Tris(triazolyl)triazine via click-chemistry: A C_3 electron-deficient core with liquid crystalline and luminescent properties

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Supporting Information

Table of Contents

General experimental details

Thermal measurements: Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed with a DSC-MDSC TA instruments Q-1000 and Q-2000; and TA Q-5000, respectively. Liquid crystal textures were studied using an Olympus BX-50 polarizing microscope equipped with a Linkam TMS91 hot stage and a CS196 hot-stage central processor. Microphotographs were taken with a digital camera Olympus DP12-2.
X-ray Diffraction measurements: were performed in a Pinhole camera (Anton-Paar) operating with a point focused Ni-filtered Cu- K_α beam (λ = 0.71073 Å).
NMR, IR and optical spectroscopic measurements: ^{1}H (300 and 400 MHz) and ^{13}C (100 MHz) were measured in $CDCl_3$ on a BRUKER ARX-300 and BRUKER AVANCE-400 instrument. IR spectra on NaCl pellets were recorded using a Thermo Nicolet Avatar 380 spectrophotometer. UV/Vis absorption spectra were collected on an ATI-Unicam UV4-200 instrument. Fluorescence spectra were recorded with a Perkin-Elmer LS50B spectrophotometer.
Electrochemical measurements: Cyclic voltammetry experiments were performed in 0.1 M tetrabutyl ammonium hexafluorophosphate solutions in dry, oxygen free dichloromethane. Graphite was used as the working electrode, platinum gauze as the auxiliary electrode, and Ag/AgCl as the reference electrode, which was checked against Fc/Fc* couple after each measurement.

Synthesis and characterization

2,4,6-tris[(trimethylsilyl)ethynyl]-1,3,5-triazine (1). was prepared by adapting the procedure described in *Org. Lett.*, **2001**, 15, 2419-2421 by Tobe et. al.

Azides 2-4 have been prepared by diazotization of alkoxylated anilines followed by addition of sodium azide according to the procedure reported by H. Gallardo et. al. in *Liquid Crystals*, **2008**, 6, 719-725. Polyalkoxylated anilines were obtained by reduction of a nitrocompound with a Pd catalyst. **Nitro compounds** (3,4-di-*n*-decyloxynitrobenzene and 3,4,5-tri-*n*-decyloxynitrobenzene) and their corresponding **anilines** (3,4-di-*n*-decyloxyaniline and 3,4,5-tri-*n*-decyloxyaniline) were prepared as reported by Serrano et al. in *Chem. Mater.* **2004***, 16*, 3308-3317 and *Liquid Crystals*, **2003**, *30*, 651-661 and showed identical spectroscopic properties to those reported therein. 4-*n*-decyloxyaniline is commercially available.

