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

# Triphenylamine- and triazine-containing hydrogen bonded complexes: liquid crystalline supramolecular semiconductors

Beatriz Feringán,[a] Roberto Termine,[b] Attilio Golemme,*[b] José M. Granadino-Roldán,[c] Amparo Navarro,*[c] Raquel Giménez,*[a] and Teresa Sierra,*[a]

## Supporting information

## Experimental details

All reagents were purchased from Aldrich and used without further purification. Anhydrous $CH_2Cl_2$ and THF were purchased from Scharlab and dried by using a solvent purification system.

$^1H$ NMR and $^{13}C$ NMR spectra were acquired on a Bruker AV400 spectrometer. The experiments were performed at room temperature in different deuterated solvents ($CDCl_3$ or $CD_2Cl_2$). Chemical shifts are given in ppm relative to TMS and the solvent residual peak was used as the internal standard.

Infrared spectra were recorded on a Bruker Vertex 70 FT-IR spectrometer. The samples were prepared on KBr pellets with a concentration of the product of 1-2% (w/w).

Mass spectra were obtained on a MICROFLEX Bruker (MALDI+) spectrometer with a dithranol matrix.

Elemental analyses were performed using a Perkin-Elmer 240C microanalyzer.

The mesophases were examined by polarizing optical microscopy using a polarizing optical microscope Olympus BX51 equipped with an Olympus DP12 digital camera and connected to a Linkam THMS600 hot stage and a Linkam TMS94 controller. Thermogravimetric analyses (TGA) were performed under a nitrogen atmosphere with a heating rate of 10°C $min^{-1}$ using a TA Instruments Q5000. Transition temperatures and enthalpies were obtained by differential scanning calorimetry with DSC TA instruments Q-20 and Q-2000 at heating and cooling rates of 10 $^oC$ $min^{-1}$. The apparatus were previously calibrated with indium (156.6 $^oC$, 28.44 J $g^{-1}$).

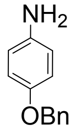
Powder X-ray experiments were performed in a Pinhole diffractometer (Anton Paar) operating with a point focused Ni-filtered Cu-Kα beam. The samples were held in Lindemann glass capillaries (0.7 and 0.9 mm diameter) and heated with a variable-temperature attachment. The diffraction patterns were collected on photographic films.

Cyclic voltamperometry measurements were carried out using an Autolab PGSTAT204 potentiostat with a three-electrode cell. As working electrode a glass-ceramic disc electrode was used and a platinum electrode was used as the auxiliary electrode. As reference electrode an Ag | AgCl electrode was used. In addition, ferrocene was used as an internal standard, so once the measures were taken, ferrocene was added to the solutions and the voltammograms to measure the potential of the redox pair ferrocene-ferrocenium (FOC), which was used as an internal reference. The cyclic voltammetry experiments in solution were carried out in solutions with approximate concentrations of studied compounds of $10^{-4}$ M and 0.1 M of TBAPF6 in dichloromethane. For cyclic voltammetric measurements in thin film, the films were prepared by drop-casting a solution of the complex in dichloromethane on the working electrode and the measurements were made in 0.1 M solution of TBAPF6 in acetonitrile. All the experiments were carried out in argon atmosphere.

Full geometry optimization of the complex was performed using the long-range corrected (LC) hybrid density ωB97XD functional[1] which accounts for dispersion interactions, together with the 6-31G** basis set implemented in the Gaussian 09 program package (version D.01).[2] The molecular geometry of the neutral, anionic and cationic states of the **T3C$_1$**, **TPA3C$_1$** and **T3C$_1$-2BnOC$_1$-TPA2C$_1$** complex were fully optimized in gas phase at the same level of theory. The long side chains were replaced with methoxy groups to reduce the computational cost. The individual **T3C$_1$** and **TPA3C$_1$** units were also included in our study for comparative purposes.

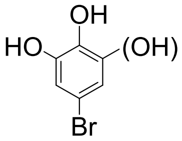
# Synthesis and characterization

### 4-bencyloxyaniline (1)



A suspension of 1.00 g (4.2 mmol) of 4-benzyloxyaniline hydrochloride in 50 mL of diethyl ether was prepared in an Erlenmeyer. 8 mL of a 1M aqueous solution of NaOH (8 mmol of NaOH) were added dropwise onto this suspension. The mixture was stirred for 15 minutes. After this time, the organic phase was separated, washed with water, dried with anhydrous $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure to obtain the product as a yellowish solid. Yield: 82%. $^1$H NMR (400 MHz, Acetone-$d_6$), δ (ppm): 7.47 – 7.41 (m, 2H, ArH $OCH_2Ph$), 7.40 – 7.33 (m, 2H, ArH $OCH_2Ph$), 7.33 – 7.26 (m, 1H, ArH $OCH_2Ph$), 6.80 – 6.73 (m, 2H, ArH), 6.65 – 6.58 (m, 2H, ArH), 4.98 (s, 2H, $OCH_2Ph$), 4.21 (s, 2H, $NH_2$). $^{13}$C NMR (100 MHz, Acetone-$d_6$), δ (ppm): 151.8, 143.3, 139.1, 129.1, 128.3, 128.3, 116.7, 116.2, 71.1. IR (KBr, cm$^{-1}$): 3450-3100 (NH), 1512 (arC-C), 1242 (C-O).

### di- and tri-hydroxybromobenzenes (2b and 2c)[3]

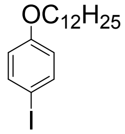


1 mmol of 4-Bromo-1,2-dimethoxybenzene or 5-bromo-1,2,3-trimethoxybenzene were dissolved in 2mL of dry $CH_2Cl_2$ (2 mL per mmol of precursor) under argon atmosphere. With the flask immersed in an ice / NaCl bath at -10 °C, 1.2 mmol per mmol of hydroxyl group to be unprotected of $BBr_3$ (1 M solution in $CH_2Cl_2$) were slowly added. The reaction was maintained at 25 °C for 20 h. After this time, the excess of $BBr_3$ was destroyed by slowly adding water until HBr vapors were no longer observed. The mixture was extracted with ethyl acetate and the organic phases were combined, washed with distilled water (until the pH of the aqueous phase was neutral) and saturated NaCl solution, dried with anhydrous $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure, obtaining the pure product.

**4-bromo-1,2-dihydroxybenzene (2b).** Yield.: 93%. $^1$H NMR (300 MHz, Acetone-$d_6$), δ (ppm):8.28 (s, 1H, ArOH), 8.12 (s, 1H, ArOH), 6.98 (d, *J* = 2.3 Hz, 1H, ArH), 6.84 (dd, *J* = 8.4, 2.3 Hz, 1H, ArH), 6.76 (d, *J* = 8.4 Hz, 1H, ArH).

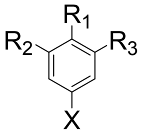
**5-bromo-1,2,3-trihydroxybenzene (2c).** Yield.: 90%. $^1$H NMR (300 MHz, Acetone-$d_6$), δ (ppm): 8.22 (s, 2H, ArOH), 7.50 (s, 1H, ArOH), 6.55 (s, 2H, ArH).

**1-dodecyloxy-4-iodobenzene (3a)**[4]



5.20 g (23.6 mmol) of 4-iodophenol, 6.60 g (47.8 mmol) of dry $K_2CO_3$ and 0.40 g (47.8 mmol) of KI are dissolved/suspended in 60 mL of butanone. After the addition of 7.27 g (29.2 mmol) of 1-bromododecane, the reaction mixture was stirred under reflux for 15 hours. Then, the solid was filtered off and the solvent was evaporated under reduced pressure. The product was purified by flash chromatography in silica gel varying the polarity of the eluent from hexane to hexane / ethyl acetate 10/1. After recrystallization from ethanol, the pure product was obtained as a white solid. Yield: 69%. $^1$H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.56 – 7.51 (m, 2H, ArH), 6.71 – 6.63 (m, 2H, ArH), 3.91 (t, *J* = 6.6 Hz, 2H, $OCH_2$), 1.81 – 1.71 (m, 2H, $CH_2$), 1.50 – 1.20 (m, 18H, $CH_2$), 0.88 (t, *J* = 6.9 Hz, 3H, $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$), δ (ppm): 159.2, 138.3, 117.1, 82.5, 68.3, 32.1, 29.8, 29.8, 29.7, 29.7, 29.5, 29.5, 29.3, 26.1, 22.8, 14.3. IR (KBr, cm$^{-1}$): 2917 (Csp$^3$-H), 2849 (Csp$^3$-H), 1588 (arC-C), 1489 (arC-C), 1474 (arC-C), 1464 (arC-C), 1285 (C-O), 1249 (C-O).

**4-bromo-1,2-didodecyloxybenzene (3b) and 5-bromo-1,2,3-tridodecyloxybenzene (3c)**[3]

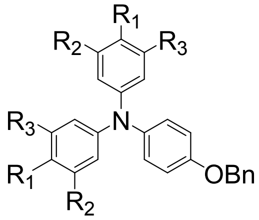


20.0 mmol of the corresponding arylbromide (**2b-c**) and 5.53 g (40.0 mmol) per hydroxyl group of dry $K_2CO_3$ were dissolved in 100 mL of DMF. The reaction mixture was heated and 25.0 mmol of 1-Bromododecane per hydroxyl group were added. The reaction mixture was stirred at 100 °C for 24 hours. After this time, it was allowed to cool to room temperature, poured into water and extracted with diethyl ether. The combined organic phases were washed with distilled water and saturated NaCl solution, dried with anhydrous $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure and the product was purified by flash chromatography in silica gel varying the polarity of the eluent from hexane to hexane / ethyl acetate 9/1. After recrystallization from ethanol, the pure product was obtained as a white solid.

**4-bromo-1,2-didodecyloxybenzene (3b).** Yield: 64%. $^1$H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.02 – 6.94 (m, 2H, ArH), 6.78 – 6.70 (m, 1H, ArH), 3.96 (t, *J* = 6.6 Hz, 2H, $OCH_2$), 3.95 (t, *J* = 6.6 Hz, 2H, $OCH_2$), 1.87 – 1.73 (m, 4H, $CH_2$), 1.50 – 1.40 (m, 4H, $CH_2$), 1.39 – 1.20 (m, 32H, $CH_2$), 0.88 (t, *J* = 6.8 Hz, 6H, $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$), δ (ppm): 150.2, 148.5, 123.6, 117.1, 115.3, 112.9, 69.7, 69.5, 32.1, 29.8, 29.8, 29.8, 29.6, 29.5, 29.4, 29.3, 26.1, 22.8, 14.3. IR (KBr, cm$^{-1}$): 2914 (Csp$^3$-H), 2848 (Csp$^3$-H), 1505 (arC-C), 1463 (arC-C), 1251 (C-O), 1220 (C-O).

**5-bromo-1,2,3-tridodecyloxybenzene (3c).** Yield: 54%. $^1$H NMR (400 MHz, $CDCl_3$), δ (ppm): 6.67 (s, 2H, ArH), 3.93 (t, *J* = 6.5 Hz, 4H, $OCH_2$), 3.90 (t, *J* = 6.6 Hz, 2H, $OCH_2$), 1.83 – 1.67 (m, 6H, $CH_2$), 1.51 – 1.40 (m, 6H, $CH_2$), 1.39 – 1.21 (m, 48H, $CH_2$), 0.88 (t, *J* = 6.9 Hz, 9H, $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$), δ (ppm): 154.0, 137.6, 115.7, 110.3, 73.6, 69.4, 32.1, 32.1, 30.4, 29.9, 29.9, 29.9, 29.8, 29.8, 29.8, 29.7, 29.5, 29.5, 29.4, 26.2, 26.2, 22.8, 14.3. IR (KBr, cm$^{-1}$): 2918 (Csp$^3$-H), 2848 (Csp$^3$-H), 1585 (arC-C), 1500 (arC-C), 1468 (arC-C), 1223 (C-O).

***N,N*-bis(aryl)-4-benzyloxyaniline (4a-c)**



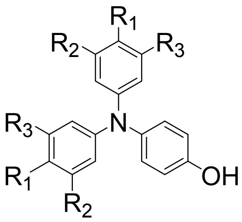
In a Schlenk under argon, 150 mg (0.16 mmol) of tris(dibenzylideneacetone)dipalladium(0) and 32 mg (0.16 mmol) of tris(tert-butyl)phosphine were dissolved in 15 mL of dry toluene under argon in a Schlenk tube. In a second Schlenk tube, and also under argon, 0.80 g (4.0 mmol) of 4-benzyloxyaniline (**1**), 11.6 mmol of the corresponding aromatic halide (**3a-c**) and 2.60 g (23.2 mmol) of potassium tert-butoxide were suspended in 25 mL of dry toluene. The solution of the first Schlenk was transferred with a cannula to the second Schlenk and the reaction mixture was stirred at 90 °C for 21 hours. After this time, the reaction mixture was cooled to room temperature, diluted with 250 mL of ethyl acetate and washed with distilled water (4x150 mL) and saturated NaCl solution (50 mL). The organic phase was dried with anhydrous MgSO$_4$, filtered and the solvent was evaporated under reduced pressure. The product was purified following the appropriate procedure in each case:

**N,N-bis(4-dodecyloxyphenyl)-4-benzyloxyaniline (4a)** was purified by flash chromatography on silica gel varying the polarity of the eluent from hexane to hexane / ethyl acetate 80/1 to obtain the product as a yellowish oil. Yield: 83%. $^1$H NMR (400 MHz, Acetone-d$_6$), δ (ppm): 7.51 – 7.44 (m, 2H, ArH OCH$_2$Ph), 7.42 – 7.36 (m, 2H, ArH OCH$_2$Ph), 7.35 – 7.29 (m, 1H, ArH OCH$_2$Ph), 6.95 – 6.88 (m, 8H, ArH TPA), 6.86 – 6.79 (m, 4H, ArH TPA), 5.07 (s, 2H, OCH$_2$Ph), 3.94 (t, *J* = 6.5 Hz, 4H, OCH$_2$), 1.81 – 1.69 (m, 4H, CH$_2$), 1.52 – 1.21 (m, 36H, CH$_2$), 0.88 (t, *J* = 6.9 Hz, 6H, CH$_3$). $^{13}$C NMR (100 MHz, Acetone-d$_6$), δ (ppm): 155.7, 155.1, 143.2, 142.7, 138.6, 129.3, 128.6, 128.4, 125.7, 125.3, 116.4, 116.0, 70.8, 68.8, 32.6, 30.4, 30.4, 30.4, 30.1, 30.1, 26.8, 23.3, 14.4. IR (KBr, cm$^{-1}$): 2924 (Csp$^3$-H), 2853 (Csp$^3$-H), 1503 (arC-C), 1468 (arC-C), 1236 (C-O).

***N,N*-bis(3,4-didodecyloxyphenyl)-4-benzyloxyaniline (4b)** was purified by flash chromatography on silica gel varying the polarity of the eluent from hexane to hexane / ethyl acetate 40/1 and subsequent recrystallization in acetone to obtain the product as an off-white solid. Yield: 80% $^1$H NMR (400 MHz, Acetone-d$_6$, 40 °C), δ (ppm): 7.51 – 7.44 (m, 2H, ArH OCH$_2$Ph), 7.42 – 7.36 (m, 2H, ArH OCH$_2$Ph), 7.35 – 7.29 (m, 1H, ArH OCH$_2$Ph), 7.00 – 6.90 (m, 4H, ArH TPA), 6.83 (d, *J* = 8.6 Hz, 2H, ArH TPA), 6.65 (d, *J* = 2.6 Hz, 2H, ArH TPA), 6.48 (dd, *J* = 8.6, 2.6 Hz, 2H, ArH TPA), 5.08 (s, 2H, OCH$_2$Ph), 3.96 (t, *J* = 6.4 Hz, 4H, OCH$_2$), 3.85 (t, *J* = 6.4 Hz, 4H, OCH$_2$), 1.81 – 1.66 (m, 8H, CH$_2$), 1.57 – 1.22 (m, 72H, CH$_2$), 0.89 (t, *J* = 6.9 Hz, 12H, CH$_3$). $^{13}$C NMR (100 MHz, Acetone-d$_6$, 40 °C), δ (ppm): 155.6, 151.1, 146.2, 143.5, 143.0, 138.7, 129.3, 128.6, 128.5, 126.1, 116.9, 116.6, 116.5, 111.9, 71.0, 70.6, 69.9, 32.7, 30.5, 30.5, 30.4, 30.3, 30.2, 30.2, 27.0, 26.9, 23.4, 14.4. IR (KBr, cm$^{-1}$): 2918 (Csp$^2$-H), 2850 (Csp$^2$-H), 1506 (arC-C), 1468 (arC-C), 1231 (C-O).

