Electronic Supporting Information for:

Functional Star-shaped Tris(triazolyl)triazines: Columnar Liquid Crystal, Fluorescent, Solvatofluorochromic and Electrochemical Properties

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General experimental details

^{1}H NMR and ^{13}C NMR spectra were measured on Bruker ARX 300 and Bruker AVANCE 400 spectrometers. Chemical shifts are given in ppm relative to TMS and the solvent residual peak was used as the internal standard.

Microanalyses were performed with a LECO CHNS-932 microanalyzer. IR spectra were recorded on a Thermo Nicolet Avatar 380 FTIR spectrophotometer between NaCl pellets. Mass spectra were obtained on MICROFLEX Bruker (MALDI+) spectrometer.

Mesophase analysis was performed using a Linkam THMS600 hot stage and an Olympus polarizing microscope BX51 equipped with an Olympus DP12 digital camera. Transition temperatures and enthalpies were obtained by differential scanning calorimetry with a DSC-MDSC Q-20 and Q-2000 from TA Instruments at heating and cooling rates of 10 ºC/min. The apparatus were previously calibrated with indium (156.6 ºC, 28.44 J/g). Thermogravimetric analysis was performed with a Q-5000IR thermobalance from TA Instruments under nitrogen flow.

Powder X-ray diffraction patterns were obtained using a pinhole camera (Anton Paar) operating with a point focused Ni-filtered Cu-Kα beam. The sample was held in Lindemann glass capillaries (0.9 and 1 mm diameter) and heated, when necessary, with a variable-temperature attachment. The diffraction patterns were collected on flat photographic film.

Optical absorption spectra were recorded with a UV4-200 UV-Vis spectrophotometer from ATI Unicam. Fluorescence spectra were recorded with a Perkin-Elmer LS50B system. Thin films were prepared by drop casting from dichloromethane solutions onto a quartz substrate and measured by front-detection.

CD spectra were recorded in a Jasco J-810. Neat samples were prepared on a quarzt plate, heated to form the isotropic liquid state and cooled to room temperature.

Cyclic voltammetry (CV) measurements were performed with a Metrohm μ-Autolab ECO-Chemie potentiostat, using a glassy carbon working electrode, Pt counter electrode, and Ag/AgCl reference electrode in a three-electrode cell. The experiments were carried out under argon, in CH_2Cl_2, with Bu_4NPF_6 as supporting electrolyte (0.1 M). Scan rate was 100 mV s^{-1}. The potential was checked against ferrocene/ferrocenium (FOC) couple after each measurement (E^o = 4.8 eV). LUMO energy levels were calculated as the difference between -4.8 eV and $E_{1/2}^{red}$ vs FOC (eV).

Synthesis and characterization

Compounds 2,4,6-tris[1'-(4''-n-decyloxyphenyl)-1',2',3'-triazol-4'-yl)]-1,3,5-triazine (**T3**), 2,4,6-tris[1'-(4''-n-decyloxyphenyl)-1',2',3'-triazol-4'-yl)]-1,3,5-triazine (**T6**) and 2,4,6-tris[1'-(4''-n-decyloxyphenyl)-1',2',3'-triazol-4'-yl)]-1,3,5-triazine (**T9**) were prepared by the procedure described in *Org. Lett.*, **2010**, *12*, 1404-1407 by *Beltran et al.*

General procedure for the synthesis of aromatic azides (A/A*)

6.6 mmol of the appropriate poly(alcoxylated)benzoic acid (4-decyloxybenzoic acid, 3,4-didecyloxybenzoic acid, 3,4,5-tridecyloxybenzoic acid, 4-(3',7'-dimethyloctyloxy)benzoic acid, 3,4-bis(3',7'-dimethyloctyloxy)benzoic acid or 3,4,5-tris(3',7'-dimethyloctyloxy)benzoic acid), 6.6 mmol of 4-azidophenol and 0.1 mmol of 4-dimethylaminopyridine were dissolved in dry dichloromethane (50 mL). The reaction mixture was cooled down to 0 ºC and 6.6 mmol of N, N'-dicyclohexylcarbodiimide (DCC) was slowly added. After adding the last portion of DCC the cooling bath was removed and the mixture was stirred at room temperature for 24 hours. The solid was removed by filtration and the solvent was evaporated. The crude was purified by column chromatography with silica gel as the stationary phase and the eluent indicated below for each compound.

4'-azidophenyl 4-decyloxybenzoate (**A1**) was obtained in quantitative yield as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm 0.88 (t, *J* = 7.3 Hz, 3H, CH_3), 1.27 (m, 12H, CH_2), 1.43-1.53 (m, 2H, CH_2), 1.78-1.85 (m, 2H, CH_2), 4.04 (t, *J* = 6.5 Hz, 2H, OCH_2), 6.96-6.98 (m, AA'XX', 2H, ArH), 7.06-7.08 (m, AA'XX', 2H, ArH), 7.19-7.21 (m, AA'XX', 2H, ArH), 8.11-8.14 (m, AA'XX', 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm 14.1, 22.7, 26.0, 29.1, 29.3, 29.4, 29.5, 31.6, 31.9, 68.3, 114.3, 119.8, 121.2, 123.2, 132.3, 137.3, 147.3, 163.6, 164.9; IR (NaCl) ν, cm^{-1} 2905 (C-C), 2849 (C-C), 2105 (N_3), 1738 (C=O), 1606 (arC), 1511 (arC), 1501 (arC), 1263 (C-O); Anal. Calcd for $C_{23}H_{29}N_3O_3$: C, 69.85; H, 7.39; N, 10.62 Found: C, 69.52; H, 7.58; N, 10.39; MALDI$^+$ (dithranol): 418.2 $[M+Na]^+$ (Calcd for $C_{23}H_{29}N_3NaO_3$: 418.2); R_f: 0.6 (ethyl acetate/hexane 1/9).

4'-azidophenyl 3,4-didecyloxybenzoate (**A2**) was purified by column chromatography with ethyl acetate/hexane 1/9 as eluent to give a white solid. Yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm 0.89-0.86 (m, 6H, CH_3), 1.26 (m, 24H, CH_2), 1.44-1.51 (m, 4H, CH_2), 1.81-1.90 (m, 4H, CH_2), 4.04-4.09 (m, 4H, OCH_2), 6.92 (d, *J* = 8.5 Hz, 1H, ArH), 7.06-7.08 (m, AA'XX', 2H, ArH), 7.18-

7.21 (m, AA'XX', 2H, ArH), 7.64 (d, J = 2.0 Hz, 1H, ArH), 7.79 (dd, J = 2.0 Hz, J = 8.5 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm 14.1, 22.7, 26.1, 29.3, 29.4, 29.6, 29.7, 30.3, 31.9, 32.0, 69.1, 106.8, 114.3, 119.8, 121.2, 123.1, 123.2, 132.3, 138.4, 148.1, 153.4, 163.7, 164.9; IR (NaCl) ν, cm^{-1} 2920 (C-C), 2109 (N_3), 1730 (C=O), 1594 (arC), 1514 (arC), 1263 (C-O); Anal. Calcd for $C_{33}H_{49}N_3O_4$: C, 71.83; H, 8.95; N, 7.62 Found: C, 71.75; H, 8.93; N, 7.42; MALDI$^+$ (dithranol): 574.4 $[M+Na]^+$ (Calcd for $C_{33}H_{49}N_3NaO_4$: 574.4); R_f: 0.8 (ethyl acetate/hexane 1/9).