General procedure for the synthesis of TTT compounds 5-7

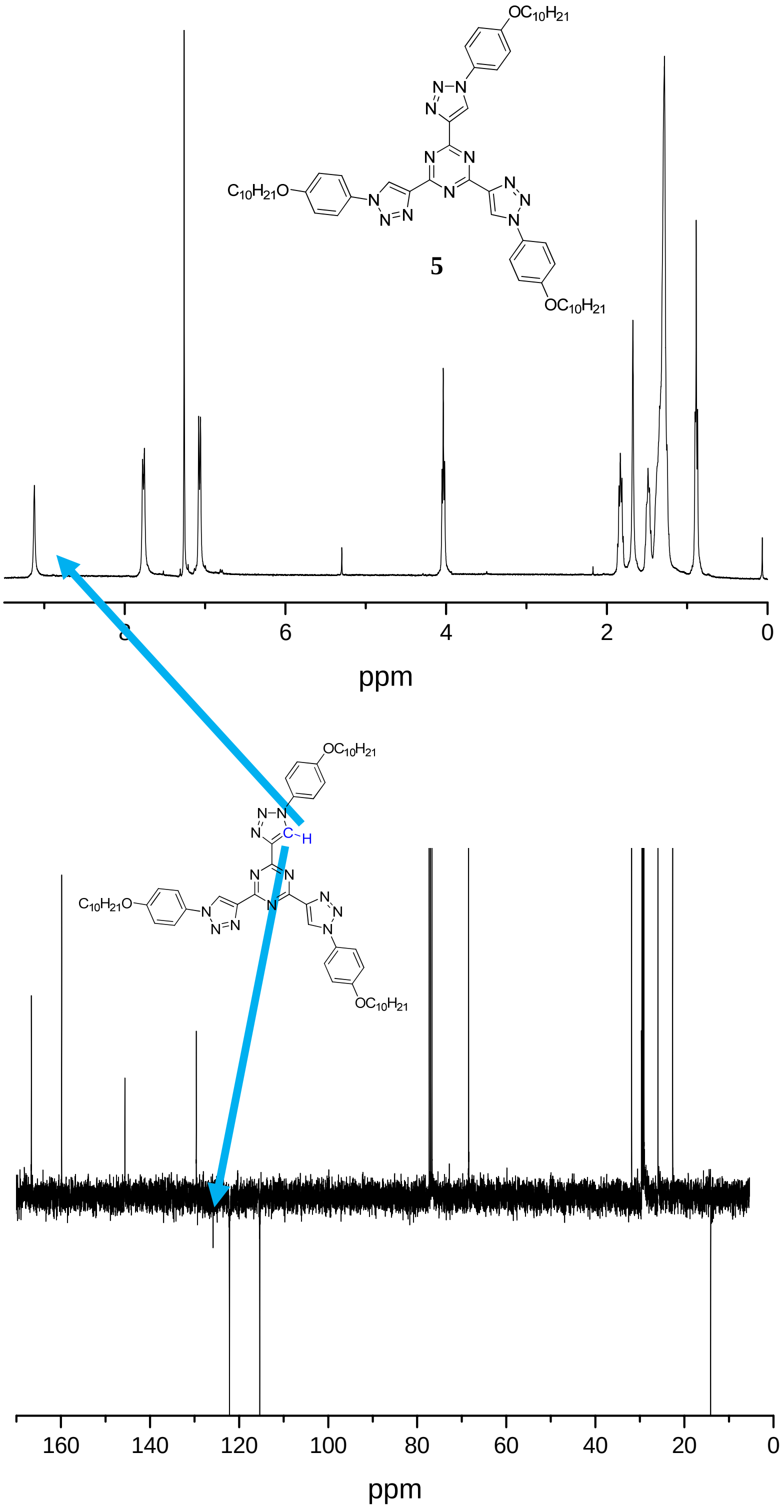
0.77 mmol of **1** and 2.39 mmol of **2-4** were dissolved in THF / H_2O (5 mL/5 mL). The solution was stirred for 3 minutes. Then, 0.23 mmol of sodium ascorbate, 0.11 mmol of copper(II) sulphate and 2.3 mmol of TBAF 1 M in THF were added. The flask was kept in dark for 12 hours. The reaction mixture was extracted with dichloromethane/water 2/1 (3x15 mL) and the combined organic layers were dried over $MgSO_4$. The solvent was evaporated, and the residue was purified by column chromatography with silica gel as the stationary phase and the suitable eluent.

2,4,6-tris[1-(4-*n*-decyloxyphenyl)-1,2,3-triazol-4-yl]-1,3,5-triazine (5) was purified by column chromatography with ethyl acetate/dichloromethane 9.5/0.5 as eluent to give **5** as a yellow solid. Yield: 45%.
^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm 0.88 (t, *J*= 7.0 Hz, 9H, CH_3), 1.27 (m, 36H, CH_2), 1.44-1.51 (m, 6H, CH_2), 1.78-1.85 (m, 6H, CH_2), 4.02 (t, *J*= 6.6 Hz, 6H, OCH_2), 7.04 (m, AA'XX', 6H, ArH), 7.74 (m, AA'XX', 6H, ArH), 9.12 (s, 3H, triazole); ^{13}C NMR APT (100 MHz, $CDCl_3$) δ, ppm 14.1, 22.7, 25.9, 29.1, 29.3, 29.4, 29.5, 29.7, 31.9, 68.5, 115.4, 122.1, 128.8, 129.6, 145.6, 159.8, 166.6; IR (NaCl) υ, cm^{-1} 2924 (C-C), 2854 (C-C), 1513 (triazole), 1251 (C-O); Anal. Calcd for $C_{57}H_{78}N_{12}O_3$: C, 69.91; H, 8.03; N, 17.16 Found: C, 69.82; H, 8.13; N, 16.89; HRMS (MALDI+, dithranol): 1001.6160 $[M+Na]^+$ (Calcd for $C_{57}H_{78}N_{12}NaO_3$: 1001.6217); Rf = 0.22 (ethyl acetate/dichloromethane 9.5/0.5).

