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Electronic Supplementary Information (ESI) for

Supramolecular synthesis with *N*-Hetero-tolanes: Liquid crystals, hydrogen-bonded and halogen-bonded co-crystals

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1. Materials and methods

UV/Vis studies were carried out on a PerkinElmerLamba XLS+ spectrometer.

2. Synthesis and compound characterization

The manipulation of all air and/or water sensitive compounds was carried out using standard inert atmosphere techniques. All chemicals were used as received from commercial sources without further purification. Anhydrous solvents were used as received from commercial sources.

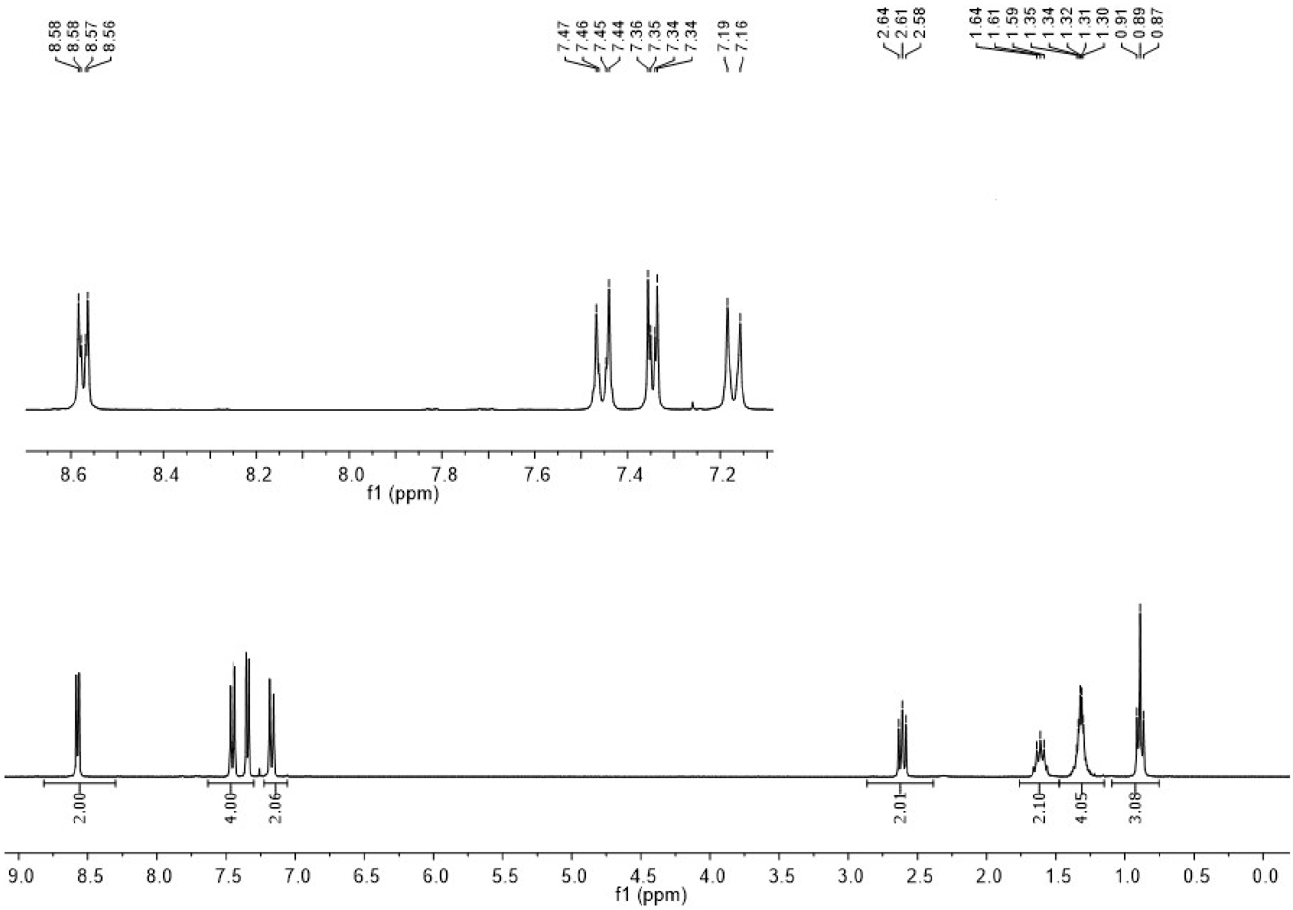
Nuclear magnetic resonance spectra were recorded on 400 MHz spectrometers at ambient probe temperature. Chemical shifts for ^{1}H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform: δ = 7.26 ppm). ^{13}C NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard ($^{13}CDCl_3$: 77.16 ppm).

General procedure for the Sonogashira coupling: In a Schlenk tube, 1-ethynyl-4-pentylbenzene (0.6 ml, 3.1 mmol) was dissolved in a mixture of dry THF (2 ml) and triethylamine (2 ml) and the solution was degassed by three freeze-thaw cycles before purging with argon. 4-Iodopyridine or 3-iodopyridine (454 mg, 2.2 mmol), bis(triphenylphosphine) palladium (II) chloride (78 mg, 0.11 mmol) and copper (I) iodide (42 mg, 0.22 mmol) were then added to the solution. The reaction mixture was stirred at room temperature under argon atmosphere for 16 h. The mixture was then diluted with CH_2Cl_2 (100 ml) and washed with water (100 ml), saturated aqueous NH_4Cl (100 ml) and brine (100 ml). The organic layer was dried over anhydrous $MgSO_4$ and the solvents were removed by rotary evaporation. The crude product was further purified by flash chromatography (SiO_2, $CHCl_3$ and then $CHCl_3$ with 1% methanol).