***N,N*-bis(3,4,5-tridodecyloxyphenyl)-4-benzyloxyaniline (4c)** was purified by column chromatography on silica gel varying the polarity of the eluent from hexane to hexane / ethyl acetate 40/1 and subsequent recrystallization in acetone to obtain the product as an off-white solid. Yield: 79%. $^1$H NMR (400 MHz, Acetone-d$_6$, 40 °C), δ (ppm): 7.51 – 7.44 (m, 2H, ArH OCH$_2$Ph), 7.42 – 7.36 (m, 2H, ArH OCH$_2$Ph), 7.35 – 7.29 (m, 1H, ArH OCH$_2$Ph), 7.07 – 7.01 (m, 2H, ArH TPA), 6.99 – 6.93 (m, 2H, ArH TPA), 6.27 (s, 4H, ArH TPA), 5.09 (s, 2H, OCH$_2$Ph), 3.92 (t, *J* = 6.4 Hz, 4H, OCH$_2$), 3.82 (t, *J* = 6.3 Hz, 8H, OCH$_2$), 1.78 – 1.65 (m, 12H, CH$_2$), 1.59 – 1.22 (m, 108H, CH$_2$), 0.95 – 0.83 (m, 18H, CH$_3$). $^{13}$C NMR (100 MHz, Acetone-d$_6$, 40 °C), δ (ppm): 156.1, 154.4, 144.8, 142.2, 138.6, 135.1, 129.3, 128.7, 128.5, 127.3, 116.6, 103.8, 73.8, 70.9, 69.7, 32.7, 31.3, 30.6, 30.6, 30.6, 30.5, 30.5, 30.5, 30.5, 30.3, 30.2, 30.2, 30.2, 27.1, 27.0, 23.4, 14.4. IR (KBr, cm$^{-1}$): 2917 (Csp$^2$-H), 2848 (Csp$^2$-H), 1588 (arC-C), 1502 (arC-C), 1468 (arC-C), 1231 (C-O).

**4-[*N,N*-bis(aryl)amino]phenol (5a-c)**



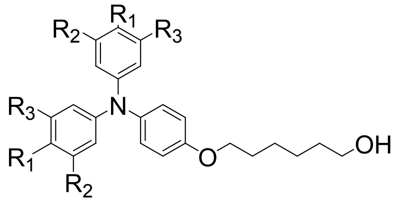
3.00 g of the corresponding triarylamine **4a-c** were dissolved in 75 mL of dry THF and stirred under argon atmosphere at room temperature. 0.30 g of Pd / C (10% by weight) were added. After three vacuum-argon cycles, the mixture was stirred under hydrogen atmosphere at room temperature for 18 hours. After this time, it was diluted with ethyl acetate and filtered through celite®. The solvent was evaporated under reduced pressure and the product was purified following the appropriate procedure in each case.

**4-[*N,N*-bis(4-dodecyloxyphenyl)]aminophenol (5a)** was purified by flash chromatography on silica gel varying the polarity of the eluent from hexane to hexane / ethyl acetate 10/1 to obtain the product as a grayish oil. Yield: 90%. $^1$HNMR (400 MHz, Acetone-d$_6$), δ (ppm): 8.09 (s, 1H, ArOH, TPA-OH), 6.93 – 6.72 (m, 12H, ArH TPA), 3.94 (t, *J* = 6.5 Hz, 4H, OCH$_2$), 1.81 – 1.69 (m, 4H, CH$_2$), 1.54 – 1.21 (m, 36H, CH$_2$), 0.88 (t, *J* = 6.9 Hz, 6H, CH$_3$). $^{13}$C NMR (100 MHz, Acetone-d$_6$), δ (ppm): 155.4, 154.0, 143.0, 141.8, 126.4, 125.2, 116.8, 116.0, 68.8, 32.6, 30.4, 30.4, 30.3, 30.1, 30.1, 26.8, 23.3, 14.4. IR (KBr, cm$^{-1}$): 3500-3100 (OH), 2929 (Csp$^3$-H), 2855 (Csp$^3$-H), 1501 (arC-C), 1468 (arC-C), 1235 (C-O).

**4-[*N,N*-bis(3,4-didodecyloxyphenyl)]aminophenol (5b)** was purified by flash chromatography on silica gel by varying the polarity of the eluent from hexane to hexane / ethyl acetate 10/1 and subsequent recrystallization in acetone to obtain the product as an off-white solid. Yield: 93%. $^1$H NMR (400 MHz, Acetone-d$_6$, 40 °C), δ (ppm): 7.99 (s, 1H, , ArOH TPA-OH), 6.94 – 6.88 (m, 2H, ArH TPA), 6.81 (d, *J* = 8.6 Hz, 2H, ArH TPA), 6.80 – 6.74 (m, 2H, ArH TPA), 6.63 (d, *J* = 2.6 Hz, 2H, ArH TPA), 6.46 (dd, *J* = 8.6, 2.6 Hz, 2H, ArH TPA), 3.95 (t, *J* = 6.4 Hz, 4H, OCH$_2$), 3.85 (t, *J* = 6.4 Hz, 4H, OCH$_2$), 1.82 – 1.65 (m, 8H, CH$_2$), 1.57 – 1.23 (m, 72H, CH$_2$), 0.89 (t, *J* = 6.8 Hz, 12H, CH$_3$). $^{13}$C NMR (100 MHz, Acetone-d$_6$, 40 °C), δ (ppm): 154.4, 151.1, 145.8, 143.9, 141.5, 127.1, 116.9, 116.7, 116.4, 111.5, 70.7, 69.9, 32.7, 30.5, 30.5, 30.5, 30.5, 30.5, 30.4, 30.4, 30.2, 30.2, 27.0, 26.9, 23.4, 14.4. IR (KBr, cm$^{-1}$): 3500-3100 (OH), 2919 (Csp$^3$-H), 2850 (Csp$^3$-H), 1503 (arC-C), 1468 (arC-C), 1232 (C-O).

**4-[*N,N*-bis(3,4,5-tridodecyloxyphenyl)]aminophenol (5c)** was purified by flash chromatography on silica gel varying the polarity of the eluent from hexane to hexane / ethyl acetate 10/1 and subsequent recrystallization in acetone to obtain the product as an off-white solid. Yield: 93%. $^1$H NMR (400 MHz, Acetone-d$_6$, 40 °C), δ (ppm): 8.08 (s, 1H, ArOH TPA-OH), 7.00 – 6.94 (m, 2H, ArH TPA), 6.83 – 6.77 (m, 2H, ArH TPA), 6.26 (s, 4H, ArH TPA), 3.91 (t, *J* = 6.4 Hz, 4H, OCH$_2$), 3.83 (t, *J* = 6.3 Hz, 8H, OCH$_2$), 1.78 – 1.65 (m, 12H, CH$_2$), 1.59 – 1.22 (m, 108H, CH$_2$), 0.89 (t, *J* = 6.8 Hz, 18H, CH$_3$). $^{13}$C NMR (100 MHz, Acetone-d$_6$, 40 °C), δ (ppm): 154.9, 154.3, 145.0, 140.7, 134.8, 128.1, 117.0, 103.4, 73.8, 69.7, 32.7, 31.3, 30.6, 30.6, 30.6, 30.5, 30.5, 30.5, 30.5, 30.3, 30.2, 30.2, 27.1, 27.0, 23.4, 14.4. IR (KBr, cm$^{-1}$): 3500-3100 (OH), 2919 (Csp$^3$-H), 2850 (Csp$^3$-H), 1591 (arC-C), 1502 (arC-C), 1467 (arC-C), 1232 (C-O).

**6-[4-(*N,N*-bis(4-dodecyloxyphenyl)amino)phenoxy]-1-hexanol (6a-c)**



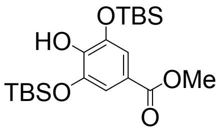
3.2 mmol of the corresponding 4-[*N,N*-bis(aryl)amino]phenol (**5a-c**), 2.8 g (20.2 mmol) of dry $K_2CO_3$ and 0.36 g (2.2 mmol) of KI were dissolved in 100 mL of DMF in a round bottom flask. The reaction mixture was heated and 0.92 g (5.1 mmol) of 6-bromo-1-hexanol were added. The reaction mixture was stirred at 100 °C for 16 hours. After this time, it was allowed to cool to room temperature, poured into water and extracted with a 1/1 hexane / ethyl acetate mixture. The combined organic phases were washed with distilled water and saturated NaCl solution, dried with anhydrous $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure and the product was purified by flash chromatography on silica gel using mixtures hexane / ethyl acetate of increasing polarity (from 15/1 to 1/1).

**6-[4-(*N,N*-bis(4-dodecyloxyphenyl)amino)phenoxy]-1-hexanol (6a).** Yellowish oil. Yield: 71% $^1H$ NMR (400 MHz, Acetone-$d_6$), δ (ppm): 6.93 – 6.87 (m, 6H, ArH TPA), 6.85 – 6.79 (m, 6H, ArH TPA), 3.95 (t, *J* = 6.5 Hz, 2H, $OCH_2$), 3.94 (t, *J* = 6.5 Hz, 4H, $OCH_2$), 3.55 (td, *J* = 6.4, 5.3 Hz, 2H, $CH_2OH$), 3.36 (t, *J* = 5.3 Hz, 1H, OH), 1.81 – 1.70 (m, 6H, $CH_2$), 1.59 – 1.23 (m, 42H, $CH_2$), 0.88 (t, *J* = 6.9 Hz, 6H, $CH_3$). $^{13}C$ NMR (100 MHz, Acetone-$d_6$), δ (ppm): 155.6, 142.8, 125.6, 116.0, 68.8, 68.8, 62.4, 33.8, 32.7, 30.4, 30.4, 30.4, 30.4, 30.2, 30.1, 30.1, 26.8, 26.7, 26.5, 23.3, 14.4. IR (NaCl, $cm^{-1}$): 3500-3100 (OH), 2924 ($Csp^3$-H), 2854 ($Csp^3$-H), 1503 (arC-C), 1469 (arC-C), 1236 (C-O).

**6-[4-(*N,N*-bis(3,4-didodecyloxyphenyl)amino)phenoxy]-1-hexanol (6b)** was further recrystallized from acetone to obtain the product as a yellowish solid. Yield: 74%. $^1H$ NMR (400 MHz, Acetone-$d_6$, 40 °C), δ (ppm): 6.98 – 6.93 (m, 2H, ArH TPA), 6.86 – 6.79 (m, 4H, ArH TPA), 6.64 (d, *J* = 2.6 Hz, 2H, ArH TPA), 6.47 (dd, *J* = 8.6, 2.6 Hz, 2H, ArH TPA), 3.96 (t, *J* = 6.5 Hz, 2H, $OCH_2$), 3.96 (t, *J* = 6.4 Hz, 4H, $OCH_2$), 3.85 (t, *J* = 6.4 Hz, 4H, $OCH_2$), 3.56 (td, *J* = 6.4, 5.3 Hz, 2H, $CH_2OH$), 3.25 (t, *J* = 5.3 Hz, 1H, OH), 1.82 – 1.66 (m, 10H, $CH_2$), 1.60 – 1.23 (m, 78H, $CH_2$), 0.89 (t, *J* = 6.8 Hz, 12H, $CH_3$). $^{13}C$ NMR (100 MHz, Acetone-$d_6$, 40 °C), δ (ppm): 156.0, 151.1, 146.0, 143.6, 142.5, 126.3, 116.8, 116.6, 116.1, 111.8, 70.6, 69.9, 68.9, 62.5, 33.8, 32.7, 32.7, 30.5, 30.5, 30.5, 30.5, 30.5, 30.5, 30.3, 30.3, 30.3, 30.2, 30.2, 30.2, 27.0, 26.9, 26.8, 26.6, 23.4, 14.4. IR (KBr, $cm^{-1}$): 3500-3100 (OH), 2918 ($Csp^3$-H), 2850 ($Csp^3$-H), 1508 (arC-C), 1469 (arC-C), 1231 (C-O).

**6-[4-(*N,N*-bis(3,4,5-tridodeciloxyphenyl)amino)phenoxy]-1-hexanol (6c)** was further recrystallized from acetone to obtain the product as a yellowish solid. Yield: 72%. $^1H$ NMR (400 MHz, Acetone-$d_6$, 40 °C), δ (ppm): 7.05 – 6.98 (m, 2H, ArH TPA), 6.90 – 6.82 (m, 2H, ArH TPA), 6.26 (s, 4H, ArH TPA), 3.97 (t, *J* = 6.5 Hz, 2H, $OCH_2$), 3.91 (t, *J* = 6.3 Hz, 4H, $OCH_2$), 3.82 (t, *J* = 6.3 Hz, 8H, $OCH_2$), 3.56 (td, *J* = 6.2, 4.9 Hz, 2H, $CH_2OH$), 3.27 (t, *J* = 4.9 Hz, 1H, OH), 1.84 – 1.64 (m, 14H, $CH_2$), 1.61 – 1.23 (m, 114H, $CH_2$), 0.89 (t, *J* = 6.7 Hz, 18H, $CH_3$). $^{13}C$ NMR (100 MHz, Acetone-$d_6$, 40 °C), δ (ppm): 156.5, 154.3, 144.8, 141.7, 135.0, 127.4, 116.1, 103.6, 73.8, 69.7, 68.9, 62.5, 33.8, 32.7, 31.3, 30.6, 30.6, 30.5, 30.5, 30.5, 30.3, 30.2, 30.2, 27.1, 27.0, 26.8, 26.6, 23.4, 14.4. IR (KBr, $cm^{-1}$): 3500-3100 (OH), 2919 ($Csp^3$-H), 2849 ($Csp^3$-H), 1589 (arC-C), 1503 (arC-C), 1468 (arC-C), 1238 (C-O).

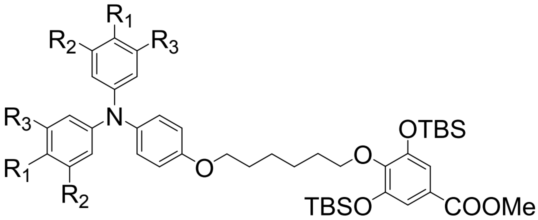
**Methyl 3,5-bis(*tert*-butyldimethylsilyloxy)-4-hydroxybenzoate (7)**[4]



3.15 g (16.8 mmol) of methyl 3,4,5-trihydroxybenzoate and 3.51 g (51.6 mmol) of imidazole are dissolved in 15 mL of DMF in a round bottom flask under argon atmosphere and cooled in an ice bath. A solution of 5.29 g (34.0 mmol) of tert-butyldimethylsilyl chloride in 20 mL of DMF was added dropwise. The reaction was stirred at room temperature for 15 hours. After this time, the reaction mixture was poured into water and extracted with ethyl acetate (2x75 mL). The combined organic phases were washed with distilled water and with saturated $NH_4Cl$ solution, dried with anhydrous $MgSO_4$ and filtered over celite®. The solvent was evaporated under reduced pressure and the product was purified by flash chromatography on silica gel using a mixture hexane / $CH_2Cl_2$ 2:1 as eluent. The product was obtained as a yellowish oil that crystallized on cooling to give a white solid. Yield: 67%.

$^1$H NMR (300 MHz, $CD_2Cl_2$), δ (ppm): 7.20 (s, 2H, ArH), 5.67 (s, 1H, OH), 3.82 (s, 3H, $OCH_3$), 1.01 (s, 18H, Si-C-$(CH_3)_3$), 0.24 (s, 12H, Si-$CH_3$).

**Methyl 3,5-bis(*tert*-butyldimethylsilyloxy)-4-[6-[4-(*N,N*-bis(aryl)amino)phenoxy]hexyloxy] benzoate (8a-c)**



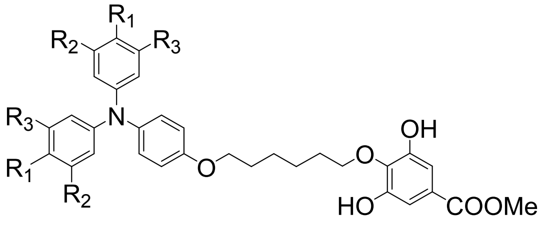
0.89 g (2.2 mmol) of methyl 3,5-bis(tert-butyldimethylsilyloxy)-4-hydroxybenzoate (15), 2.1 mmol of the corresponding triphenylamine with hexyloxy spacer and a terminal hydroxyl group (16a-c) and 0.63 g (2.4 mmol) of triphenylphosphine were dissolved in a round bottom flask in 60 mL of dry THF under argon atmosphere. In an, 0.64 mg (3.2 mmol) of DIAD were dissolved in 15 mL of dry THF and added dropwise into the reaction mixture. The reaction was stirred at room temperature for 16 hours. After this time, it was poured into a mixture of water (150 mL) and ethyl acetate (150 mL). The organic phase was separated, washed with saturated NaCl solution, dried with anhydrous $MgSO_4$ and filtered. The solvent was evaporated under educed pressure and the product was purified by flash chromatography on silica gel using the appropriate eluent in each case.

