Electronic Supplementary Information (ESI)

Contents

1. Experimental Details

1.1 General

NMR experiments

NMR experiments were performed on a Bruker Avance 400 spectrometer, operating at frequency of 400.13 MHz for ^{1}H and 100.61 MHz for ^{13}C.

^{1}H NMR diffusion measurements were performed using stimulated echo sequence with bipolar gradient pulses. Diffusion time (Δ) was set within the interval 50-150 ms. The pulsed gradients were incremented from 2 to 95% of the maximum strength in sixteen spaced steps with a duration (δ) of 2.6 to 4 ms. Data were acquired in dichlorometane and tetrahydrofuran deuterated with sample rotation and the temperature was controlled at 298 K to minimize convection effects.

Infrared spectra (IR)

IR spectra for all the complexes were obtained by using a Mattson Genesis II FTIR spectrophotometer in the 400-4000 cm^{-1} spectral range.

Polarized optical microscopy (POM)

The textures of the mesophases were studied with an optical microscope (Olympus) with crossed polarizers and connected to a Linkam TMS600 hot stage and a Linkam THMS central processor.

Differential scanning calorimetry (DSC) and Thermal Gravimetric Analysis (TGA)

Measurements of the transition temperatures were made using a TA instrument 2000 differential scanning calorimeter (DSC) with a heating or cooling rate of 10ºC/min. The apparatus was calibrated with indium (156.6 ºC, 28.44 J/g) and tin (232.1 ºC, 60.5 J/g).

X-ray diffraction

X-ray diffraction studies were carried out at room temperature using a Pinhole camera (Anton-Paar) operating with a point focused Ni-filtered Cu Kα beam. The sample was

held in Lindemann glass capillaries (1 mm diameter) and heated, when necessary, with a variable-temperature attachment. The diffraction patterns were collected on a flat photographic film perpendicular to the x-ray beam.

Determination of number of molecules per unit cell (Z).

The relationship between the density (ρ) of the complexes **M-XD** in the mesophase and the number of the molecules in the unit cell (Z) is given by the following equation:

$$\rho = (M/N)/(V/Z), \qquad (2)$$

Where M is the molar mass (g/mol) of the complex, N is the Avogadro number, and V the unit cell volume (cm^3). Assuming that the density of the complexes should not be far from 1 g/cm^3. For a hexagonal unit cell $V = (\sqrt{3}/2)\, a^2\, h\, 10^{-24}$, and for a rectangular unit cell $V = a\, b\, h\, 10^{-24}$; *a, b* are the 2D lattice constants and *h* the stacking distance. Although a scattering maximum corresponding to *h* is not detected in the X-ray patterns of the Col_r mesophases, its value is assumed to be equal to that experimentally found for the Col_h mesophase (3.4 Å).

Circular Dichroism (CD)

CD spectra were recorded in a Jasco J-810. Neat samples were prepared by casting a tetrahydrofuran solution of the material, at 2wt %, onto a quartz plate and subsequent melting above the clearing point. As heating stage, a Mettler FP82, with a central processor Mettler FP80, was used conveniently modified to fix within the sample holder of the CD spectrometer.

Absorbance an Fluorescence measurements

UV/Vis absorption spectra were collected on an ATI-Unicam UV4-200 instrument. Fluorescence spectra were recorded with a Perkin-Elmer LS50B spectrophotometer. Both measurements were performed in dichloromethane solution.

To the optical absorption and emission measurements in solid and mesophase were used the same films used for the CD measurements.

Fluorescence quantum yields

The relative quantum yields of fluorescence (ϕF) for all compounds were determined according to:

$$\phi_{unk} = \phi_{std} (I_{unk} / A_{unk}) (A_{std} / I_{std}) (\eta_{std}/n_{unk})^2, \quad (1)$$

where W_{std} is the fluorescence yield of quinine sulfate standard (ϕ_{std} = 0.546 in 1M H_2SO_4 at 298 K), I_{unk} and I_{std} are the integrated emission intensities of the sample and the standard, respectively, A_{unk} and A_{std} are the absorbances of the sample and standard, respectively, at the desired wavelength λ_{exc} (318; 324 nm) such that absorbance was less than 0.10, and η_{unk} and η_{std} are the refractive indexes of the sample and standard solutions.

Determination of E_g

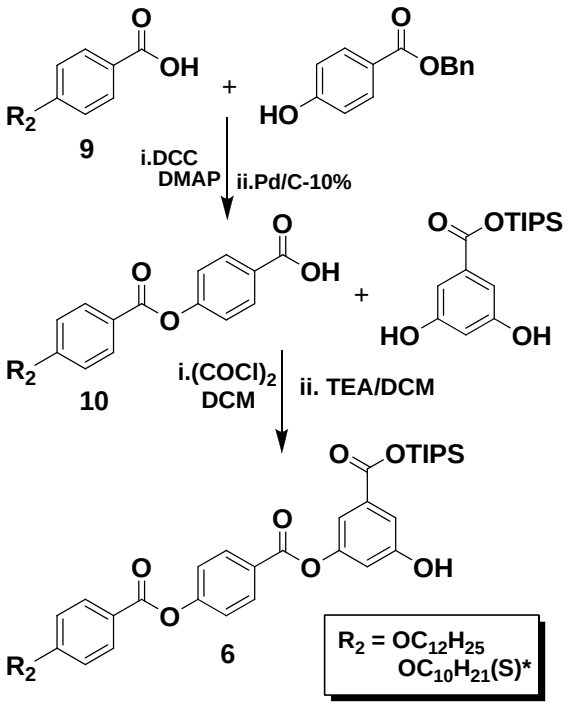
The E_g wavelengths were obtained from the derivative of the UV curves, giving the midpoint between the threshold energy at which the lowest energy absorption band starts increasing and that at which it starts decreasing.

Convertion 100nm = 12.4125 eV.

1.2 Synthesis

Dodecyl-1,3,5-triazine-2,4,6-triamine (M); The synthesis of this compound was described in: J. Barberá, L. Puig, P. Romero, J. L. Serrano, T. Sierra, J. Am. Chem. Soc., 2006, 128, 4487.

Triisopropylsilyl 3,5-dihydroxybenzoate was prepared according to the procedure described in Vera, F.; Tejedor, R. M.; Romero, P.; Barberá, J.; Ros, M. B.; Serrano, J. L.; Sierra, T. *Angew. Chem. Int. Ed*., 2007, *46*, 1873-1877



Scheme 1. Synthetic route of the intermediate **6.**

Benzyl 4-[4-(dodecyloxy)benzoyloxy]benzoate.