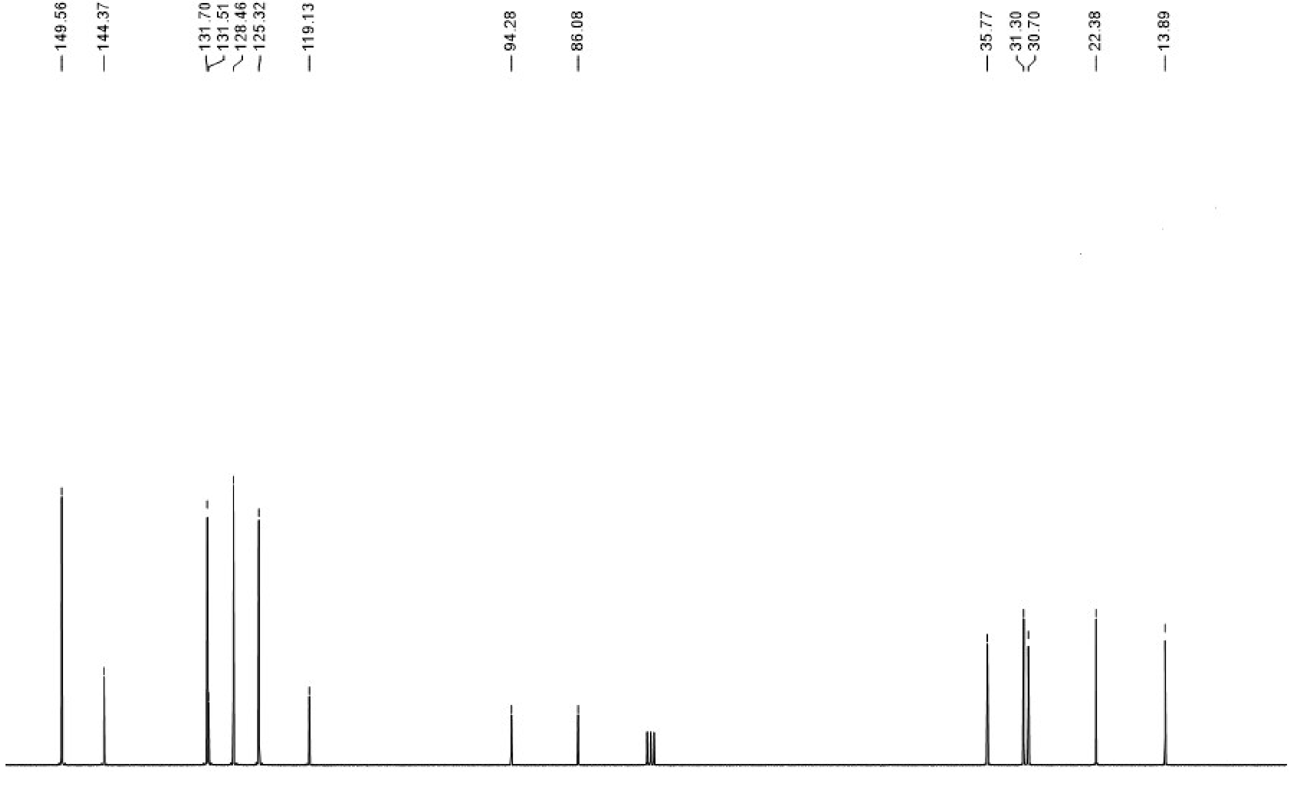
4-[(4-pentylphenyl)ethynyl]pyridine (**1**) is isolated as a brown solid. Yield: 374 mg (68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.58 - 7.34 (m, 6H),7.18 (d, J = 8.1 Hz, 2H), 2.61 (t, J = 7.5 Hz, 2H), 1.61 (q, J = 7.5 Hz, 2H), 1.31 (m, 4H), 0.89 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C = 149.6, 144.4, 131.7, 131.5, 128.5, 125.3, 119.1, 94.3, 86.1, 35.8, 31.3, 30.7, 22.4, 13.9 ppm. EI$^+$-HRMS, found: 249.1525; calculated for $C_{18}H_{19}N$: 249.1517.

2-[(4-pentylphenyl)ethynyl]pyridine (**2**) is obtained as a yellow oil. Yield: 232 mg (71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.62 - 7.21 (m, 6H), 7.18 (d, J = 8.0 Hz, 2H), 2.72 – 2.51 (m, 2H), 1.65 – 1.57 (m, 2H), 1.38 – 1.27 (m, 4H), 0.97 – 0.82 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C= 150.0, 144.3, 136.1, 132.4, 128.6, 128.5, 127.1, 122.6, 119.4, 89.6, 88.1, 35.9, 30.9, 30.3, 22.5, 14.1 ppm. EI$^+$-HRMS, found: m/z 249.1526; calculated for $C_{18}H_{19}N$: 249.1517.

3-[(4-pentylphenyl)ethynyl]pyridine (**3**) is obtained as a brown oil. Yield: 402 mg (73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.76 - 7.26 (m, 6H), 7.18 (d, J = 8.3 Hz, 2H), 2.62 (t, J = 7.3 Hz, 2H), 1.62 (q, J = 7.3 Hz, 2H), 1.31 (m, 4H), 0.89 (t, J = 6.9 Hz, 3H) ppm;^{13}C NMR (100 MHz, $CDCl_3$) δ_C= 152.1, 148.3, 143.9, 138.2, 131.6, 128.5, 122.9, 120.6, 119.6, 92.9, 85.3, 35.8, 31.4, 30.8, 22.5, 14.0 ppm. EI$^+$-HRMS, found: m/z 249.1510; calculated for $C_{18}H_{19}N$: 249.1517.