4'-azidophenyl 3,4,5-tridecyloxybenzoate (**A3**) was obtained in quantitative yield as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm 0.87-0.91 (m, 9H, CH_3), 1.29 (m, 36H, CH_2), 1.46-1.55 (m, 6H, CH_2), 1.72-1.87 (m, 6H, CH_2), 4.03-4.09 (m, 6H, OCH_2), 7.05-7.07 (m, AA'XX', 2H, ArH), 7.17-7.20 (m, AA'XX', 2H, ArH), 7.41 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm 14.0, 22.6, 26.0, 29.2, 29.3, 29.5, 29.6, 29.7, 30.3, 31.9, 69.1, 73.5, 108.4, 119.8, 123.1, 123.5, 137.4, 143.1, 147.9, 152.9, 164.8; IR (NaCl) ν, cm^{-1} 2927 (C-C), 2854 (C-C), 2114 (N_3), 1737 (C=O), 1586 (arC), 1502 (arC), 1189 (C-O); Anal. Calcd for $C_{43}H_{69}N_3O_5$: C, 72.94; H, 9.82; N, 5.93 Found: C, 73.12; H, 9.78; N, 6.12; MALDI$^+$ (dithranol): 721.1 $[M+2Na-1H]^+$ (Calcd for $C_{43}H_{68}N_3Na_2O_5$: 721.1). R_f: 0.8 (ethyl acetate/hexane 1/9).

4''-azidophenyl 4-(3',7'-dimethyloctyloxy)benzoate (**A1***) was purified by column chromatography with ethyl acetate /hexane 0.5/9.5 as eluent to give a white solid. Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm 0.88 (t, J = 6.6 Hz, 3H, CH_3), 0.96 (d, J = 6.5 Hz, 3H, CH_3), 1.12-1.40 (m, 9H, CH_2), 1.49-1.77 (m, 3H, CH_2), 1.83-1.97 (m, 1H, CH), 4.04-4.13 (m, 2H, OCH_2), 6.95-6.99 (m, AA'XX', 2H, ArH), 7.05-7.08 (m, AA'XX', 2H, ArH), 7.18-7.22 (m, AA'XX', 2H, ArH), 8.11-8.15 (m, AA'XX', 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm 19.6, 22.6, 22.7, 24.6, 24.7, 25.4, 27.9, 29.8, 35.9, 37.2, 39.2, 66.7, 114.3, 119.8, 121.2, 123.2, 132.3, 137.3, 147.9, 163.6, 164.9; IR (NaCl) ν, cm^{-1} 2922 (C-C), 2117 (N_3), 1735 (C=O), 1608 (arC), 1497 (arC), 1258 (C-O); Anal. Calcd for $C_{23}H_{29}N_3O_3$: C, 69.85; H, 7.39; N, 10.62 Found: C, 70.40; H, 7.71; N, 10.46; MALDI$^+$ (dithranol): 418.3 $[M+Na]^+$ (Calcd for $C_{23}H_{29}N_3NaO_3$: 418.2); R_f: 0.6 (ethyl acetate/hexane 1/9).

4''-azidophenyl 3,4-bis(3',7'-dimethyloctyloxy)benzoate (**A2***) was purified by column chromatography with ethyl acetate/hexane 0.5/9.5 as eluent to give a light yellow solid. Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm 0.86 (t, J = 6.6 Hz, 6H, CH_3), 0.87 (d, J = 6.6 Hz, 6H, CH_3), 0.96 (d, J = 6.4 Hz, 6H, CH_3), 0.97 (d, J = 6.4 Hz, 6H, CH_3), 1.11-1.21 (m, 12H, CH_2), 1.24-1.46 (m, 6H, CH_2), 1.47-1.59 (m, 3H, CH_3), 1.62-1.76 (m, 3H, CH_3), 1.86-1.94 (m, 2H, CH), 4.06-4.16 (m, 4H, OCH_2), 7.06-7.08 (m, AA'XX', 2H, ArH), 7.18-7.20 (m, AA'XX', 2H, ArH), 7.65 (d, J =

2.02 Hz, 1H, ArH), 7.80 (dd, *J* = 2.02 Hz, *J* = 8.6 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm 19.6, 19.7, 22.5, 22.6, 24.7, 27.9, 29.9, 35.9, 36.1, 37.2, 39.2, 67.4, 67.7, 111.8, 114.4, 119.8, 121.2, 123.2, 137.4, 148.0, 148.6, 153.9, 165.0; IR (NaCl) ν, cm^{-1} 2926 (C-C), 2115 (N_3), 1742 (C=O), 1589 (arC), 1495 (arC), 1276 (C-O); Anal. Calcd for $C_{33}H_{49}N_3O_4$: C, 71.83; H, 8.95; N, 7.62 Found: C, 71.64; H, 8.90; N, 7.43; MALDI$^+$ (dithranol): 574.6 $[M+Na]^+$ (Calcd for $C_{33}H_{49}N_3NaO_4$: 574.4) R_f: 0.8 (ethyl acetate/hexane 1/9).

4''-azidophenyl 3,4,5-tris(3',7'-dimethyloctyloxy)benzoate (**A3***) was obtained in quantitative yield as a yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm 0.88 (d, *J* = 6.6 Hz, 12H, CH_3), 0.89 (d, *J* = 6.6 Hz, 6H, CH_3), 0.96 (d, *J* = 6.4 Hz, 12H, CH_3), 0.97 (d, *J* = 6.4 Hz, 12H, CH_3), 1.19-1.23 (m, 8H, CH_2), 1.25-1.40 (m, 10H, CH_2), 1.51-1.80 (m, 9H, CH_2), 1.83-1.95 (m, 3H, CH), 4.05-4.16 (m, 6H, OCH_2), 7.06-7.08 (m, AA'XX', 2H, ArH), 7.19-7.21 (m, AA'XX', 2H, ArH), 7.42 (s, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm 19.5, 22.6, 22.7, 24.6, 27.9, 29.5, 29.8, 36.2, 37.3, 37.4, 39.2, 39.3, 67.5, 71.7, 108.4, 119.8, 123.1, 123.6, 137.5, 143.0, 147.9, 152.9, 164.9; IR (NaCl) ν, cm^{-1} 2934 (C-C), 2136 (N_3), 1740 (C=O), 1591 (arC), 1504 (arC), 1195 (C-O); Anal. Calcd for $C_{43}H_{69}N_3O_5$: C, 72.94; H, 9.82; N, 5.93 Found: C, 73.56; H, 9.81; N, 5.81; MALDI$^+$ (dithranol): 721.1 $[M+2Na-1H]^+$ (Calcd for $C_{43}H_{68}N_3Na_2O_5$: 721.1) R_f: 0.8 (ethyl acetate/hexane 0.5/9.5).