**Methyl 3,5-bis(*tert*-butyldimethylsilyloxy)-4-[6-[4-(*N,N*-bis(4-dodecyloxyphenyl)amino) phenoxy]hexyloxy]benzoate (8a)** was purified by flash chromatography on silica gel by varying the polarity of the eluent from hexane to hexane / ethyl acetate 40/1 to obtain the product as a colorless oil. Yield: 80%. $^1$H NMR (400 MHz, Acetone-d$_6$, 40 $^o$C), δ (ppm): 7.22 (s, 2H, ArH), 6.94 – 6.88 (m, 6H, ArH TPA), 6.85 – 6.79 (m, 6H, ArH TPA), 4.05 (t, *J* = 7.0 Hz, 2H, $OCH_2$), 3.96 (t, *J* = 6.4 Hz, 2H, $OCH_2$), 3.95 (t, *J* = 6.5 Hz, 4H, $OCH_2$), 3.84 (s, 3H, $OCH_3$), 1.87 – 1.70 (m, 8H, $CH_2$), 1.59 – 1.23 (m, 40H, $CH_2$), 1.04 (s, 18H, Si-C-$(CH_3)_3$), 0.88 (t, J = 6.9 Hz, 6H, $CH_3$), 0.24 (s, 12H, Si-$CH_3$). $^{13}$C NMR (100 MHz, Acetone-d$_6$, 40 $^o$C), δ (ppm): 166.7, 155.7, 155.7, 150.7, 147.5, 142.9, 142.9, 125.9, 125.7, 125.6, 116.7, 116.2, 116.2, 73.7, 69.0, 68.8, 52.4, 32.7, 31.0, 30.4, 30.4, 30.4, 30.2, 30.2, 30.1, 26.9, 26.8, 26.5, 26.2, 23.4, 19.0, 14.4, -4.1. IR (NaCl, cm$^{-1}$): 2926 (Csp$^3$-H), 2855 (Csp$^3$-H), 1725 (C=O), 1576 (arC-C), 1503 (arC-C), 1470 (arC-C), 1236 (C-O).

**Methyl 3,5-bis(*tert*-butyldimethylsilyloxy)-4-[6-[4-(*N,N*-bis(3,4-didodecyloxyphenyl)amino) phenoxy]hexyloxy]benzoate (8b)** was purified by column chromatography on silica gel by varying the polarity of the eluent from hexane to hexane / ethyl acetate 30/1 to obtain the product as an off-white solid. Yield: 66%. $^1$H NMR (400 MHz, Acetone-d$_6$, 40 °C), δ (ppm): 7.22 (s, 2H, ArH), 6.99 – 6.92 (m, 2H, ArH TPA), 6.87 – 6.78 (m, 4H, ArH TPA), 6.64 (d, *J* = 2.6 Hz, 2H, ArH TPA), 6.47 (dd, *J* = 8.6, 2.6 Hz, 2H, ArH TPA), 4.05 (t, *J* = 7.0 Hz, 2H, OCH$_2$), 3.96 (t, *J* = 6.4 Hz, 2H, OCH$_2$), 3.95 (t, *J* = 6.4 Hz, 4H, OCH$_2$), 3.85 (t, *J* = 6.4 Hz, 4H, OCH$_2$), 3.84 (s, 3H, OCH$_3$), 1.87 – 1.66 (m, 12H, CH$_2$), 1.59 – 1.23 (m, 76H, CH$_2$), 1.04 (s, 18H, Si-C-(CH$_3$)$_3$), 0.89 (t, *J* = 6.9 Hz, 12H, CH$_3$), 0.24 (s, 12H, Si-CH$_3$). $^{13}$C NMR (100 MHz, Acetone-d$_6$, 40 °C), δ (ppm): 166.7, 156.0, 151.0, 150.7, 147.5, 146.0, 143.6, 142.5, 126.3, 125.9, 116.8, 116.7, 116.6, 116.1, 111.8, 73.7, 70.6, 69.9, 68.8, 52.4, 32.7, 32.7, 31.0, 30.5, 30.5, 30.5, 30.5, 30.4, 30.3, 30.2, 30.2, 27.0, 26.9, 26.9, 26.6, 26.3, 23.4, 19.0, 14.4, -4.1. IR (KBr, cm$^{-1}$): 2922 (Csp$^3$-H), 2850 (Csp$^3$-H), 1725 (C=O), 1576 (arC-C), 1506 (arC-C), 1469 (arC-C), 1230 (C-O).

**Methyl 3,5-bis(*tert*-butyldimethylsilyloxy)-4-[6-[4-(*N,N*-bis(3,4,5-tridodecyloxyphenyl)amino) phenoxy]hexyloxy]benzoate (8c)** was purified by silica gel column chromatography by varying the polarity of the eluent from hexane to hexane / ethyl acetate 30/1 to obtain the product as a yellowish solid. Yield: 55%. $^1$H NMR (400 MHz, Acetone-d$_6$, 40 °C), δ (ppm): 7.22 (s, 2H, ArH), 7.06 – 6.99 (m, 2H, ArH TPA), 6.90 – 6.83 (m, 2H, ArH TPA), 6.26 (s, 4H, ArH TPA), 4.05 (t, *J* = 7.0 Hz, 2H, OCH$_2$), 3.98 (t, *J* = 6.5 Hz, 2H, OCH$_2$), 3.92 (t, *J* = 6.4 Hz, 4H, OCH$_2$), 3.84 (s, 3H, OCH$_3$), 3.82 (t, *J* = 6.3 Hz, 8H, OCH$_2$), 1.87 – 1.66 (m, 16H, CH$_2$), 1.60 – 1.23 (m, 112H, CH$_2$), 1.04 (s, 18H, Si-C-(CH$_3$)$_3$), 0.89 (t, *J* = 6.8 Hz, 18H, CH$_3$), 0.24 (s, 12H, Si-CH$_3$). $^{13}$C NMR (100 MHz, Acetone-d$_6$, 40 °C), δ (ppm): 166.7, 156.5, 154.3, 150.7, 147.5, 144.8, 141.7, 135.0, 127.4, 125.9, 116.7, 116.1, 103.7, 73.8, 73.7, 69.7, 68.8, 52.4, 32.7, 31.3, 31.0, 30.6, 30.6, 30.6, 30.5, 30.5, 30.5, 30.5, 30.3, 30.2, 27.1, 27.0, 26.9, 26.6, 26.3, 23.4, 19.0, 14.4, -4.1. IR (KBr, cm$^{-1}$): 2921 (Csp$^3$-H), 2850 (Csp$^3$-H), 1728 (C=O), 1588 (arC-C), 1503 (arC-C), 1468 (arC-C), 1239 (C-O).

### Methyl 3,5-dihydroxy-4-[6-[4-(*N,N*-bis(aryl)amino)phenoxy]hexyloxy]benzoate (9a-c)



In an argon flask, 1.6 mmol of the corresponding methyl ester 8a-c were dissolved in 20 mL of dry THF, and put in an ice bath. 3.5 mL (3.5 mmol) of 1M TBAF solution in THF were added dropwise. The reaction was stirred at room temperature for 10 minutes. After this time, the reaction mixture was poured into water and extracted with ethyl acetate (x3). The combined organic phases were washed with saturated NaCl solution, dried with anhydrous MgSO$_4$ and filtered. The solvent was evaporated under reduced pressure and the product was purified by flash chromatography on silica gel using hexane / ethyl acetate 6/1 as eluent.

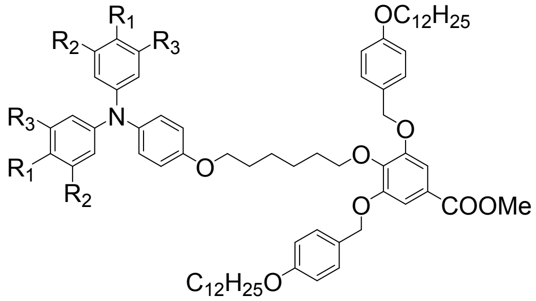
**Methyl 3,5-dihydroxy-4-[6-[4-(*N,N*-bis(4dodecyloxyphenyl)amino)phenoxy]hexyloxy] benzoate (9a)** was obtained as a grayish oil. Yield: quantitative. $^1$H NMR (400 MHz, Acetone-d$_6$, 40 °C), δ (ppm): 8.06 (s, 2H, ArOH), 7.10 (s, 2H, ArH), 6.93 – 6.88 (m, 6H, ArH TPA), 6.86 – 6.79 (m, 6H, ArH TPA), 4.17 (t, *J* = 6.8 Hz, 2H, OCH$_2$), 3.96 (t, *J* = 6.4 Hz, 2H, OCH$_2$), 3.95 (t, *J* = 6.5 Hz, 4H, OCH$_2$), 3.81 (s, 3H, OCH$_3$), 1.87 – 1.70 (m, 8H, CH$_2$), 1.57 – 1.25 (m, 40H, CH$_2$), 0.88 (t, *J* = 6.9

Hz, 6H, $CH_3$). $^{13}C$ NMR (100 MHz, Acetone-$d_6$, 40 °C), δ (ppm): 167.0, 155.8, 155.7, 151.2, 142.9, 142.9, 139.6, 126.3, 125.7, 125.7, 116.2, 110.0, 73.5, 69.0, 68.9, 52.1, 32.7, 30.7, 30.4, 30.4, 30.4, 30.2, 30.2, 30.1, 30.1, 26.9, 26.7, 26.4, 23.4, 14.4. IR (NaCl, $cm^{-1}$): 3600-3100 (OH), 2924 ($Csp^3$-H), 2854 ($Csp^3$-H), 1700 (C=O), 1505 (arC-C), 1471 (arC-C), 1236 (C-O).

**Methyl 3,5-dihydroxy-4-[6-[4-(*N,N*-bis(3,4-didodecyloxyphenyl)amino)phenoxy]hexyloxy] benzoate (9b)** was obtained as a grayish oil. Yield: quantitative. $^1H$ NMR (400 MHz, Acetone-$d_6$, 40 °C), δ (ppm): 8.04 (s, 2H, ArOH), 7.10 (s, 2H, ArH), 6.98 – 6.92 (m, 2H, ArH TPA), 6.87 – 6.79 (m, 4H, ArH TPA), 6.64 (d, *J* = 2.6 Hz, 2H, ArH TPA), 6.47 (dd, *J* = 8.6, 2.6 Hz, 2H, ArH TPA), 4.17 (t, *J* = 6.8 Hz, 2H, $OCH_2$), 3.96 (t, *J* = 6.4 Hz, 2H, $OCH_2$), 3.95 (t, *J* = 6.4 Hz, 4H, $OCH_2$), 3.85 (t, *J* = 6.4 Hz, 4H, $OCH_2$), 3.81 (s, 3H, $OCH_3$), 1.87 – 1.66 (m, 12H, $CH_2$), 1.59 – 1.23 (m, 76H, $CH_2$), 0.89 (t, J = 6.9 Hz, 12H, $CH_3$). $^{13}C$ NMR (100 MHz, Acetone-$d_6$, 40 °C), δ (ppm): 167.0, 156.0, 151.2, 151.0, 146.0, 143.6, 142.5, 139.6, 126.3, 126.3, 116.8, 116.6, 116.1, 111.7, 110.0, 73.5, 70.6, 69.9, 68.9, 52.1, 32.7, 32.7, 30.7, 30.5, 30.5, 30.5, 30.4, 30.3, 30.2, 27.0, 26.9, 26.7, 26.4, 23.4, 14.4. IR (KBr, $cm^{-1}$): 3600-3100 (OH), 2915 ($Csp^3$-H), 2850 ($Csp^3$-H), 1684 (C=O), 1504 (arC-C), 1470 (arC-C), 1250 (C-O), 1222 (C-O).

**Methyl 3,5-dihydroxy-4-[6-[4-(*N,N*-bis(3,4,5-tridodecyloxyphenyl)amino)phenoxy]hexyloxy] benzoate (9c)** was obtained as a grayish oil. Yield: quantitative. $^1H$ NMR (400 MHz, Acetone-$d_6$, 40 °C), δ (ppm): 8.03 (s, 2H, ArOH), 7.10 (s, 2H, ArH), 7.05 – 7.00 (m, 2H, ArH TPA), 6.90 – 6.84 (m, 2H, ArH TPA), 6.26 (s, 4H, ArH TPA), 4.18 (t, *J* = 6.8 Hz, 2H, $OCH_2$), 3.98 (t, *J* = 6.5 Hz, 2H, $OCH_2$), 3.92 (t, *J* = 6.4 Hz, 4H, $OCH_2$), 3.83 (t, *J* = 6.3 Hz, 8H, $OCH_2$), 3.81 (s, 3H, $OCH_3$), 1.87 – 1.66 (m, 16H, $CH_2$), 1.61 – 1.23 (m, 112H, $CH_2$), 0.89 (t, *J* = 6.9 Hz, 18H, $CH_3$). $^{13}C$ NMR (100 MHz, Acetone-$d_6$, 40 °C), δ (ppm): 167.0, 156.6, 154.4, 151.2, 144.9, 141.7, 139.6, 135.1, 127.5, 126.3, 116.1, 110.0, 103.7, 73.8, 73.5, 69.8, 68.9, 52.1, 32.7, 31.3, 30.7, 30.6, 30.6, 30.6, 30.5, 30.5, 30.5, 30.5, 30.3, 30.2, 27.1, 27.0, 26.7, 26.4, 23.4, 14.4. IR (KBr, $cm^{-1}$): 3600-3100 (OH), 2922 ($Csp^3$-H), 2851 ($Csp^3$-H), 1720 (C=O), 1589 (arC-C), 1503 (arC-C), 1468 (arC-C), 1240 (C-O).

**Methyl 3,5-bis(4-dodecyloxybenzyloxy)-4-[6-[4-(*N,N*bis(aryl)amino)phenoxy]hexyloxy] benzoate (10a-c)**



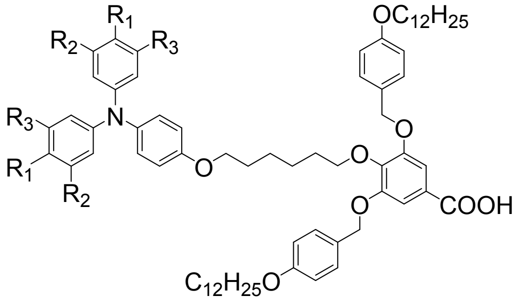
1.5 mmol of the corresponding compound **9a-c**, 1.65 g (11.9 mmol) of dry $K_2CO_3$ and 0.20 g (1.2 mmol) of KI were dissolved/suspended in 100 mL of DMF in a round bottom flask. The reaction mixture was heated and 2.35 g (7.6 mmol) of 4-dodecyloxybenzyl chloride[5] were added. The reaction was stirred at 100 °C for 15 hours. After this time, it was allowed to cool to room temperature, poured into water and extracted with a 1/1 hexane / ethyl acetate mixture. The combined organic phases were washed with distilled water and saturated NaCl solution, dried with anhydrous $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure and the product was purified by flash chromatography on silica gel using mixtures from hexane to hexane / ethyl acetate 10/1 as eluent.

**Methyl 3,5-bis(4-dodecyloxybenzyloxy)-4-[6-[4-(*N,N*-bis(4-dodecyloxyphenyl)amino) phenoxy]hexyloxy]benzoate (10a).** Colorless oil. Yield: 38%. $^1$H NMR (400 MHz, Acetone-$d_6$, 40 °C), δ (ppm): 7.45 – 7.38 (m, 6H, ArH), 6.97 – 6.87 (m, 10H, ArH + ArH TPA), 6.84 – 6.78 (m, 6H, ArH TPA), 5.08 (s, 4H, $OCH_2Ph$), 4.06 (t, *J* = 6.3 Hz, 2H, $OCH_2$), 3.98 (t, *J* = 6.5 Hz, 4H, $OCH_2$), 3.95 (t, *J* = 6.5 Hz, 4H, $OCH_2$), 3.88 (t, *J* = 6.5 Hz, 2H, $OCH_2$), 3.85 (s, 3H, $OCH_3$), 1.81 – 1.63 (m, 12H, $CH_2$), 1.54 – 1.23 (m, 76H, $CH_2$), 0.88 (t, *J* = 6.8 Hz, 12H, $CH_3$). $^{13}$C NMR (100 MHz, Acetone-$d_6$, 40 °C), δ (ppm): 166.9, 160.2, 155.7, 155.7, 153.7, 144.2, 142.9, 142.9, 130.3, 130.0, 125.9, 125.7, 125.6, 116.2, 116.2, 115.4, 110.1, 73.9, 71.8, 69.0, 68.9, 68.7, 52.4, 32.7, 31.1, 30.4, 30.4, 30.2, 30.1, 26.9, 26.9, 26.6, 26.6, 23.4, 14.4. IR (KBr, $cm^{-1}$): 2920 ($Csp^3$-H), 2851 ($Csp^3$-H), 1717 (C=O), 1504 (arC-C), 1468 (arC-C), 1238 (C-O).