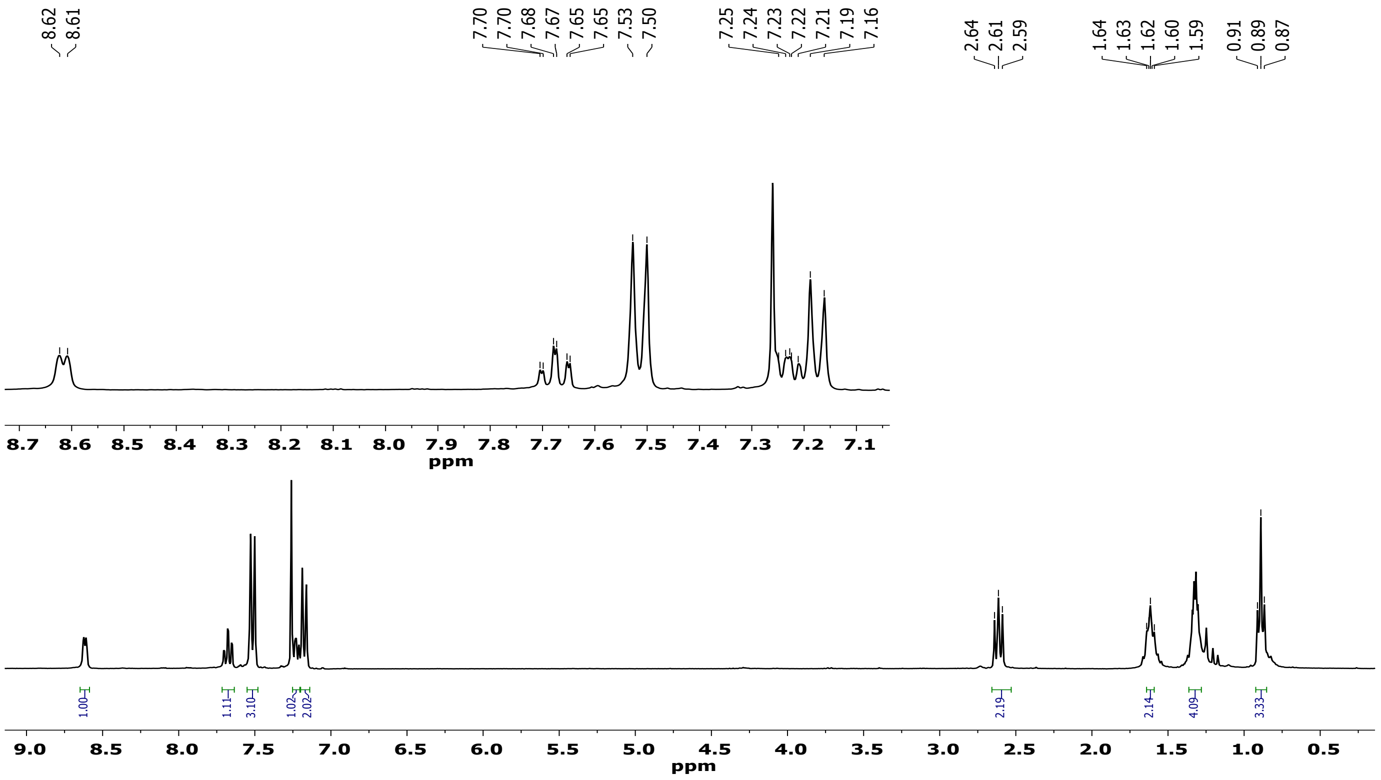


^{1}H NMR spectrum of **1** (400 MHz, CDCl$_3$).

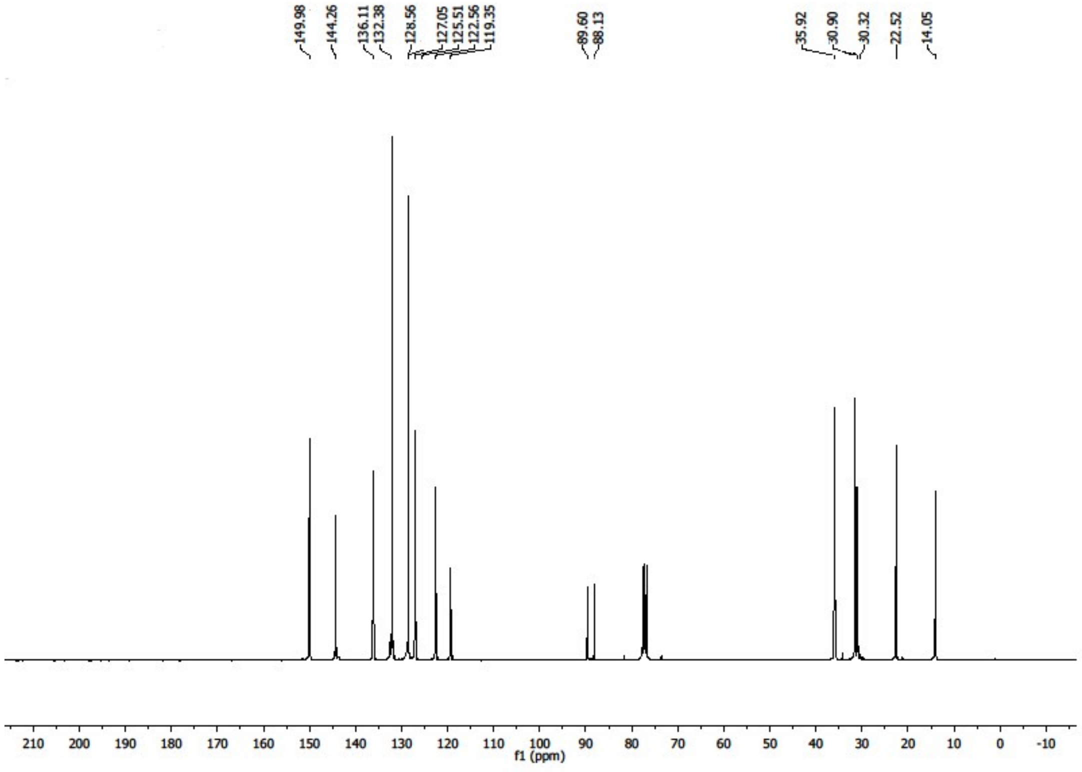


^{13}C NMR spectrum of **1** (100 MHz, CDCl$_3$).

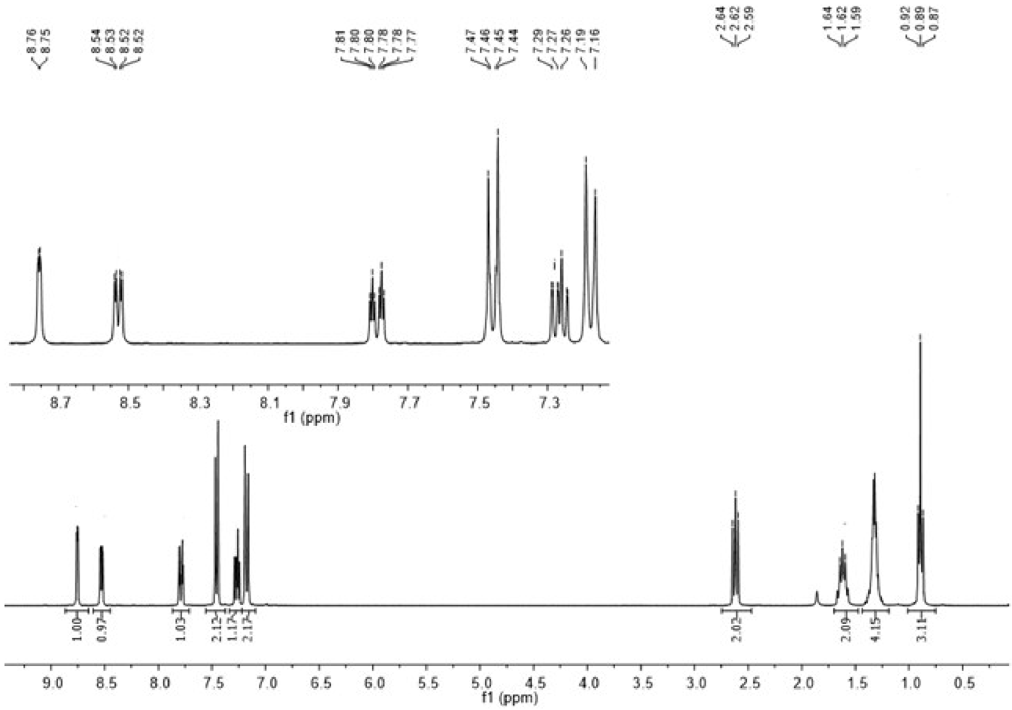
^{1}H NMR spectrum of **2** (400 MHz, CDCl$_3$).



