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ELECTRONIC SUPPLEMENTARY INFORMATION (ESI) FOR:

Structural Characterization and Physical Properties of New Tetrabenzopentaphene Mesogens

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Materials and techniques

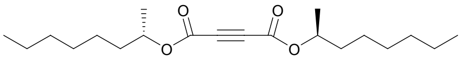
Commercial reagents and dry solvents were purchased from ABCR GmbH, Aldrich Chemical Co., or Strem Chemicals Inc., and were used without further purification. *n*-BuLi was used in solution in hexane (2.40 M). TLC was performed on Merck silica gel 60 F_{254}; chromatograms were visualized with UV light (254 and 360 nm). Flash column chromatography was performed on Merck silica gel 60 (ASTM 230-400 mesh). ^1H and ^{13}C NMR spectra were recorded at 250.13 and 62.83 MHz (Bruker DPX-250 instrument) or 300 and 75 MHz (Varian Mercury-300 instrument), respectively. High- or low-temperature NMR spectra were recorded on either a Bruker AMX-500 or a Varian Inova-750 instrument. Low-resolution electron impact mass spectra (EI-LRMS) were determined at 70 eV on a HP-5988A instrument. High-resolution mass spectra (HRMS) and FAB (positive FAB in 3-nitrobenzyl alcohol) were obtained on a Micromass Autospec spectrometer. MALDI-TOF spectra were determined on a Bruker Autoflex instrument. IR spectra were recorded on a Mattson Cygnus 100 spectrophotometer. Melting points were measured on a Gallenkamp instrument.

Mesophase analysis was performed using an Olympus BH-2 polarizing microscope equipped with a Linkam THMS600 hot-stage and an Olympus DP12 digital camera. Transition temperatures and enthalpies were obtained by differential scanning calorimetry using a DSC-MDSC 2910 and a Q-1000 from TA Instruments, at heating and cooling rates of 10 ºC min^{-1}. The apparatus were previously calibrated with indium (156.6 ºC, 28.44 J g^{-1}). Powder X-ray diffraction patterns were obtained using a pinhole camera (Anton Paar) operating with a point focused Ni-filtered Cu-Kα radiation. 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. Exposure times from 2 to 12 hours were applied depending on the sample and the experiment.

Single crystals of **1** suitable for X-ray diffraction were grown by slow evaporation of a THF/MeOH solution. Measurements were made on a KappaCCD2000 diffractometer. Structure was solved using SHELXL-97. Cambridge Crystallogaphic Data Centre (CCDC) 656872 record contains the supplementary crystallographic data for this paper; these data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif. *Optical absorption spectra* were recorded with a UV4-200 UV-Vis spectrophotometer from ATI-Unicam.

Photoconductivity measurements: Cells were made by overlapping two ITO covered glass slides without any alignment agent, controlling the thickness with 5 µm glass spacers. The real thickness, measured by considering interference fringes around 1000 nm[13] was 5.1 µm. Cells were filled by capillarity in the isotropic phase at 270 °C and then cooled to room temperature in the crystalline phase. Photoconductivity was measured by applying a DC electric field and then measuring the current flowing through the cell, with and without light exposure, with a Keithley 6517A electrometer. Since photogeneration depends on the light power density I, results are presented in terms of the σ_{ph}/I ratio. A 300 W Xenon-lamp (LOT Oriel) was used as a light source and the desired wavelength was selected by a motorized monochromator (Oriel Instruments, Cornerstone^{TM} 260 1\4 M, model 74100). The actual power of the radiation incident on the sample $I \sim 3$ mW cm^{-2} was measured by using a power meter (UV Silicon Probe 70282 LOT Oriel).

- *Synthetic details and spectroscopic data for alkyne* ***4***.



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A mixture of (*S*)-2-octanol (1.39 mL, 8.76 mmol), acetylenedicarboxylic acid (250 mg, 2.19 mmol) and concentrated H_2SO_4 (20 µL) in THF (2 mL) was refluxed for 14 hours. Then H_2O (10 mL) and Et_2O (10 mL) were added, the phases were separated and the aqueous layer was extracted with Et_2O (5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2; 5:95 Et_2O/hexane), affording **4** (718 mg, 97%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) : δ = 5.08-4.96 (m, 2H), 1.71-1.45 (m, 4H), 1.30-1.22 (m, 16H), 1.26 (d, *J* = 6.2 Hz, 6H), 0.86 (t, *J* = 6.0 Hz, 6H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 151.6 (2C), 76.5 (2C), 74.7 (2CH), 35.7 ($2CH_2$), 31.6 ($2CH_2$), 29.0 ($2CH_2$), 25.2 ($2CH_2$), 22.5 ($2CH_2$), 19.7 ($2CH_3$), 14.0 ($2CH_3$) ppm. LRMS (CI^+): *m/z* (%): 339 (100) [M^+ + 1]. HRMS (CI^+) for $C_{20}H_{35}0_4$, calculated: 339.2535, found: 339.2531. IR (CsI): 2957, 2932, 2860, 1721 cm^{-1}. $[\alpha]_D$ = +31.9º (c = 11.7, $CHCl_3$).

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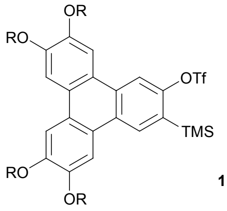
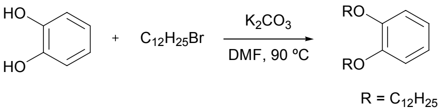
- *Synthetic details and spectroscopic data for aryne precursor **1b**.*



1b, R = $C_{12}H_{25}$

1,2-Bis(dodecyloxy)benzene.[1]



A mixture of catechol (5.00 g, 45.4 mmol), 1-bromododecane (40 mL, 167 mmol) and K_2CO_3 (74 g, 536 mol) in DMF (100 mL) was heated at 90 ºC for 14 hours. After this time, the mixture was filtered over a small plug of Al_2O_3 and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (200 mL) and washed with H_2O (3 x 150 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2; 1:2 CH_2Cl_2/hexane), affording 1,2-bis(dodecyloxy)benzene (17.2 g, 85%) as a white solid. M.p. = 45-48 ºC (lit. m.p.[1] = 47-48 ºC). ^1H NMR (250 MHz, $CDCl_3$): δ = 6.88 (s, 4H), 3.99 (t, *J* = 6.6 Hz, 4H), 1.84-1.60 (m, 4H), 1.56-1.26 (m, 36H), 0.88 (t, *J* = 6.6 Hz, 6H) ppm. LRMS (EI^+): *m/z* (%): 446 (100) [M^+].