**Methyl 3,5-bis(4-dodecyloxybenzyloxy)-4-[6-[4-(*N,N*-bis(3,4-didodecyloxyphenyl)amino) phenoxy]hexyloxy]benzoate (10b).** Off-white solid. Yield: 36%. $^1$H NMR (400 MHz, Acetone-$d_6$, 40 °C), δ (ppm): 7.46 – 7.37 (m, 6H, ArH), 6.98 – 6.90 (m, 6H, ArH + ArH TPA), 6.85 – 6.78 (m, 4H, ArH TPA), 6.64 (d, *J* = 2.5 Hz, 2H, ArH TPA), 6.47 (dd, *J* = 8.6, 2.5 Hz, 2H, ArH TPA), 5.09 (s, 4H, $OCH_2Ph$), 4.06 (t, *J* = 6.3 Hz, 2H, $OCH_2$), 3.98 (t, *J* = 6.5 Hz, 4H, $OCH_2$), 3.95 (t, *J* = 6.4 Hz, 4H, $OCH_2$), 3.89 (t, *J* = 6.4 Hz, 2H, $OCH_2$), 3.85 (s, 3H, $OCH_3$), 3.84 (t, *J* = 6.4 Hz, 4H, $OCH_2$), 1.81 – 1.63 (m, 16H, $CH_2$), 1.56 – 1.23 (m, 112H, $CH_2$), 0.89 (t, *J* = 6.3 Hz, 18H, $CH_3$). $^{13}$C NMR (100 MHz, Acetone-$d_6$, 40 °C), δ (ppm): 166.9, 160.2, 156.0, 153.7, 151.1, 146.0, 144.2, 143.6, 142.5, 130.3, 130.0, 126.3, 125.9, 116.8, 116.6, 116.1, 115.4, 111.7, 110.1, 73.9, 71.8, 70.6, 69.9, 68.9, 68.7, 52.4, 32.7, 31.1, 30.5, 30.5, 30.5, 30.4, 30.3, 30.2, 30.2, 30.1, 30.0, 29.8, 29.6, 29.5, 29.3, 27.0, 26.9, 26.9, 26.6, 23.4, 14.4. IR (KBr, $cm^{-1}$): 2920 ($Csp^3$-H), 2851 ($Csp^3$-H), 1719 (C=O), 1506 (arC-C), 1469 (arC-C), 1232 (C-O).

**Methyl 3,5-bis(4-dodecyloxybenzyloxy)-4-[6-[4-(*N,N*-bis(3,4,5-tridodecyloxyphenyl)amino) phenoxy]hexyloxy]benzoate (10c).** Off-white solid. Yield: 37%. $^1$H NMR (300 MHz, Acetone-$d_6$), δ (ppm): 7.46 – 7.39 (m, 6H, ArH), 7.07 – 7.01 (m, 2H, ArH TPA), 6.97 – 6.90 (m, 4H, ArH), 6.89 – 6.84 (m, 2H, ArH TPA), 6.26 (s, 4H, ArH TPA), 5.10 (s, 4H, $OCH_2Ph$), 4.05 (t, *J*= 6.1 Hz, 2H, $OCH_2$), 3.98 (t, *J* = 6.5 Hz, 4H, $OCH_2$), 3.90 (t, *J* = 6.3 Hz, 6H, $OCH_2$), 3.85 (s, 3H, $OCH_3$), 3.80 (t, *J* = 6.3 Hz, 8H, $OCH_2$), 1.80 – 1.64 (m, 20H, $CH_2$), 1.58 – 1.24 (m, 148H, $CH_2$), 0.92 – 0.81 (m, 24H, $CH_2$).

### 3,5-bis(4-dodecyloxybenzyloxy)-4-[6-[4-(*N,N*-bis(aryl)amino)phenoxy]hexyloxy]benzoic acids



0.4 mmol of the corresponding methyl benzoate precursor **11a-c** were dissolved in 20 mL of 1,4-dioxane. The solution was heated to 80 °C and 0.20 g (3.6 mmol) of KOH dissolved in 1.5 mL of distilled water were added. The reaction was stirred at 80 °C for 16 hours. After this time, the reaction mixture was cooled to room temperature, diluted with distilled water, put in an ice bath and acidified to pH 3 with 1N HCl. After stirring the mixture for 4 hours, it was extracted with ethyl acetate (3x50mL). The combined organic phases were washed with distilled water and saturated NaCl solution, dried with anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the product was purified following the appropriate procedure in each case.

**3,5-bis(4-dodecyloxybenzyloxy)-4-[6-[4-(*N,N*-bis(4-dodecyloxyphenyl)amino)phenoxy] hexyloxy]benzoic acid (A-2BnOC$_{12}$-TPA2C$_{12}$)** was purified by flash chromatography on silica gel using mixture hexane/ethyl acetate as eluent (from hexane to hexane / ethyl acetate 1/1) to obtain the product as a yellowish soft solid. Yield: 63%. $^1$H NMR (400 MHz, Acetone-d$_6$, 40 °C), δ (ppm): 7.46 – 7.40 (m, 6H, ArH), 6.97 – 6.88 (m, 10H, ArH + ArH TPA), 6.85 – 6.79 (m, 6H, ArH TPA), 5.10 (s, 4H, OCH$_2$Ph), 4.06 (t, *J* = 6.3 Hz, 2H, OCH$_2$), 3.99 (t, *J* = 6.5 Hz, 4H, OCH$_2$), 3.95 (t, *J* = 6.5 Hz, 4H, OCH$_2$), 3.89 (t, *J* = 6.5 Hz, 2H, OCH$_2$), 1.81 – 1.64 (m, 12H, CH$_2$), 1.54 – 1.24 (m, 76H, CH$_2$), 0.88 (t, *J* = 6.8 Hz, 12H, CH$_3$). $^{13}$C NMR (100 MHz, Acetone-d$_6$, 40 °C), δ (ppm): 167.3, 160.2, 155.7, 153.6, 144.1, 142.9, 142.9, 130.3, 130.0, 126.2, 125.7, 116.2, 116.2, 115.4, 110.4, 73.9, 71.8, 69.0, 68.9, 68.7, 32.7, 31.1, 30.5, 30.4, 30.3, 30.2, 30.1, 30.1, 30.1, 29.9, 29.7, 26.9, 26.9, 26.6, 26.6, 23.4, 14.4. IR (KBr, cm$^{-1}$): 3500-2400 (COOH), 2924 (Csp$^3$-H), 2854 (Csp$^3$-H), 1683 (C=O), 1503 (arC-C), 1469 (arC-C), 1237 (C-O). MS (MALDI+, dithranol): 1431.9 [M]$^+$, 1454.9 [M+Na]$^+$, 1476.9 [M-H+2Na]$^+$. EA (%): calc. for $C_{93}H_{139}NO_{10}\cdot H_2O$: C 77.08, H 9.81, N 0.97; exp.: C 76.88, H 10.12, N 0.95.

**3,5-bis(4-dodecyloxybenzyloxy)-4-[6-[4-(*N,N*-bis(3,4-didodecyloxyphenyl)amino)phenoxy] hexyloxy]benzoic acid (A-2BnOC$_{12}$-TPA4C$_{12}$)** was purified by recrystallization from acetone to obtain the product as an off-white solid. Yield: 71%. $^1$H NMR (400 MHz, Acetone-d$_6$, 40 °C), δ (ppm): 7.47 – 7.39 (m, 6H, ArH), 7.00 – 6.90 (m, 6H, ArH + ArH TPA), 6.86 – 6.78 (m, 4H, ArH TPA), 6.64 (d, *J* = 2.5 Hz, 2H, ArH TPA), 6.47 (dd, *J* = 8.6, 2.5 Hz, 2H, ArH TPA), 5.10 (s, 4H, OCH$_2$Ph), 4.06 (t, *J* = 6.2 Hz, 2H, OCH$_2$), 3.98 (t, *J* = 6.5 Hz, 4H, OCH$_2$), 3.95 (t, *J* = 6.4 Hz, 4H, OCH$_2$), 3.89 (t, *J* = 6.5 Hz, 2H, OCH$_2$), 3.84 (t, *J* = 6.4 Hz, 4H, OCH$_2$), 1.81 – 1.64 (m, 16H, CH$_2$), 1.56 – 1.24 (m, 112H, CH$_2$), 0.93 – 0.84 (m, 18H, CH$_3$). $^{13}$C NMR (100 MHz, Acetone-d$_6$, 40 °C), δ (ppm): 167.3, 160.2, 156.0, 153.6, 151.1, 146.0, 144.1, 143.6, 142.5, 130.3, 130.0, 126.3, 126.2, 116.8, 116.6, 116.1, 115.4, 111.7, 110.4, 73.9, 71.8, 70.6, 69.9, 68.9, 68.7, 32.7, 31.1, 30.5, 30.5, 30.5, 30.3, 30.2, 30.2, 30.1, 30.1, 29.9, 29.7, 27.0, 26.9, 26.9, 26.6, 23.4, 14.4. IR (KBr, cm$^{-1}$): 3500-2400 (COOH), 2921 (Csp$^3$-H), 2851 (Csp$^3$-H), 1685 (C=O), 1506 (arC-C), 1468 (arC-C), 1248 (C-O), 1232 (C-O). MS (MALDI+, dithranol): 1800.3 [M]$^+$, 1823.3 [M+Na]$^+$, 1845.4 [M-H+2Na]$^+$. EA (%): calc. for $C_{117}H_{187}NO_{12}\cdot H_2O$: C 77.31, H 10.48, N 0.77; exp.: C 77.59, H 10.24, N 0.92.

**3,5-bis(4-dodecyloxybenzyloxy)-4-[6-[4-(*N,N*-bis(3,4,5-tridodecyloxyphenyl)amino)phenoxy] hexyloxy]benzoic acid (A-2BnOC$_{12}$-TPA6C$_{12}$)** was purified by recrystallization from acetone to obtain the product as an off-white solid. Yield: 57%. $^1$H NMR (400 MHz, Acetone-d$_6$, 40 °C), δ (ppm): 7.47 – 7.40 (m, 6H, ArH), 7.08 – 7.01 (m, 2H, ArH TPA), 6.97 – 6.91 (m, 4H, ArH), 6.90 – 6.84 (m, 2H, ArH TPA), 6.27 (s, 4H, ArH TPA), 5.10 (s, 4H, OCH$_2$Ph), 4.07 (t, *J* = 6.2 Hz, 2H, OCH$_2$), 3.99 (t, *J* = 6.5 Hz, 4H, OCH$_2$), 3.92 (t, *J* = 6.4 Hz, 6H, OCH$_2$), 3.82 (t, *J* = 6.3 Hz, 8H, OCH$_2$), 1.81 – 1.65 (m, 20H, CH$_2$), 1.59 – 1.24 (m, 148H, CH$_2$), 0.94 – 0.85 (m, 24H, CH$_2$). $^{13}$C NMR (100 MHz, Acetone-d$_6$, 40 °C), δ (ppm): 167.3, 160.2, 156.6, 154.4, 153.6, 144.8, 144.1, 141.7, 135.0, 130.3, 130.1, 127.5, 126.2, 116.2, 115.4, 110.4, 103.6, 73.9, 73.8, 71.8, 69.7, 68.9, 68.7, 32.7, 31.3, 31.1, 30.6, 30.6, 30.5, 30.5, 30.5, 30.5, 30.3, 30.2, 30.1, 30.1, 29.9, 29.7, 27.1, 27.0, 26.9, 26.6, 23.4, 14.4. IR (KBr, cm$^{-1}$): 3500-2400 (COOH), 2921 (Csp$^3$-H), 2851 (Csp$^3$-H), 1688 (C=O), 1589 (arC-C), 1516 (arC-C), 1502 (arC-C), 1468 (arC-C), 1240 (C-O). MS (MALDI+, dithranol): 2167.6 [M]$^+$. EA (%): calc. for $C_{141}H_{235}NO_{14}\cdot H_2O$: C 77.46, H 10.93, N 0.64; exp.: C 77.43, H 10.46, N 0.66.

## MS MALDI characterization of the acids

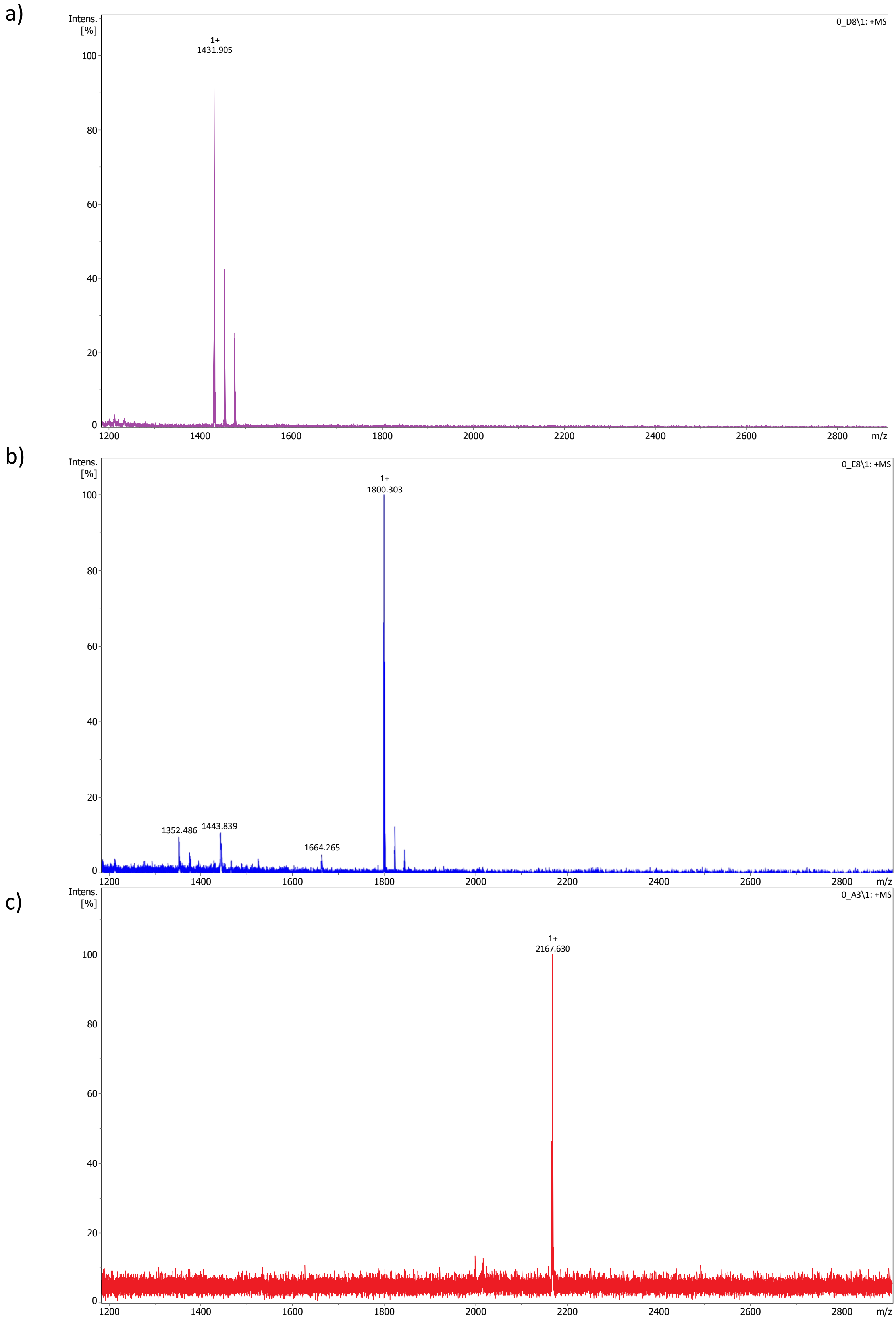
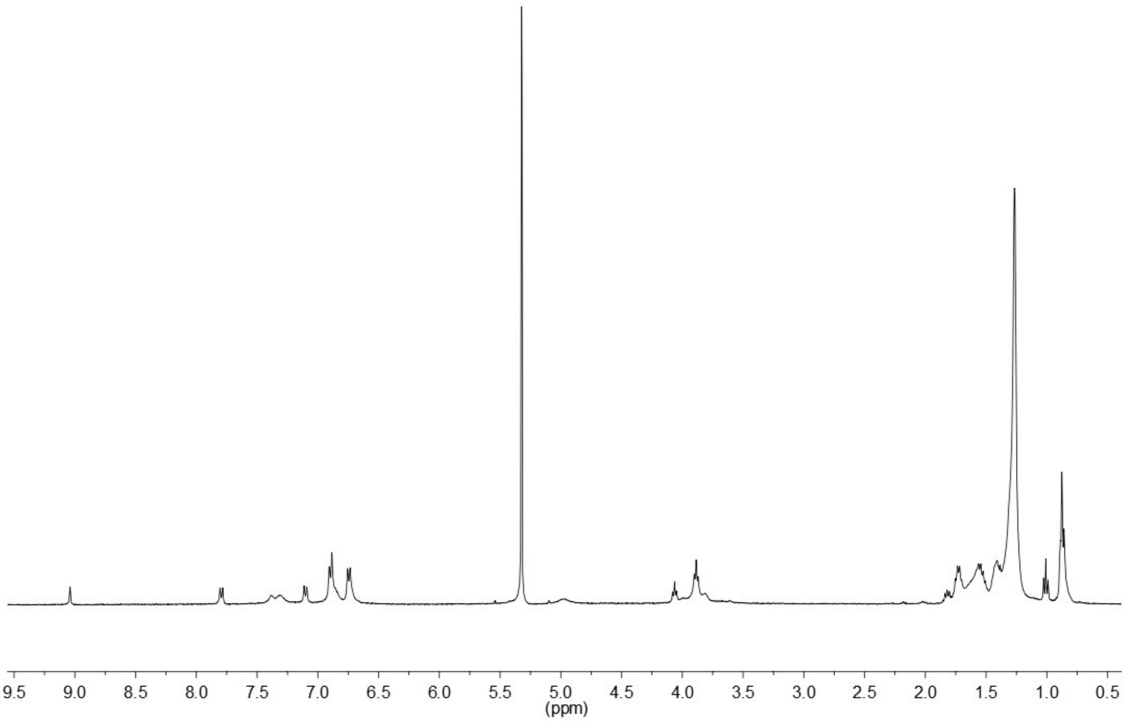