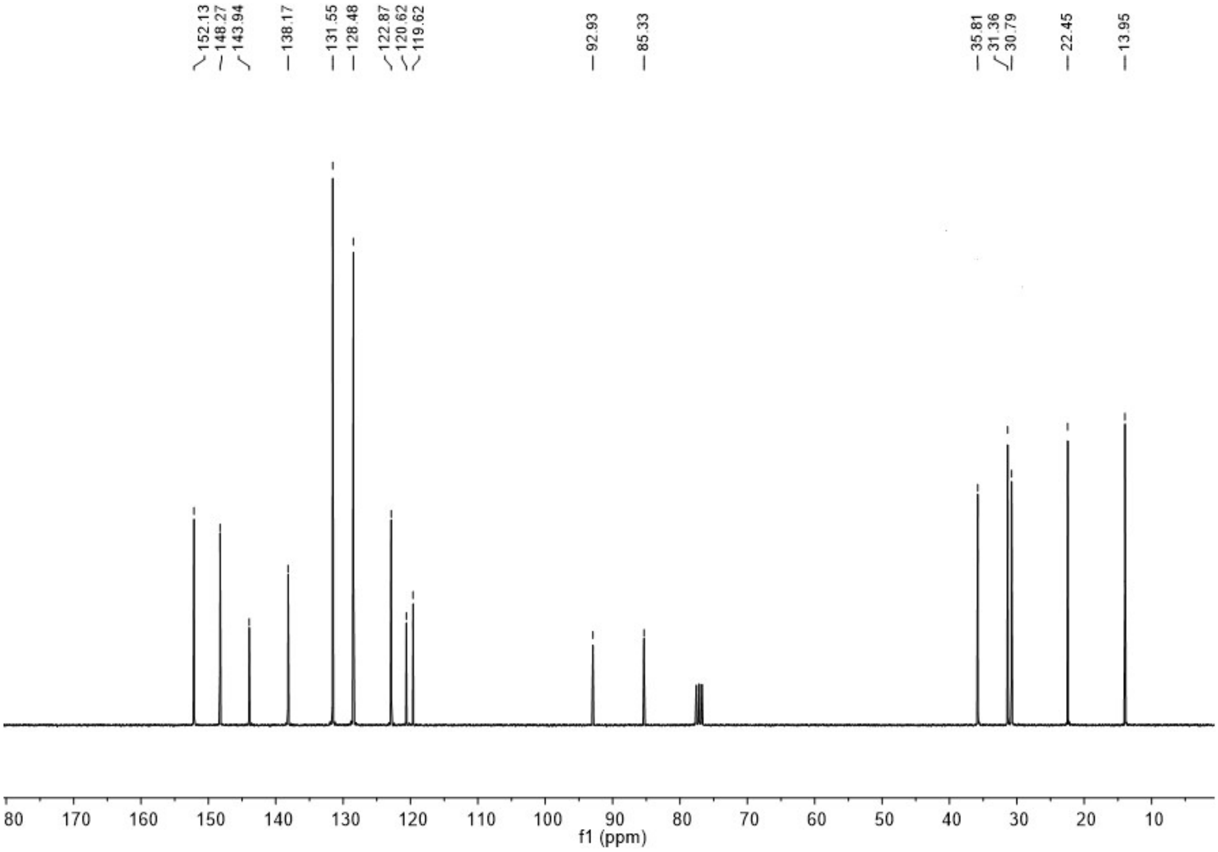
^{13}C NMR spectrum of **2** (100 MHz, CDCl$_3$).



^{1}H NMR spectrum of **3** (400 MHz, CDCl$_3$).



^{13}C NMR spectrum of **3** (100 MHz, CDCl)



2. Thermal properties.

The thermal analyses (DSC) were carried out at the inter-departamental research service unit at the UAM on a Discovery Instruments apparatus with a Tzero aluminum hermetic sample holder with quantities between 1.493 (**1**H$^+$×Terephthalate) and 2.167mg(**1**×HCl).

Differential scanning calorimetry (DSC) of ternary **1**H$^+$×Terephthalate co-crystals.

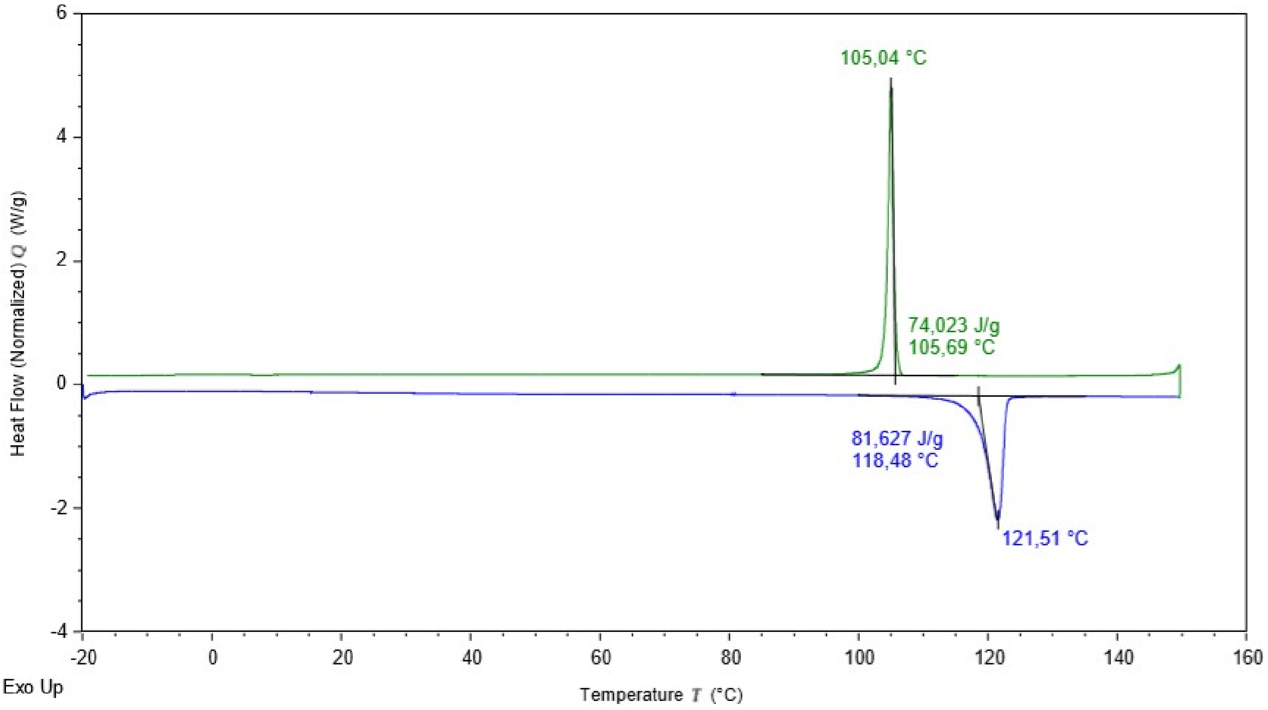


Figure S1. First heating scan: green; first cooling scan: blue.