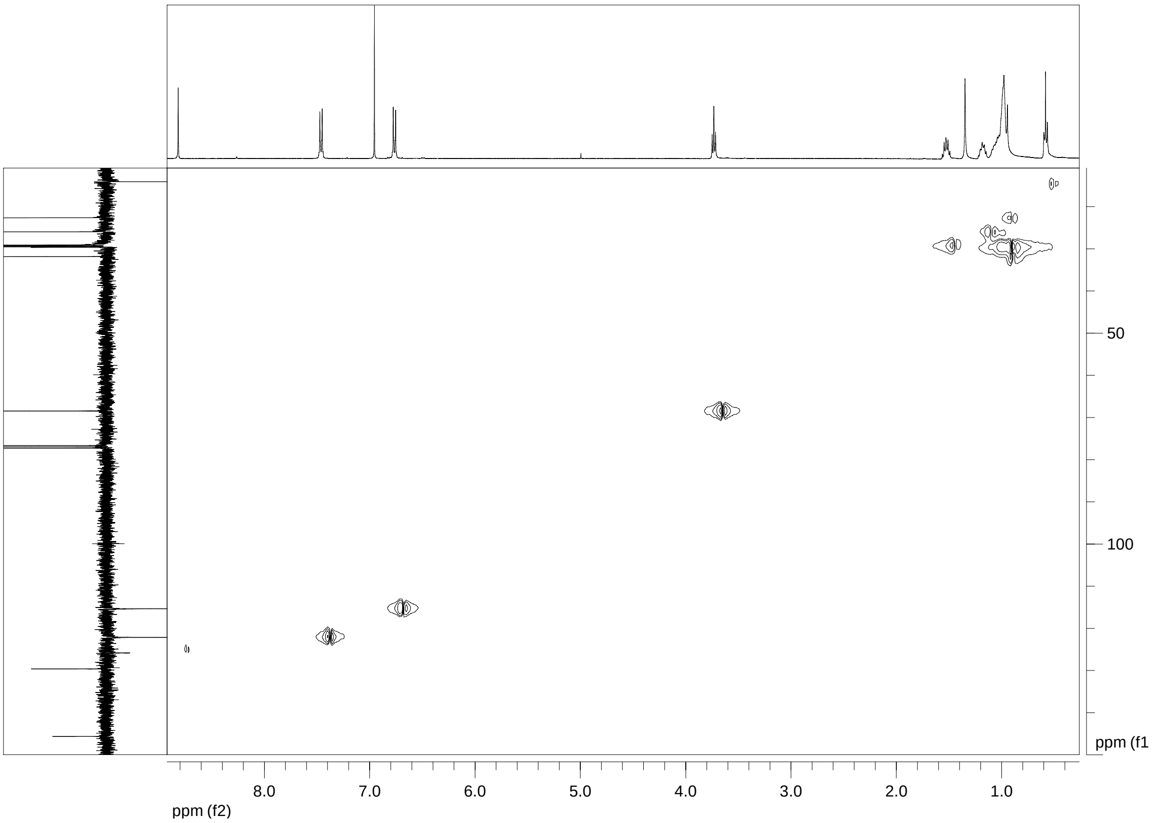
2,4,6-tris-[1-(3,4-di-*n*-decyloxyphenyl)-1,2,3-triazol-4-yl]-1,3,5-triazine (6) was purified by column chromatography with ethyl acetate/dichloromethane 9.5/0.5 as eluent to give **6** as a yellow paste. Yield 51%.
^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm 0.86-0.89 (m, 18H, CH_3), 1.27 (m, 72H, CH_2), 1.44-1.54 (m, 12H, CH_2), 1.82-1.93 (m, 12H, CH_2), 4.04-4.13 (m, 12H, OCH_2), 7.01 (d, *J*= 8.9 Hz, 3H, ArH), 7.36 (m, 6H, ArH), 9.18 (s, 3H, triazole); ^{13}C NMR APT (100 MHz, $CDCl_3$) δ, ppm 14.1, 22.7, 26.0, 29.2, 29.3, 29.4, 29.6, 29.7, 31.9, 69.5, 106.5, 112.8, 113.6, 125.0, 130.0, 135.2, 145.6, 150.0, 166.8; IR (NaCl) υ, cm^{-1} 2922 (C-C), 2851 (C-C), 1514 (triazole), 1251 (C-O); Anal. Calcd for $C_{87}H_{138}N_{12}O_6$: C, 72.16; H, 9.61; N, 11.61 Found: C, 72.18; H, 9.66; N, 11.49; HRMS (MALDI+, dithranol): 1470.0760 $[M+Na]^+$ (Calcd for $C_{87}H_{138}N_{12}NaO_6$: 1470.0760); Rf = 0.26 (ethyl acetate/dichloromethane 9.5/0.5).