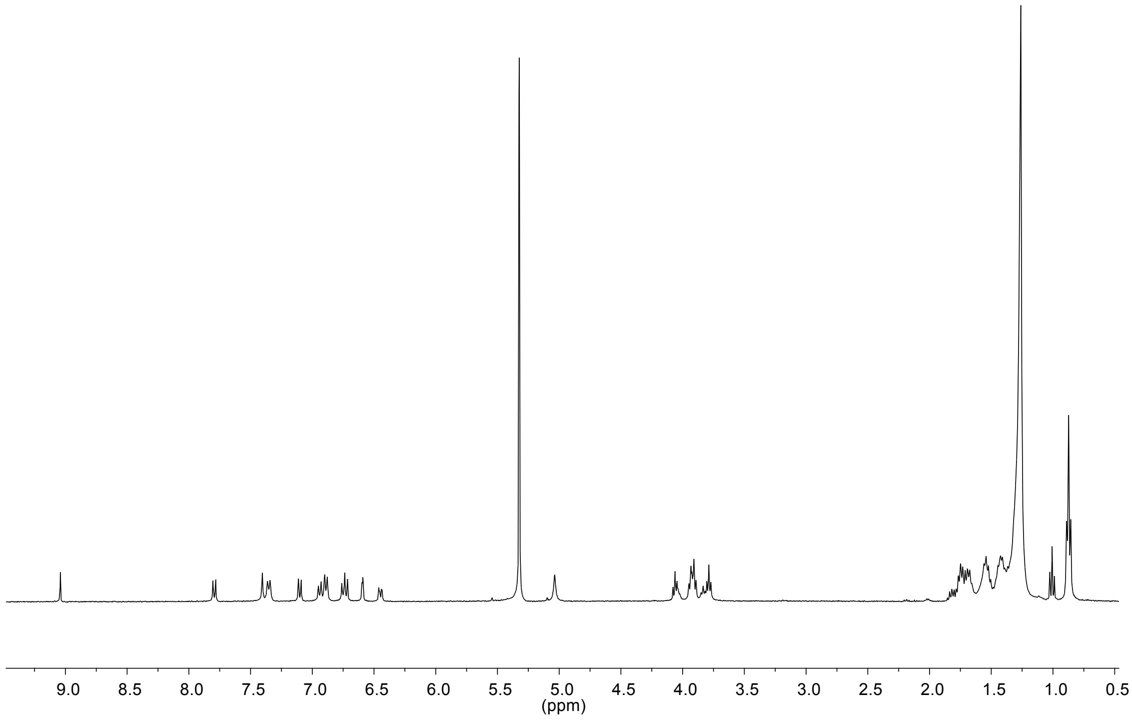
**Figure S1.** MS spectra of acids (a) **A-2BnOC$_{12}$-TPA2C$_{12}$,** (b) **A-2BnOC$_{12}$-TPA4C$_{12}$** and (c) **A-2BnOC$_{12}$-TPA6C$_{12}$**.

**NMR characterization**

a)



b)



c)

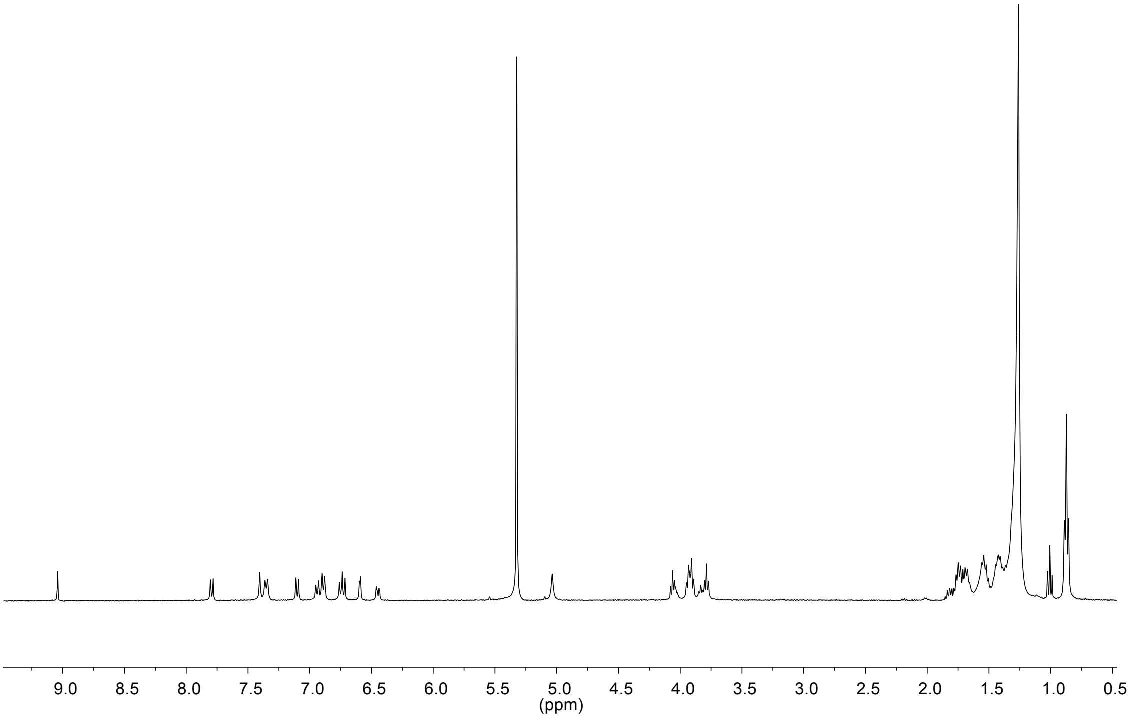


**Figure S2.** $^1$H NMR spectra in $CD_2Cl_2$ of the solution of **T3C$_4$** and each of the acids (a) **A-2BnOC$_{12}$-TPA2C$_{12}$,** (b) **A-2BnOC$_{12}$-TPA4C$_{12}$** and (c) **A-2BnOC$_{12}$-TPA6C$_{12}$**, in a 1:3 ratio, respectively.

**FTIR**

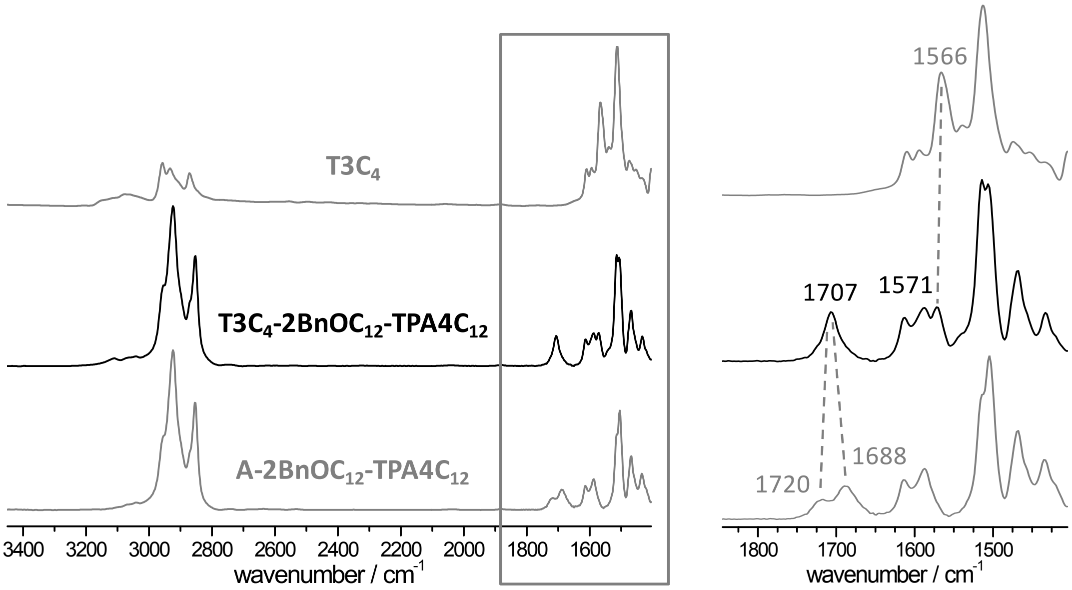


**Figure S3**. FTIR spectra measured in KBr pellets at r.t. of **T3C$_4$**, the acid **A-2BnOC$_{12}$-TPA4C$_{12}$** and the corresponding supramolecular complex **T3C$_4$-2BnOC$_{12}$-TPA4C$_{12}$**.

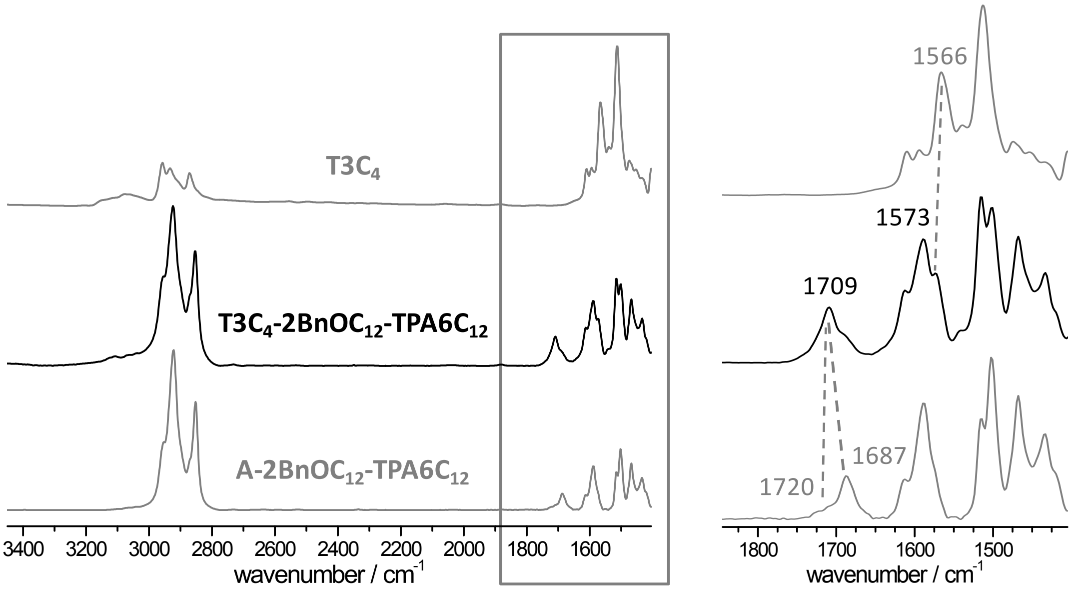
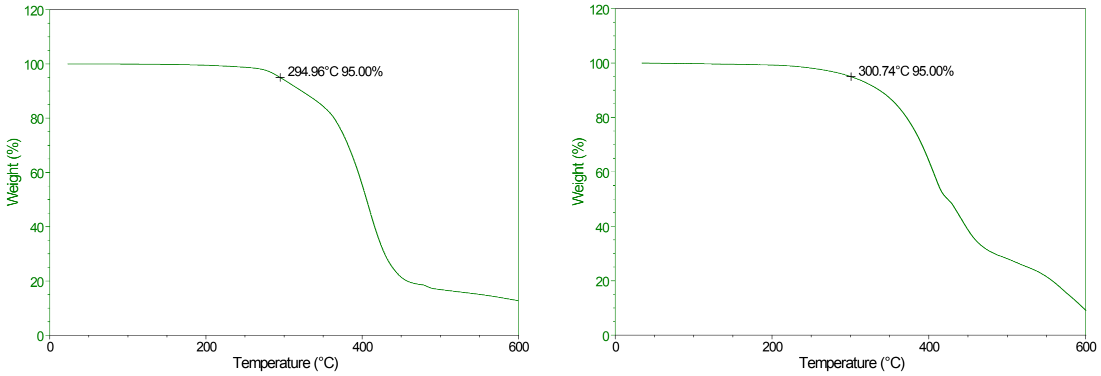


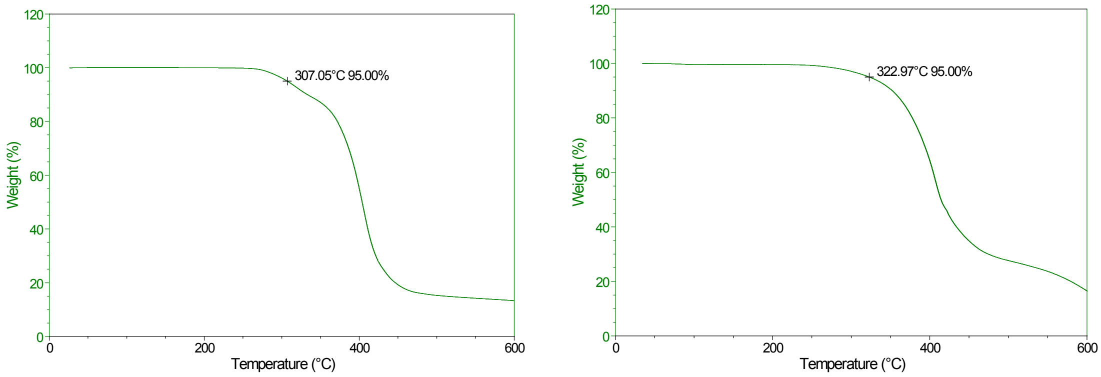
**Figure S4**. FTIR spectra measured in KBr pellets at r.t. of **T3C$_4$**, the acid **A-2BnOC$_{12}$-TPA6C$_{12}$** and the corresponding supramolecular complex **T3C$_4$-2BnOC$_{12}$-TPA6C$_{12}$**.

# Thermal stability. Thermogravimetric analysis

**T3C$_4$-2BnOC$_{12}$-TPA2C$_{12}$** **A-2BnOC$_{12}$-TPA2C$_{12}$**



**T3C$_4$-2BnOC$_{12}$-TPA4C$_{12}$** **A-2BnOC$_{12}$-TPA4C$_{12}$**



**T3C$_4$-2BnOC$_{12}$-TPA6C$_{12}$** **A-2BnOC$_{12}$-TPA6C$_{12}$**

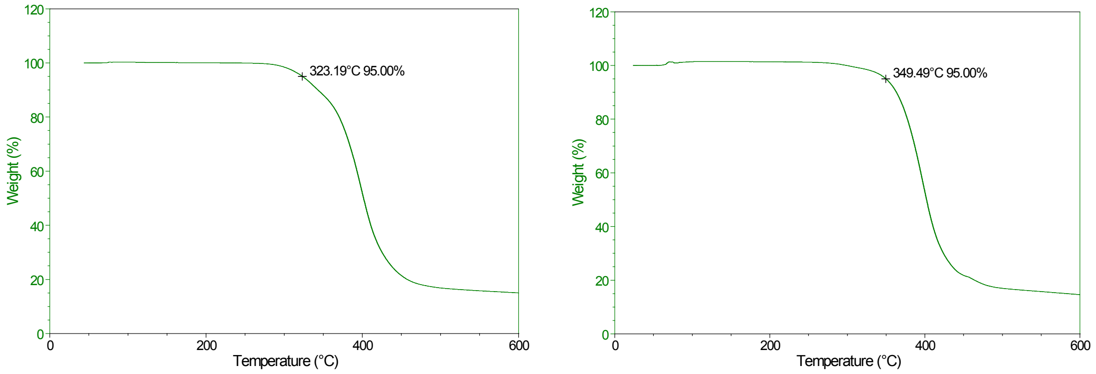


**Figure S5**. TGA thermograms of complexes and their corresponding acid component. Shown is the temperature at which a 5% weight loss is observed.