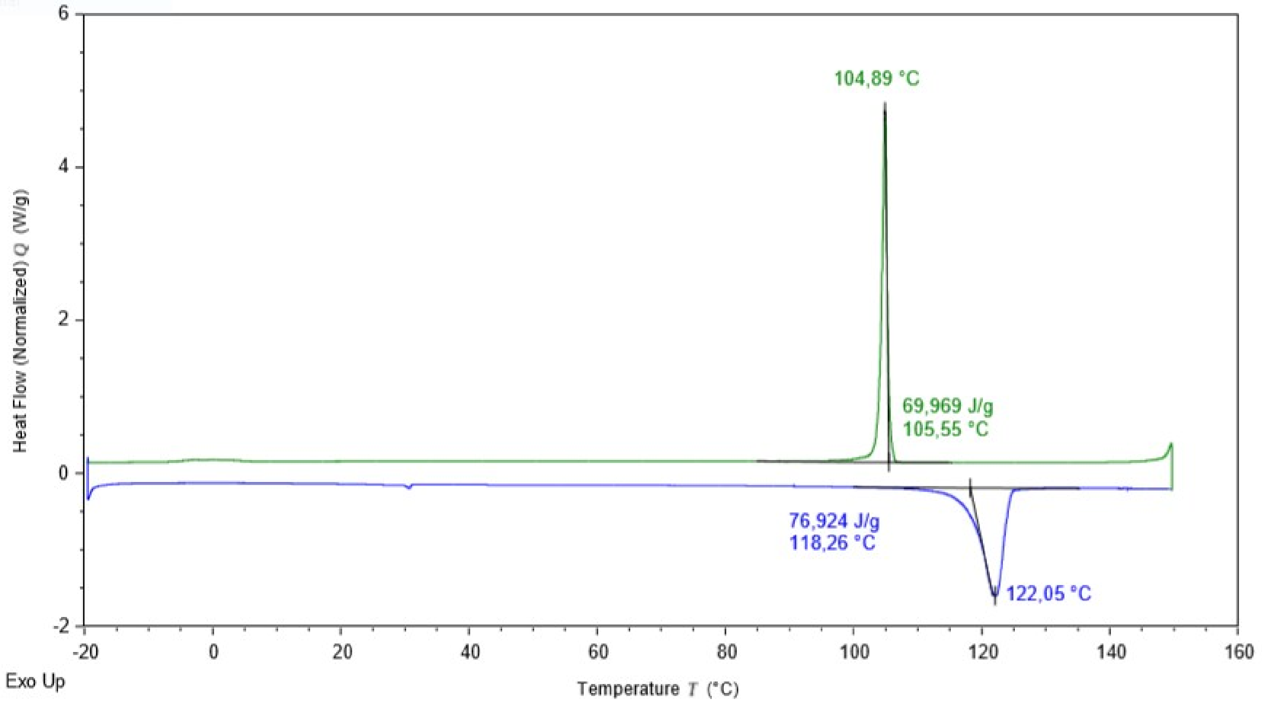
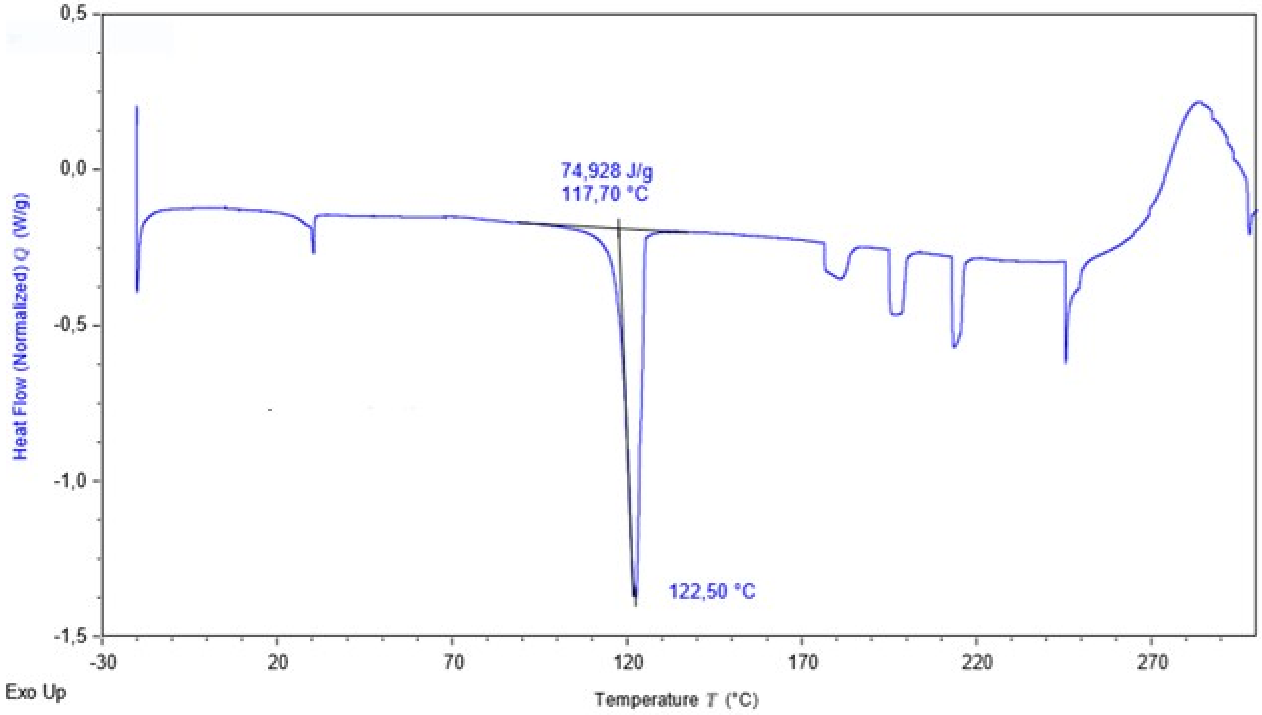
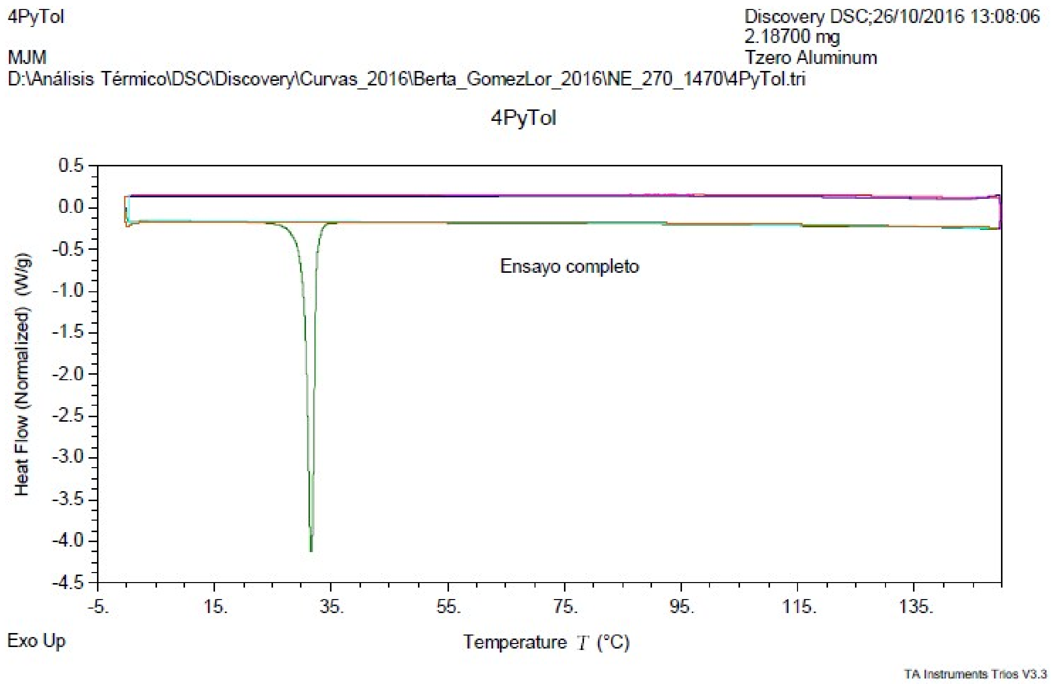


