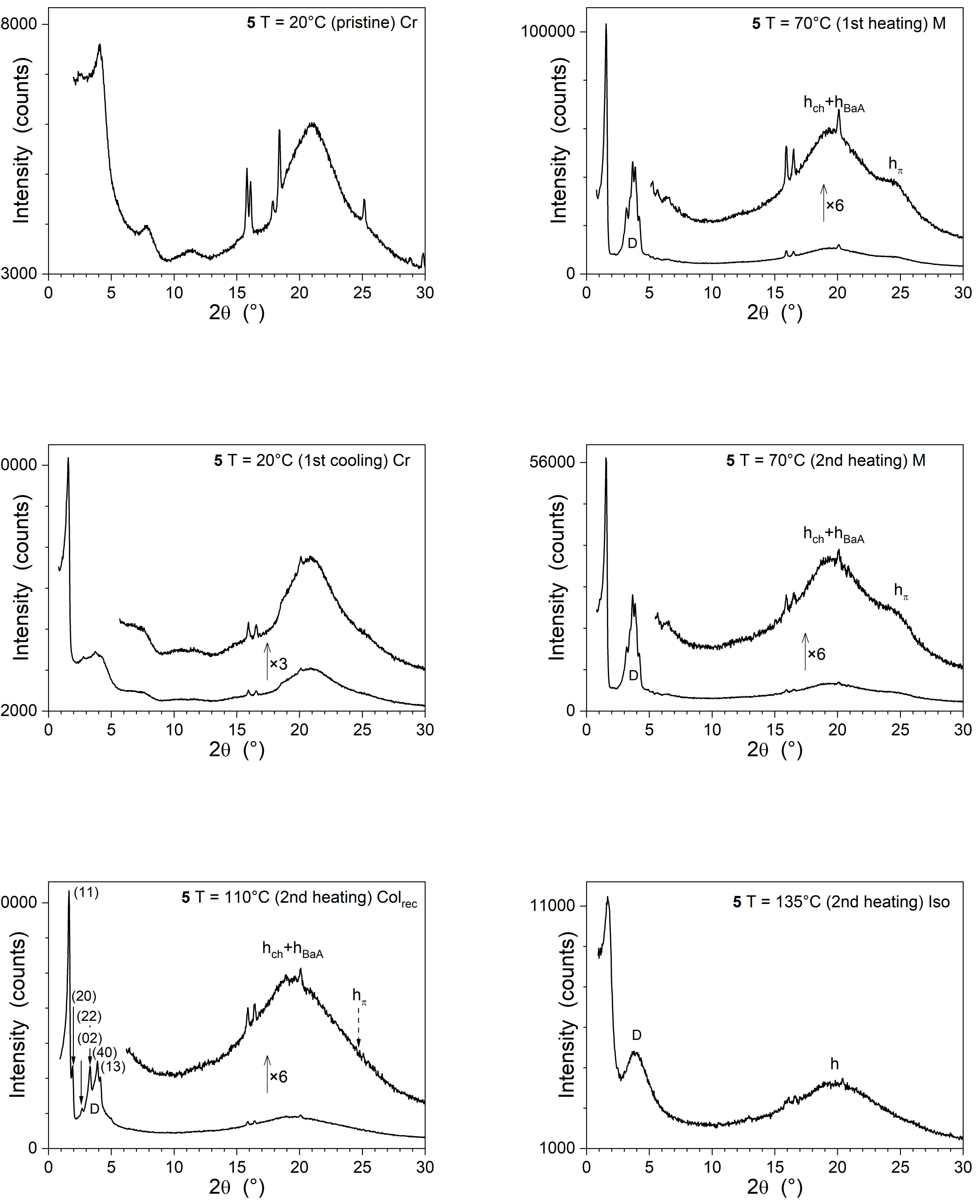


Figure S18. S/WAXS patterns of **5** at various temperatures.