The corresponding carboxylic acid (4-(dodecyloxy)benzoic acid or 4-((S)-3,7-dimethyloctyloxy)benzoic acid) (2 mmol), benzyl 4-hydroxybenzoate (2 mmol) DCC (2.4 mmol), and a catalytic amount of DMAP in dichloromethane (40 mL) was stirred at room temperature under argon atmosphere for 24 h. The resulting precipitate was filtered off and washed with dichloromethane (50 mL). The solvent was evaporated and the crude product was purified by column chromatography (eluent hexane/ethyl acetate (8:2)). **Yield:** 86%, m.p.: 55°C. **IR** (KBr): 2956, 2916, 2849, 1729, 1602, 1510, 1469, 1292 (C-O), 1254 (C_{Ar}-O), 1163, 1021, 1082, 893, 842, 759cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.16, (d, J = 7.6 Hz, 2H), 8.13 (d, J = 7.6 Hz, 2H), 7.46 (d, J = 6.8 Hz, 2H), 7.40 (t, J = 7.2 Hz, 2H), 7.36 (d, J = 6.8 Hz, 2H), 7.29 (d, J = 9.0 Hz, 2H), 6.98 (d, J = 9.0 Hz, 2H), 5.38 (s, 2H), 4.04 (t, J = 7.0 Hz, 2H), 1,83 (q, J = 7.0 Hz, 2H), 1.48 (m, 2H), 1.28 (m, 12H), 0.89 (t, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 165.7, 164.3, 163.7, 154.8, 135.9, 132.3, 131.2, 128.5, 128.2, 128.1, 127.5, 121.8, 120.9,

114.3, 68.3, 66.7, 31.9, 29.6, 29.6, 29.5, 29.5, 29.3, 29.0, 25.9, 22.7, 14.1. **MALDI-MS** *m/z*= 517.4 $[M]^+$.

Benzyl 4-[4-(S-3,7-dimethyloctyloxy)benzoyloxy]benzoate.

Yield: 74%, m.p.: 61°C. **IR** (KBr): 2955, 2920, 1729 (C=O), 1709 (C=O) 1601, 1511, 1469, 1255 (C_{Ar}-O), 1164, 1082, 890, 850cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.15, (d, J = 8.0 Hz, 2H), 8.13 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 7.2 Hz, 2H), 7.40 (t, J = 7.2 Hz, 2H), 7.35 (t, J = 7.2 Hz, 1H), 7.29 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 5.38 (s, 2H), 4.04 (t, J = 7.0 Hz, 2H), 1.92-1.82 (m, 1H), 1.76-1.60 (m, 2H), 1.58-1.50 (m, 1H), 1.38-1.24 (m, 3H), 1.22-1.11 (m, 3H), 0.96 (d, J = 6.8 Hz, 3H), 0.87 (d, J = 6.8 Hz, 6H).

4-[4-(dodecyloxy)benzoyloxy]benzoic acid (10; R=$OC_{12}H_{25}$).

To a solution of the benzyl precursor (7.5 mmol) dissolved in tetrahydrofuran (15 ml) was added the palladium hydroxide on carbon 20% W/W (320 mg, 10%) and immediately led to the suspension of hydrogenation equipment. The reaction was subjected at a pressure of 60 barr of hydrogen gas for 7 hours. The suspension was filtered through Celite and washed with 70 mL of tetrahydrofuran. The solution obtained was concentrated resulting in a gray solid. The product **10** was recrystallized in ethanol.

Yield: 98%, m.p.: 54°C. **IR** (KBr): 2920, 2850, 1731, 1689, 1602, 1511, 1422, 1293 (C-O), 1255 (C_{Ar}-O), 1160, 1065, 1019, 846, 761, 690, 666 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.19, (d, J = 8.8 Hz, 2H), 8.14 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 4.05 (t, J = 6.8 Hz, 2H), 1,83 (q, J = 7.0 Hz, 2H), 1.48 (m, 2H), 1.28 (m, 12H), 0.89 (t, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 166.6, 163.4, 162.8, 153.6, 131.4, 130.3, 127.6, 120.8, 119.9, 113.5, 67.4, 30.9, 28.7, 28.7, 28.6, 28.6, 28.4, 28.1, 25.0, 21.7, 13.3.

4-[4-(S-3,7-dimethyloctyloxy)benzoyloxy]benzoic acid (10; R=$OC_{10}H_{21}$(S))*. Yield: 93%. **IR** (KBr): 3400-2500, 2923, 2850, 1732 (C=O) 1688, 1507, 1422, 1291 (C-O), 1255 (C_{Ar}-O), 1206, 1157, 1062, 846, 763cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.20 (d, J = 8.4 Hz, 2H), 8.15 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 4.05 (m, 2H), 1.92-1.82 (m, 1H), 1.76-1.60 (m, 2H), 1.58-50 (m, 1H), 1.38-1.24 (m, 3H), 1.22-1.11(m, 3H), 0,96 (d, J = 6.8 Hz, 3H), 0.87 (d, J = 6.8 Hz, 6H).

Triisopropylsilyl 3-{4-[4-(dodecyloxy)benzoyloxy]benzoyloxy}-5-hydroxybenzoate (6; R=$OC_{12}H_{25}$).

The corresponding carboxylic acid **9** (2 mmol) and oxalyl chloride (2.2 mmol) was put in 30 mL of dichloromethane and stirred for 4h at room temperature. The solvent and excess of oxalyl chloride were evaporated under vacuum affording the acid chloride, which was used without further purification. To a three-necked round bottomed flask with argon inlet–outlet containing the compound triisopropylsilyl 3,5-dihydroxybenzoate (4 mmol) dissolved in dichloromethane (30 mL) and triethylamine (1 mL), the respective acid chloride in 5 mL of dichloromethane was added dropwise. The mixture was stirred at room temperature for 12 h. The reaction is filtered on celite and the organic layer was additionally washed with water (3x30 mL), brine (1x30 mL) and dried with Na_2SO_4. The solvents were evaporated to give a white solid, the product was purified by column chromatography (eluent hexane/ethyl acetate (8:2)).

Yield: 35%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.26, (d, J = 8.4 Hz, 2H), 8.15, (d, J = 8.4 Hz, 2H), 7.46, (d, J = 12.8 Hz, 2H), 7.37, (d, J = 8.4 Hz, 2H), 6.99, (d, J = 8.4 Hz, 2H), 6.96 (t, J = 2.4 Hz, 1H), 6.22 (s, 1H), 4.05 (t, J = 6.4 Hz, 2H), 1,83 (q, J = 7.2 Hz, 2H), 1.51-135 (m, 5H), 1.27 (m, 16H), 1.13 (d, J = 7.6Hz, 18H), 0.88 (t, J = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 165.4, 164.4, 164.3, 163.8, 156.8, 155.5, 151.5, 133.7,

132.4, 131.4, 126.4, 122.2, 120.8, 115.5, 114.9, 114.4, 114.1, 68.4, 31.9, 29.6, 29.6, 29.5, 29.5, 29.3, 29.0, 26.0, 22.7, 17.8, 14.1, 12.0.