2,4,6-tris[1-(3,4,5-tri-*n*-decyloxyphenyl)-1,2,3-triazol-4-yl]-1,3,5-triazine (7) was purified by column chromatography with ethyl acetate/dichloromethane 10/0.4 as eluent to give **7** as a brown paste. Yield: 48%.
^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm 0.88 (m, 27H, CH_3), 1.28 (m, 108H, CH_2), 1.44-1.55 (m, 18H, CH_2), 1.84-1.91 (m, 18H, CH_2), 4.02 (t, *J*= 6.4 Hz, 6H, OCH_2), 4.09 (t, *J*= 6.4 Hz, 12H, OCH_2), 7.07 (s, 6H, ArH), 9.17 (s, 1H, triazole); ^{13}C NMR APT (100 MHz, $CDCl_3$) δ, ppm 14.1, 22.7, 26.0, 26.1, 29.3, 29.4, 29.6, 29.7, 29.8, 30.3, 31.9, 69.5, 73.7, 99.2, 126.1, 131.8, 138.7, 145.6, 153.9, 166.7; IR (NaCl) υ, cm^{-1} 2923 (C-C), 2853 (C-C), 1508 (triazole), 1244 (C-O); Anal. Calcd for $C_{117}H_{198}N_{12}O_9$: C, 73.30; H, 10.41; N, 8.77 Found: C, 73.51; H, 10.50; N, 8.47; MS (MALDI+, DCTB): 1938.68 $[M+Na]^+$; Rf = 0.76 (ethyl acetate/dichloromethane 10/0.4).

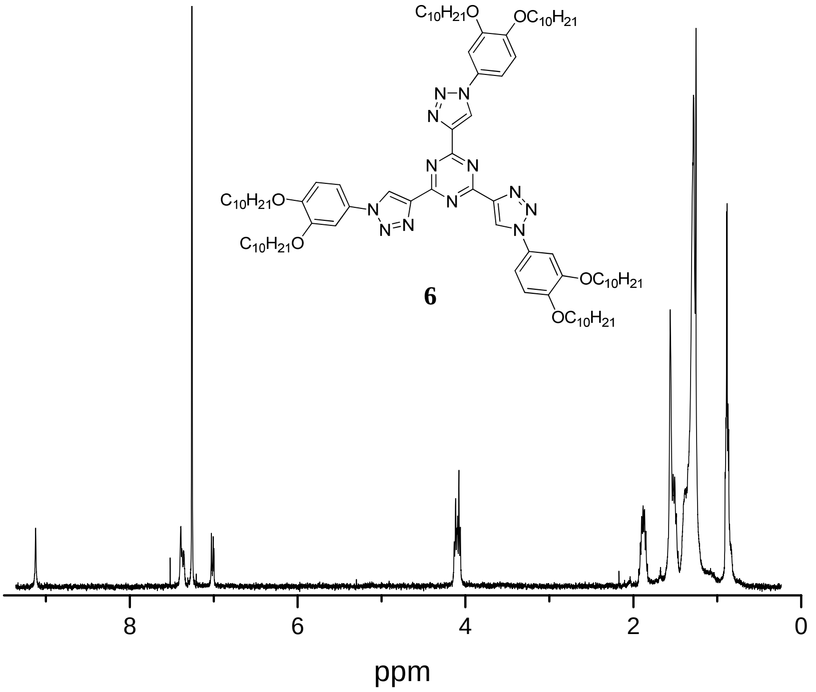
^{1}H NMR and ^{13}C NMR spectra of compound 5