## Liquid crystalline properties

### Liquid crystalline properties of the acids

All acids showed liquid crystalline behavior at room temperature on cooling the isotropic liquid. By POM, no characteristic textures were observed (Figure S6). The acid **A-2BnOC12-TPA2C12** showed a hexagonal columnar mesophase as confirmed by X-ray diffraction (Figure S10a and Table S2). Acids **A-2BnOC$_{12}$-TPA4C$_{12}$** and **A-2BnOC$_{12}$-TPA6C$_{12}$** showed a complex thermal behavior in their DSC thermograms (Table S1 and Figures S8-S9). Unfortunately, X-ray diffractograms did not allow to obtain further information in order to assign the mesophase (Figure S10 and Table S2).

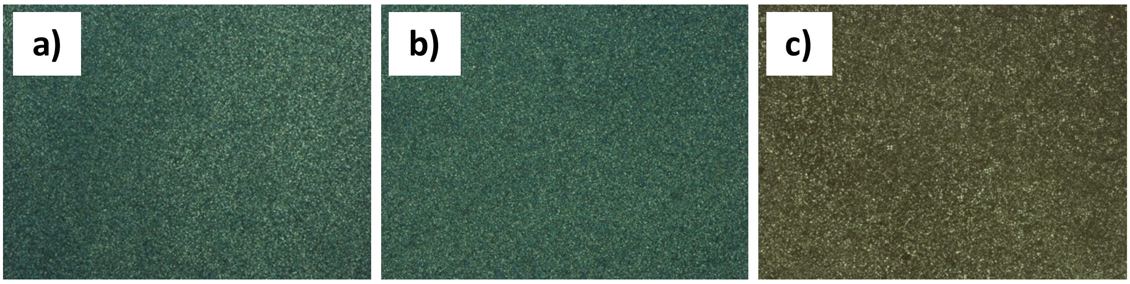


**Figure S6.** (a) **A-2BnOC$_{12}$-TPA2C$_{12}$**, r.t. (cooling), (b) **A-2BnOC$_{12}$-TPA4C$_{12}$** 55°C (cooling) and (c) **A-2BnOC$_{12}$-TPA6C$_{12}$**, r.t. (cooling).

**Table S1.** Thermal properties (transition temperatures and enthalpies) of the triphenylamine-containing benzoic acids.

| **Acid** | **Thermal properties (T °C, [ΔH kJ/mol])** |
|---|---|
| **A-2BnOC$_{12}$-TPA2C$_{12}$** | Col$_h$ 60 [6.0] I (a) |
| **A-2BnOC$_{12}$-TPA4C$_{12}$** | Cr 64 [88.2] I (a) |
| | I 56 [5.8] M 3 [23.8] X (b) |
| | X 12 [23.8] M 38 [-7.9] M + Cr 56 -60 [34.0] I (c) |
| **A-2BnOC$_{12}$-TPA6C$_{12}$** | Cr 66 [158.3] I (a) |
| | I 24 [3.8] M (b) |
| | M 33 [-54.8] Cr' 49 [55.9] Cr' + I 54 [-25.5] Cr 65 [57.4] I (c) |

(a) 1st heating, (b) 1st cooling and (c) 2nd heating

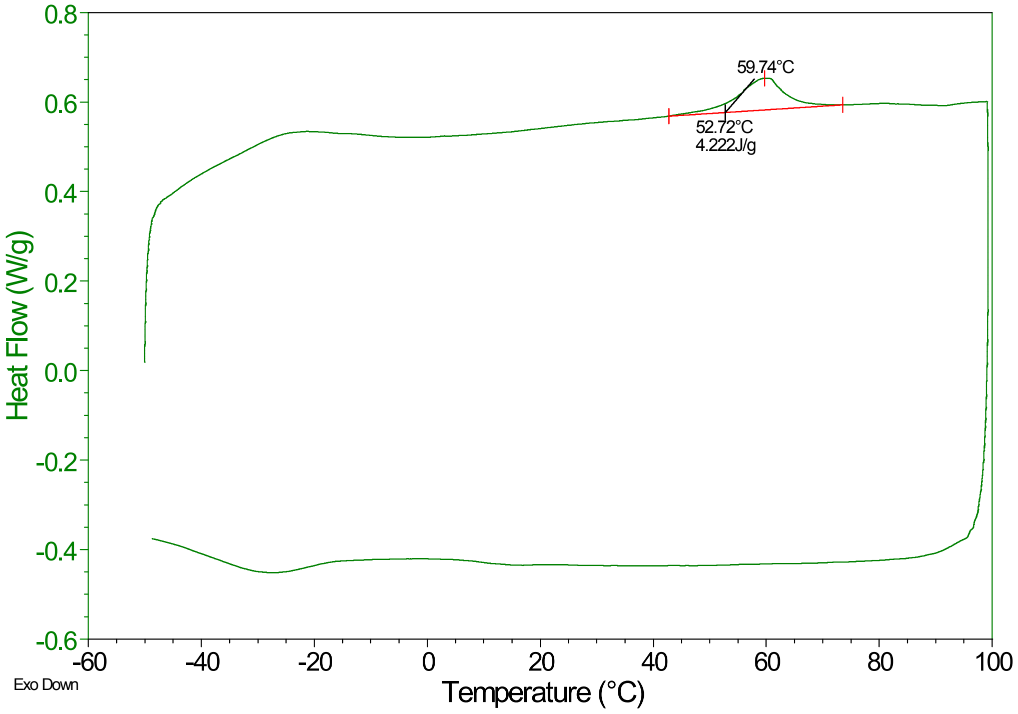


**Figure S7.** DSC thermogram of acid **A-2BnOC$_{12}$-TPA2C$_{12}$** (1st heating/cooling cycle, 10$^{o}$C/min).

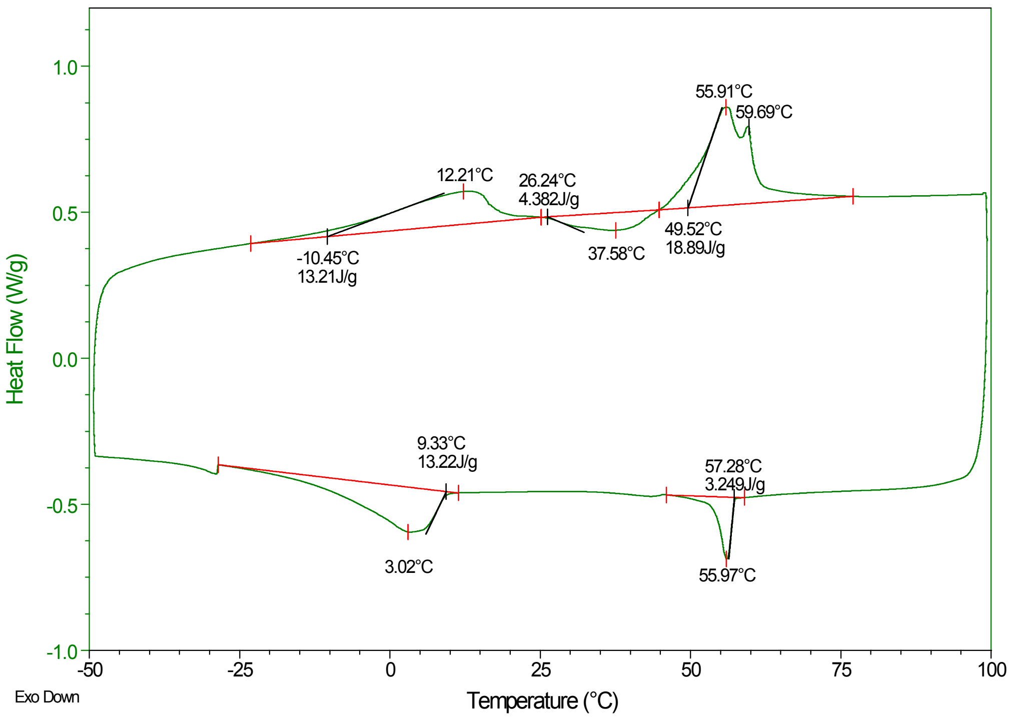


**Figure S8.** DSC thermogram of acid **A-2BnOC$_{12}$-TPA4C$_{12}$** (2nd heating-cooling cycle, 10$^{o}$C/min).

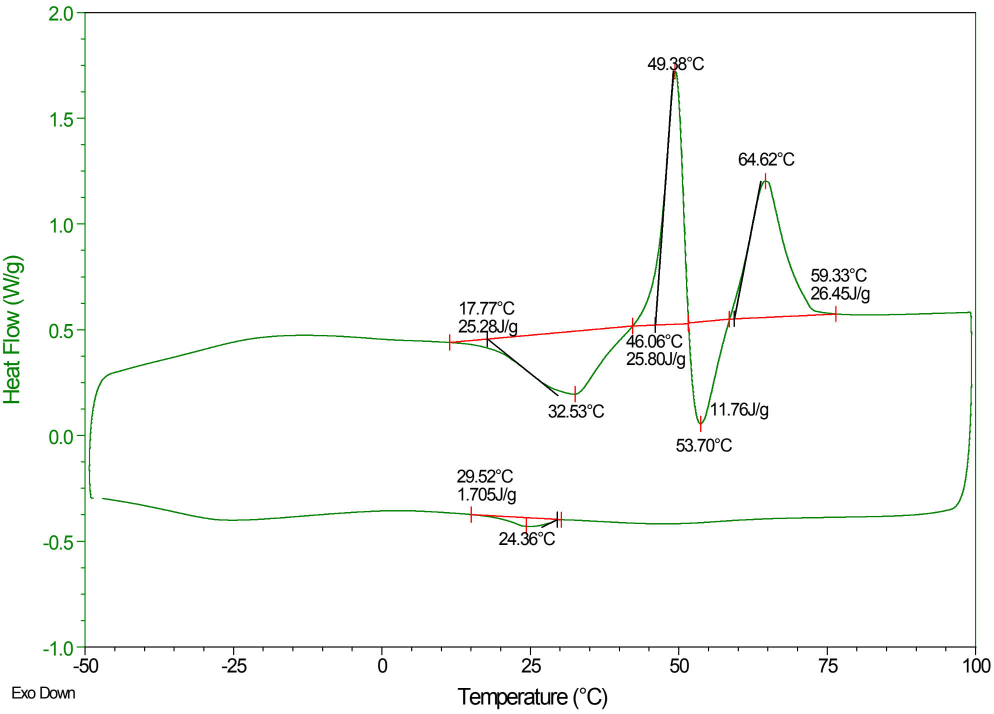


**Figure S9.** DSC thermogram of acid **A-2BnOC$_{12}$-TPA6C$_{12}$** (2nd heating-cooling cycle, 10°C/min).

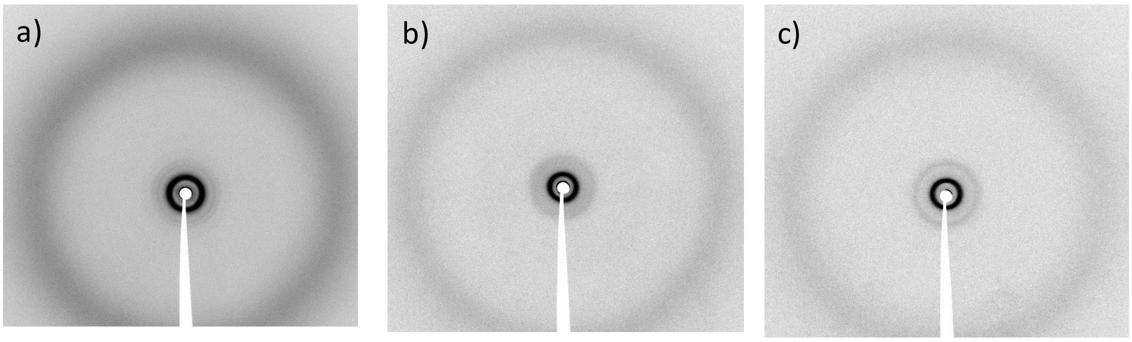


**Figure S10.** X-ray diffractograms of the triphenylamine-containing benzoic acids, recorded at room temperature in samples cooled from the isotropic liquid of (a) **A-2BnOC$_{12}$-TPA2C$_{12}$**, (b) **A-2BnOC$_{12}$-TPA4C$_{12}$**, and (c) **A-2BnOC$_{12}$-TPA6C$_{12}$**.

**Table S2.** X-ray diffraction data of the triphenylamine-containing benzoic acids.

| Acid | T (°C) | Mesophase | $d_{obs}$ (Å) |
|---|---|---|---|
| **A-2BnOC$_{12}$-TPA2C$_{12}$** | r.t. | Col$_h$ | 38.9<br>22.4<br>19.5<br>4.5 (dif) |
| **A-2BnOC$_{12}$-TPA4C$_{12}$** | r.t. | M[a] | 49.3<br>21.8<br>4.5 (dif) |
| **A-2BnOC$_{12}$-TPA6C$_{12}$** | r.t. | M[a] | 46.6<br>21.0<br>4.5 (dif) |

[a] The structural parameters of the mesophase could not be determined from the maxima observed in the diffraction patterns.

## Liquid crystalline properties of the supramolecular complexes

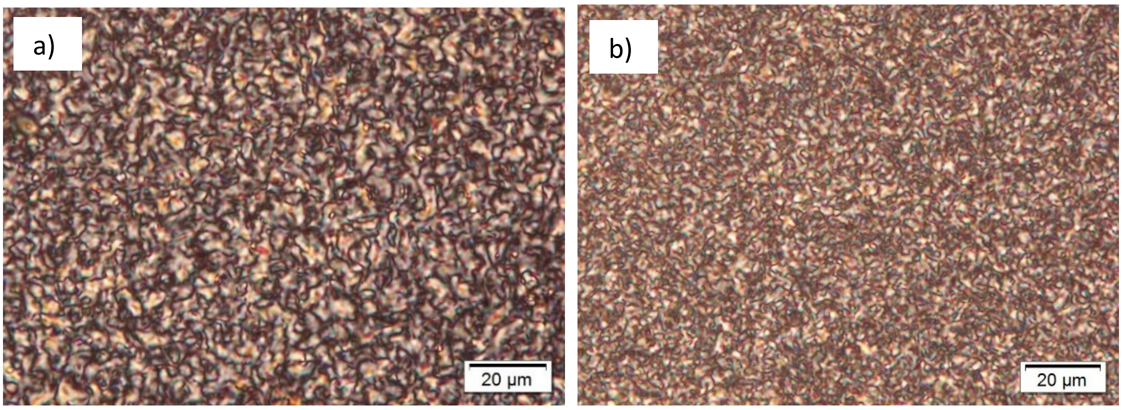


**Figure S11.**Photomicrographs of textures observed by POM, on cooling from the isotropic liquid, for (a) **T3C$_4$-2BnOC$_{12}$-TPA4C$_{12}$** at 75 °C, 0.1 °C/min, and (b) **T3C$_4$-2BnOC$_{12}$-TPA6C$_{12}$** at 55 °C, 1 °C/min.