General procedure for the synthesis of compounds TB/TB*

0.77 mmol of 2,4,6-tris[(trimethylsilyl)ethynyl]-1,3,5-triazine and 2.39 mmol of an aromatic azide **A**/**A*** 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 tetrabutylammonium fluoride (TBAF) (2.3 mL, 1 M in THF) were added. The flask was kept in dark and stirred for 12 hours. The reaction mixture was extracted with dichloromethane/water 2/1 (3 x 15 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 indicated below.

4,4',4''-(4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(1,2,3-triazole-1-yl))triphenyl tris(4-decyloxybenzoate) (**TB3**) was purified by column chromatography with ethyl acetate/dichloromethane 1/10 as eluent to give a white solid. Yield: 32%. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm 0.88 (t, *J* = 7.0 Hz, 9H, CH_3), 1.28 (m, 36H, CH_2), 1.45-1.52 (m, 6H, CH_2), 1.80-1.87 (m, 6H, CH_2), 4.10 (t, *J* = 6.5 Hz, 6H, OCH_2), 6.98-7.02 (m, AA'XX', 6H, ArH), 7.45-7.49 (m, AA'XX', 6H, ArH), 7.95-7.99 (m,

AA'XX', 6H, ArH), 8.15-8.18 (m, AA'XX', 6H, ArH), 9.24 (s, 3H, triazole); ^{13}C NMR APT (100 MHz, $CDCl_3$) δ, ppm 14.1, 22.7, 26.0, 29.1, 29.3, 29.4, 29.6, 31.9, 68.4, 114.4, 120.8, 121.8, 123.5, 125.8, 132.4, 134.0, 146.0, 151.7, 163.8, 164.5, 166.8; IR (NaCl) υ, cm^{-1} 2921 (C-C), 2853 (C-C), 1722 (C=O), 1514 (triazole), 1257 (C-O); Anal. Calcd for $C_{78}H_{90}N_{12}O_9$: C, 69.93; H, 6.77; N, 12.55 Found: C, 69.69; H, 6.77; N, 12.73; Rf = 0.10 (ethyl acetate/dichloromethane 1/10).

4,4',4''-(4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(1,2,3-triazole-1-yl))triphenyl tris(3,4-didecyloxybenzoate) (**TB6**) was purified by column chromatography with ethyl acetate/dichloromethane 0.5/10 as eluent to give a yellow solid. Yield: 41%. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm 0.85-0.98 (m, 18H, CH_3), 1.28 (m, 72H, CH_2), 1.45-1.52 (m, 12H, CH_2), 1.81-1.89 (m, 12H, CH_2), 4.05-4.09 (m, 12H, OCH_2), 6.93 (d, *J* = 8.6 Hz, 3H, ArH), 7.44-7.46 (m, AA'XX', 6H, ArH), 7.7 (d, *J* = 1.9 Hz, 3H, ArH), 7.82 (dd, *J* = 1.9 Hz, *J* = 8.4 Hz, 3H, ArH), 7.92-7.96 (m, AA'XX', 6H, ArH), 9.20 (s, 3H, triazole); ^{13}C NMR APT (100 MHz, $CDCl_3$) δ, ppm 14.1,22.6, 25.9, 26.0, 28.9, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 31.8, 69.0, 69.3, 111.8, 114.5, 120.8, 121.6, 123.4, 124.5, 125.8, 133.7, 145.8, 148.6, 151.6, 154.0, 164.5, 166.6; IR (NaCl) υ, cm^{-1} 2915 (C-C), 2854 (C-C), 1726 (C=O), 1512 (triazole), 1233 (C-O); Anal. Calcd for $C_{108}H_{150}N_{12}O_{12}$: C, 71.73; H, 8.36; N, 9.29 Found: C, 71.30; H, 8.50; N, 8.97; Rf = 0.25 (ethyl acetate/dichloromethane 1/10).

4,4',4''-(4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(1,2,3-triazole-1-yl))triphenyl tris(3,4,5-tridecyloxybenzoate) (**TB9**) was purified by column chromatography with ethyl acetate/dichloromethane 0.37/10 as eluent to give TB9 as a brown paste. Yield: 28%. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm 0.86-0.90 (m, 27H, CH_3), 1.28 (m, 108H, CH_2), 1.46-1.53 (m, 18H, CH_2), 1.54-1.74 (m, 18H, CH_2), 4.05-4.09 (m, 18H, OCH_2), 7.43 (s, 6H, ArH), 7.45-7.47 (m, AA'XX', 6H, ArH), 7.95-7.98 (m, AA'XX', 6H, ArH), 9.24 (s, 3H, triazole); ^{13}C NMR APT (100 MHz, $CDCl_3$) δ, ppm 14.1, 22.6, 22.7, 26.0, 26.1, 29.3, 29.4, 29.5, 29.6, 29.7, 30.3, 31.9, 31.9, 69.3, 73.6, 108.6, 121.8, 123.2, 123.5, 125.9, 133.9, 143.3, 145.9, 151.6, 153.0, 164.6, 166.7; IR (NaCl) υ, cm^{-1} 2926 (C-C), 2849 (C-C), 1726 (C=O), 1506 (triazole), 1196 (C-O); Anal. Calcd for $C_{138}H_{210}N_{12}O_{15}$: C, 72.79; H, 9.30; N, 7.38 Found: C, 73.08; H, 9.31; N, 7.16; Rf = 0.40 (ethyl acetate/dichloromethane 1/25).

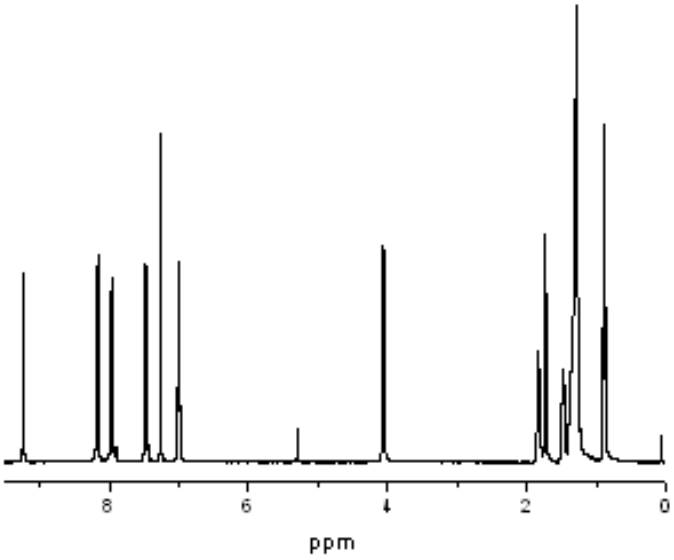
4,4',4''-(4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(1,2,3-triazole-1-yl))triphenyl tris(4-(3,7-dimethyloctyloxy)benzoate) (**TB3***) was purified by column chromatography with ethyl acetate/dichloromethane 1/10 as eluent to give a yellow paste. Yield: 39%.
^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm 0.88 (d, *J* = 6.5 Hz, 18H, CH_3), 0.97 (d, *J* = 6.1 Hz, 9H, CH_3), 1.15-1.41 (m, 12H, CH_2), 1.48-1.75 (m, 9H, CH_2), 1.84-1.92 (m, 9H, CH_2), 4.06-4.13 (m, 6H,