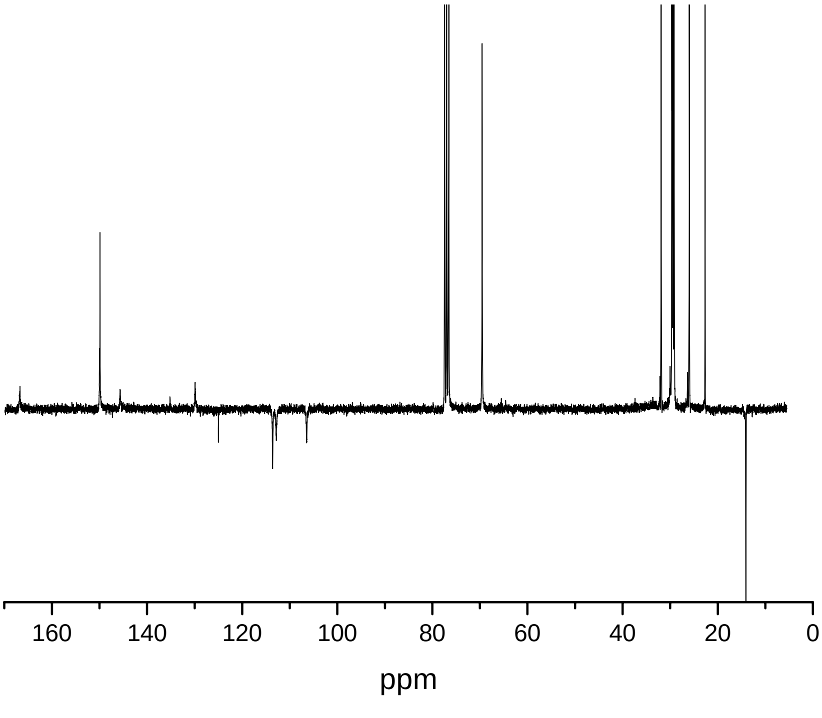


^{1}H-^{13}C HSQC spectrum of compound 5

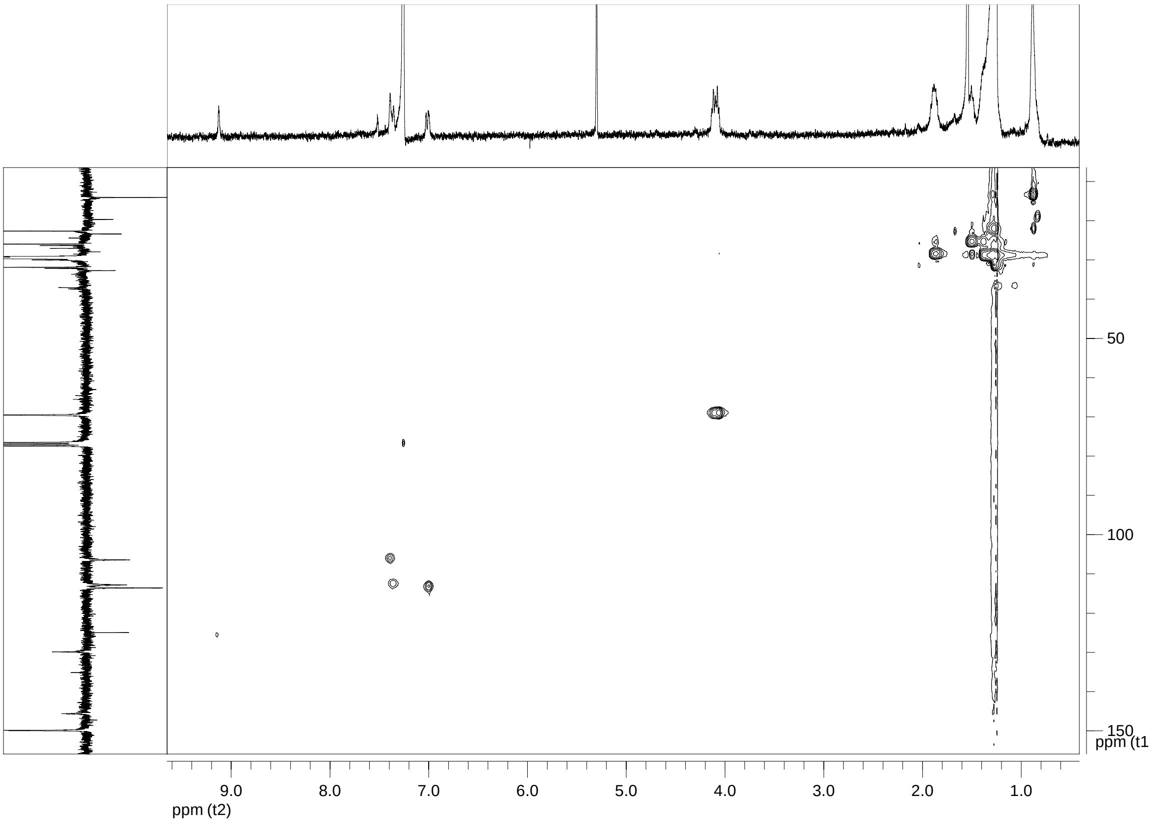


^{1}H NMR and ^{13}C NMR spectra of compound 6

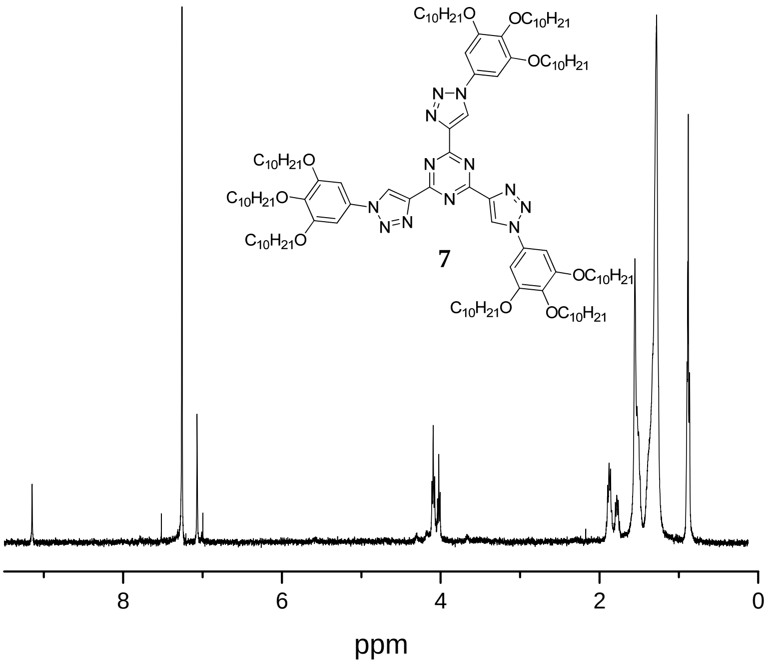


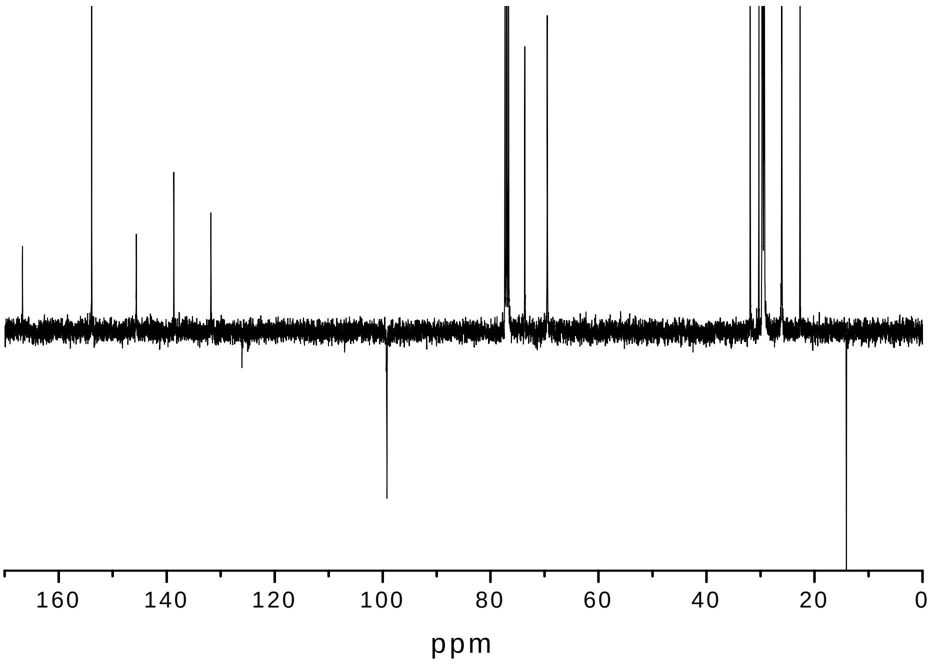