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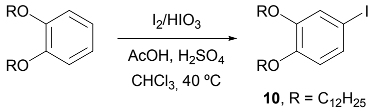
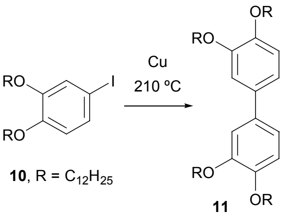
[1] Tahara, K.; Furukawa, S.; Uji-i, H.; Uchino, T.; Ichikawa, T.; Zhang, J.; Mamdouh, W.; Sonoda, M.; De Schryver, F. C.; De Feyter, S.; Tobe, Y. *J. Am. Chem. Soc.*, **2006**, *128*, 16613.

1,2-Bis(dodecyloxy)-4-iodobenzene (**10**).[2]



A mixture of 1,2-bis(dodecyloxy)benzene (7.98 g, 17.9 mmol), I_2 (1.69 g, 6.64 mmol), glacial acetic acid (21 mL), H_2O (7.0 mL), concentrated H_2SO_4 (0.30 mL) and HIO_3 (789 mg, 4.48 mmol) in $CHCl_3$ (20 mL) was heated at 40 ºC for 14 hours. Then 10% aqueous Na_2SO_3 solution (20 mL) and $CHCl_3$ (30 mL) were added and the mixture was stirred for 0.5 hours. The phases were separated and the aqueous layer was extracted with $CHCl_3$ (30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2; 1:3 CH_2Cl_2/hexane), affording 1,2-bis(dodecyloxy)-4-iodobenzene (**10**, 9.54 g, 93%) as a white solid. M.p. = 58-60 ºC. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.17 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.12 (d, *J* = 1.8 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 1H), 3.94 (t, *J* = 6.6 Hz, 4H), 1.83-1.71 (m, 4H), 1.55-1.26 (m, 36H), 0.88 (t, *J* = 6.4 Hz, 6H) ppm. LRMS (EI$^+$): *m/z* (%): 572 (18) [M$^+$]. HRMS (EI$^+$) for $C_{30}H_{53}O_2I$, calculated: 572.3090, found: 572.3088.

3,3',4,4'-Tetrakis(dodecyloxy)biphenyl (**11**).



A mixture of 1,2-bis(dodecyloxy)-4-iodobenzene (**10**, 858 mg, 1.50 mmol) and Cu (powder, 979 mg, 15.4 mmol) was heated at 210 ºC for 14 hours. After this time, $CHCl_3$ (20 mL) was added, and the mixture was filtered over a small plug of SiO_2 and concentrated under reduced pressure. The residue

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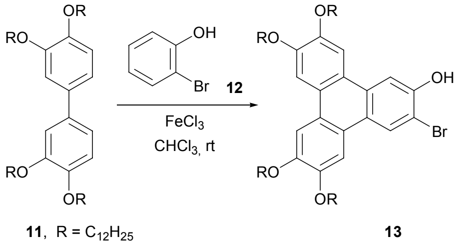
[2] (a) Foster, E. J.; Babuin, J.; Nguyen, N.; Williams, V. E. *Chem. Commun.*, **2004**, *18*, 2052.
(b) Kikkawa, Y.; Koyama, E.; Tsuzuki, S.; Fujiwara, K.; Miyake, K.; Tokuhisa, H.; Kanesato, M. *Langmuir*, **2006**, *22*, 6910.

was purified by column chromatography (SiO_2; 1:3 $CHCl_3$/hexane), affording 3,3',4,4'-tetrakis(dodecyloxy)biphenyl (**11**, 636 mg, 95%) as a white solid. M.p. = 90-92 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.07 (s, 2H), 7.05 (dd, J = 7.5, 1.7 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 4.05 (t, J = 6.7 Hz, 4H), 4.02 (t, J = 6.7 Hz, 4H), 1.89-1.77 (m, 8H), 1.63-1.15 (m, 72H), 0.88 (t, J = 6.6 Hz, 12H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 149.3 (2C), 148.5 (2C), 134.4 (2C), 119.3 (2CH), 114.2 (2CH), 113.2 (2CH), 69.54 ($2CH_2$), 69.46 ($2CH_2$), 31.9 ($4CH_2$), 29.7 ($12CH_2$), 29.5 ($8CH_2$), 29.4 ($8CH_2$), 26.1 ($4CH_2$), 22.7 ($4CH_2$), 14.1 ($4CH_3$) ppm. LRMS (CI$^+$): m/z (%): 892 (14) [M$^+$+1]. HRMS (CI$^+$) for $C_{60}H_{107}O_4$, calculated: 891.8169, found: 891.8154.

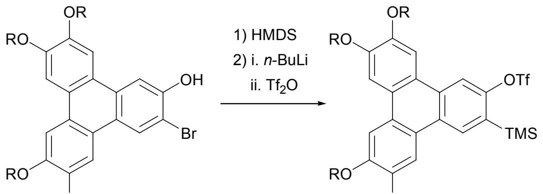
3-Bromo-6,7,10,11-tetrakis(dodecyloxy)-2-triphenylenol (**13**).



A mixture of 3,3',4,4'-tetrakis(dodecyloxy)biphenyl (**11**, 300 mg, 0.34 mmol), 2-bromophenol (**12**, 0.47 mL, 4.04 mmol) and $FeCl_3$ (1.02 g, 6.34 mmol) in $CHCl_3$ (20 mL) was stirred at room temperature for 30 minutes. Then MeOH (80 mL) was added and the mixture was stirred for 14 hours. After this time, the resulting suspension was concentrated under reduced pressure and $CHCl_3$ (20 mL) was added. The mixture was filtered over a small plug of SiO_2 and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2; 1:2 $CHCl_3$/hexane), affording 3-bromo-6,7,10,11-tetrakis(dodecyloxy)-2-triphenylenol (**13**, 282 mg, 79%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.49 (s, 1H), 8.00 (s, 1H), 7.80 (s, 1H), 7.76 (s, 2H), 7.75 (s, 1H), 5.69 (s, 1H), 4.28-4.13 (m, 8H), 2.01-1.85 (m, 8H), 1.58-1.18 (m, 72H), 0.88 (t, J = 6.6 Hz, 12H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 150.1 (C), 149.8 (C), 149.24 (C), 149.18 (C), 149.0 (C), 130.3 (C), 126.5 (CH), 124.5 (C), 124.4 (C), 123.3 (C), 122.5 (2C), 110.1 (C), 108.5 (CH), 107.2 (CH), 106.9 (CH), 106.7

(CH), 106.4 (CH), 69.7 (CH_2), 69.6 (CH_2), 69.4 (CH_2), 69.2 (CH_2), 31.9 ($4CH_2$), 29.73 ($8CH_2$), 29.68 ($12CH_2$), 29.5 ($4CH_2$), 29.4 ($4CH_2$), 26.2 ($4CH_2$), 22.7 ($4CH_2$), 14.1 ($4CH_3$) ppm. LRMS (MALDI-TOF), *m/z* (%): 1060.8 [M^+ (^{81}Br), 100], 1058.8 [M^+ (^{79}Br), 81]. HRMS (FAB^+) for $C_{66}H_{107}O_5{}^{81}Br$, calculated: 1060.7214, found: 1060.7214; for $C_{66}H_{107}O_5{}^{79}Br$, calculated: 1058.7302, found: 1058.7265. UV/Vis ($CHCl_3$): λ_{max} (ε) = 350 (3670), 314 (26960), 279 (107600), 271 (sh, 89250), 262 (sh, 63000 mol^{-1} dm^3 cm^{-1}) nm.