Triisopropylsilyl 3-{4-[4-(S-3,7-dimethyloctyloxy)benzoyloxy]benzoyloxy}-5-hydroxybenzoate (6; R=$OC_{10}H_{21}$* (S)). Yield: 30%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.27, (d, J = 8.8 Hz, 2H), 8.15, (d, J = 8.8 Hz, 2H), 7.46 (m, 2H), 7.37, (d, J = 8.8 Hz, 2H), 6.99, (d, J = 8.8 Hz, 2H), 6.96 (t, J = 2.4 Hz, 1H), 4.10 (m, 2H), 1.91-1.81 (m, 1H), 1.74-1.58 (m, 2H) 1.57-1.49 (m, 1H), 1.45-1.25 (m, 3H), 1.19 (m, 3H), 1.13 (d, J = 7.6 Hz, 18H), 0.96 (d, J = 6.4 Hz, 3H) 0.87 (d, J = 6.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 165.3, 164.4, 164.3, 163.8, 156.6, 155.5, 151.6, 133.8, 132.4, 131.9, 126.5, 122.2, 120.8, 115.6, 114.8, 114.4, 114.0, 66.7, 39.2, 37.2, 36.0, 29.8, 28.0, 24.6, 22.7, 22.6, 19,6, 17.8, 12.0. **MALDI-MS** *m/z*= 713.4 $[M+Na]^+$.

4-(S-3,7-dimethyloctyloxy)benzonitrile (1a) and 4-(R-3,7-dimethyloctyloxy)benzonitrile (1b) ; A mixture of 4-hydroxybenzonitrile (33.5 mmol), K_2CO_3 (100 mmol), (S) or (R) -1-bromo-3,7-dimethyloctane (36.9 mmol) and 100 mL butanone was stirred under reflux. The reaction was monitored by TLC and was complete after 18h. After cooling, the reaction mixture was filtered off and washed with butanone. The filtrate was concentrated and the residue recrystallized from ethanol. **Yield:** 91%, m.p.: oil. **IR** (KBr): 2954, 2927, 2869, 2225 (CN), 1606, 1509, 1469, 1302, 1258 (C-O), 1171 (C_{Ar}-O), 834, 547 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.54, (d, J = 9.2 Hz, 2H, Ar-*H*), 6.91 (d, J = 9.2 Hz, 2H, Ar-*H*), 4.01 (m, 2H, O*C*H_2-), 1,82 (m, 1H, -C*H*-$(CH_3)_2$), 1.64-1.56 (m, 2H, OCH_2CH_2-), 1,55-1.48 (m, 1H, -C*H*-$(CH_2)_2$-(CH_3)), 1.34-1.23 (m, 3H, -CH_2), 1.18-1.13 (m, 3H, -CH_2), 0.93 (d, J = 6.8 Hz, 3H, -CH_3), 0.86 (d, J = 6.8Hz, 6H, -(CH_3)$_2$). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 162.3, 133.7, 119.1, 115.0, 103.5, 66.6, 39.0, 37.1, 35.7, 29.6, 27.8, 24.5, 22.5, 22.4, 19.5.

4-(dodecyloxy)benzonitrile (1c). **Yield:** 86%, m.p.: 45°C. **IR** (KBr): 2950, 2916, 2869, 2848, 2218 (CN), 1607, 1573, 1508, 1474, 1302, 1288 (C-O), 1256 (C_{Ar}-O), 1170, 1046, 1033, 823, 812, 546 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.49, (d, J = 8.8 Hz, 2H, Ar-*H*), 6.85 (d, J = 8.8 Hz, 2H, Ar-*H*), 3.91 (t, J = 6.5 Hz, 2H, O*C*H_2-), 1,72 (q, J = 6.5 Hz, 2H, OCH$_2$*C*H_2-), 1.37 (m, 2H, OCH$_2$CH$_2$*C*H_2-), 1.19 (m, 16H, -*C*H_2-), 0.80 (t, J = 7.0 Hz, 3H, -*C*H_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 162.4, 133.8, 119.3, 115.1, 103.6, 68.4, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 28.9, 22.6, 14.1.

5-[4-(S-3,7-dimethyloctyloxy)phenyl]tetrazole (2a) and 5-[4-(R-3,7-dimethyloctyloxy)phenyl]tetrazole (2b). 4-((S)-3,7-dimethyloctyloxy)benzonitrile **1a** (10.4 mmol), NaN_3 (31.3 mmol), NH_4Cl (31.3 mmol), and dimethylformamide (50 mL) were stirred at 110 °C for 12 h. The suspension was then poured into 350 mL of water/ice, after that the solution was acidification with concentrated HCl until pH~1. The crude product was collected by suction filtration and recrystallized from ethanol. **Yield:** 78%, m.p.: 120°C. **IR** (KBr): 3064, 2948, 2866, 2694, 2615, 2466, 1613, 1501, 1266, 1177, 1047, 982, 837, 751, 526cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$ and DMSO) δ: 11.79 (s, 1H, HN-), 8.10, (d, J = 8.8 Hz, 2H, Ar-*H*), 7.00 (d, J = 8.8 Hz, 2H, Ar-*H*), 4.02 (m, 2H, O*C*H_2-), 1.86-1.78 (m, 1H, -*C*H-(CH_3)$_2$), 1.66-1.55 (m, 2H, OCH$_2$*C*H_2-), 1.54-1.46 (m, 1H, -*C*H-(CH_2)$_2$-(CH_3)), 1.33-1.28 (m, 3H, -*C*H_2), 1.17-1.12 (m, 3H, -*C*H_2), 0.94 (t, J = 6.4 Hz, 3H, -*C*H_3), 0.85 (d, J= 6.4Hz, 6H, -*C*H_3). **^{13}C NMR** (100 MHz, $CDCl_3$ and DMSO) δ: 162.0, 155.9, 129.3, 115.4, 114.9, 66.7, 39.2, 37.3, 36.0, 29.8, 27.9, 24.7, 22.7, 22.6, 19.6. **ESI-MS** *m/z*= 303.1 $[M]^+$.

5-[4-(dodecyloxy)phenyl]tetrazole (2c). **Yield:** 55%, m.p.: 154°C. **IR** (KBr): 2934, 2914, 2870, 2850, 2685, 2545, 2468, 1892, 1612, 1507, 1470, 1255, 1180, 1056, 987, 831, 751cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$ and DMSO) δ: 7.60, (d, J = 8.8 Hz, 2H, Ar-

H), 6.61 (d, J = 8.8 Hz, 2H, Ar-*H*), 3.62 (t, J = 6.4 Hz, 2H, OC*H*$_2$-), 1,40 (m, 2H, OCH$_2$C*H*$_2$-), 1.08 (m, 2H, OCH$_2$CH$_2$C*H*$_2$-), 0.86 (m, 16H, -C*H*$_2$-), 0.47 (t, J = 6.5 Hz, 3H, -C*H*$_3$). **^{13}C NMR** (100 MHz, $CDCl_3$ and DMSO) δ: 160.4, 127.9, 114.2, 67.3, 30.9, 28.7, 28.7, 28.6, 28.4, 28.4, 28.2, 25.0, 21.7, 13.3. **ESI-MS** *m/z*= 331.2 $[M]^+$.