^1H-^{13}C HSQC spectrum of compound 6

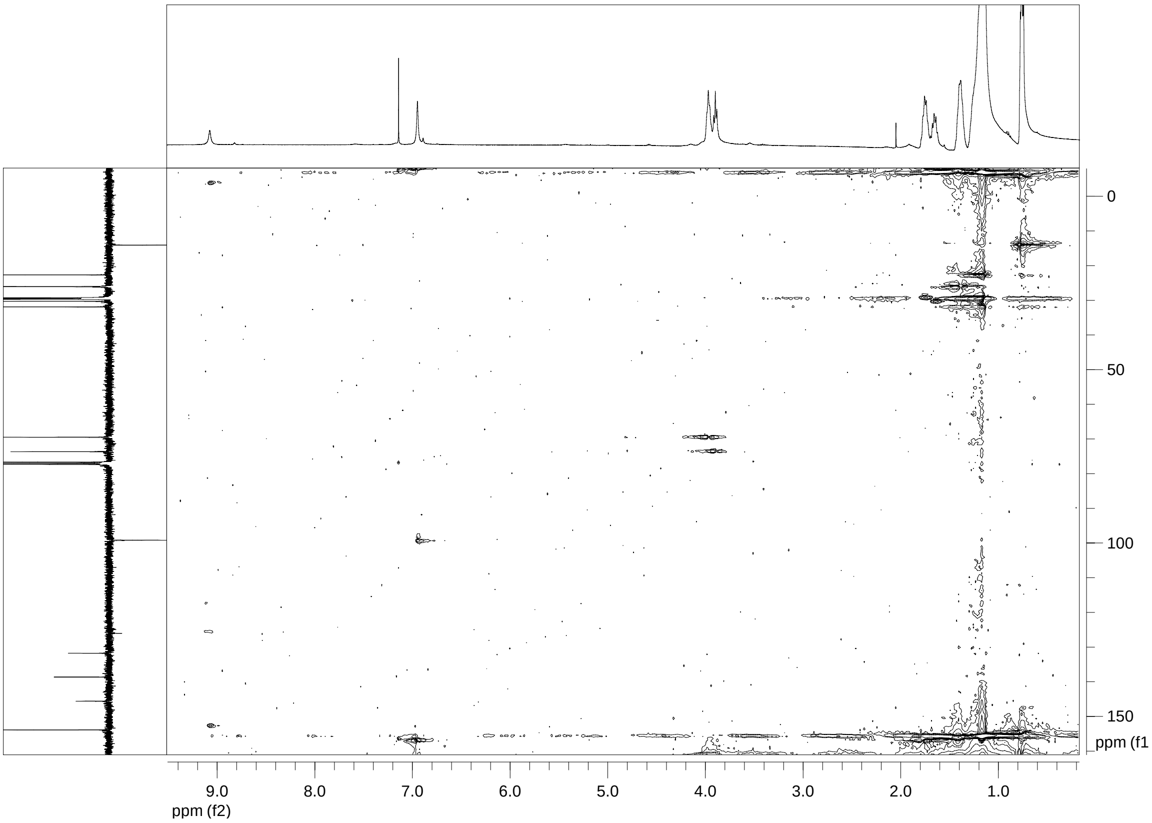


^{1}H NMR and ^{13}C NMR spectra of compound 7

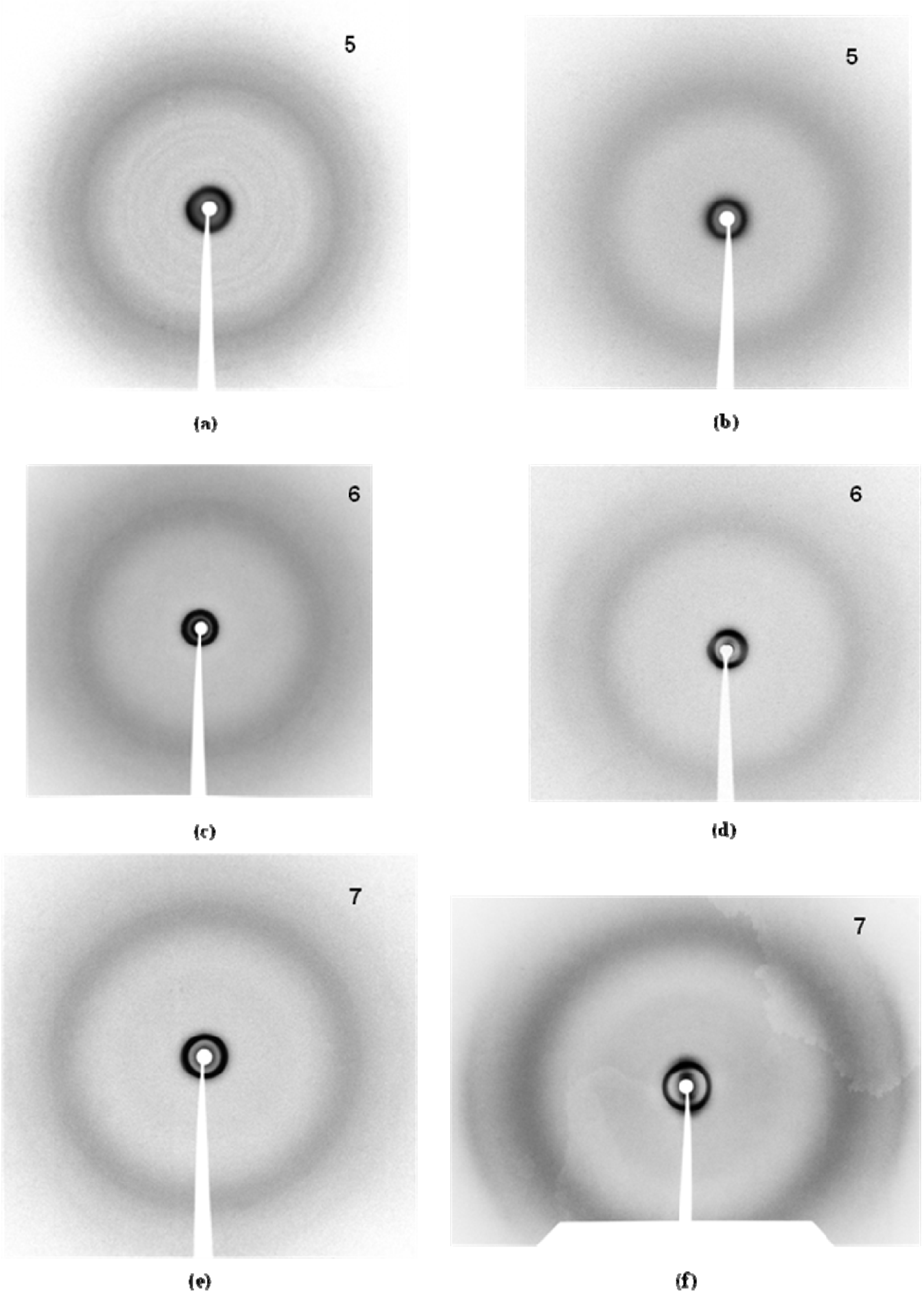




^{1}H-^{13}C HSQC spectrum of compound 7



X-ray diffractograms



(a) (b)

(c) (d)

(e) (f)

Room temperature XRD patterns for **5**: (a) crystalline order and (b) mesophase (Col$_h$); **6**: (c) mesophase (Col$_h$) and (d) partially aligned sample; **7**: (e) mesophase (Col$_h$) and (f) partially aligned sample.