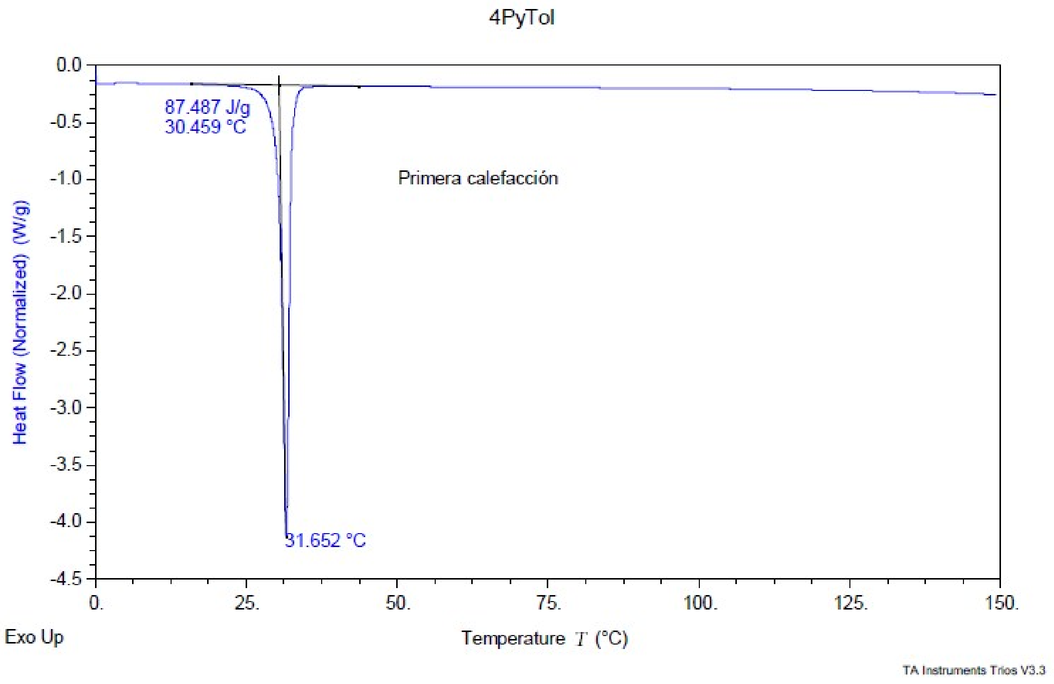
Figure S2. Second heating scan: green; second cooling scan: blue.



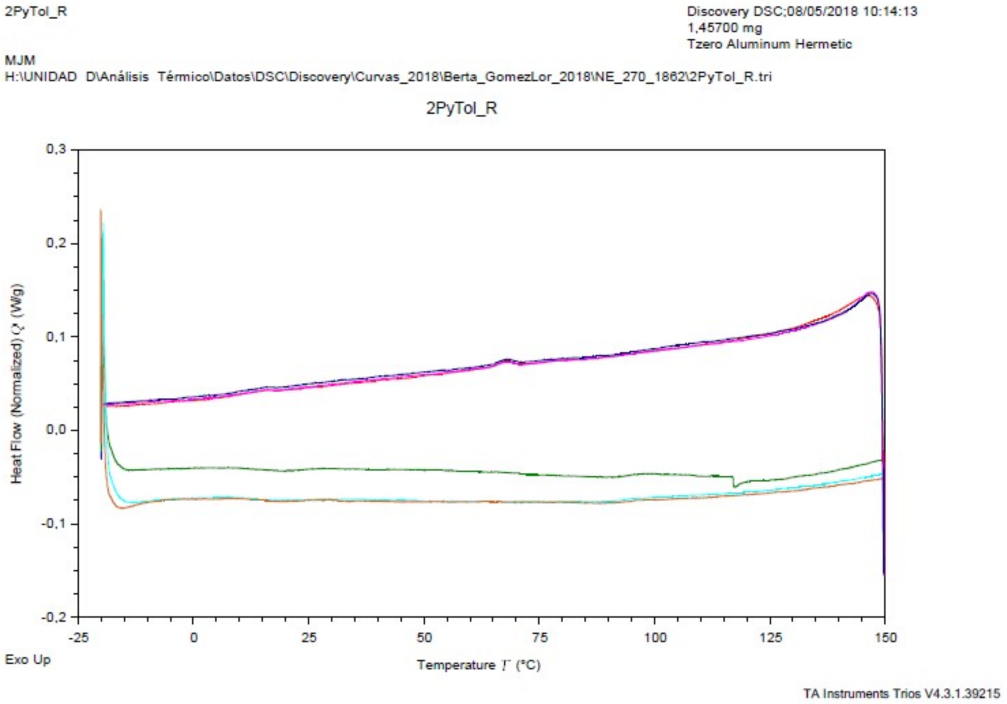
Third heating scan.

Differential scanning calorimetry (DSC) of **1**.





Differential scanning calorimetry (DSC) of **2**.