2,3,6,7-Tetrakis(dodecyloxy)-10-(trimethylsilyl)triphenylen-11-yl trifluoromethanesulfonate (**1b**).



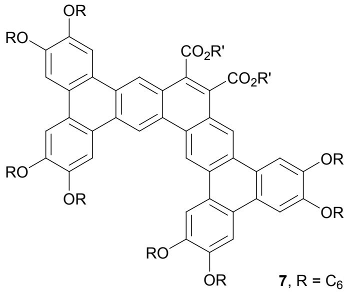
13, R = $C_{12}H_{25}$ **1b**

A solution of 3-bromo-6,7,10,11-tetrakis(dodecyloxy)-2-triphenylenol (**13**, 0.85 g, 0.80 mmol) and HMDS (340 µL, 1.6 mmol) in THF (5 mL) was refluxed for 1 h. The solvent was evaporated under reduced pressure, and the residue was subjected to vacuum to remove excess NH_3 and unreacted HMDS. ^{1}H NMR of the crude residue showed quantitative formation of the corresponding silyl ether. This crude product was dissolved in THF (16 mL), TMEDA was added (0.24 mL, 1.6 mmol) and the solution was cooled to -100°C (external temperature). *n*-BuLi (570 µL, 4.2 M, 2.4 mmol) was added dropwise and the reaction mixture was stirred for 1 h while the temperature reached -60°C. The mixture was again cooled to -100°C, Tf_2O (570 µL, 3.2 mmol) was added dropwise and stirring was kept up for 90 min while the temperature reached to -50°C. Then, saturated aqueous $NaHCO_3$ (20 mL) and Et_2O (10 mL) was added, the phases were separated, and the aqueous layer was extracted with Et_2O (2 x 20 mL) and CH_2Cl_2 (2 x 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2; 3:2 CH_2Cl_2/hexane), affording **1b** (421 mg, 44%) as a yellowish solid. M.p. =

48-50 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.60 (s, 1H), 8.36 (s, 1H), 7.98 (s, 1H), 7.83 (s, 1H), 7.82 (s, 2H), 4.30-4.20 (m, 8H), 2.03-1.90 (m, 8H), 1.77-1.13 (m, 72H), 0.89 (t, *J* = 6.6 Hz, 12H), 0.52 (s, 9H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 153.5 (C), 150.4 (C), 150.1 (C), 149.22 (C), 149.18 (C), 131.4 (CH), 131.2 (C), 129.3 (C), 127.4 (C), 125.0 (C), 124.5 (C), 122.6 (C), 122.4 (C), 118.9 (c, *J* = 320 Hz, CF_3), 113.0 (CH), 107.2 (CH), 106.9 (CH), 106.8 (2CH), 69.60 (CH_2), 69.57 ($2CH_2$), 69.3 (CH_2), 31.9 ($4CH_2$), 29.7 ($14CH_2$), 29.5 ($6CH_2$), 29.4 ($6CH_2$), 29.3 ($2CH_2$), 26.2 ($4CH_2$), 22.7 ($4CH_2$), 14.1 ($4CH_3$), -0.6 ($3CH_3$, TMS) ppm. LRMS (FAB^+), *m/z* (%): 1185 (M^+, 100). HRMS (FAB^+) for $C_{70}H_{115}O_7F_3SiS$, calculated: 1184.8085, found: 1184.8137. UV/Vis ($CHCl_3$): λ_{max} (ε) = 369 (1960), 348 (3440), 280 (109600), 274 (sh, 94900 mol^{-1} dm^3 cm^{-1}) nm.

*Synthetic details and spectroscopic data for tetrabenzopentaphenes 7, **8**, **9** and **14**.*

Bis(tert-butyl) 2,3,6,7,14,15,18,19-octakis(hexyloxy)tetrabenzo[*a,c,m,o*]pentaphene-10,11-dicarboxylate (**7**).



7, R = C_6H_{13}, R' = ^tBu

Finely powdered anhydrous CsF (32 mg, 0.21 mmol) was added to a solution of 2,3,6,7-tetrakis(hexyloxy)-10-(trimethylsilyl)triphenylen-11-yl trifluoromethanesulfonate[3] (**1a**, 60 mg, 0.071 mmol), bis(tert-butyl) acetylenedicarboxylate (**3**, 35 mg, 0.16 mmol) and $Pd(PPh_3)_4$ (8.2 mg, 7 μmol) in 10.5:1 CH_3CN/THF (4.4 mL). After stirring 14 h at room temperature under Ar atmosphere, the solvent was evaporate and the residue was purified by column chromatography (SiO_2; CH_2Cl_2/hexane, from 1:1 to 3:1; then CH_2Cl_2/Et_2O/hexane, from 2:1:17 to 6:1:13), to yield the cyclotrimer 2,3,6,7,12,13,16,17,22,23,26,27-dodecakis(hexyloxy)hexabenzo[a,c,k,m,u,w]trinaphthylene[3] (7.3 mg, 16%) and bis(tert-butyl) 2,3,6,7,14,15,18,19-octakis(hexyloxy)tetrabenzo[a,c,m,o]pentaphene-10,11-dicarboxylate (**7**, 28.2 mg, 54%) as a yellow solid. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ = 9.67 (s, 2H), 8.66 (s, 2H), 8.55 (s, 2H), 7.85 (s, 2H), 7.69 (s, 2H), 7.54 (s, 2H), 4.66 (t, *J* = 5.7 Hz, 4H), 4.31 (t, *J* = 6.5 Hz, 4H), 4.22 (t, *J* = 6.7 Hz, 4H), 3.99 (t, *J* = 6.5 Hz, 4H), 2.13-1.90 (m, 16H), 1.76 (s, 18H), 1.69-1.57 (m, 16H), 1.53-1.37 (m, 32H), 1.02-0.94 (m, 24H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 167.5 (2C), 150.1 (2C), 149.2 (2C), 149.0 (2C), 148.8 (2C), 130.3 (2C), 128.5 (2C), 128.2 (2C), 127.6 (2C), 125.2 (2C), 124.8 (2C), 123.9 (2C), 123.5 (2C), 123.2 (2C), 120.7 (2CH), 116.2 (2CH), 108.5 (2CH), 106.78 (2CH), 106.75 (2CH), 105.9 (2CH), 82.1 (2C), 69.5 ($2CH_2$), 69.4 ($2CH_2$), 69.2 ($2CH_2$), 68.8 ($2CH_2$), 32.0 ($2CH_2$), 31.85 ($2CH_2$), 31.79 ($4CH_2$), 29.9 ($2CH_2$), 29.7 ($2CH_2$), 29.6 ($2CH_2$), 29.5

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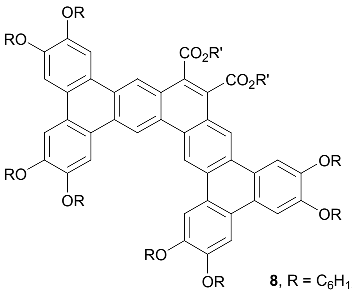
[3] Romero, C.; Peña, D.; Pérez, D.; Guitián, E. *Chem. Eur. J.* **2006**, *12*, 5677.