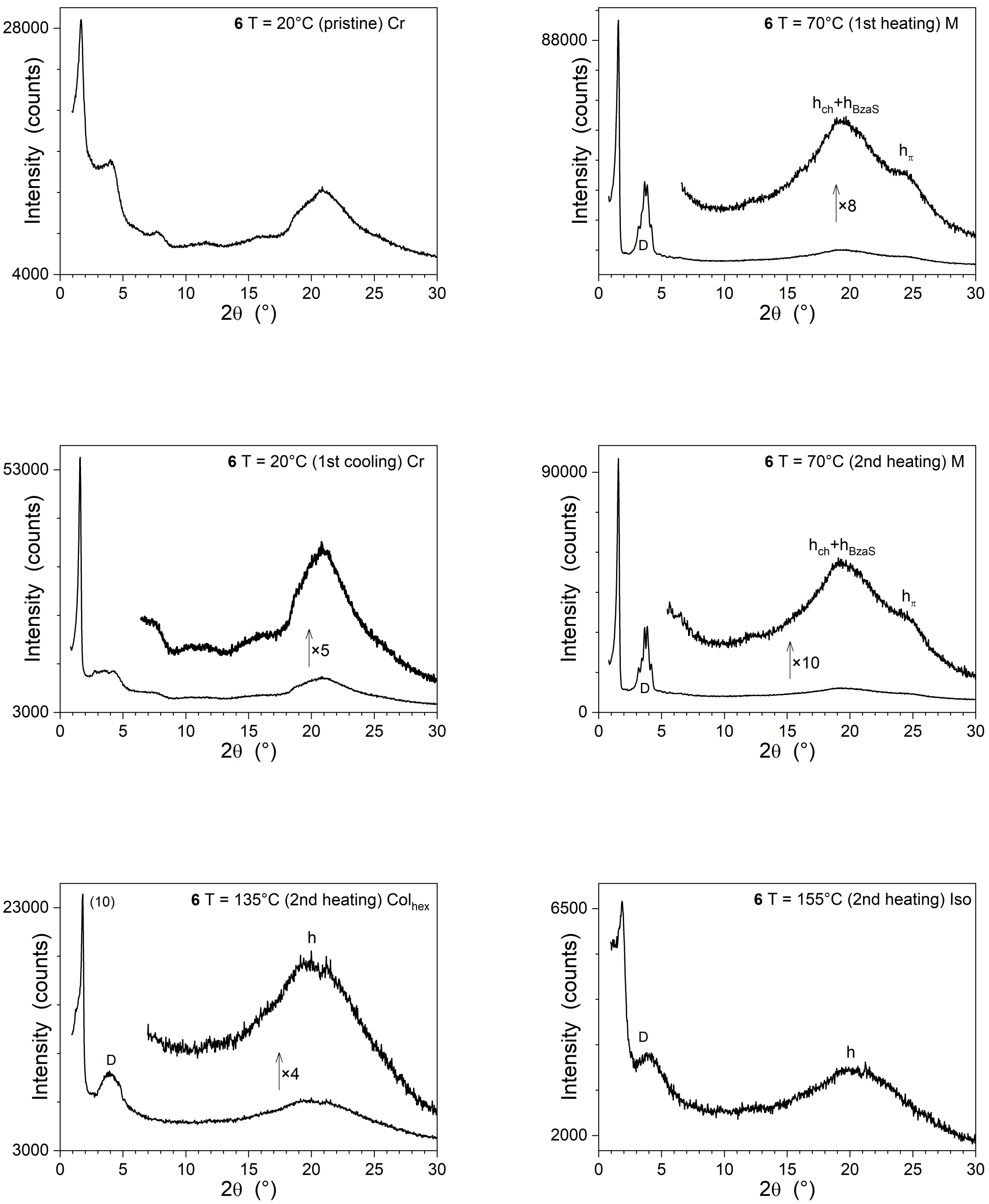


Figure S19. S/WAXS patterns of **6** at various temperatures.