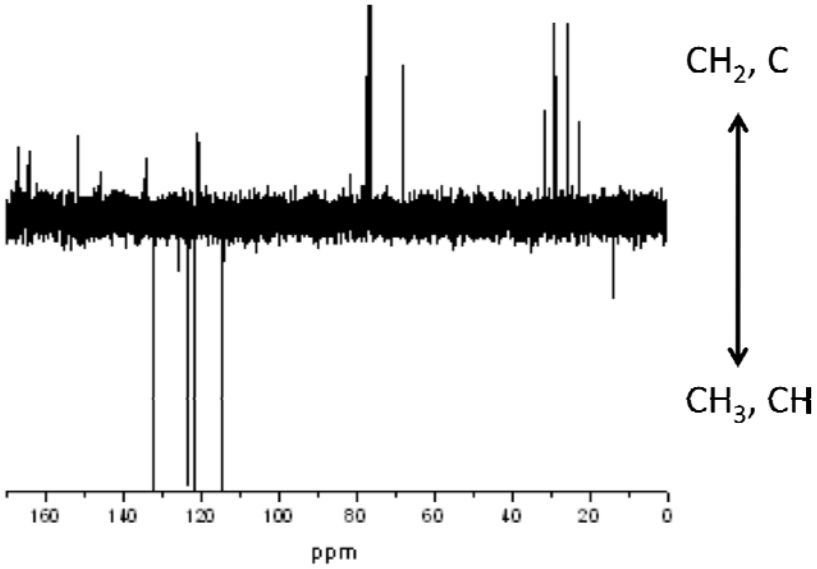
OCH_2), 6.99-7.02 (m, AA'XX', 6H, ArH), 7.46-7.49 (m, AA'XX', 6H, ArH), 7.96-7.98 (m, AA'XX', 6H, ArH), 8.16-8.19 (m, AA'XX', 6H, ArH), 9.24 (s, 3H, triazole); ^{13}C NMR APT (100 MHz, $CDCl_3$) δ, ppm 19.6, 22.6, 22.7, 24.6, 27.9, 29.8, 35.9, 37.2, 39.2, 66.7, 114.4, 120.9, 121.7, 123.4, 125.7, 132.8, 133.8, 145.9, 151.6, 163.7, 164.4, 166.6; IR (NaCl) υ, cm^{-1} 2951 (C-C), 2864 (C-C), 1736 (C=O), 1514 (triazole), 1246 (C-O); Anal. Calcd for $C_{78}H_{90}N_{12}O_9$: C, 69.93; H, 6.77; N, 12.55 Found: C, 69.61; H, 6.87; N, 12.45; Rf = 0.22 (ethyl acetate/dichloromethane 1/5).

4,4',4''-(4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(1,2,3-triazole-1-yl))triphenyl tris(3,4-di-(3,7-dimethyloctyloxy)benzoate) (**TB6***) was purified by column chromatography with ethyl acetate/dichloromethane 1/10 as eluent to give a yellow paste. Yield: 42%.
^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm 0.88 (d, *J* = 6.6 Hz, 18H, CH_3), 0.87 (d, *J* = 6.6 Hz, 18H, CH_3), 0.97 (d, *J* = 6.3 Hz, 9H, CH), 0.98 (d, *J* = 6.3 Hz, 9H, CH), 1.11-1.21 (m, 36H, CH_2), 1.30-1.41 (m, 18H, CH_2), 1.48-1.58 (m, 9H, CH_2/CH), 1.63-1.78 (m, 9H, CH_2/CH), 1.79-1.97 (m, 6H, CH_2), 4.09-4.16 (m, 12H, OCH_2), 6.96 (d, J= 8.6 Hz, 3H, ArH), 7.46-7.49 (m, AA'XX', 6H, ArH), 7.68 (d, *J* = 1.8 Hz, 3H, ArH), 7.85 (dd, *J* = 1.8 Hz, *J* = 8.6 Hz, 3H, ArH), 7.95-7.99 (m, AA'XX', 6H, ArH), 9.27 (s, 3H, triazole); ^{13}C NMR APT (100 MHz, $CDCl_3$) δ, ppm 19.6, 19.7, 22.6, 22.7, 24.7, 27.9, 29.9, 35.9, 36.1, 37.3, 37.7, 39.3, 67.4, 67.7, 111.8, 114.4, 120.8, 121.7, 123.5, 124.5, 133.9, 145.9, 148.7, 151.7, 154.1, 164.7, 166.7; IR (NaCl) υ, cm^{-1} 2926 (C-C), 2849 (C-C), 1726 (C=O), 1506 (triazole), 1189 (C-O); Anal. Calcd for $C_{108}H_{150}N_{12}O_{12}$: C, 71.73; H, 8.36; N, 9.29 Found: C, 71.77; H, 8.50; N, 9.11; Rf = 0.34 (ethyl acetate/dichloromethane 1/10).

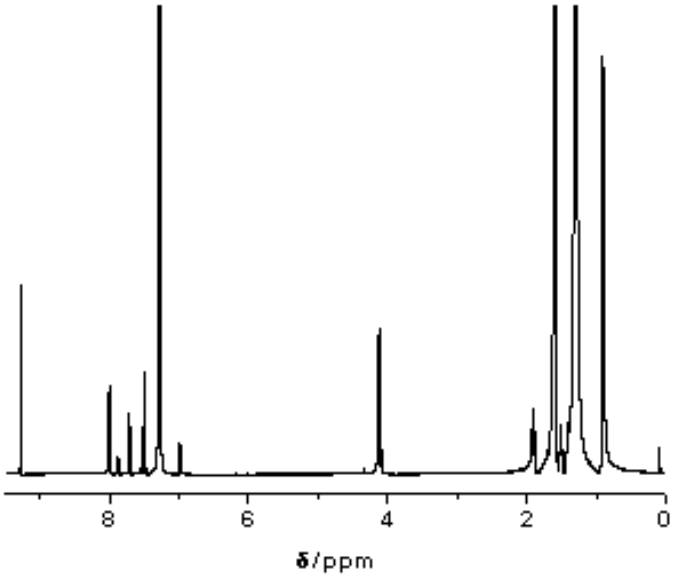
4,4',4''-(4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(1,2,3-triazole-1-yl))triphenyl tris(3,4,5-tri-(3,7-dimethyloctyloxy)benzoate) (**TB9***) was purified by column chromatography with ethyl acetate/dichloromethane 1/10 as eluent to give an amber paste. Yield: 36%.
^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm 0.87 (d, *J* = 6.6 Hz, 36H, CH_3), 0.88 (d, *J* = 6.6 Hz, 18H, CH_3), 0.95 (d, *J* = 6.3 Hz, 18H, CH_3), 0.96 (d, *J* = 6.3 Hz, 9H, CH_3), 1.11-1.22 (m, 24H, CH_2), 1.29-1.42 (m, 30H, CH_2), 1.48-1.78 (m, 27H, CH_2), 1.82-1.95 (m, 9H, CH_2), 4.05-4.09 (m, 18H, OCH_2), 7.45 (s, 6H, ArH), 7.45-7.49 (m, AA'XX', 6H, ArH), 7.96-8.00 (m, AA'XX', 6H, ArH), 9.27 (s, 3H, triazole); ^{13}C NMR APT (100 MHz, $CDCl_3$) δ, ppm 19.5, 19.6, 22.5, 22.6, 22.7, 24.7, 27.9, 29.6, 29.7, 29.8, 36.3, 37.3, 37.5, 39.2, 39.3, 67.6, 71.8, 108.6, 121.8, 123.2, 123.5, 134.0, 143.3, 146.0, 151.6, 153.0, 164.6, 166.7; IR (NaCl) υ, cm^{-1} 2924 (C-C), 2866 (C-C), 1728 (C=O), 1509 (triazole), 1196 (C-O); Anal. Calcd for $C_{138}H_{210}N_{12}O_{15}$: C, 72.79; H, 9.30; N, 7.38 Found: C, 73.19; H, 9.40; N, 7.05; Rf = 0.44 (ethyl acetate/dichloromethane 1/10).