(2CH$_2$), 28.5 (6CH$_3$), 26.3 (2CH$_2$), 26.0 (2CH$_2$), 25.94 (2CH$_2$), 25.90 (2CH$_2$), 22.8 (2CH$_2$), 22.7 (6CH$_2$), 14.1 (8CH$_3$) ppm. LRMS (MALDI-TOF): *m/z* (%): 1479 (83) [M$^+$]. HRMS (MALDI-TOF) for $C_{96}H_{134}O_{12}$, calculated: 1478.9870; found: 1478.9923. IR (CsI): 2926, 2857, 1714 cm^{-1}. UV/Vis (CHCl$_3$): λ_{max} (ε) = 416 (13800), 380 (46400), 359 (63900), 346 (50180), 329 (43500), 298 (74300), 280 (58800), 257 (52700 mol^{-1} dm^3 cm^{-1}) nm.

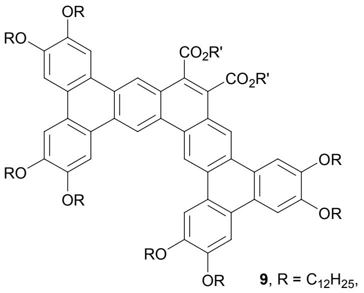
Bis[(1*S*)-1-methylheptyl] 2,3,6,7,14,15,18,19-octakis(hexyloxy)tetrabenzo[*a,c,m,o*] pentaphene-10,11-dicarboxylate (**8**).



8, R = C$_6$H$_{13}$, R' = (*S*)-2-Octyl

Finely powdered anhydrous CsF (27 mg, 0.18 mmol) was added to a solution of 2,3,6,7-tetrakis(hexyloxy)-10-(trimethylsilyl)triphenylen-11-yl trifluoromethanesulfonate (**1a**) (50 mg, 0.059 mmol), bis[(1*S*)-1-methylheptyl] acetylenedicarboxylate (**4**, 44 mg, 0.13 mmol) and Pd(PPh$_3$)$_4$ (6.8 mg, 5.9 µmol) in 10.5:1 CH$_3$CN/THF (3.7 mL). After stirring 14 h at room temperature under Ar atmosphere, the solvent was evaporate and the residue was purified by column chromatography (SiO$_2$; CH$_2$Cl$_2$/hexane, from 1:1 to 3:1; then CH$_2$Cl$_2$/Et$_2$O/hexane, from 2:1:17 to 6:1:13), to yield bis[(1*S*)-1-methylheptyl] 2,3,6,7,14,15,18,19-octakis(hexyloxy)tetrabenzo[a,c,m,o]pentaphene-10,11-dicarboxylate (**8**, 34 mg, 72%) as a yellow solid. ^{1}H NMR (500 MHz, 303 K, CDCl$_3$): δ = 9.91 (s, 2H), 9.12 (s, 2H), 8.41 (s, 2H), 8.03 (s, 2H), 7.88 (s, 2H), 7.85 (s, 2H), 5.46-5.40 (m, 2H), 4.44 (t, *J* = 6.1 Hz, 4H), 4.30 (t, *J* = 6.5 Hz, 4H), 4.26 (t, *J* = 6.6 Hz, 4H), 4.24-4.18 (t, *J* = 6.6 Hz, 4H), 2.05-1.93 (m, 18H), 1.79-1.55 (m, 24H), 1.49-1.35 (m, 40H), 1.30-1.18 (m, 8H), 1.00-0.90 (m, 24H), 0.84-0.80 (m, 6H) ppm. ^{13}C-NMR (75 MHz, CDCl$_3$) δ = 168.1 (2C), 150.4 (2C), 149.9 (2C), 149.4 (2C), 149.1 (2C), 130.1 (2C), 129.0 (2C), 128.6 (2C), 128.5 (2C), 125.4 (2C), 125.2 (2C), 124.5 (2C), 123.5 (2C), 123.3 (2C), 121.1 (2CH), 116.5 (2CH), 108.2 (2CH), 107.4 (2CH), 107.3 (2CH), 107.2 (2CH), 73.4 (2CH), 69.8 (2CH$_2$), 69.64 (2CH$_2$), 69.56 (2CH$_2$), 69.4 (2CH$_2$), 36.1 (2CH$_2$), 31.84 (2CH$_2$), 31.75 (2CH$_2$), 31.7 (6CH$_2$), 29.8 (2CH$_2$), 29.5 (2CH$_2$), 29.44 (2CH$_2$), 29.42 (2CH$_2$), 29.3 (2CH$_2$), 26.1 (2CH$_2$), 25.9 (4CH$_2$), 25.8 (2CH$_2$), 25.6 (2CH$_2$), 22.7 (8CH$_2$), 22.6 (2CH$_2$), 20.2 (2CH$_3$), 14.1 (8CH$_3$), 14.0 (2CH$_3$) ppm. LRMS (MALDI-TOF): *m/z* (%): 1591 (100) [M$^+$]. HRMS (MALDI-TOF) for $C_{104}H_{150}O_{12}$, calculated: 1591.1122; found: 1591.1093. IR (CsI): 2953, 2928, 2858, 1716 cm^{-1}. UV/Vis (CHCl$_3$): λ_{max} (ε) = 410 (9540), 380 (29144), 360 (40021), 349 (31820), 330 (25370), 297 (53679), 291 (sh, 52075), 276 (45870), 260 (41300 mol^{-1} dm^3 cm^{-1}) nm.

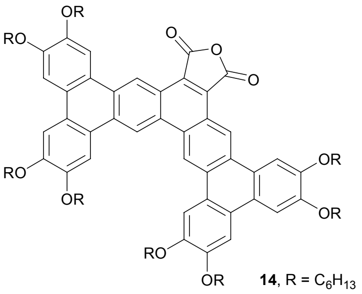
Dimethyl 2,3,6,7,14,15,18,19-octakis(dodecyloxy)tetrabenzo[*a,c,m,o*]pentaphene-10,11-dicarboxylate (**9**).