Table S1. XRD data

The relationship between the density (ρ) of the compounds in the mesophase and the number of molecules per unit cell (Z) is given by the equation : $\rho = (M/N)/(V/Z)$, where M is the molar mass of the pure compound, N the Avogadro number, and V the unit cell volume (cm^3): $V = (\sqrt{3}/2) \times a^2c \times 10^{-24}$

Compound	Phase	Lattice constants (Å)$^{)}$	d_{obs} (Å)	*hkl*	*Z*	Calcd. density (g/cm^3)	D (Å) [a]
5	Col$_h$	$a = 35.6$	30.8	100	2	0.9	49.0
			4.5 (br)				
6	Col$_h$	$a = 37.2$	32.2	100	2	1.1	49.8
		$c = 3.5$	4.5 (br)				
			3.5	001			
7	Col$_h$	$a = 32.9$	28.5	100	1	0.9	50.1
		$c = 3.5$	4.3 (br)				
			3.5	001			

[a] Van der Waals diameter of the molecular structures estimated using ChemBio3D Ultra Software, version 11.0.1. The optimized structures had their energy minimized using the MM2 energy minimization method.

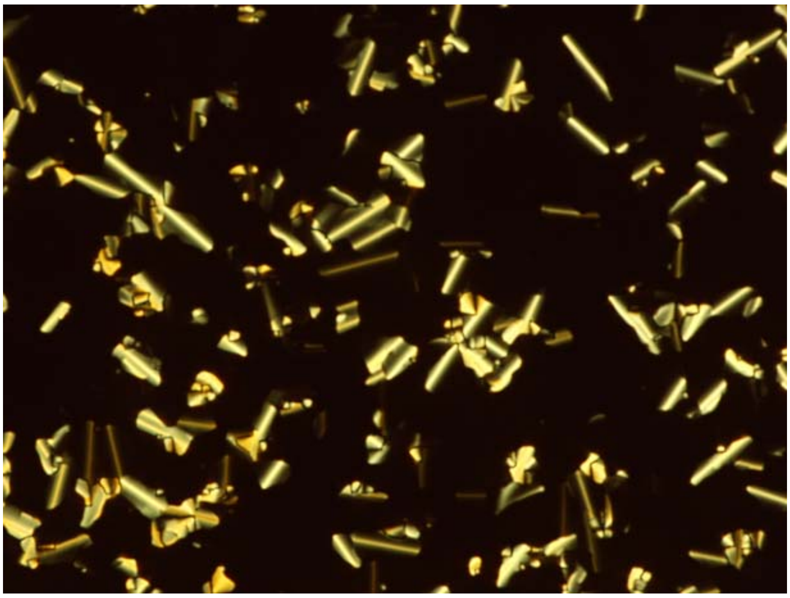
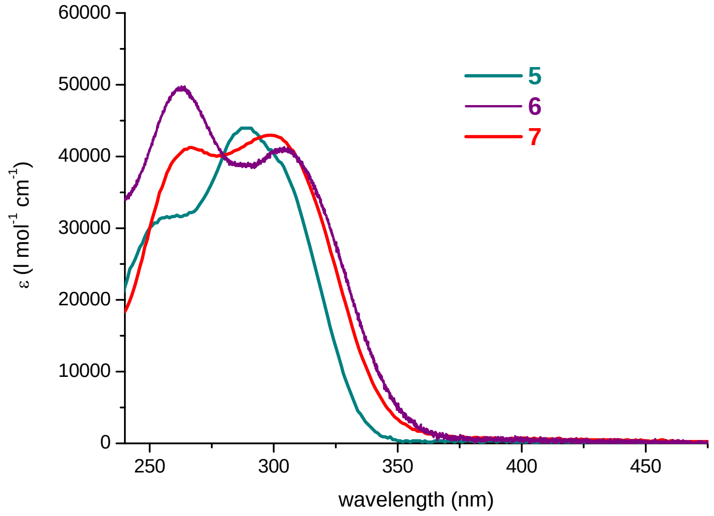


Figure S1. Polarized optical photomicrograph of a 50/50 mixture between **5** and **6** at 110 ºC.

UV-Vis absorption spectra in THF



Cyclic voltammetry plots