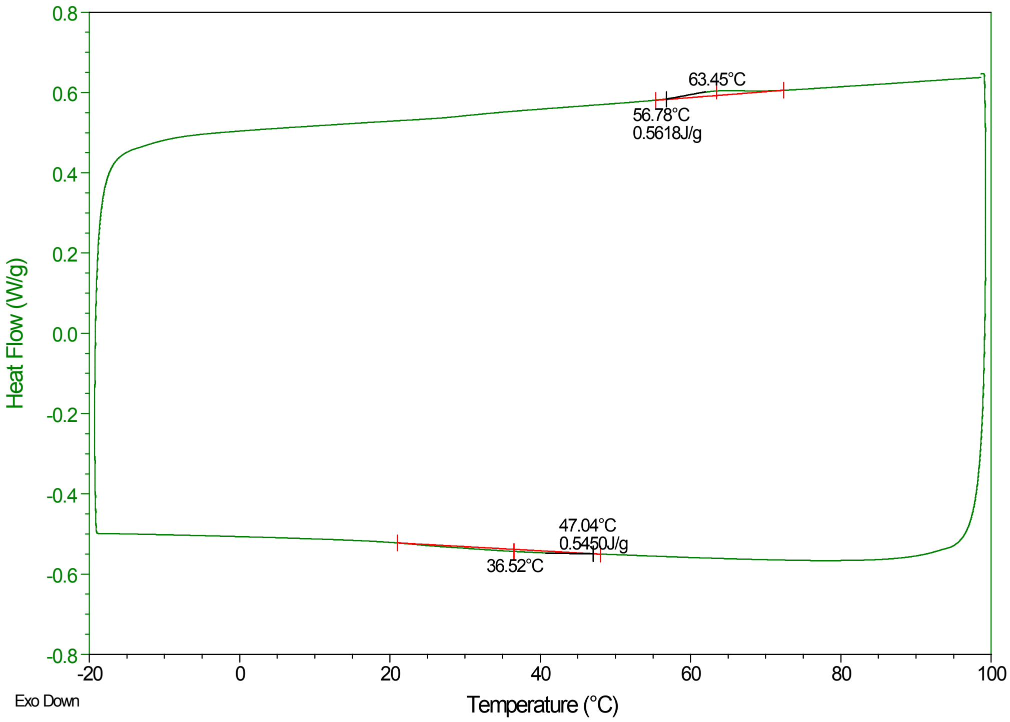


**Figure S12.** DSC thermogram of **T3C$_4$-2BnOC$_{12}$-TPA2C$_{12}$** (2nd heating-cooling cycle, 10°C/min).

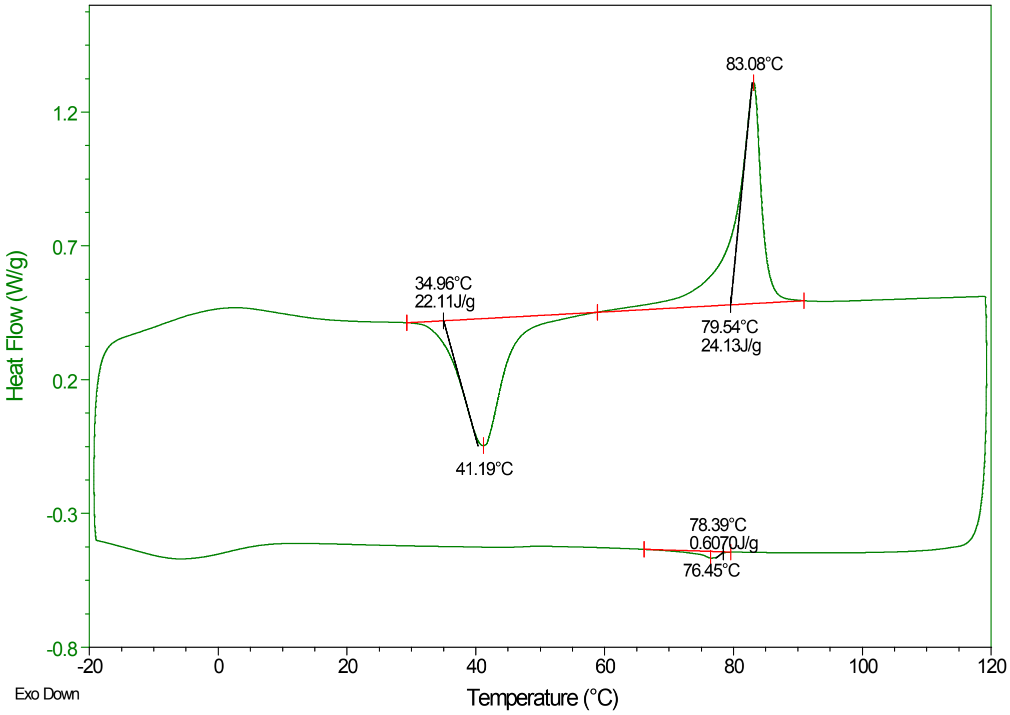


**Figure S13.** DSC thermogram of **T3C$_4$-2BnOC$_{12}$-TPA4C$_{12}$** (2nd heating-cooling cycle, 10$^o$C/min).

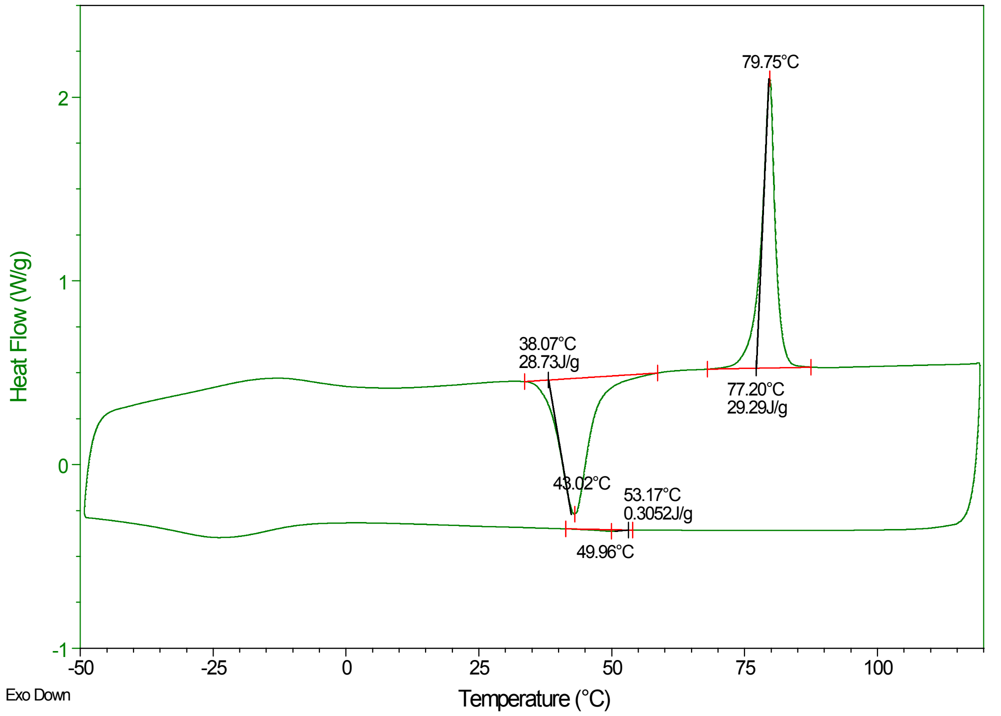


**Figure S14.** DSC thermogram of **T3C$_4$-2BnOC$_{12}$-TPA6C$_{12}$** (2nd heating-cooling cycle, 10$^o$C/min).

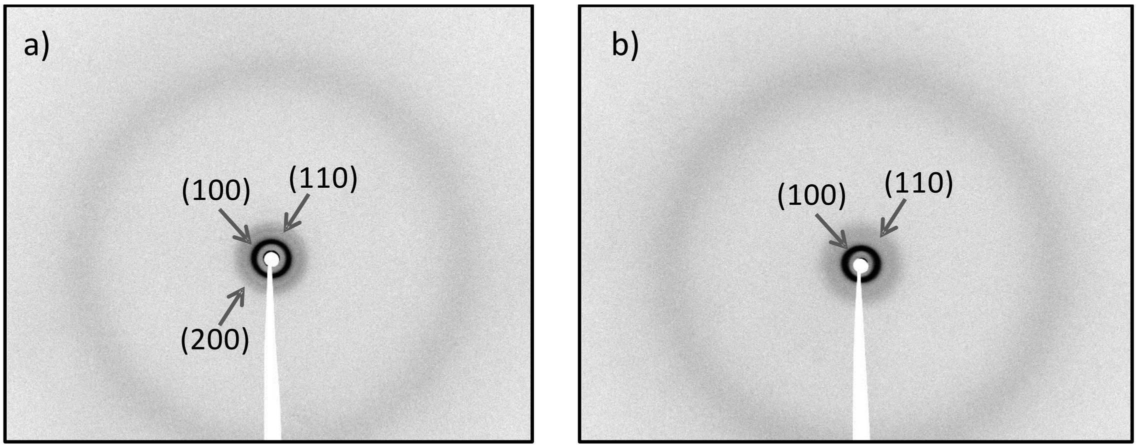


**Figure S15**. X-ray diffractograms taken at r.t. for the supramolecular complexes cooled from the isotropic liquid: (a) **T3C$_4$-2BnOC$_{12}$-TPA4C$_{12}$** and (b) **T3C$_4$-2BnOC$_{12}$-TPA6C$_{12}$**.

**Table S3.** X-ray diffraction data of the supramolecular complexes **T3C$_4$-2BnOC$_{12}$-TPA2C$_{12}$**, **T3C$_4$-2BnOC$_{12}$-TPA4C$_{12}$** and **T3C$_4$-2BnOC$_{12}$-TPA6C$_{12}$**.

| **Complex** | **T (°C)** | **Mesophase** | **Lattice parameters** | **d$_{obs}$ (Å)** | **d$_{calc}$ (Å)** | **Miller index (hkl)** |
|---|---|---|---|---|---|---|
| **T3C$_4$-2BnOC$_{12}$-TPA2C$_{12}$** | r.t. | Col$_h$ | *a* = 46.2 Å | 40.0<br>23.1<br>20.0<br>4.5 (dif) | 40.0<br>23.1<br>20.0 | 100<br>110<br>200 |
| **T3C$_4$-2BnOC$_{12}$-TPA4C$_{12}$** | r.t. | Col$_h$ | *a* = 54.3 Å | 47.0<br>27.4<br>23.1<br>4.5 (dif) | 47.0<br>27.1<br>23.5 | 100<br>110<br>200 |
| **T3C$_4$-2BnOC$_{12}$-TPA6C$_{12}$** | r.t. | Col$_h$ | *a* = 55.1 Å | 47.7<br>27.7<br>4.5 (dif) | 47.7<br>27.5 | 100<br>110 |

# Electrochemical studies

## Electrochemical properties of the supramolecular complexes

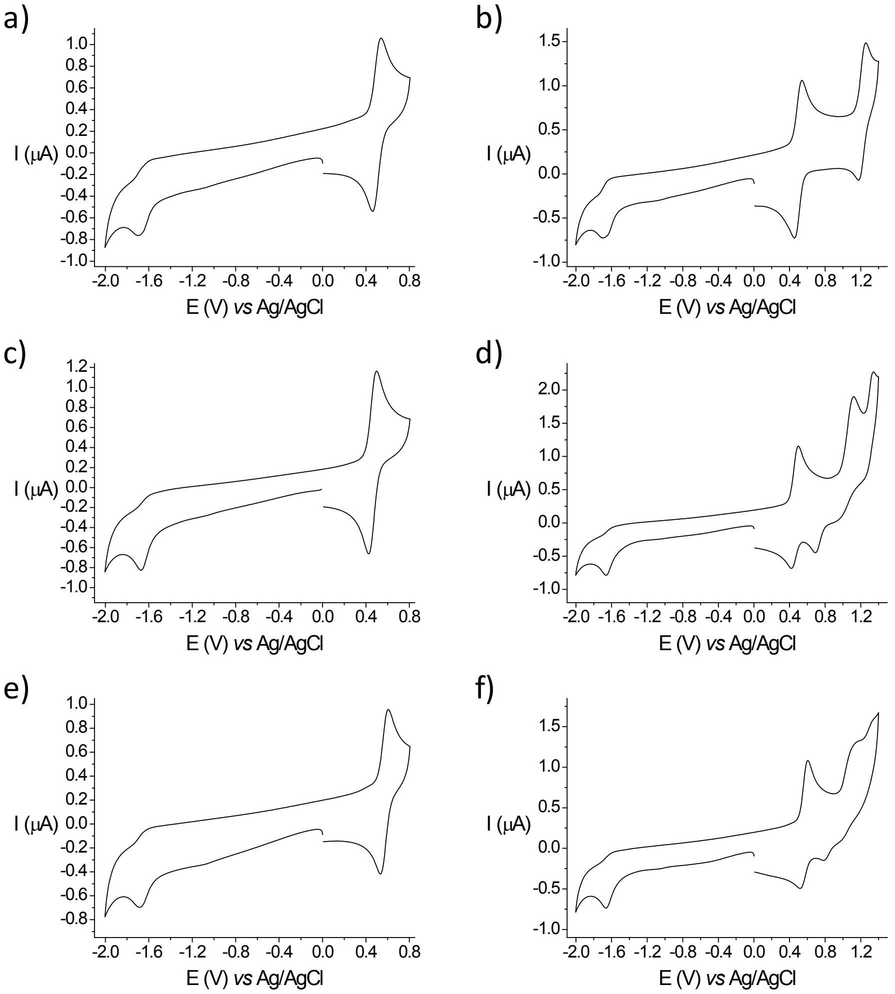


**Figure S16.** Cyclic voltamperograms in 0.1 M $TBAPF_6$ solution in $CH_2Cl_2$ of the supramolecular complexes (a, b) **T3C$_4$-2BnOC$_{12}$-TPA2C$_{12}$**, (c, d) **T3C$_4$-2BnOC$_{12}$-TPA4C$_{12}$** and (e, f) **T3C$_4$-2BnOC$_{12}$-TPA6C$_{12}$**.

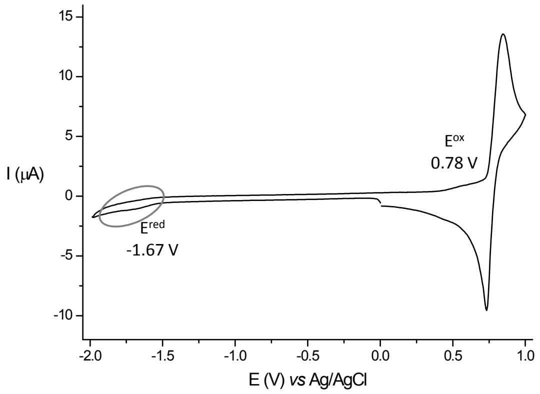


**Figure S17.** Cyclic voltamperogram of complex **T3C$_4$-2BnOC$_{12}$-TPA2C$_{12}$** film in 0.1 M $TBAPF_6$ solution in acetonitrile.

## Electrochemical properties of the acids

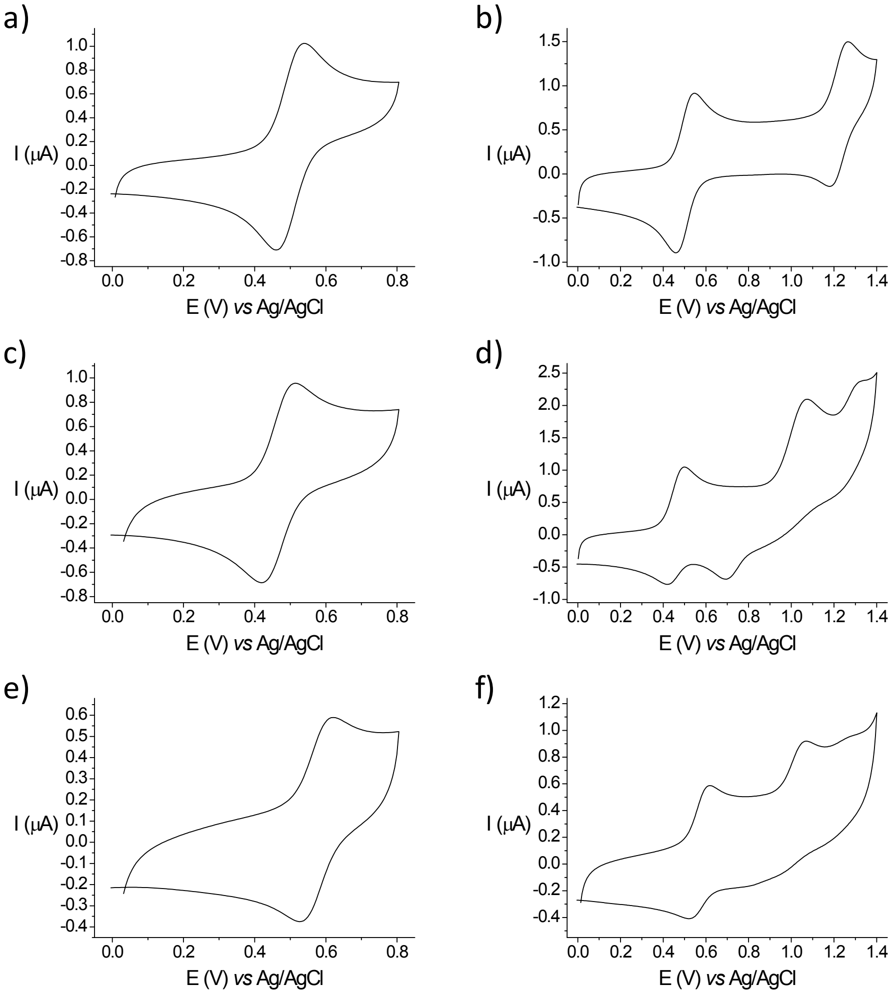


**Figure S18.** Cyclic voltamperograms in 0.1 M $TBAPF_6$ solution in $CH_2Cl_2$ of the acids (a, b) **A-2BnOC$_{12}$-TPA2C$_{12}$**, (c, d) **A-2BnOC$_{12}$-TPA4C$_{12}$** y (e, f) **A-2BnOC$_{12}$-TPA6C$_{12}$**.