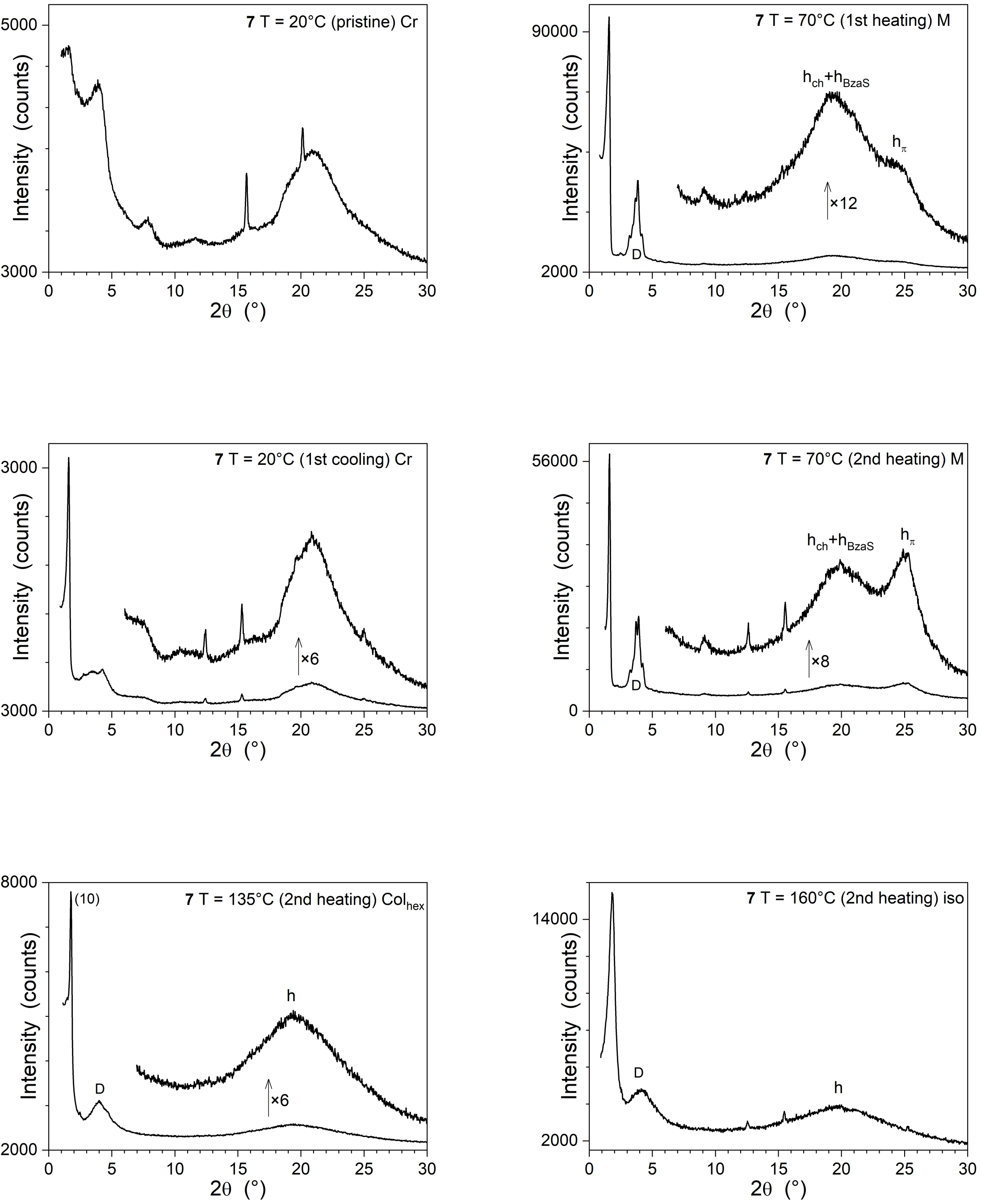


Figure S20. S/WAXS patterns of **7** at various temperatures.