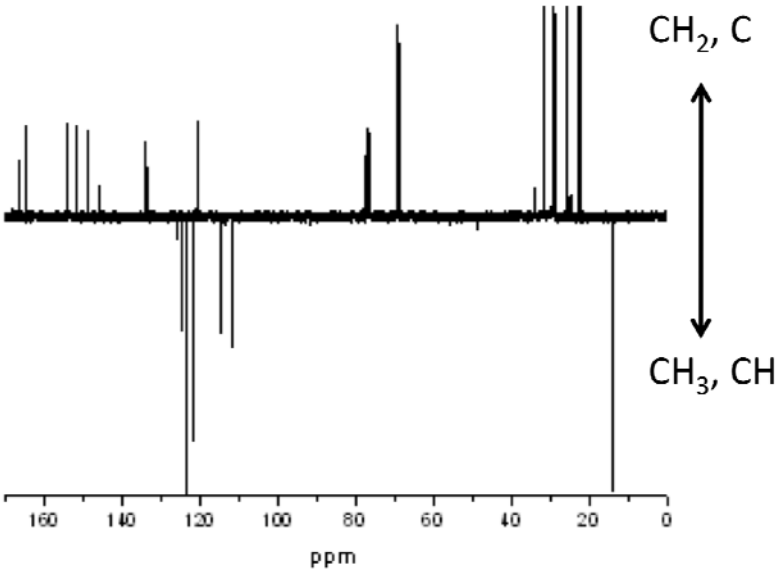
^{1}H NMR and ^{13}C NMR spectra of compound TB3



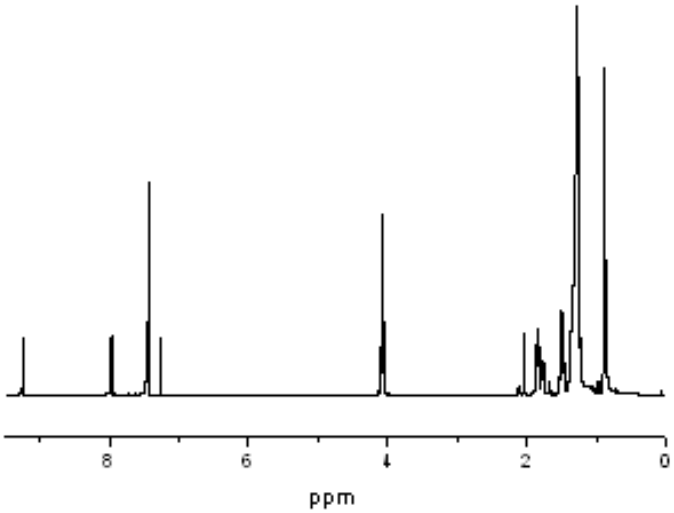


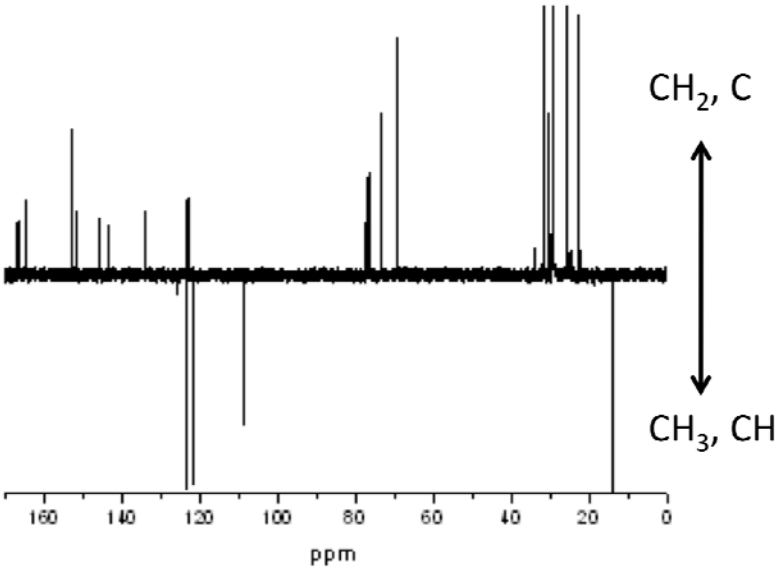
^{1}H NMR and ^{13}C NMR spectra of compound TB6