9, R = $C_{12}H_{25}$, R' = Me

Finely powdered anhydrous CsF (46 mg, 0.31 mmol) was added to a solution of 2,3,6,7-tetrakis(dodecyloxy)-10-(trimethylsilyl)triphenylen-11-yl trifluoromethanesulfonate (**1b**, 60 mg, 0.051 mmol), dimethyl acetylenedicarboxylate (**2**, 14 μL, 0.11 mmol) and Pd(PPh$_3$)$_4$ (6.0 mg, 5.2 μmol) in 1:1 CH$_3$CN/THF (10.2 mL). After stirring 14 h at room temperature under Ar atmosphere, the solvent was evaporate and the residue was purified by column chromatography (SiO$_2$; CH$_2$Cl$_2$/hexane, from 1:1 to 3:1; then CH$_2$Cl$_2$/Et$_2$O/hexane, from 3:1:16 to 4:2:4), to yield dimethyl 2,3,6,7,14,15,18,19-octakis(dodecyloxy)tetrabenzo[*a,c,m,o*]pentaphene-10,11-dicarboxylate (**9**, 30 mg, 57%) as a yellow solid. ^{1}H NMR (400 MHz, 298 K, CDCl$_3$): δ = 9.57 (s, 2H), 8.86 (s, 2H), 8.38 (s, 2H), 7.75 (s, 2H), 7.70 (s, 2H), 7.64 (s, 2H), 4.51 (t, *J* = 5.6 Hz, 4H), 4.26 (t, *J* = 6.2 Hz, 4H), 4.18 (t, *J* = 6.2 Hz, 4H), 4.10 (t, *J* = 5.6 Hz, 4H), 4.06 (s, 6H), 2.09-1.91 (m, 16H), 1.78-1.19 (m, 144H), 1.02-0.82 (m, 24H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 168.7 (2C), 150.3 (2C), 149.6 (2C), 148.9 (4C), 129.7 (2C), 128.8 (2C), 128.3 (2C), 127.9 (2C), 125.2 (2C), 124.7 (2C), 124.0 (2C), 123.23 (2C), 123.19 (2C), 121.0 (2CH), 116.1 (2CH), 108.4 (2CH), 106.9 (2CH), 106.8 (4CH), 69.6 ($2CH_2$), 69.5 ($2CH_2$), 69.3 ($2CH_2$), 68.8 ($2CH_2$), 52.4 ($2CH_3$), 32.0 ($8CH_2$), 29.8 ($24CH_2$), 29.75 ($16CH_2$), 29.70 ($8CH_2$), 29.4 ($8CH_2$), 26.7 ($2CH_2$), 26.4 ($2CH_2$), 26.3 ($4CH_2$), 22.7 ($8CH_2$), 14.1 ($8CH_3$) ppm. LRMS (MALDI-TOF): *m/z* (%): 2068 (M^+, 100). HRMS (MALDI-TOF) for $C_{138}H_{218}O_{12}$, calculated: 2067.6443; found: 2067.6345. IR (CsI): 2956, 2925, 2854, 1711 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 420 (17600), 380 (58000), 362 (75150), 330 (sh, 47190), 300 (96650), 280 (sh, 74800), 263 (69052 mol^{-1} dm^3 cm^{-1}) nm.

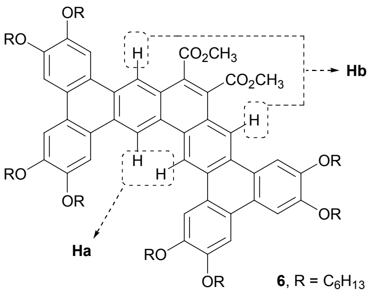
2,3,6,7,14,15,18,19-Octakis(hexyloxy)tetrabenzo[*a,c,m,o*]pentaphene-10,11-dicarboxylic anhydride (**14**).



14, R = C_6H_{13}

A solution of KOH (240 mg, 4.30 mmol) in EtOH (2.4 mL) was added to a suspension of dimethyl 2,3,6,7,14,15,18,19-octakis(hexyloxy)tetrabenzo[*a,c,m,o*]pentaphene-10,11-dicarboxylate (**6**, 103 mg, 0.073 mmol) in EtOH/dioxane (1:1, 18 mL) and the mixture was heated to 110 ºC for 140 min under Ar atmosphere. Then, at room temperature, Et_2O (10 mL) and 10% aqueous solution of HCl (15 mL) were added, turning the colour of the organic phase to red. The phases were separated, the aqueous phase was extracted with $CHCl_3$ (3 x 10 mL) and the combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The red residue was purified by filtration over a small plug of SiO_2 ($CHCl_3$) to yield **14** (99 mg, 99 %) as a red solid. ^1H NMR (400 MHz, 313 K, $CDCl_3$): δ = 8.87 (s, 2H), 8.35 (s, 2H), 7.47 (s, 2H), 7.36 (s, 2H), 7.02 (s, 2H), 6.87 (s, 2H), 4.23 (t, *J* = 5.5 Hz, 4H), 3.85 (t, *J* = 5.8 Hz, 4H), 3.84 (t, *J* = 5.6 Hz, 4H), 3.62 (t, *J* = 6.2 Hz, 4H), 2.05-1.96 (m, 4H), 1.87-1.68 (m, 12H), 1.56-1.33 (m, 48H), 1.03 (t, *J* = 6.9 Hz, 6H), 1.00-0.91 (m, 18H) ppm. ^{13}C-NMR (100 MHz, 313 K, $CDCl_3$): 163.8 (2C), 150.6 (2C), 149.6 (2C), 148.9 (2C), 148.8 (2C), 129.44 (2C), 129.35 (2C), 127.9 (2C), 127.3 (2C), 125.0 (2C), 123.5 (2C), 122.3 (2C), 122.2 (2C), 121.2 (2C), 119.2 (2CH), 115.2 (2CH), 107.2 (2CH), 106.17 (2CH), 106.16 (2CH), 105.5 (2CH), 68.9 ($2CH_2$), 68.8 ($2CH_2$), 68.4 ($2CH_2$), 68.7 ($2CH_2$), 32.3 ($2CH_2$), 31.95 ($2CH_2$), 31.93 ($2CH_2$), 31.84 ($2CH_2$), 30.3 ($2CH_2$), 29.6 ($4CH_2$), 29.4 ($2CH_2$), 26.4 ($2CH_2$), 26.0 ($2CH_2$), 25.88 ($2CH_2$), 25.86 ($2CH_2$), 22.9 ($2CH_2$), 22.74 ($2CH_2$), 22.69 ($4CH_2$), 14.2 ($2CH_3$), 14.1 ($4CH_3$), 14.0 ($2CH_3$) ppm. LRMS (MALDI-TOF): *m/z* (%): 1349 (M^+, 100). HRMS (MALDI-TOF) for $C_{88}H_{116}O_{11}$, calculated: 1348.8512, found: 1348.8473. IR (KBr): 2955, 2926, 2855, 1828 (weak), 1758, 1736 (weak) cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 496 (13700), 384 (41100), 294 (68900), 254 (45400 mol^{-1} dm^3 cm^{-1}) nm.

- *NMR study for compound **6**.*



See: Tobe, Y.; Utsumi, N.; Kawabata, K.; Nagano, A.; Adachi, K.; Araki, S.; Sonoda, M.; Hirose, K.; Naemura, K. *Journal of the American Chemical Society* **2002**, *124*, 5350-5364.