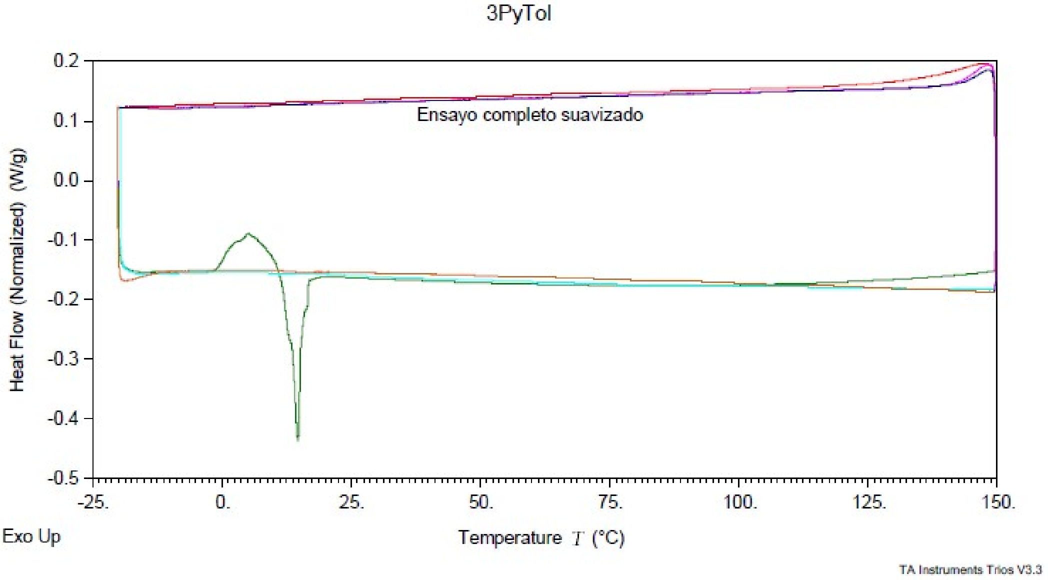
Differential scanning calorimetry (DSC) of **3**.

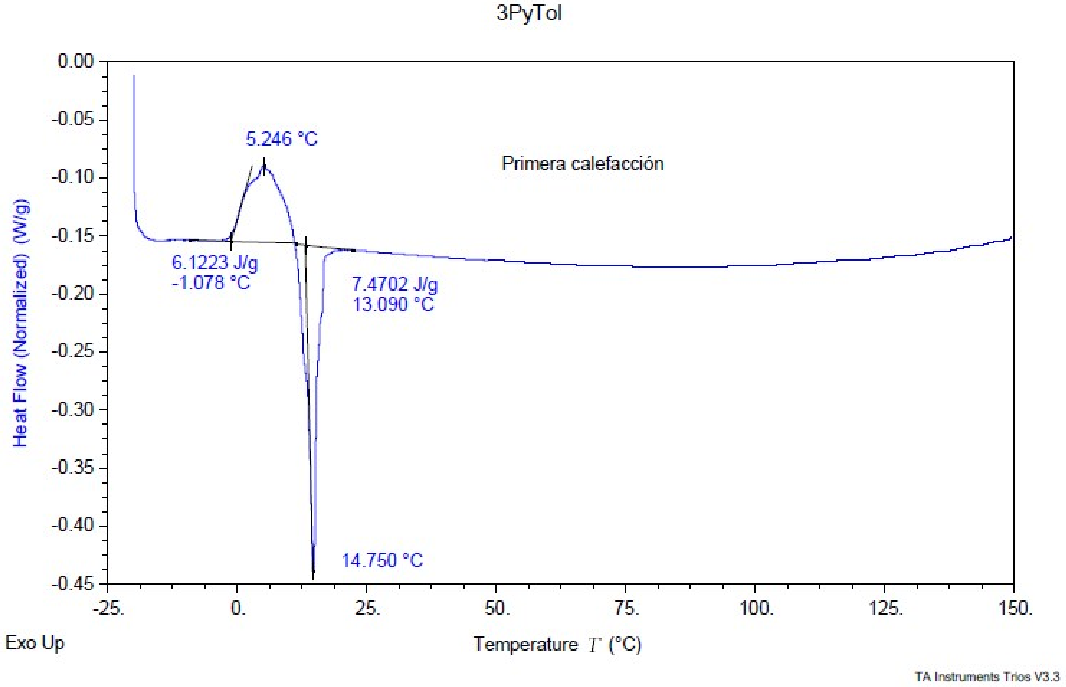
3PyTol

MJM

D:\Análisis Térmico\DSC\Discovery\Curvas_2016\Berta_GomezLor_2016\NE_270_1470\3PyTol.tri

Discovery DSC;27/10/2016 4:04:49
2.02100 mg
Tzero Aluminum Hermetic





3.1. Crystallization.

1×HCl.Compound **1 (**0.053 g, 2.12 mmol)is dissolved in ethanol (2 ml)andwater (1 ml). Concentrated HCl (37%)is added to the mixture and slow solvent evaporation at r.t. yields crystals of **1**×HClsuitable for XRD spectroscopy.

1H$^+$×Terephthalate. Compound 1 (0.050 g, 2.0 mmol) and terephthalic acid (0.016 g, 0.96 mmol) are dissolved in a 1.1 mixture of EtOH : H_20 (3 mL) and filtered over celite. The remaining solution is evaporated slowly at r.t. until a crystalline solid appears.

1×Diiodo-tetrafluoro benzene. XRD quality crystals are obtained upon slow evaporation of THF (3 mL) at r.t. used to dissolve **1**(0.050 g, 2.0 mmol)and1,4,-diiodo-tetarfluoro benzene (0.040 g, 1.0 mmol).

2×Diiodo-tetrafluoro benzene**. 2**(0.024 g, 0.96 mmol) and1,4,-diiodo-tetarfluoro benzene(0.019 g, 0.47 mmol)are heated in acetonitrile (3 mL) for 24 h. Upon cooling to r.t. followed by slow solvent evaporation suitable crystals ofthe halogen bond complex appeared.

3.2. Single-Crystal Structure Determination.

Crystals were selected under a polarizing optical microscope for a single crystal X-ray diffraction experiment. Single-crystal X-ray data were obtained on a Bruker four-circle κ diffractometer equipped with a Cu INCOATED microsource, operated at 50 W power (50 kV, 1.00 mA) to generate Cu Kα radiation (λ = 1.54178 Å), and a Bruker VANTEC 500 area detector (micro gap technology). Diffraction data were collected by exploring over a hemisphere of the reciprocal space in a combination of φ and ω scans to reach a resolution of 0.85 Å, using a Bruker APEX2 software suite (each exposure covering 1° in ω or φ). Unit cell dimensions were determined for a least-squares fit of the reflections with $I > 4\sigma$. The structures were solved by intrinsic phase methods. The hydrogen atoms were fixed at their calculated positions using distances and angle constraints. All calculations were performed using APEX3[1] software for data collection and OLEX2[2] and SHELXL[3]for resolution and refinement of the structure. Mercury[4] has been used for structural figures and supramolecular packing studies.