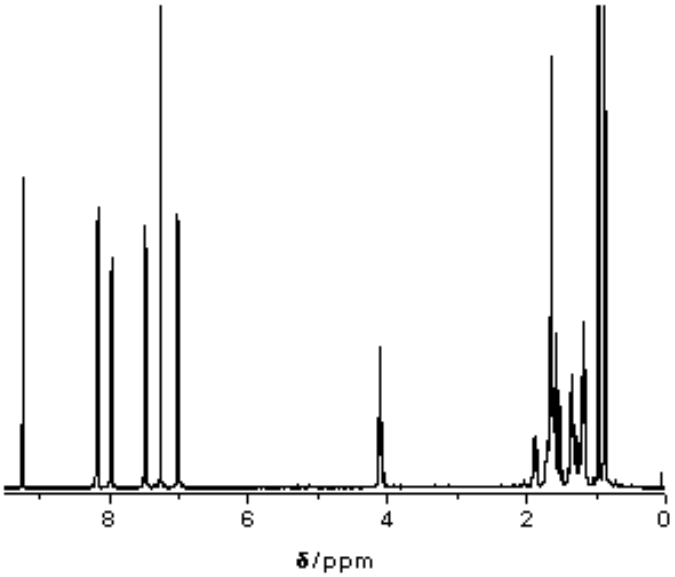


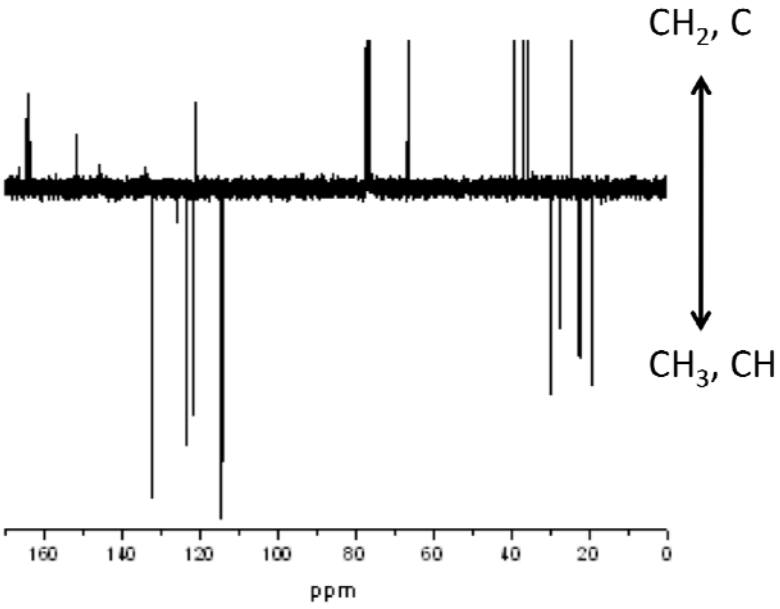
^{1}H NMR and ^{13}C NMR spectra of compound TB9



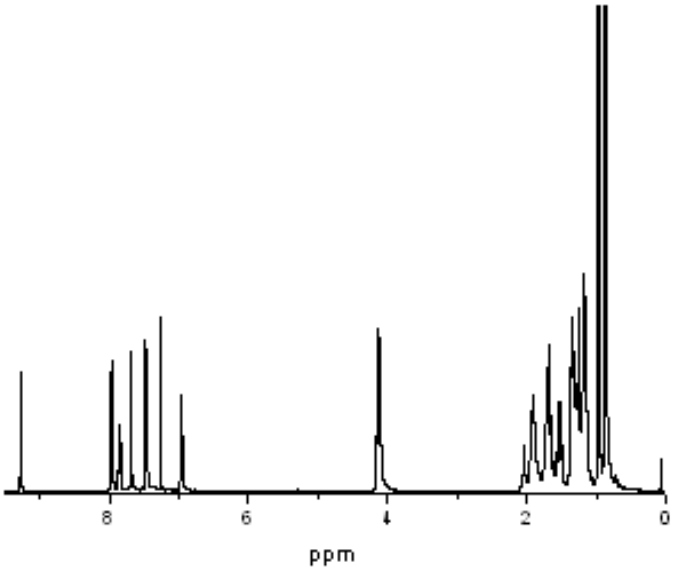


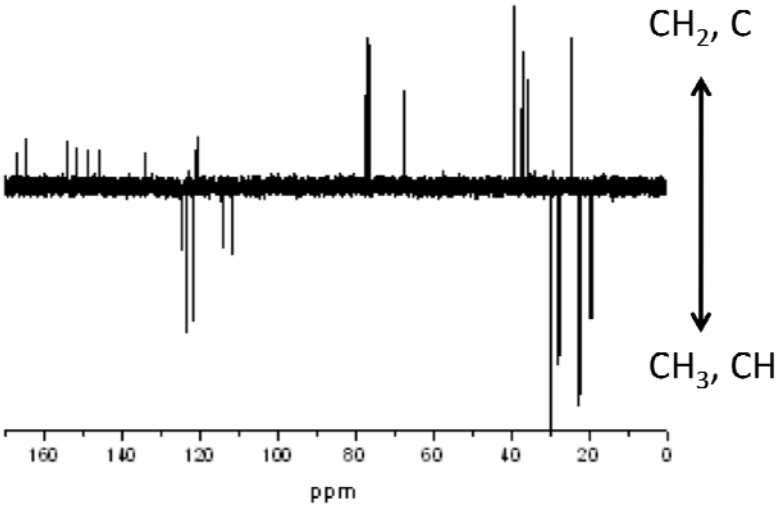
^{1}H NMR and ^{13}C NMR spectra of compound TB3*



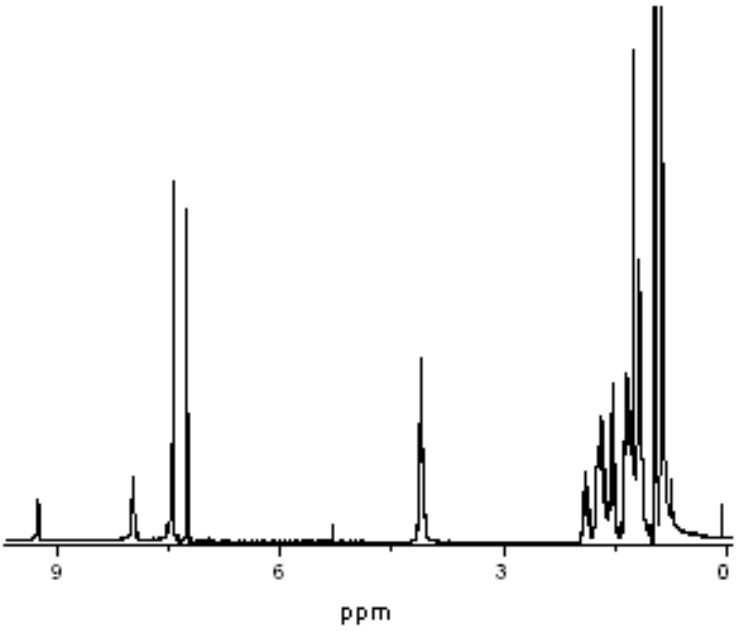


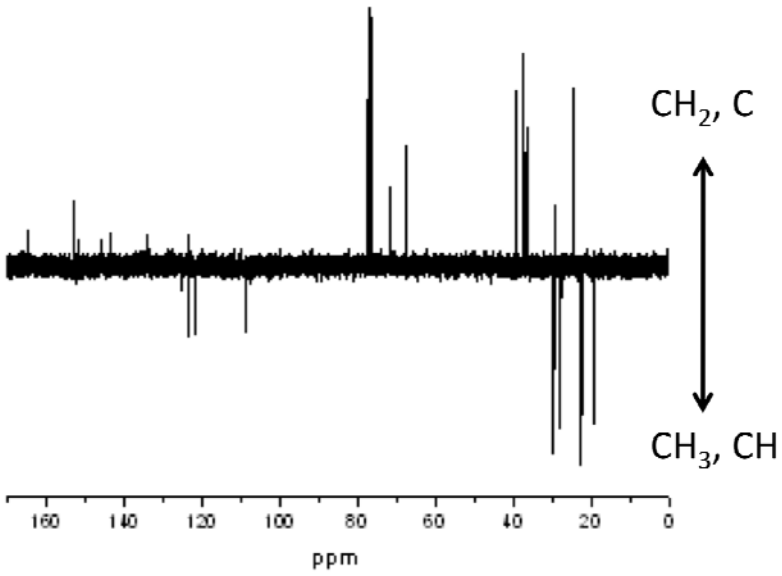
^{1}H NMR and ^{13}C NMR spectra of compound TB6*