	263	***273***	***283***	***293***	***303***	***T (K)***
C (mM)						
15.0	9.390	9.450	9.5100	9.560	9.600	
7.51	9.530	9.580	9.6300	9.680	9.720	
3.76	9.650	9.690	9.7300	9.770	9.800	
1.88	9.750	9.790	9.8200	9.840	9.860	
0.939	9.830	9.850	9.8700	9.890	9.900	
0.470	9.880	9.890	9.9100	9.920	9.930	
0.235	9.910	9.920	9.9300	9.940	9.940	
0.117	9.930	9.940	9.9400	9.950	9.950	

Chemical shifts (ppm) for the most downfield signal (Ha) in the ^{1}H NMR spectrum of compound **6** in $CDCl_3$

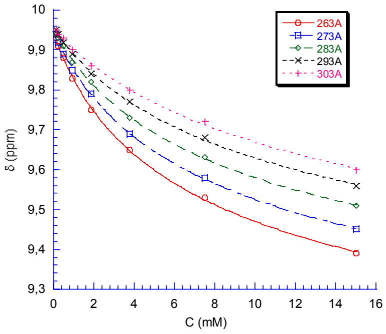
	263	***273***	***283***	***293***	***303***	***T (K)***
C (mM)						
15.0	8.680	8.730	8.780	8.840	8.900	
7.51	8.810	8.870	8.920	8.980	9.030	
3.76	8.950	8.990	9.040	9.080	9.120	
1.88	9.060	9.100	9.140	9.170	9.200	
0.939	9.150	9.180	9.200	9.230	9.250	
0.470	9.210	9.230	9.250	9.260	9.280	
0.235	9.250	9.260	9.270	9.280	9.290	
0.117	9.270	9.280	9.290	9.290	9.300	

Chemical shifts (ppm) for the second most downfield signal (Hb) in the ^{1}H NMR spectrum of compound **6** in $CDCl_3$.

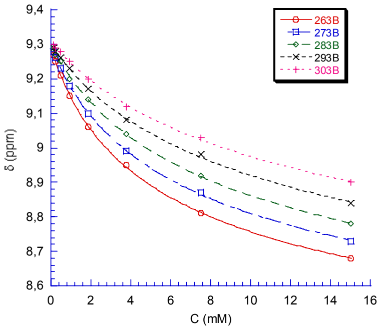
Infinite association model

$$\delta = \delta_m + (\delta_a - \delta_m)\left(1 + \frac{1 - \sqrt{4K_E C_t + 1}}{2K_E\, C_t}\right)$$

Assuming $K_2 = K_3 = K_4 = \ldots = K_n = K_E$



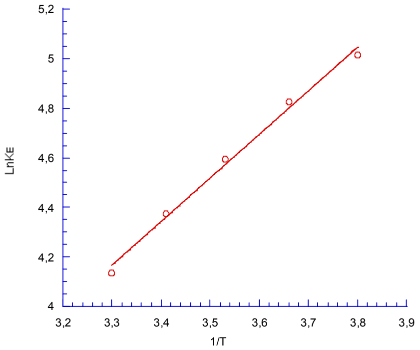
Chemical shift dependence for signal Ha



Chemical shift dependence for signal Hb

***T* (K)**	**303**	**293**	**283**	**273**	**263**
δm (Ha)	9.953 ± 0.004	9.955 ± 0.003	9.950 ± 0.002	9.947 ± 0.004	9.943 ± 0.003
δa (Ha)	8.010 ± 0.132	8.069 ± 0.078	7.982 ± 0.046	7.863 ± 0.068	7.747 ± 0.050
K_E (Ha)	58.4 ± 7.9	81.1 ± 7.5	97.0 ± 5.5	114.4 ± 9.5	133.1 ± 8.3
δm (Hb)	9.308 ± 0.003	9.299 ± 0.003	9.298 ± 0.003	9.294 ± 0.002	9.290 ± 0.003
δa (Hb)	7.182 ± 0.095	7.066 ± 0.084	7.022 ± 0.064	7.056 ± 0.036	7.024 ± 0.031
K_E (Hb)	66.5 ± 6.2	77.9 ± 6.4	101 ± 7	135 ± 6	168 ± 7
K_E (Av)	**62.4**	**79.5**	**99.0**	**125**	**150**

δm = Calculated chemical shifts for the aromatic protons of monomer
δa = Calculated chemical shifts for the aromatic protons of aggregates
K_E = Associations constants (M^{-1}) calculated independently for different aromatic protons (Ha and Hb)
K_E (Av) = Average association constants (M^{-1})



Van't Hoff plot

y = -1,6409 + 1,7598x R= 0,99635

ΔH_E = - 14.4 kJ mol^{-1}

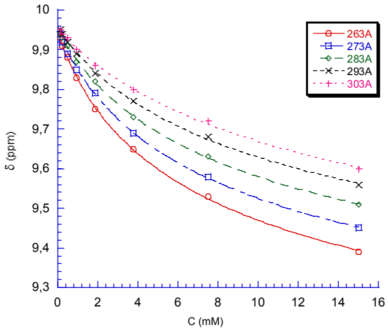
ΔS_E = - 13.0 J mol^{-1} K^{-1}

ΔG_E (298K) = - 10.5 kJ mol^{-1}

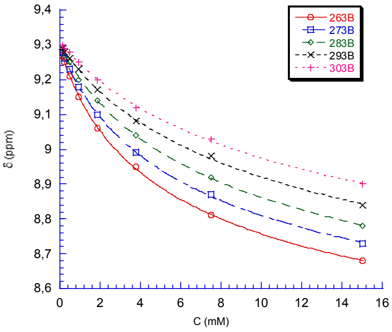
K_E (298K) = 71.5 M^{-1}

Monomer-dimer model

$$\delta = \delta_{\mathrm{m}} + (\delta_{\mathrm{d}} - \delta_{\mathrm{m}})\left(1 + \frac{1-\sqrt{8K_2C_{\mathrm{t}}+1}}{4K_2C_{\mathrm{t}}}\right)$$



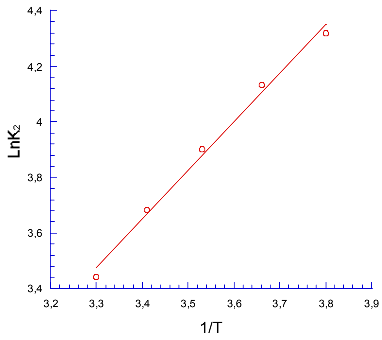
Chemical shift dependence for signal Ha



Chemical shift dependence for signal Hb

T **(K)**	**303**	**293**	**283**	**273**	**263**
δm (Ha)	9.953 ± 0.004	9.955 ± 0.003	9.951 ± 0.002	9.947 ± 0.004	9.943 ± 0.003
δd (Ha)	8.981 ± 0.0667	9.012 ± 0.040	8.966 ± 0.024	8.905 ± 0.035	8.845 ± 0.026
K_2 (Ha)	29.2 ± 4.0	40.5 ± 3.7	48.5 ± 2.7	57.2 ± 4.8	66.5 ± 4.1
δm (Hb)	9.308 ±0.003	9.299 ± 0.003	9.298 ± 0.003	9.294 ± 0.002	9.290 ± 0.003
δd (Hb)	8.245 ± 0.048	8.182 ± 0.043	8.160 ± 0.033	8.175 ± 0.018	8.157 ± 0.016
K_2 (Hb)	33.3 ± 3.1	38.9 ± 3.2	50.5 ± 3.4	67.4 ± 2.9	83.9 ± 3.4
K_2 (Av)	**31.2**	**39.7**	**49.5**	**62.3**	**75.2**