Methyl 4-{5-[4-(S-3,7-dimethyloctyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoate (4a) and Methyl 4-{5-[4-(R-3,7-dimethyloctyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoate (4b). The 4-(methoxycarbonyl)benzoic acid (6 mmol) was put in 30 mL of dichloromethane. Oxalyl dichloride (12 mmol) was added to the suspension, after 10 min three drops of DMF were added, to catalysis of the acid chloride, the mixture was stirred for 4h. The solvent was removed under reduced pressure and to the residue 5 ml of pyridine was added; 4-((S)-3,7-dimethyloctyloxy)benzonitrile (6 mmol) dissolved in 10 ml of pyridine was then added dropwise. The mixture was heated under reflux until for 4h, the evolution of N_2 is a strong evidence of the reaction. After cooling, the solution was poured into ice/water (250 ml) and the precipitate was collected by filtration. The product was purified by chromatography on basic alumina, eluting with hexane/ethyl acetate (95:5). **Yield:** 84%, m.p.: 134°C. **IR** (KBr): 2953, 2925, 2869, 1716(C=O), 1614, 1497, 1281, 1251, 1176, 1099, 739, 711cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.2 (s, 4H, Ar-*H*), 8.05 (d, J = 8.8 Hz, 2H, Ar-*H*), 7.01 (d, J = 8.8 Hz, 2H, Ar-*H*), 4.06 (m, 2H, OC*H*$_2$-), 3.95 (s, 3H, $COCH_3$), 1.87-1.80 (m, 1H, -C*H*-$(CH_3)_2$), 1.68-1.58 (m, 2H, -CH_2C*H*$_2$), 1.59-1.49 (m, 1H, -C*H*-$(CH_2)_2$-(CH_3)), 1.35-1.24 (m, 3H, -C*H*$_2$), 1.18-1.13 (m, 3H, -C*H*$_2$), 0.95 (t, J = 6.4 Hz, 3H, -CH_3), 0.86 (d, J= 6.4Hz, 6H, -CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 166.1, 165.0, 163.3, 162.1, 132.5, 130.2, 128.7, 127.8, 126.6, 115.7, 115.0, 66.6, 52.4, 39.1, 37.1, 35.9, 29.7, 27.9, 24.6, 22.6, 22.5, 19.5. **MALDI-MS** *m/z* = 459.2 $[M+Na]^+$.

Methyl 4-{5-[4-(dodecyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoate (4c). **Yield:** 73%, m.p.: 126°C. **IR** (KBr): 2955, 2918, 1721(C=O), 1615, 1497, 1284, 1254, 1101, 738, 713cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.19 (s, 4H, Ar-*H*), 8.07 (d, J = 9.2 Hz, 2H, Ar-*H*), 7.02 (d, J = 9.2 Hz, 2H, Ar-*H*), 4.03 (t, J = 6.4 Hz, 2H, OCH_2-), 3.96 (s, 3H, $COCH_3$), 1.82 (q, J = 6.4 Hz, 2H, -OCH_2CH_2), 1.47 (m, 2H, -$OCH_2CH_2CH_2$), 1.26 (m, 16H, -CH_2), 0.88 (t, J = 7.2 Hz, 3H, -CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 166.2, 164.5, 162.2, 130.2, 128.8, 127.9, 126.7, 115.8, 115.0, 81.7, 68.3, 52.4, 31.9, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 29.1, 26.0, 22.7, 14.1. **MALDI-MS** *m/z* = 465.3 $[M]^+$.

4-{5-[4-(S-3,7-dimethyloctyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoic acid (5a) and 4-{5-[4-(R-3,7-dimethyloctyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoic acid (5b). In a round bottom flask the compound **4a** or **4b** (5 mmol) and KOH (10 mmol) in mixture of EtOH:H_2O (7:3, 60 mL) were refluxed under stirring for 2h. After cooling, the resulting solution was acidified with HCl 5M until pH~1. The crude precipitate was filtered-off, washed with water and recrystallized from EtOH to afford desired product. **Yield:** 93%, m.p.: 245 °C. **IR** (KBr): 3070, 2953, 2925, 2868, 2670, 2542, 1683(C=O), 1610, 1494, 1423, 1365, 1249, 1175, 739, 714cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$ and DMSO) δ: 8.11, (s, 4H, Ar-*H*), 7.98 (d, J = 8.8 Hz, 2H, Ar-*H*), 6.96 (d, J = 8.8 Hz, 2H, Ar-*H*), 4.01 (m, 2H, OCH_2-), 1.80-1.74 (m, 1H, -C*H*-$(CH_3)_2$), 1.62-1.50 (m, 2H, OCH_2CH_2-), 1.49-1.40(m, 1H, -C*H*-$(CH_2)_2$-(CH_3)) 1.27-1.20 (m, 3H, -CH_2), 1.16-1.07 (m, 3H, -CH_2), 0.88 (t, J = 6.6 Hz, 3H, -CH_3), 0.79 (d, J = 6.6Hz, 6H, -CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$ and DMSO) δ: 166.8, 164.4, 162.8, 161.5, 133.1, 129.9, 128.1, 126.8, 125.9, 115.1, 114.5, 66.0, 38.5, 36.6, 35.4, 29.1, 27.3, 24.0, 22.1, 22.0, 19.1. **MALDI-MS** *m/z* = 423.2 $[M]^+$.

4-{5-[4-(dodecyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoic acid (5c). **Yield:** 99%, m.p.: 253°C. **IR** (KBr): 2954, 2920, 2848, 1683(C=O), 1613, 1496, 1384, 1250, 739cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$ and DMSO) δ: 8.11 (d, J = 2.0 Hz, 4H, Ar-*H*), 7.98 (d, J = 8.8 Hz, 2H, Ar-*H*), 6.99 (d, J = 8.8 Hz, 2H, Ar-*H*), 3.98 (t, J = 7.0 Hz, 2H, OC*H*$_2$-), 1,74 (q, J = 7.0 Hz, 2H, -OCH$_2$C*H*$_2$), 1.41 (m, 2H, -OCH$_2$CH$_2$C*H*$_2$), 1.20 (m, 16H, -C*H*$_2$-), 0.80 (t, J = 7.0 Hz, 3H, -C*H*$_3$). **^{13}C NMR** (100 MHz, $CDCl_3$ and DMSO) δ: 165.4, 163.2, 161.7, 160.5, 132.2, 128.8, 127.2, 125.8, 125.0, 114.1, 113.6, 66.6, 30.2, 27.9, 27.9, 27.8, 27.6, 27.6, 27.4, 24.3, 21.0, 12.6. **MALDI-MS** *m/z*= 451.3 $[M]^+$.