^{1}H NMR and ^{13}C NMR spectra of compound TB9*





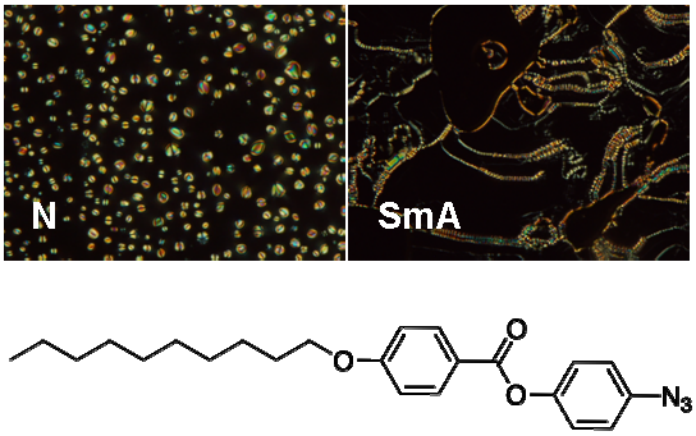


Figure S1. Microphotograph of the textures observed by POM on cooling compound **A1**, nematic at 69 ºC (left), smectic A at 43 ºC (right). Temperatures (ºC) (enthalpy values (kJ/mol)).

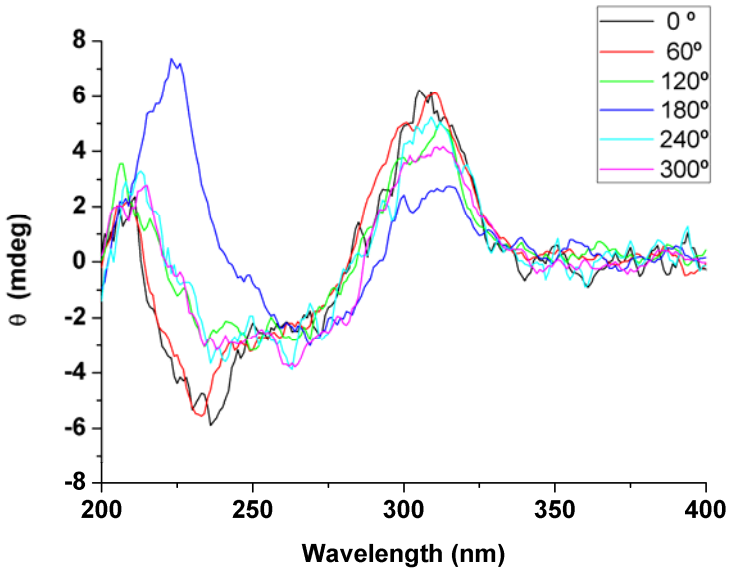


Figure S2. CD spectra of **TB6*** recorded at different angles of rotation of the sample.

Contact miscibility tests

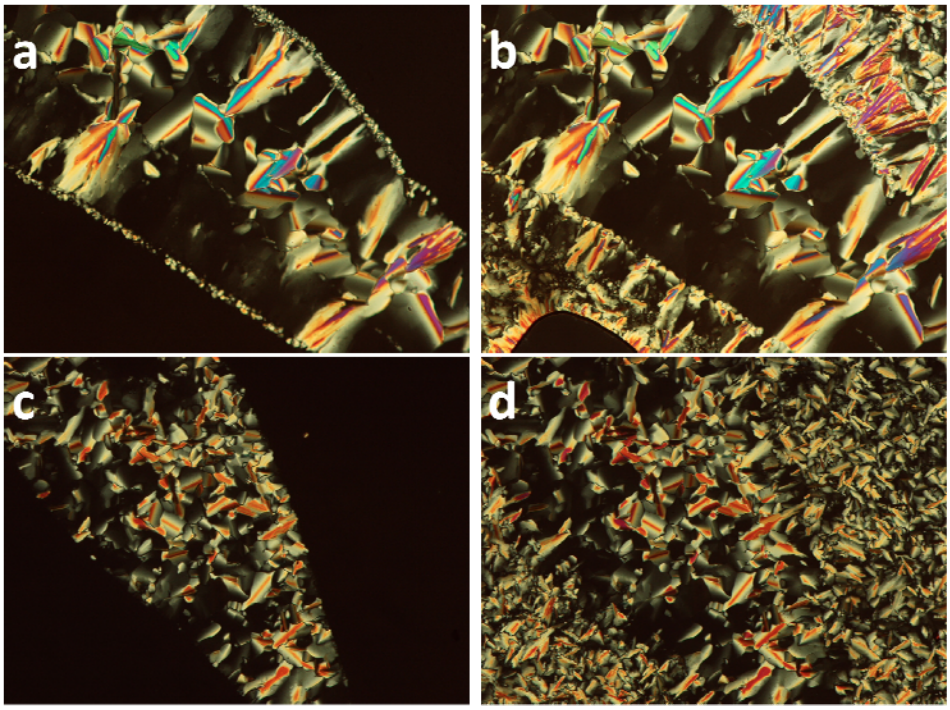


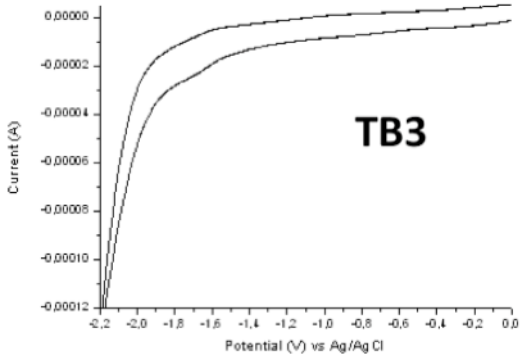
Figure S3. Polarized optical photomicrograph of a 50/50 mixture between **TB6/TB9** at (a) 186 ºC and (b) 120 ºC; and between **TB6*/TB9** at (c) 190 ºC and (d) 100 ºC.

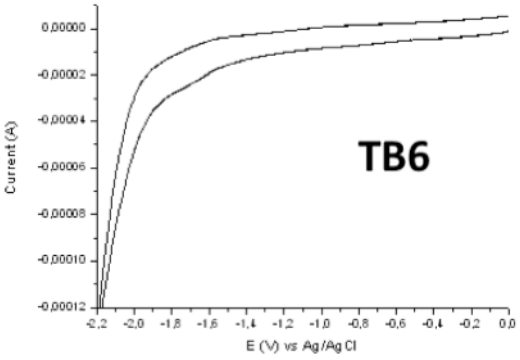
Table S1. TGA/DTA and XRD data.