δm = Calculated chemical shifts for the aromatic protons of monomer
δd = Calculated chemical shifts for the aromatic protons of dimers
K_2 = Dimerization constants (M^{-1}) calculated independently for different aromatic protons (Ha and Hb)
K_2 (Av) = Average dimerization constants (M^{-1})



Van't Hoff plot

——— y = -2,3341 + 1,7598x   R= 0,99635

ΔH_2 = - 14.6 kJ mol^{-1}

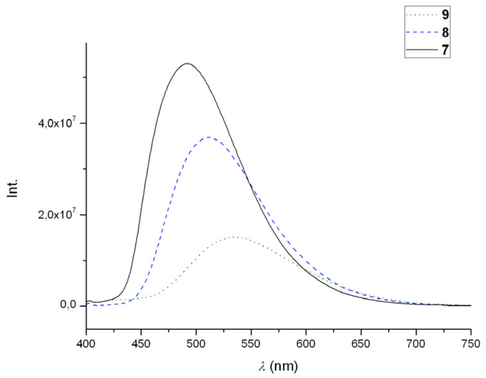
ΔS_2 = - 19.4 J mol^{-1} K^{-1}

ΔG_2 (298K) = - 8.8 kJ mol^{-1}

K_2 (298K)= 35.6 M^{-1}

- ***Gelation experiments.*** In a typical experiment 5-10 mg of compound **14** was weighted in a 2 mL vial with screw cap and 1 mL of the appropriate solvent was added. The vial was sealed tightly, heated until affording homogeneous and fluid solutions and allowed to cool to 5 ºC for 10 min. Gelation is considered to have occurred when a homogeneous solid material is obtained that does not flow when the capped vial is turned upside down at room temperature. The minimal gelation concentration can be obtained repeating this procedure by dilution of the sample with subsequent volumes of solvent.

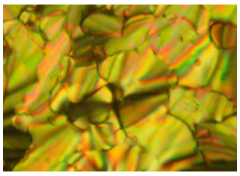
- Emission spectra of compounds **7 - 9** in solution (1 µM in THF, excitation at 360 nm).



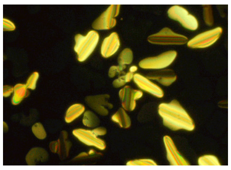
- POM, DSC, TGA and XRD of compounds **6-9** and **14**.

Compound 6

Microphotographs of the hexagonal columnar mesophase:

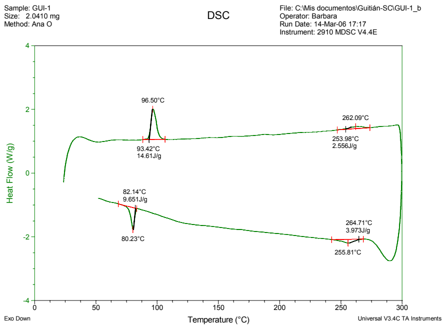


193ºC, heating process, x 200

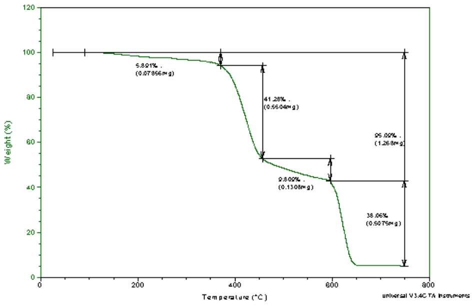


237ºC, cooling process, x 200

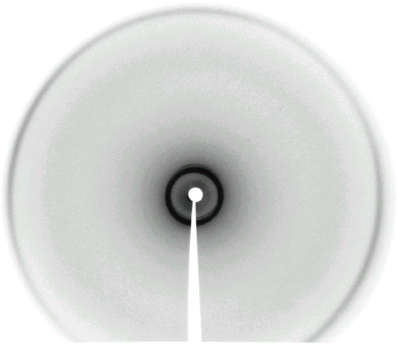
DSC:



TGA-DTA:



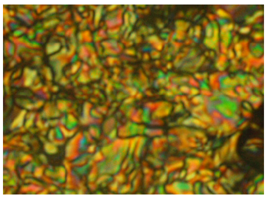
XRD pattern of compound **6** recorded at 115ºC (Col$_{ho}$):



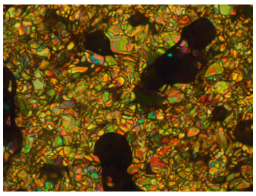
Compound 7

Microphotographs of the mesophase observed and of the decomposition process:

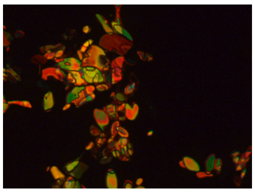
Heating process:



164ºC, x400

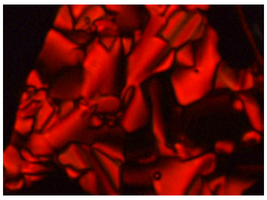


182ºC, x400



199ºC, x400

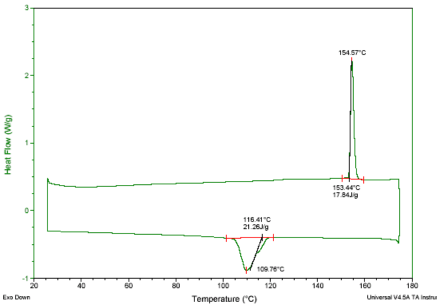
Decomposition to anhydride **14** occurs:



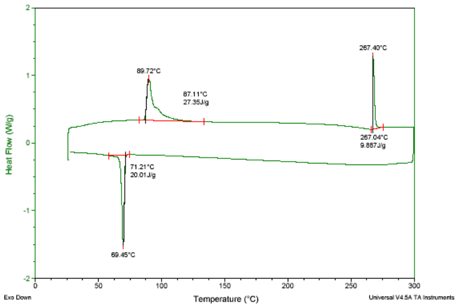
242ºC, x400

DSC:

1st heating scan:

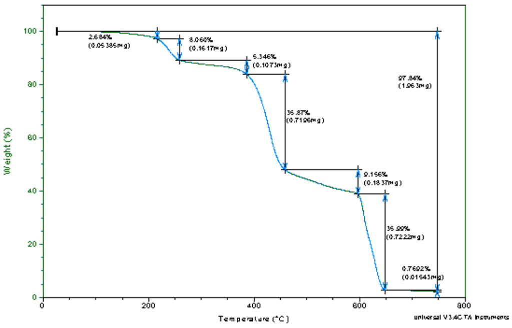


6th heating scan:

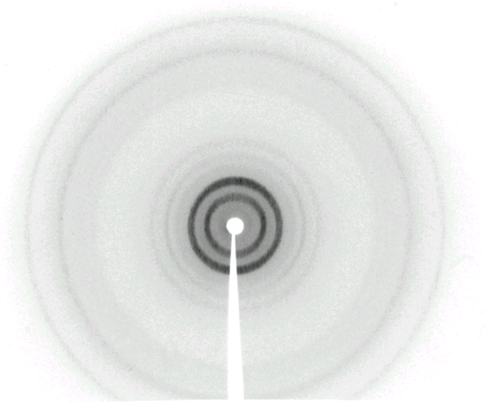


Conversion to anhydride is complete

TGA-DTA:

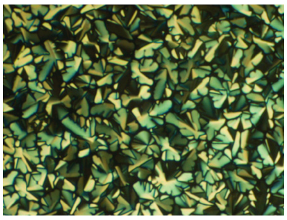


XRD pattern of compound **7** recorded at 160ºC:



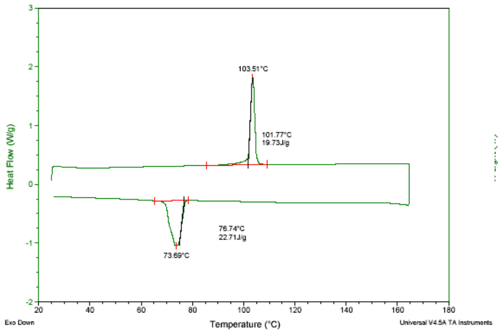
Compound **8**

Microphotograph of the rectangular columnar mesophase:

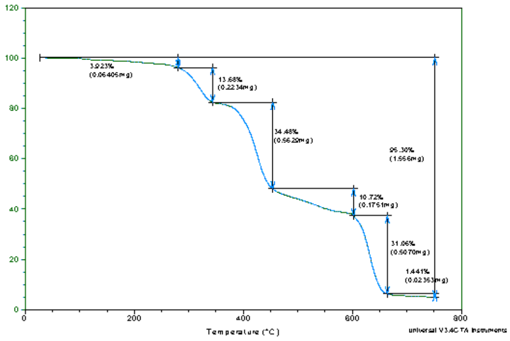


83ºC, cooling process, x200

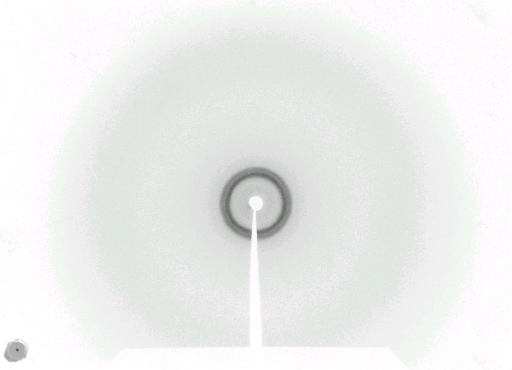
DSC:



TGA-DTA:

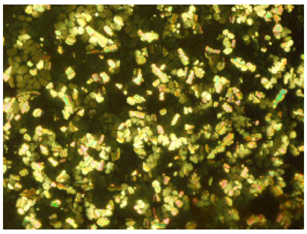


Small-angle region of the XRD pattern of compound **8** recorded at 110ºC (Col_r):

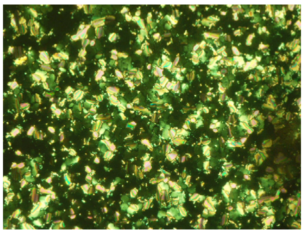


Compound **9**

Microphotographs of the hexagonal columnar mesophase:

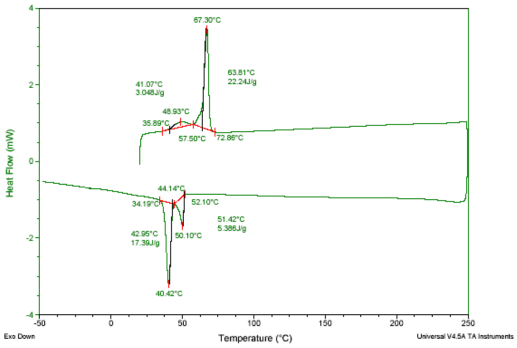


93ºC, cooling process, x200

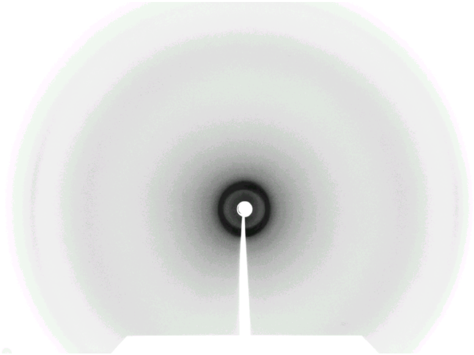


86ºC, heating process, x200

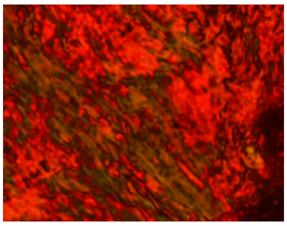
DSC:



XRD pattern of compound **9** recorded at 80ºC (Col$_{ho}$):



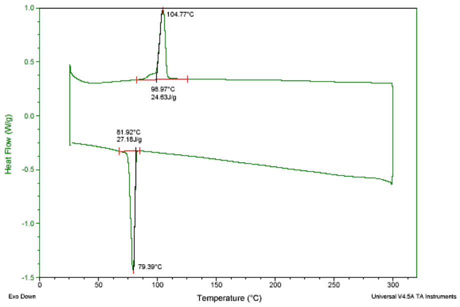
Compound **14**
Microphotograph of the hexagonal columnar mesophase:

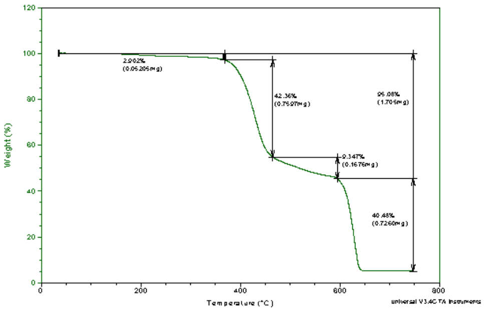


109ºC, heating process, x200

DSC:

TGA-DTA:





XRD pattern of compound **14** recorded at 120ºC (Col_{ho}):