Triisopropylsilyl 3-{4-[4-(dodecyloxy)benzoyloxy]benzoyloxy}-5-(4-{5-[4-(dodecyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoyloxy)benzoate (7a).

A mixture of the corresponding benzoic acid **5** (**5a, 5b or 5c)** (1.2 mmol), the respective compound **6** (1.0 mmol) and (N,N-dimethylamino)pyridinium-4-toluenesulfonate (DPTS) (1.2 mmol) in dichloromethane (50 ml) was stirred under argon atmosphere. The solution was cooled in an ice bath until 0°C. Subsequently N,N'-dicyclohexylcarbodiimide (1.2 mmol) solubilized in dichloromethane was added . The mixture was stirred at room temperature for 48h. The solution was filtered passing through silica gel and the organic phase was evaporated. The resulting product was purified by flash chromatography on silica gel, eluting with hexane/ethyl acetate mixtures (9:1). **Yield:** 87%. **IR** (KBr): 2918, 2850, 1739(C=O), 1706 (C=O TIPS), 1609, 1496, 1305, 1253 (C_{Ar}-O), 1134, 1070, 834, 762, 736, 709 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.37 (d, J = 8.8 Hz, 2H), 8.30 (d, J = 1.4 Hz, 2H), 8.28 (d, J = 1.4 Hz, 2H), 8.15 (d, J = 8.8 Hz, 2H), 8.09 (d, J = 8.8 Hz, 2H), 7.87 (dd, J = 1.2 Hz, J = 1.6 Hz 1H), 7.86 (dd, J = 1.6 Hz, J = 1.6 Hz 1H), 7.46 (t, J = 2.0 Hz, 1H), 7.39 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 9.2 Hz, 2H), 4.06 (dt, J = 2.2 Hz, J = 6.8 Hz,

4H), 1,83 (q, J = 7.2 Hz, 4H),1.46 (m, 7H), 1.49-1.27 (m, 32H), 1.16 (d, J = 7.2 Hz, 18H), 0.88 (t, J = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 165.2, 164.4, 164.2, 163.9, 163.8, 163.7, 163.1, 162.5, 155.6, 151.2, 151.0, 134.0, 132.4, 131.9, 131.3, 130.9, 128.8, 128.8, 126.9, 126.2, 122.2, 121.1, 120.8, 120.4, 115.7, 115.0, 114.4, 68.4, 68.3, 31.9, 29.6, 29.6, 29.5, 29.5, 29.3, 29.1, 29.0, 26.0, 22.7, 17.8, 14.1, 12.0. **MALDI-MS** *m/z*= 1151.6 $[M]^+$.

Triisopropylsilyl 3-(4-{5-[4-(S-3,7-dimethyloctyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoyloxy)-5-{4-[4-(dodecyloxy)benzoyloxy]benzoyloxy}benzoate (7b).

Yield: 79%. **IR** (KBr): 2919, 2851, 1744 (C=O), 1705 (C=O TIPS), 1609, 1496, 1471, 1316, 1252 (C_{Ar}-O), 1134, 1055, 836, 773, 740, 713 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.37 (d, J = 8.4 Hz, 2H), 8.30 (d, J = 2.4 Hz, 2H), 8.28 (d, J = 2.4 Hz, 2H), 8.15 (d, J = 9.2 Hz, 2H), 8.10 (d, J = 8.8 Hz, 2H), 7.87 (dd, J = 1.4 Hz, J = 2.1 Hz 1H), 7.86 (dd, J = 1.4 Hz, J = 2.1 Hz 1H), 7.46 (t, J = 2.4 Hz, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 4.08 (m, 4H), 1.90-1.79 (m, 3H), 1.74-1.59 (m, 3H) 1.52-1.41 (m, 5H), 1.39-1.22 (m, 19H), 1.19 (m, 3H), 1.15 (d, J = 7.6 Hz, 18H), 0.97 (d, J = 6.8 Hz, 3H) 0.88 (d, J = 6.8 Hz, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 165.4, 164.6, 164.2, 164.1, 164.1, 163.7, 163.3, 162.8, 162.4, 155.8, 151.4, 151.5, 134.4, 132.6, 132.2, 131.5, 130.9, 129.0, 128.8, 127.1, 126.3, 122.4, 121.0, 115.9, 115.0, 114.4, 68.4, 68.7, 53.6, 39.2, 37.2, 36.1, 31.9, 29.8, 29.7, 29.7, 29.6, 29.2, 28.1, 26.1, 24.9, 22.9, 22.6, 19.7, 18.2, 14.2, 12.2. **MALDI-MS** *m/z*= 1123.6 $[M]^+$.

Triisopropylsilyl 3-(4-{5-[4-(R-3,7-dimethyloctyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoyloxy)-5-{4-[4-(dodecyloxy)benzoyloxy]benzoyloxy}benzoate (7c).

Yield: 95%. **IR** (KBr): 2919, 2868, 2852, 1744(C=O), 1705 (C=O TIPS), 1609, 1496, 1305, 1252 (C_{Ar}-O), 1134, 1055, 836, 740, 713 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ:

8.37 (d, J = 8.4 Hz, 2H), 8.30 (d, J = 2.4 Hz, 2H), 8.28 (d, J = 2.4 Hz, 2H), 8.15 (d, J = 9.2 Hz, 2H), 8.10 (d, J = 8.8 Hz, 2H), 7.87 (dd, J = 1.4 Hz, J = 2.1 Hz 1H), 7.86 (dd, J = 1.4 Hz, J = 2.1 Hz 1H), 7.46 (t, J = 2.4 Hz, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 4.08 (m, 4H), 1.90-1.79 (m, 3H), 1.74-1.59 (m, 3H) 1.52-1.41 (m, 5H), 1.39-1.22 (m, 19H), 1.19 (m, 3H), 1.15 (d, J = 7.6 Hz, 18H), 0.97 (d, J = 6.8 Hz, 3H) 0.88 (d, J = 6.8 Hz, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 165.4, 164.5, 164.3, 164.1, 164.1, 163.9, 163.3, 162.8, 162.4, 155.8, 151.4, 151.1, 134.2, 132.6, 132.1, 131.5, 131.1, 129.0, 128.9, 127.1, 126.3, 122.4, 121.0, 115.9, 115.2, 114.6, 68.5, 68.8, 53.6, 39.4, 37.4, 36.2, 32.0, 29.9, 29.8, 29.7, 29.5, 29.2, 28.1, 26.1, 24.8, 22.8, 22.7, 19.8, 18.0, 14.3, 12.2. **MALDI-MS** *m/z*= 1123.6 $[M]^+$.