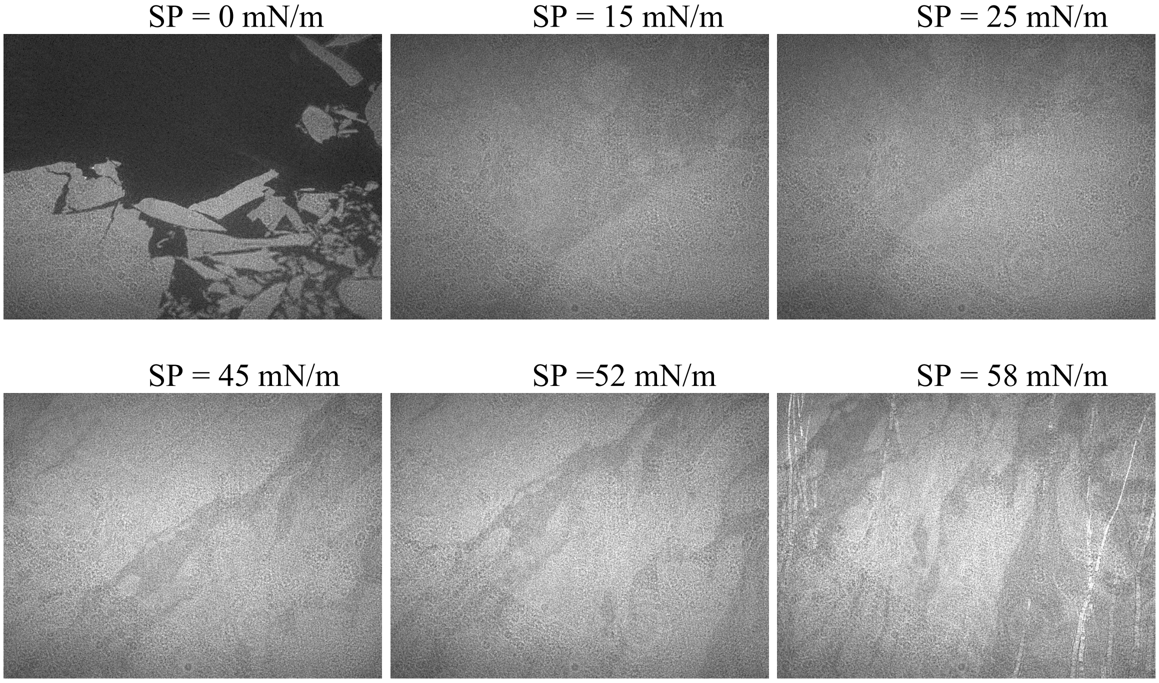
Table S1: Table of indexation of mesophases of compounds **3**-**7**

$2\theta_{exp}$	d_{exp}	I [ξ(nm)]	*hk*	$2\theta_{cal}$	d_{cal}	Mesophase parameters
Compound **3** (90°C)						
1.66	53.1	VS	11	1.666	52.99	$\mathrm{Col_{rec}}$
1.96	45.1	M	20	1.968	44.84	*a* = 89.6(9) Å
2.69	32.9	W	02	2.688	32.84	*b* = 65.6(7) Å
3.27	27.02	W	31	3.244	27.21	*A* = 5890 Å^2
3.34	26.47	S	22	3.332	26.49	(*Z* = 2)
3.93	22.46	M	40	3.937	22.42	
4.15	21.26	M	13	4.152	21.27	
3.6	25	S [7]	D			
19.7	4.5	VS [1]	$h_{ch}+h_{BzaS}$			
25.0	3.6	M [2]	h_{π}			
Compound **4** (110°C)						
1.66	53.1	VS	11	1.667	52.95	$\mathrm{Col_{rec}}$
1.94	45.6	M	20	1.938	45.54	*a* = 91.0(8) Å
2.71	32.5	W	02	2.714	32.54	*b* = 65.0(8) Å
3.33	26.47	W	22	3.334	26.48	*A* = 5927 Å^2
3.88	22.76	W	40	3.877	22.77	(*Z* = 2)
4.18	21.10	W	13	4.184	21.10	
3.9	23	S [7]	D			
19.6	4.5	VS [1]	$h_{ch}+h_{BzaS}$			
24.9	3.6	M [2]	h_{π}			
Compound **5** (110°C)						
1.65	53.3	VS	11	1.660	53.18	$\mathrm{Col_{rec}}$
1.94	45.4	S	20	1.951	45.23	*a* = 90.4(7) Å
2.68	32.9	W	02	2.686	32.87	*b* = 65.7(3) Å
3.32	26.58	M	22	3.320	26.59	*A* = 5947 Å^2
3.91	22.60	M	40	3.903	22.62	(*Z* = 2)
4.15	21.28	M	13	4.146	21.29	
3.8	23	M [10]	D			
19.6	4.5	VS [1]	$h_{ch}+h_{BzaS}$			
24.9	3.6	M [2]	h_{π}			
Compound **6** (115°C)						
1.64	53.7	VS	11	1.646	53.62	$\mathrm{Col_{rec}}$
1.93	45.8	S	20	1.934	45.65	*a* = 91.3(0) Å
2.66	33.2	W	02	2.665	33.13	*b* = 66.2(5) Å
3.30	26.77	M	22	3.293	26.81	*A* = 6049 Å^2
3.87	22.81	M	40	3.868	22.82	(*Z* = 2)
4.12	21.45	M	13	4.113	21.46	
3.8	23	M [7]	D			
19.6	4.5	S [1]	$h_{ch}+h_{BzaS}$			
25.1	3.5	M [2]	h_{π}			
Compound **6** (135°C)						
1.77	49.9	S	10			$\mathrm{Col_{hex}}$
4.0	22	S [5]	D			*a* = 57.6 Å
20.5	4.3	VS [1]	h			*A* = 2871 Å^2
						(*Z* = 1)