**Table S4.** Electrochemical data of the triphenylamine-containing benzoic acids in $CH_2Cl_2$.

| Acid | $E^{red}$ *vs* Ag/AgCl /V | $E_{1/2}^{ox}$ *vs* Ag/AgCl /V | $E^{red}$ *vs* FOC /V[a] | $E_{1/2}^{ox}$ *vs* FOC /V[a] | HOMO /eV[b] | LUMO /eV[c] |
|---|---|---|---|---|---|---|
| **A-2BnOC$_{12}$-TPA2C$_{12}$** | -[d] | 0.51 | - | 0.09 | -4.89 | - |
| **A-2BnOC$_{12}$-TPA4C$_{12}$** | -[d] | 0.46 | - | 0.04 | -4.84 | - |
| **A-2BnOC$_{12}$-TPA6C$_{12}$** | -[d] | 0.58 | - | 0.16 | -4.96 | - |

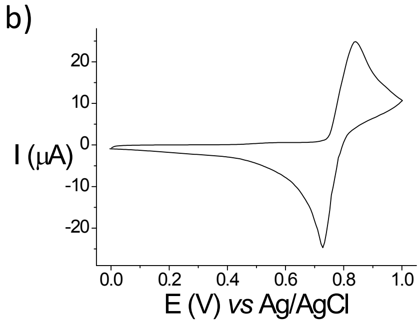


**Figure S19.** Cyclic voltamperogram of acid **A-2BnOC$_{12}$-TPA2C$_{12}$** film in 0.1 M TBAPF$_6$ solution in acetonitrile.

**Table S5.** Electrochemical data in thin film.

| **Acid** | **$E^{red}$ *vs* Ag/AgCl /V** | **$E_{1/2}^{ox}$ *vs* Ag/AgCl /V** | **$E^{red}$ *vs* FOC /V[a]** | **$E_{1/2}^{ox}$ *vs* FOC /V[a]** | **HOMO /eV[b]** | **LUMO /eV[c]** |
|---|---|---|---|---|---|---|
| **A-2BnOC$_{12}$-TPA2C$_{12}$** | -[d] | 0.77 | - | 0.34 | -5.14 | - |

## Charge mobility Measurements

The charge mobility of compound **T3C$_4$-2BnOC$_{12}$-TPA2C$_{12}$** was measured by the Space-Charge Limited Current (SCLC) method, which is commonly used to measure charge mobility in semiconductors. It entails the acquisition of the electric current flowing through the material, placed between two electrodes, as a function of the applied voltage. For low applied voltages, the current follows Ohm's law, while at higher voltages, if it is limited by a space-charge field, the current dependence on voltage is quadratic, following the Mott-Gurney law, in which the effect of the traps is neglected:

$$J = \frac{9}{8}\varepsilon_r \varepsilon_0 \mu \frac{V^2}{d^3} \tag{1}$$

where J is the current density, μ is the charge mobility, $\varepsilon_0$ is the dielectric constant of vacuum, $\varepsilon_r$ is the relative dielectric constant of the material, V is the applied voltage and d is the thickness of the device. As an example, an I/V curve acquired for compound **T3C$_4$-2BnOC$_{12}$-TPA2C$_{12}$** is shown in Figure S20.

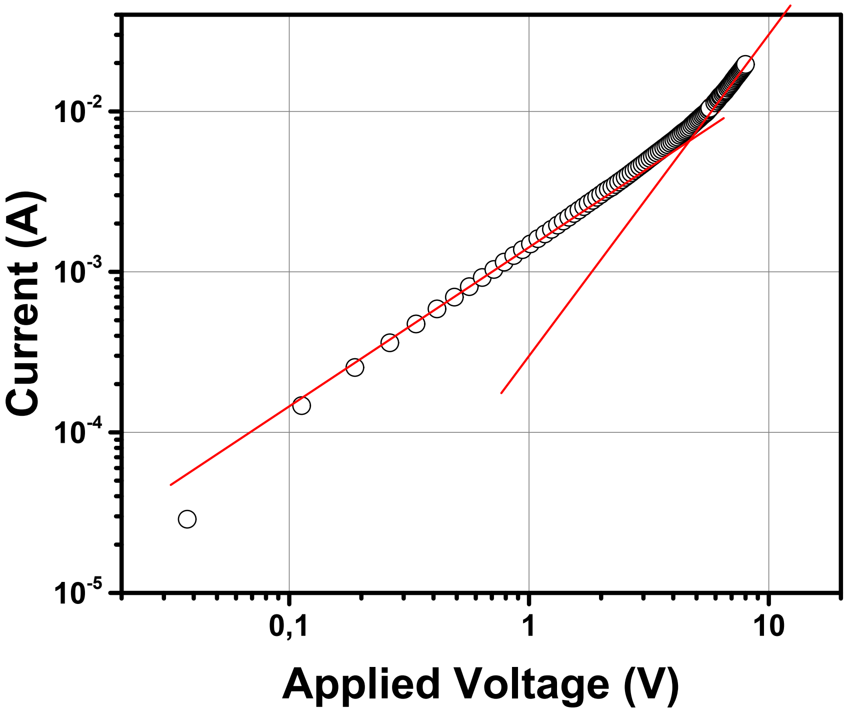


**Figure S20.** Current vs applied voltage for a sample of compound **T3C$_4$-2BnOC$_{12}$-TPA2C$_{12}$**. The red lines are not fittings, but show ideal linear and quadratic behavior.

Meaningful mobility values can be extracted form Equation 1 only if the injecting electrode can operate as a charge-reservoir for the compound, i.e. if the contact between the electrode and the material is ohmic. Usually, in order to obtain an ohmic contact, the difference between the HOMO level energy of the material (in the case of p-conductors, LUMO in the case of n-conductors) and the work function of the injecting electrode must not be higher than 0.3-0.4

eV. Since in the case of compound **$T3C_4$-$2BnOC_{12}$-$TPA2C_{12}$** the energy of HOMO level is -5.15 eV, Au electrodes (work function 5.0-5.1 eV) can be used to obtain an ohmic contact. Therefore, samples to measure hole mobility with SCLC were assembled by overlapping one glass substrate covered by five ITO stripes with another one covered by three gold stripes, controlling the thickness by glass spacers. In this way, it is possible to obtain samples with 15 independent overlapping areas of the electrodes, with an area of 0.6 $mm^2$. The samples thickness was determined by interferometry and it varied between 6 and 12 $\mu$m. In the case of the measurement of electron mobility, both sides of the measuring cells had ITO electrodes covered with ZnO.

The gold electrodes were deposited on glass by evaporation under vacuum, while the substrates covered with five ITO stripes were obtained by photolithography from commercial glass fully covered by ITO (Visiontek 12 $\Omega$/sq., 120 nm thick ITO). The ZnO electrodes were obtained from a solution prepared adding 1g of zinc acetate dehydrate to 10 mL of 2-methoxyethanol, with 0.28 g of ethanolamine as a stabilizing agent, deposited by spin coating (at 5000 RPM for 1 minute) on ITO electrodes already patterned by photolithography. After an annealing at 200°C for 60 minutes, a $\sim$ 40 nm thick ZnO layer was obtained.

Cells were prepared by placing the glass spacers on the corners of one substrate before overlapping with the second substrate. Metallic clips were used to hold together the two substrates. Epoxy glue was then used to keep the two substrates at a fixed distance before removing the metallic clips. A schematic illustration of a cell is shown in Figure S21.

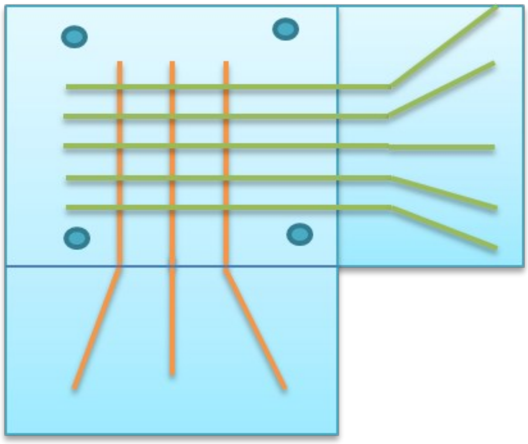


**Figure S21.** Schematic illustration of a measurement cell with three Gold electrodes and five ITO electrodes. Areas in the corners of the cell, where spacers are placed, are indicated.

The samples were prepared by placing the empty cells on a hot plate, adding some of the compound on one side and heating up to 30° C above the melting point. After waiting for the cell to be completely full, the temperature was lowered to 20°C at 0.1°C/min and a first set of I/V measurement was carried out using an electrometer, either a Keithley 6517A or a Keithley 2636B. An HP 4284A Precision LCR Meter was used to measure the capacity of the cells and obtain the dielectric constant. A POM picture of a sample is shown in fig. S22.

**Figure S22.** POM image for compound **T3C$_4$-2BnOC$_{12}$-TPA2C$_{12}$** at 20°C

The resulting currents were very low and, although a quadratic dependence of current from voltage was observed in most areas of samples, the extracted mobilities (between $10^{-8}$ and $10^{-9}$ cm$^2$ V$^{-1}$ s$^{-1}$) carry a scarce physical meaning, being limited by poor mesophase alignment and/or by poor injection. However, it is well known that the homogeneity of mesophase alignment can be greatly improved by slow cooling from the isotropic phase, particularly in the vicinity of the clearing point. Keeping the samples at a constant temperature for some time near the clearing point is also an effective method to slow the cooling rate. The rationale behind such behaviour is that, in slow processes, a lower number of seeds of the lower temperature phase are formed, leading to larger orientational domains and less grain boundaries. For this reason, the following thermal annealing procedure was performed: the sample was heated up to the isotropic phase and then it was cooled at 0.1° C/min down to a few tens of a degree below the clearing point, maintaining that temperature for 600 minutes and then cooled down to 20°C at 0.1° C/min. No significant improvement of the alignment was observed by POM. However, the mobility values extracted from I/V characteristics acquired after thermal annealing were greatly improved. Hole mobilities were extracted from J/V curves by using Equation 1. No dependence of mobility on the applied field was detected. Currents obtained from the samples with ZnO covered electrodes were always very low, probably because of lack of electron injection efficiency into the semiconductor. This prevented an estimation of electron mobility.

## Theoretical calculations

The charge transport was investigated following Marcus theory,[6] according to which the hopping rate constant for charge transfer ($k$) is calculated as:

$$k = \frac{4\pi}{h}\frac{1}{\sqrt{4\pi\lambda k_B T}}t^2 \exp\left(\frac{-\lambda^2}{4\lambda k_B T}\right) \tag{1}$$

where $t$ and $\lambda$ represent the charge transfer integral (or electronic coupling) and the reorganization energy, respectively.[7,8,9] The hole ($t_+$) and electron ($t_-$) transfer integrals were calculated at the ωB97XD/6-31G** level of theory for an optimized stacked dimer of the **T3C$_1$-2BnOC$_1$-TPA2C$_1$** complex using the projective method implemented in the J-from-g03 program.[10, 11] The reorganization energy was calculated from the adiabatic potential energy surface[12] according to $\lambda = \lambda_1 + \lambda_2$ , where:

$$\lambda_1 = E_{c,g} - E_{g,g} \tag{2}$$

$$\lambda_2 = E_{g,c} - E_{c,c} \tag{3}$$

where $E_{g,g}$ and $E_{c,c}$ represent the energy of the ground and charged states, respectively, and $E_{g,c}$ and $E_{c,g}$ are the energies calculated for charged and neutral forms using the optimized geometry of the neutral and charged complex, respectively (the superscript $^*$ would be + for holes and – for electrons). The Adiabatic Ionization Potential (AIP) and Adiabatic Electron Affinity (AEA) were calculated as AIP = $E_{+,+} - E_{g,g}$ and AEA= $E_{g,g}$ - $E_{-,-}$.

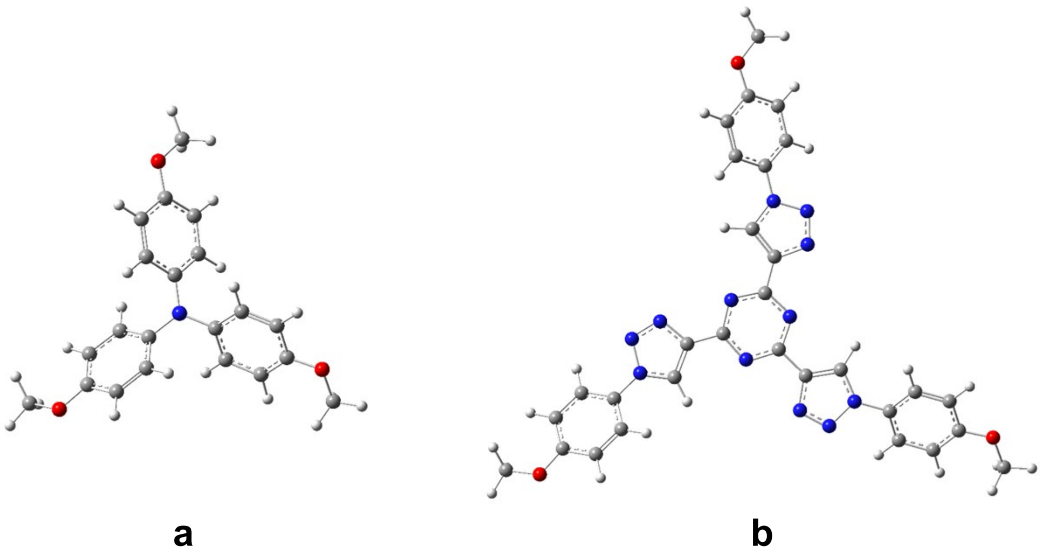


**Figure S23**. Optimized **TPA3C$_1$** (a) and the **T3C$_1$** core (b) at the ωB97XD/6-31G** level of theory.

---

[1] J.D. Chai, M. Head-Gordon, Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Phys. Chem. Chem. Phys.* 2008, **10**, 6615-6620.

[2] M. J. Frisch, et al.. Gaussian 09, revision D.01; Gaussian, Inc.:Wallingford, CT, 2009.

[3] W.-S. Li, Y. Yamamoto, T. Fukushima, A. Saeki, S. Seki, S. Tagawa, H. Masunaga, S. Sasaki, M. Takata, T. Aida, Amphiphilic molecular design as a rational strategy for tailoring bicontinuous electron donor and acceptor arrays: Photoconductive liquid crystalline oligothiophene-C(60) dyads. *J. Am. Chem. Soc.* 2008, **130**, 8886-8887.

[4] M. Yoshio, T. Kagata, K. Hoshino, T. Mukai, H. Ohno, T. Kato, One-Dimensional Ion-Conductive Polymer Films: Alignment and Fixation of Ionic Channels Formed by Self-Organization of Polymerizable Columnar Liquid Crystals. *J. Am. Chem. Soc.* 2006**, 128** (16), 5570-5577.

[5] V. Percec, D. Schlueter, Y.K. Kwon, J. Blackwell, M. Moller, P.J. Slangen, Dramatic stabilization of a hexagonal columnar mesophase generated from supramolecular and macromolecular columns by the semifluorination of the alkyl groups of their tapered building blocks. *Macromolecules* 1995, **28**, 8807-8818.

[6] R. A. Marcus, Electron Transfer Reaction in Chemistry. Theory and Experiment. *Rev. Mod. Phys.* 1993, **65**, 599-610.

[7] L. Wang, G. Nan, X. Yang, Q. Peng, Q. Li, Z. Shuai, Computational Methods for Design of Organic Materials with High Charge Mobility. *Chem. Soc. Rev*. 2010, **39**, 423-434.

[8] A. Troisi, Charge Transport in High Mobility Molecular Semiconductors: Classical Model and New Theories. *Chem. Soc. Rev*. 2011, **40**, 2347-2358.

[9] V. Coropceanu, J. Cornil, D.A. da Silva Filho, Y. Olivier, R. Silbey, J.L. Brédas, Charge Transport in Organic Semiconductors. *Chem. Rev*. 2007, **107**, 926-952.

[10] B. Baumeier, J. Kirkpatrick, D. Andrienko, Density-Functional Based Determination of Intermolecular Charge Transfer Properties for Large-Scale Morphologies. *Phys. Chem. Chem. Phys*. 2010, **12**, 11103-11113.

[11] J. Kirkpatrick, An Approximate Method for Calculating Transfer Integrals Based on the Zindo Hamiltonian. *Int. J. Quantum Chem*. 2008, **108**, 51-56.

[12] J. L. Brédas, D. Beljonne, V. Coropceanu, J. Cornil, Charge-Transfer and Energy-Transfer Processes in π-Conjugated Oligomers and Polymers: A Molecular Picture *Chem. Rev.* 2004, **104**, 4971-5004.