Triisopropylsilyl 3-{4-[4-(S-3,7-dimethyloctyloxy)benzoyloxy]benzoyloxy}-5-(4-{5-[4-(S-3,7-dimethyloctyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoyloxy)benzoate (7d). **Yield:** 84%, m.p.: 123°C. **IR** (KBr): 2919, 2862, 1741 (C=O), 1706 (C=O TIPS), 1611, 1497, 1254 (C_{Ar}-O), 1134, 1057, 834, 740, 710 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.37 (d, J = 8.8 Hz, 2H), 8.30 (d, J = 2.0 Hz, 2H), 8.28 (d, J = 2.0 Hz, 2H), 8.15 (d, J = 8.8 Hz, 2H), 8.10 (d, J = 8.8 Hz, 2H), 7.87 (dd, J = 1.2 Hz, J = 1.6 Hz 1H), 7.86 (dd, J = 1.2 Hz, J = 1.6 Hz 1H), 7.46 (t, J = 2.4 Hz, 1H), 7.39 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 9.2 Hz, 2H), 6.99 (d, J = 9.2 Hz, 2H), 4.10 (m, 4H), 1.86 (q, J = 8.8 Hz, 2H), 1.74-1.60 (m, 4H) 1.57-1.50 (m, 2H), 1.44 (m, 3H), 1.36-1.22 (m, 6H), 1.19 (m, 6H), 1.15 (d, J = 7.2 Hz, 18H), 0.97 (d, J = 6.8 Hz, 6H) 0.88 (d, J = 6.4 Hz, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 165.4, 164.6, 164.4, 164.1, 164.0, 163.9, 163.3, 162.4, 162.2, 155.8, 151.4, 151.2, 134.2, 132.6, 132.1, 131.5, 131.1, 129.0, 128.9, 127,0, 126.3, 122.4, 121.3, 121.0, 120.5, 115.9, 115.2, 114.6, 66.9, 66.8, 39.3, 37.4, 36.2, 36.2, 36.1, 29.9, 28.1, 24.8, 22.8, 22.8, 22.6, 19.8, 18.0, 17.9, 12.2 **MALDI-MS** *m/z*= 1095.6 $[M]^+$.

Triisopropylsilyl 3-{4-[4-(S-3,7-dimethyloctyloxy)benzoyloxy]benzoyloxy}-5-(4-{5-[4-(dodecyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoyloxy)benzoate (7e).

Yield: 96%. **IR** (KBr): 2921, 2851, 1745 (C=O), 1708 (C=O TIPS), 1609, 1496, 1471, 1316, 1255 (C_{Ar}-O), 1134, 1055, 836, 740, 713 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.37 (d, J = 8.8 Hz, 2H), 8.30 (d, J = 2.0 Hz, 2H), 8.28 (d, J = 2.0 Hz, 2H), 8.16 (d, J = 8.8 Hz, 2H), 8.10 (d, J = 8.8 Hz, 2H), 7.86 (dd, J = 1.6 Hz, J = 1.2 Hz 1H), 7.86 (dd, J = 1.2 Hz, J = 1.6 Hz 1H), 7.46 (t, J = 2.0 Hz, 1H), 7.39 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 4.09 (m, 2H), 4.05 (t, J = 6.4 Hz, 2H), 1.90-1.78 (m, 3H), 1.73-1.58 (m, 3H), 1.52-1.39 (m, 5H), 1.38-1.22 (m, 19H), 1.20-1.12 (m, 3H), 1.15 (d, J = 7.6 Hz, 18H), 0.97 (d, J = 6.4 Hz, 3H), 0.88 (d, J = 6.8 Hz, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 165.4, 164.6, 164.4, 164.1, 164.0, 163.9, 163.3, 162.9, 162.4, 155.8, 151.4, 151.2, 134.2, 132.6, 132.1, 131.5, 131.1, 129.0, 128.9, 127.1, 126.4, 122.4, 121.3, 121.0, 120.5, 115.9, 115.2, 114.6, 68.5, 66.9, 53.6, 39.4, 37.4, 36.1, 32.0, 30.0, 29.9, 29.8, 29.8, 29.7, 29.7, 29.5, 29.3, 28.1, 26.1, 24.8, 22.8, 22.7, 19.8, 18.0, 14.3, 12.2. **MALDI-MS** *m/z*= 1123.6 $[M]^+$.

3-{4-[4-(dodecyloxy)benzoyloxy]benzoyloxy}-5-(4-{5-[4-(dodecyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoyloxy)benzoic acid (8a or X12E12).

The compound **7a** (1.0 mmol) was dissolved in 50 mL of dichloromethane and the solution was cooling to -78°C with a bath nitrogen and isopropyl alcohol. After 10 min tetra-n-butylammonium fluoride 1M (5.0 mmol) dissolved in THF was added via syringe upon rigorous stirring. The reaction was allowed to stir for 2 h at -78°. The reaction was quenched with glacial acetic acid (6.0 mmol) and the mixture was then diluted with dichloromethane and water. The organic layer was additionally washed with water (3x30 mL), brine (1x30 mL), dried with Na_2SO_4 and concentrated. The product was purified by recrystallized in MeOH to give the final product **X12E12** as a

white solid. **Yield:** 82%, m.p.: 141.3°C. **IR** (KBr): 3200-2400 (COO-H), 2921, 2852, 1740, 1699, 1609, 1496, 1470, 1254 (C_{Ar}-O), 1162, 1133, 1058, 1015cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.36 (d, J = 11.6 Hz, 2H), 8.30 (d, J = 2.4 Hz, 2H), 8.27 (d, J = 2.4 Hz, 2H), 8.15 (d, J = 11.6 Hz, 2H), 8.10 (d, J = 12.0 Hz, 2H), 7.95 (d, J = 1.2 Hz, 1H), 7.54 (t, J = 2.8 Hz, 1H), 7.39 (d, J = 12.0 Hz, 2H), 7.04 (d, J = 12.0 Hz, 2H), 6.99 (d, J = 12.0 Hz, 2H), 4.05 (m, 4H), 1,83 (q, J = 9.0 Hz, 4H), 1.49 (m, 4H), 1.27 (m, 32H), 0.88 (t, J = 8.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$ e DMSO) δ: 166.1, 164.8, 163.6, 163.2, 162.1, 161.8, 155.4, 150.8, 150.5, 146.3, 133.2, 130.9, 130.8, 130.4, 129.2, 128.4, 128.2, 126.5, 124.9, 122.1, 120.4, 120.1, 119.5, 115.1, 114.6, 114.4, 68.0, 67.9, 31.4, 29.1, 29.1, 29.0, 29.0, 28.8, 28.6, 28.6, 25.5, 22.2, 13.7. **MALDI-MS** *m/z*= 995.5 $[M]^+$. Elemental analysis: (Requires for $C_{60}H_{70}N_2O_{11}$: C, 72.41; H, 7.09; N, 2,81% found C, 72.18; H, 7.31; N, 2.88%). TGA: 262°C.