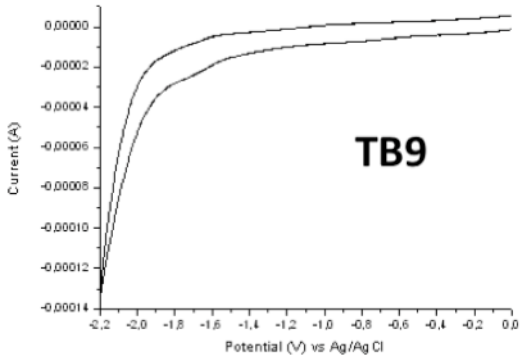
Compound	TGA 4% (ºC) [a]	DTGA (ºC) [b]	*M* (g mol^{-1})	T (ºC)	Phase	Lattice constants (Å)	***Z*** [c]
TB3	292	429	1339.6	-	-	-	-
TB6	229	399	1808.4	20	g(Col_h)	a = 42.6 c = 3.8[c]	2
				120	Col_h	a = 43.2 c = 3.7[c]	2
TB9	230	391	2277.2	20	g(Col_h)	a = 40.3 c = 5.3[c]	2
				130	Col_h	a = 41.6 c = 5.0[c]	2
TB3*	284	426	1339.6	-	-	-	-
TB6*	268	403	1808.4	20	g(Col_h)	a = 39.2 c = 4.5[c]	2
TB9*	282	407	2277.2	20	Col_h	a = 37.7 c = 6.2[c]	2

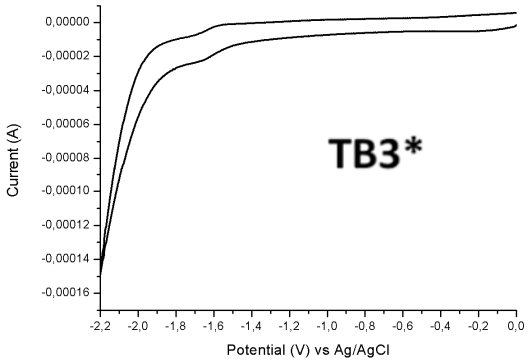
[a] Temperature corresponding to 4 % weight loss by thermogravimetric analysis. [b] Derivative of the thermogravimetric analysis indicating the temperature of the maximum weight loss. [c] Calculated with the assumption that the density of these compounds in the mesophase is 1 g cm^{-3}. The relationship 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). In the case of a hexagonal symmetry of the cell unit, the volume is calculated by the formula $V = (\sqrt{3}/2) \times a^2c \times 10^{-24}$ where a and c are the lattice constants in Å.

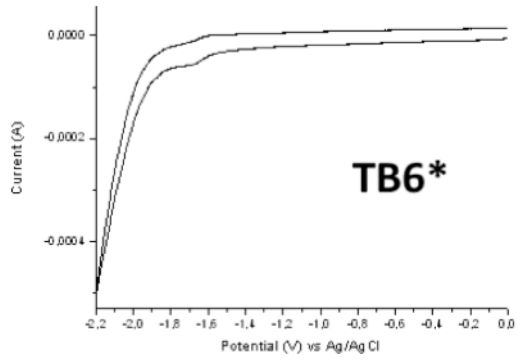
Cyclic voltammetry plots

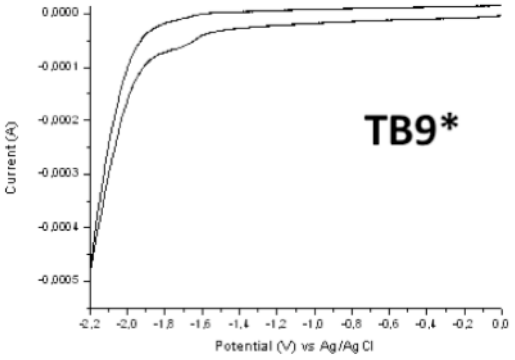












Emission spectra for series TB*

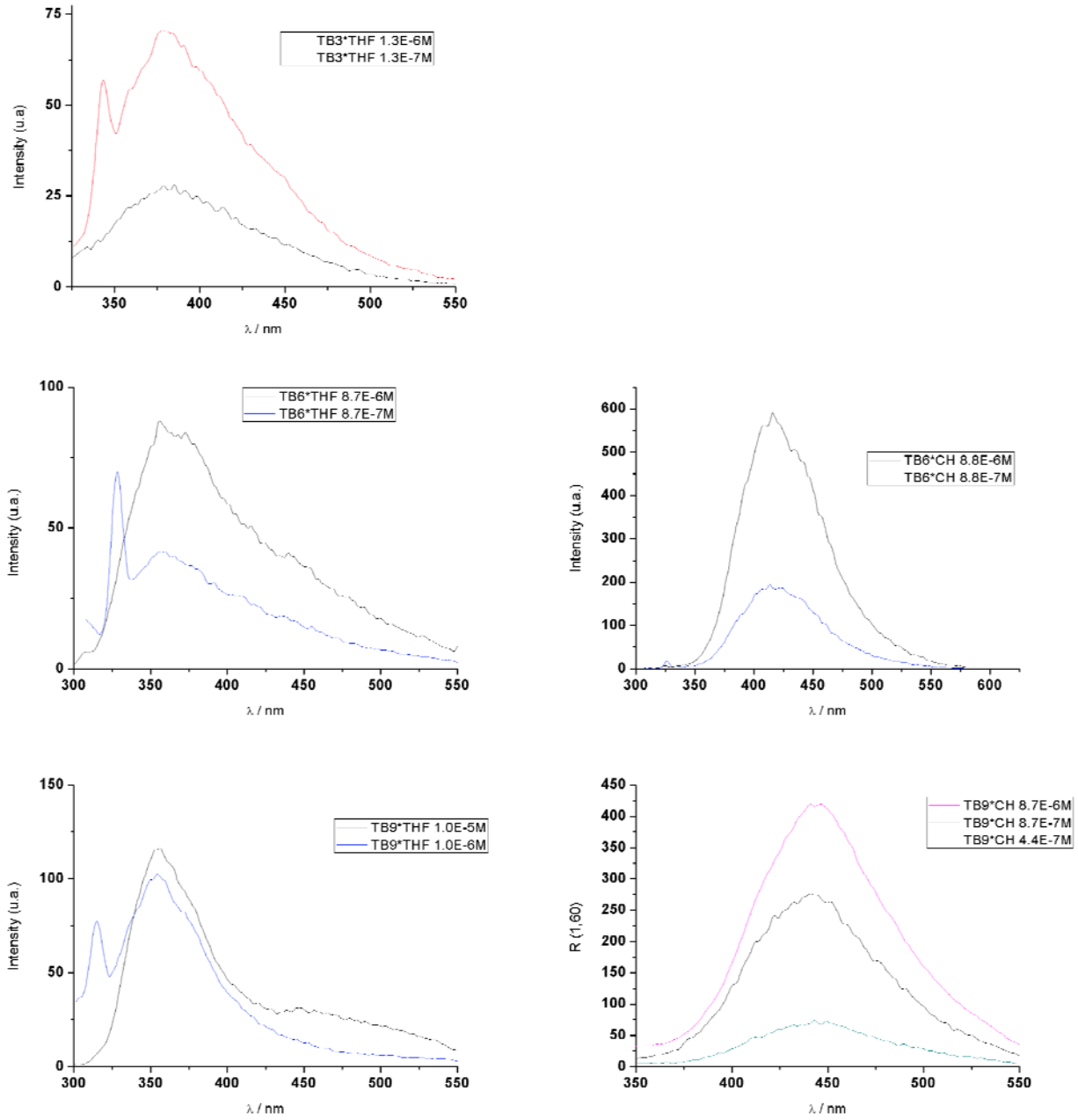


Figure S4. Emission spectra for series **TB*** in THF and cyclohexane (CH) at different molar concentrations.