Compound **7** (120°C)						
1.65	53.46	VS	11	1.652	53.43	$\mathrm{Col_{rec}}$
1.91	46.22	S	20	1.914	46.13	*a* = 92.2(5) Å
3.30	26.71	W	22	3.304	26.72	*b* = 65.5(5) Å
3.83	23.05	M	40	3.828	23.06	*A* = 6047 Å^2
4.16	21.22	W	13	4.15	21.26	(*Z* = 2)
3.8	23	S [9]	D			
19.9	4.5	VS [1]	h_{ch}+h_{BzaS}			
24.7	3.6	M [2]	h_π			
Compound **7** (135°C)						
1.76	50.3	S	10			$\mathrm{Col_{hex}}$
4.0	22	S [5]	D			*a* = 58.0 Å
20.5	4.3	VS [1]	h			*A* = 2917 Å^2
						(*Z* = 1)

$2\theta_{exp}$ (°), d_{exp} (Å), $2\theta_{cal}$ (°), d_{cal} (Å): experimental and calculated angles and d-spacings from peak position of maximum; ξ(nm): correlation length from peak width using Scherrer equation with shape factor K = 0.9 (no indication: long-range periodicity from sharp reflection); I: intensity of reflection, signal intensity code: VS = very strong, S = strong, M = medium, W = weak, VW = very weak; (*hk*) are the Miller indices of reflections from the columnar lattice; D (Å): short-range correlated periodicity from the supramolecular assembly; h_{ch} (Å), h_{BzaS} (Å): average lateral distances between molten chains and between benzylammonium/anion units; h_π (Å): average piling distance along triphenylene columns; h: overlapping average lateral distances between molecular segments; *a*, *b*, *A*, *Z*: columnar lattice parameters, lattice area and number of molecular aggregates per lattice.