3-(4-{5-[4-(S-3,7-dimethyloctyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoyloxy)-5-{4-[4-(dodecyloxy)benzoyloxy]benzoyloxy}benzoic acid (8b or X(S)10*E12).

Yield: 71%, m.p.: 151.9°C. **IR** (KBr): 3200-2400 (COO-H), 2922, 2852, 1740 (C=O), 1698, 1608, 1495, 1469, 1447, 1413, 1256 (C_{Ar}-O), 1161, 1134, 1055, 1014, 837, 739, 708 cm^{-1}. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ: 8.29 (d, J = 8.8 Hz, 2H), 8.21 (d, J = 2.0 Hz, 2H), 8.19 (d, J = 2.0 Hz, 2H), 8.05 (d, J = 8.8 Hz, 2H), 8.00 (d, J = 9.2 Hz, 2H), 7.86 (m, 2H), 7.45 (t, J = 2.4 Hz, 1H), 7.32 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 9.2 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 4.01 (m, 2H), 3.97 (t, J = 6.8 Hz, 2H), 1.82-1.69 (m, 3H), 1.66-1.51 (m, 2H), 1.49-1.35 (m, 3H), 1.32-1.14 (m, 19H), 1.13-1.04 (m, 3H), 0.88 (d, J = 6.4 Hz, 3H) 0.79 (d, J = 6.8 Hz, 9H). **^{13}C NMR** (100 MHz, CD_2Cl_2) δ: 168.5, 165.3, 164.3, 164.0, 163.9, 163.3, 162.4, 155.8, 151.6, 151.3, 132.3, 131.9, 131.6, 131.4, 130.9, 128.9, 128.8, 126.9, 126.2, 122.4, 121.3, 121.2, 120.9, 115.8, 115.1, 114.4, 68.6, 66.8, 39.3, 37.3, 36.1, 32.0, 29.9, 29.7, 29.7, 29.6, 29.6, 29.4, 29.1 28.1, 26.0, 24.7,

22.8, 22.5, 22.4, 19.5, 13.9. **MALDI-MS** *m/z*= 967.5 $[M]^+$. Elemental analysis: (Requires for $C_{58}H_{66}N_2O_{11}$: C, 72.03; H, 6.88; N, 2,90% found C, 72.02; H, 6.92; N, 2.99%). TGA: 269°C.

3-(4-{5-[4-(R-3,7-dimethyloctyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoyloxy)-5-{4-[4-(dodecyloxy)benzoyloxy]benzoyloxy}benzoic acid (8c or X(R)10*E12).

Yield: 75%, m.p.: 152.9°C. **IR** (KBr): 3200-2400 (COO-H), 2953, 2926, 2868, 1743 (C=O), 1698, 1608, 1495, 1470, 1446, 1413, 1253 (C_{Ar}-O), 1161, 1134, 1059, 1013, 835, 738, 709 cm^{-1}.**^{1}H NMR** (400 MHz, CD_2Cl_2) δ: 8.36 (d, J = 8.8 Hz, 2H), 8.29 (d, J = 2.0 Hz, 2H), 8.26 (d, J = 2.0 Hz, 2H), 8.12 (d, J = 8.8 Hz, 2H), 8.07 (d, J = 9.2 Hz, 2H), 7.93 (m, 2H), 7.52 (t, J = 2.4 Hz, 1H), 7.39 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 9.2 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 4.07 (m, 2H), 4.01 (t, J = 6.8 Hz, 2H), 1.89-1.75 (m, 3H), 1.73-1.58 (m, 2H), 1.56-1.40 (m, 3H), 1.39-1.21 (m, 19H), 1.20-1.10 (m, 3H), 0.88 (d, J = 6.8 Hz, 3H) 0.79 (d, J = 9.2 Hz, 9H). **^{13}C NMR** (100 MHz, CD_2Cl_2) δ: 168.6, 165.3, 164.3, 164.0, 163.9, 163.8, 163.3, 162.4, 155.8, 151.6, 151.4, 132.3, 131.8, 131.6, 131.3, 130.9, 128.9, 128.8, 126.9, 126.2, 122.4, 121.3, 120.9, 115.8, 115.2, 114.5, 68.6, 66.8, 39.3, 37.3, 36.1, 32.0, 29.9, 29.7, 29.7, 29.6, 29.6, 29.4, 29.2, 28.1, 26.0, 24.7, 22.8, 22.5, 22.4, 19.5, 14.0. **MALDI-MS** *m/z*= 967.7 $[M]^+$. Elemental analysis: (Requires for $C_{58}H_{66}N_2O_{11}$: C, 72.03; H, 6.88; N, 2,90% found C, 71.84; H, 6.85; N, 2.87%). TGA: 270°C.

3-{4-[4-(S-3,7-dimethyloctyloxy)benzoyloxy]benzoyloxy}-5-(4-{5-[4-(S-3,7-dimethyloctyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoyloxy)benzoic acid (8d or X(S)10*E(S)10*). Yield: 76%, m.p.: 152.8°C. **IR** (KBr): 3200-2400 (COO-H), 2922, 2852, 1748 (C=O), 1745, 1698, 1608, 1495, 1446, 1413, 1255 (C_{Ar}-O) 1161, 1133, 1055, 1015, 837, 739, 708cm^{-1}. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ: 8.36 (d, J = 8.4 Hz, 2H), 8.29 (d, J = 2.0 Hz, 2H), 8.26 (d, J = 2.0 Hz, 2H), 8.12 (d, J = 8.8 Hz, 2H), 8.07 (d,

J = 9.2 Hz, 2H), 7.93 (m, 2H), 7.52 (t, J = 2.4 Hz, 1H), 7.39 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 9.2 Hz, 2H), 4.09 (m, 4H), 1.86 (q, J = 7.2 Hz, 2H), 1.74-1.58 (m, 3H), 1.56-1.46 (m, 3H), 1.39-1.22 (m, 6H), 1.20-1.10 (m, 6H), 0.88 (d, J = 8.0 Hz, 6H) 0.79 (d, J = 6.8 Hz, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 169.2, 165.4, 164.4, 164.0, 163.8, 163.3, 162.4, 155.8, 151.5, 151.3, 155.8, 151.5, 151.3, 132.6, 132.1, 131.9, 131.4, 131.1, 129.0, 128.9, 127.1, 126.2, 122.4, 121.4, 121.3, 121.2, 121.0, 115.8, 115.2, 114.6, 66.9, 66.8, 39.4, 37.4, 36.2, 36.1, 29.9, 28.1, 24.8, 22.8, 22.7, 19.8. **MALDI-MS** *m/z*= 939.7 $[M]^+$. Elemental analysis: (Requires for $C_{56}H_{62}N_2O_{11}$: C, 71.62; H, 6.65; N, 2,98% found C, 71.49; H, 6.88; N, 3.01%). TGA: 272°C.