Table 1. Crystallographic data.

	1×HCl	**1**H$^+$×Terephthalate	**1**×Diiodo-tetrafluoro benzene	**2**×Diiodo-tetrafluoro benzene
Formula	$C_{18}H_{20}ClN$	$C_{44}H_{44}N_2O_4$	$C_{42}H_{38}N_2C_6I_2F_4$	$C_{42}H_{19}N_2C_6I_2F_4$
Formula weight	285.8	664.81	900.54	900.54
Temperature (K)	250(2)	250(2)	250(2)	250(2)
Wavelength (Å)	1.54178	1.54178	1.54178	1.54178
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/m$	P-1	$P2_1/c$	$P2_1/c$
a/Å	4.7609(5)	5.9346(6)	5.8479(3)	17.623(2)
b/Å	8.4720(1)	11.937(2)	8.0949(4)	5.4878(6)
c/Å	23.813(2)	13.426(2)	40.043(2)	20.948(2)
α/ º	90.0	73.485(9)	90.	90.0
β/ º	92.392(2)	85.966(8)	91.972(3)	108.417(7)
γ/ º	90.0	82.697(8)	90.	90.0
Volume /Å^3	959.6(2)	903.9(2)	1.894.5(1)	1922.2(4)
Z	4	1	2	2
Calc. density / g cm^{-3}	1.978	1.221	1.579	1.556
μ/mm-1	3.533	0.614	13.465	13.27
Dimensions (mm)	0.3 x 0.10 x 0.10	0.10 x 0.10 x 0.05	0.16x 0.12 x 0.08	0.30 x 0.08 x 0.08
Limiting indices				
h	$-5<h<5$	$-6<h<6$	$-5<h<6$	$-19<h<20$
K	$-9<k<10$	$-13<k<14$	$-8<k<9$	$-4<k<5$
L	$-25<l<28$	$-14<l<14$	$-40<l<47$	$-16<l<17$
F(000)	608	354	892	892
Reflections collected/unique with I > 2σ(I)	7820/1779	6788/2530	12353/2959	6850/1939
Refined parameters	111	231	227	227
GOF on F^2	1.143	1.118	1.254	1.151
R$_1$	0.0613	0.1029	0.0913	0.0631
wR$_2$	0.212	0.2674	0.1880	0.1245

4. Microscopy

POM images of **1**H$^+$×Terephthalateat different temperatures.

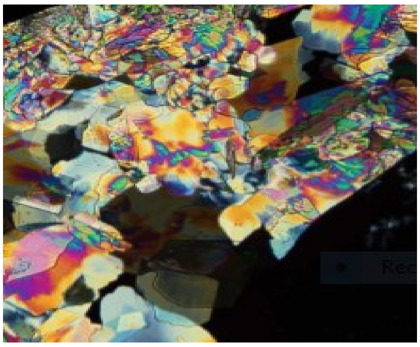


Fig S3a at 116 ºC.

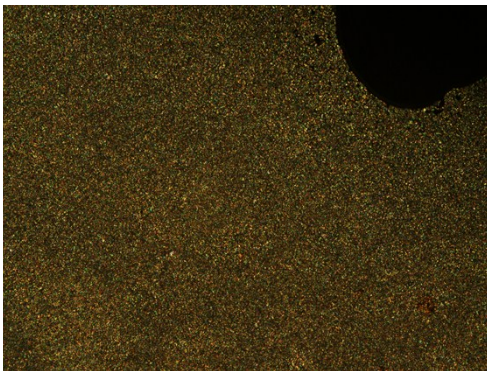


Fig S3b Texture at226 ºC

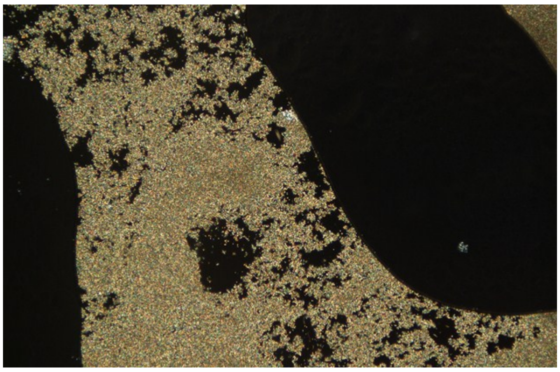
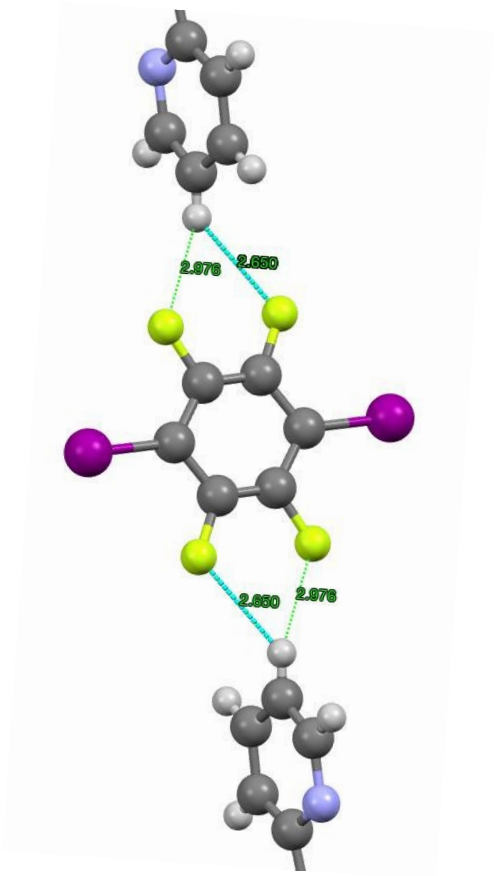


Fig S3cat 300 ºC

Fig S4. XRD image of a fragment of **2**×Diiodo-tetrafluoro benzene**.**

The F···H-C distances between the diiodo-tetrafluoro benzene and the adjacent pyridinium fragments (4-pyridyl-hydrogen) of **2** are found as 2.967 Å and 2.650 Å.This is in average 0.04 Å shorter than F···H van der Waals (vdW) distances found in the crystallographic database for comparable systems. In consequence, these vdW interactions are very weak.



References.

1.Bruker, *APEX3*Bruker AXS Inc., Madison, Wisconsin, USA. (2016).

2. OLEX2. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. &Puschmann, H., *J. Appl. Cryst.,* 2009, **42**, 339 - 341.

3.SHELXpackage. G.M. Sheldrick, Acta Cryst., 2015,**C71**, 3-8.

4.Mercury CSD 3.10. Cambridge Crystallographic Data Center. Cambridge. UK.