MicroBAM images



SP = 0 mN/m

SP = 15 mN/m

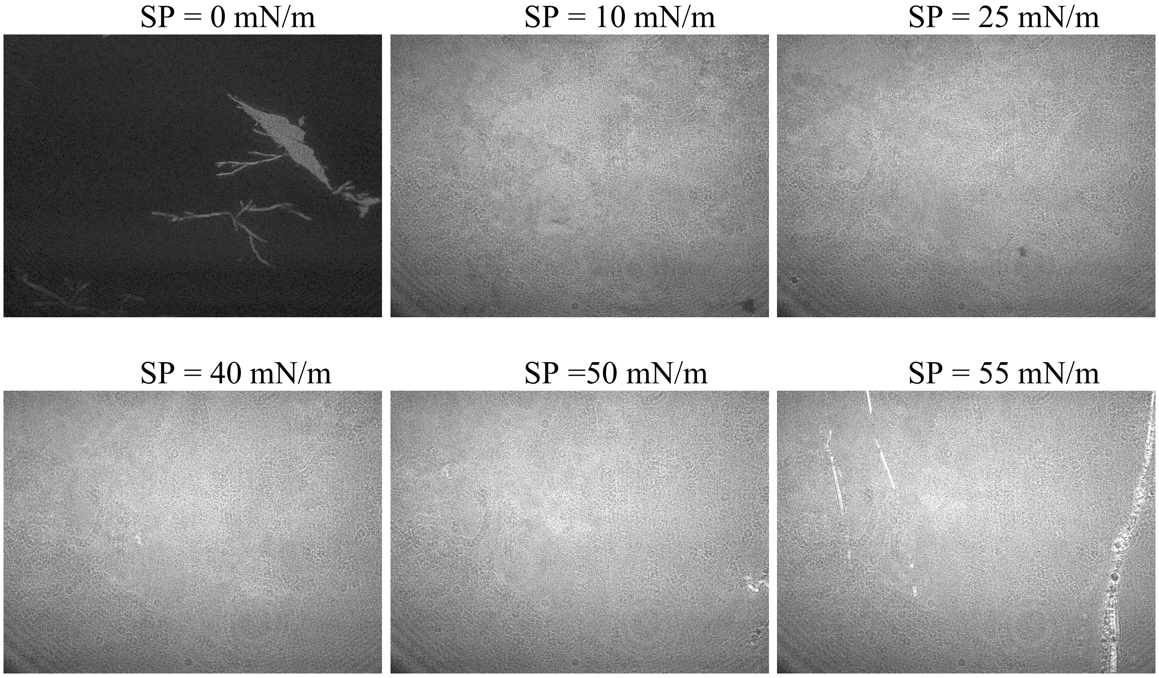
SP = 25 mN/m

SP = 45 mN/m

SP =52 mN/m

SP = 58 mN/m

Figure S21. MicroBAM images at different stages of the Langmuir films of **3**



SP = 0 mN/m

SP = 10 mN/m

SP = 25 mN/m

SP = 40 mN/m

SP =50 mN/m

SP = 55 mN/m

Figure S22. MicroBAM images at different stages of the Langmuir films of **5.**

Low-angle X-ray diffractograms of the multilayer LB films of 3 and 5. Monolayers transferred at SP = 15 mN/m upon a Z-type deposition.

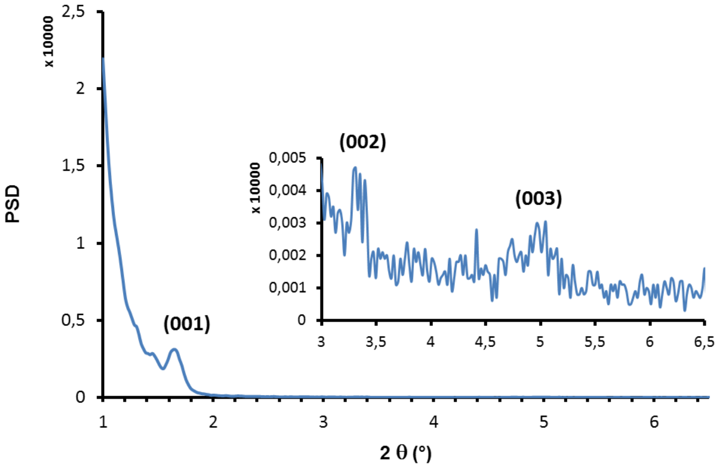


Figure S23. Diffractograms of **3**

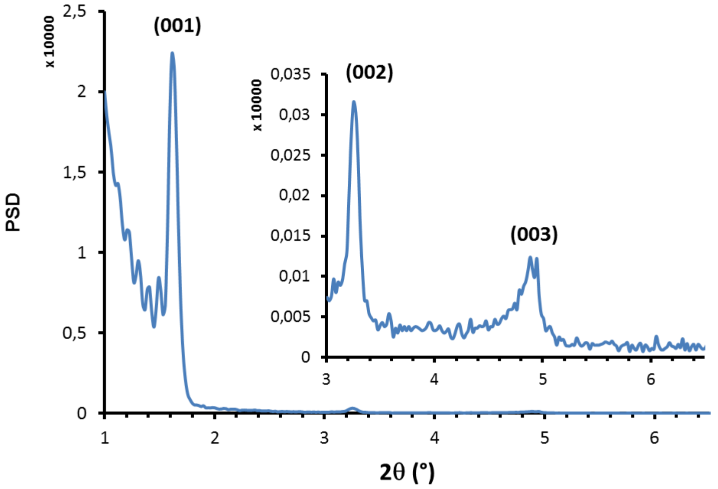


Figure S24. Diffractograms of **5**

References

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[1] J. Yu, M. Xiao, H. Tan, W. Zhu, *Thin Solid Films,* 2016, **619**, 1.

[2] E. Tritto, R. Chico, G. Sanz-Enguita, C. L. Folcia, J. Ortega, S. Coco, P. Espinet, P. *Inorg. Chem.,* 2014, **53**, 3449.