3-{4-[4-(S-3,7-dimethyloctyloxy)benzoyloxy]benzoyloxy}-5-(4-{5-[4-(dodecyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoyloxy)benzoic acid (8e or X12E(S)10*).

Yield: 95%, m.p.: 165.3°C. **IR** (KBr): 3200-2400 (COO-H), 2953, 2925 2867, 1746 (C=O livre), 1695, 1610, 1495, 1469, 1447, 1423, 1253 (C_{Ar}-O), 1134, 1073, 1013, 836, 739, 711 cm^{-1}. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ: 8.35 (d, J = 8.4Hz, 2H), 8.27 (d, J = 2.0 Hz, 2H), 8.25 (d, J = 2.0 Hz, 2H), 8.11 (d, J = 8.8 Hz, 2H), 8.06 (d, J = 8.8 Hz, 2H), 7.91 (m, 2H), 7.51 (t, J = 2.4 Hz, 1H), 7.38 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 4.08 (m, 2H), 4.02 (t, J = 6.8 Hz, 2H), 1.88-1.74 (m, 3H), 1.70-1.56 (m, 2H), 1.55-1.39 (m, 3H), 1.37-1.18 (m, 19H), 1.18-1.05 (m, 3H), 0.93 (d, J = 6.4 Hz, 3H) 0.84 (d, J = 6.8 Hz, 9H). **^{13}C NMR** (100 MHz, CD_2Cl_2) δ: 168.7, 165.3, 164.3, 164.0, 163.9, 163.8, 163.2, 162.4, 155.8, 151.5, 151.3, 132.4, 131.9, 131.7, 131.4, 130.9, 128.9, 128.8, 126.9, 126.3, 122.4, 121.3, 120.9, 115.8, 115.1, 114.5, 68.5, 66.9, 39.3, 37.3, 36.0, 32.0, 29.9, 29.7, 29.7, 29.6, 29.6, 29.4, 28.0, 26.0, 24.7, 22.8, 22.5, 22.4, 19.5, 13.9. **MALDI-MS** *m/z*= 967.6 $[M]^+$. Elemental analysis: (Requires for

$C_{58}H_{66}N_2O_{11}$: C, 72.03; H, 6.88; N, 2,90% found C, 71.77; H, 6.90; N, 2.91%). TGA: 270°C.

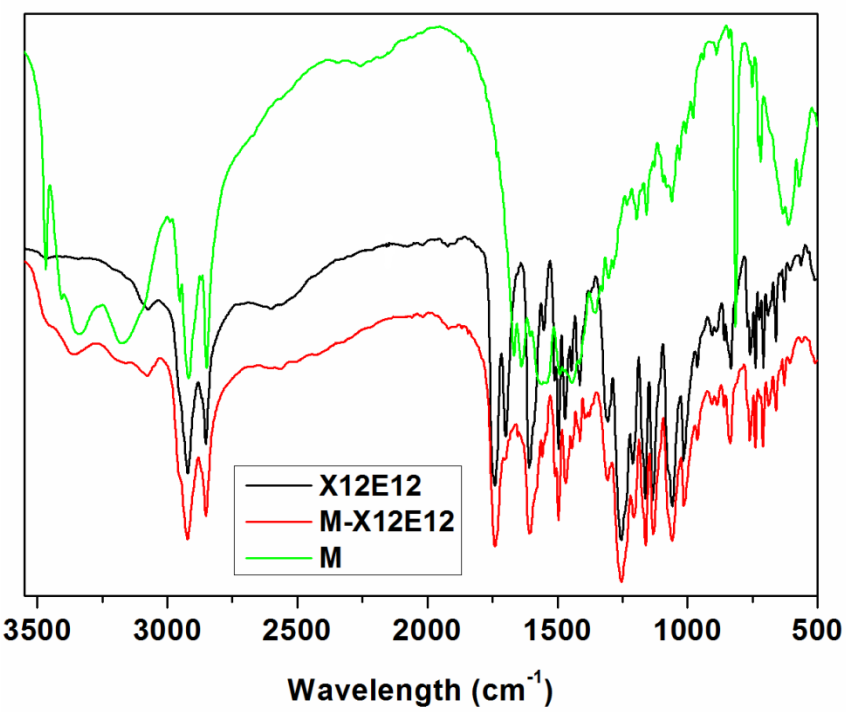
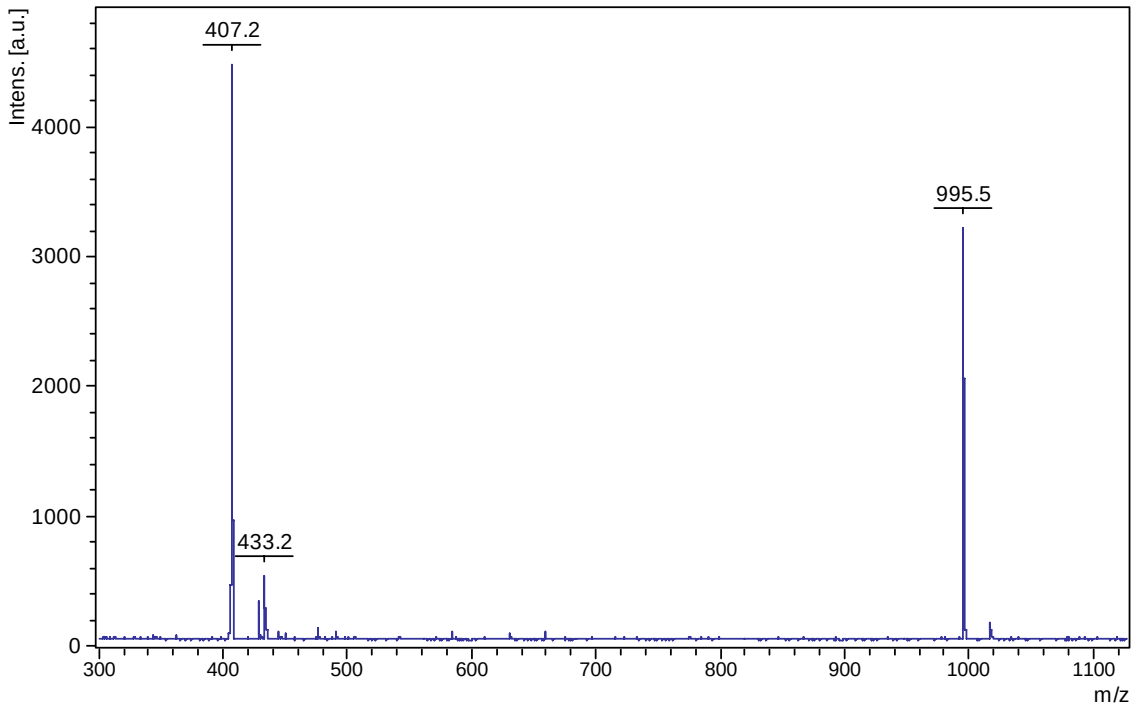
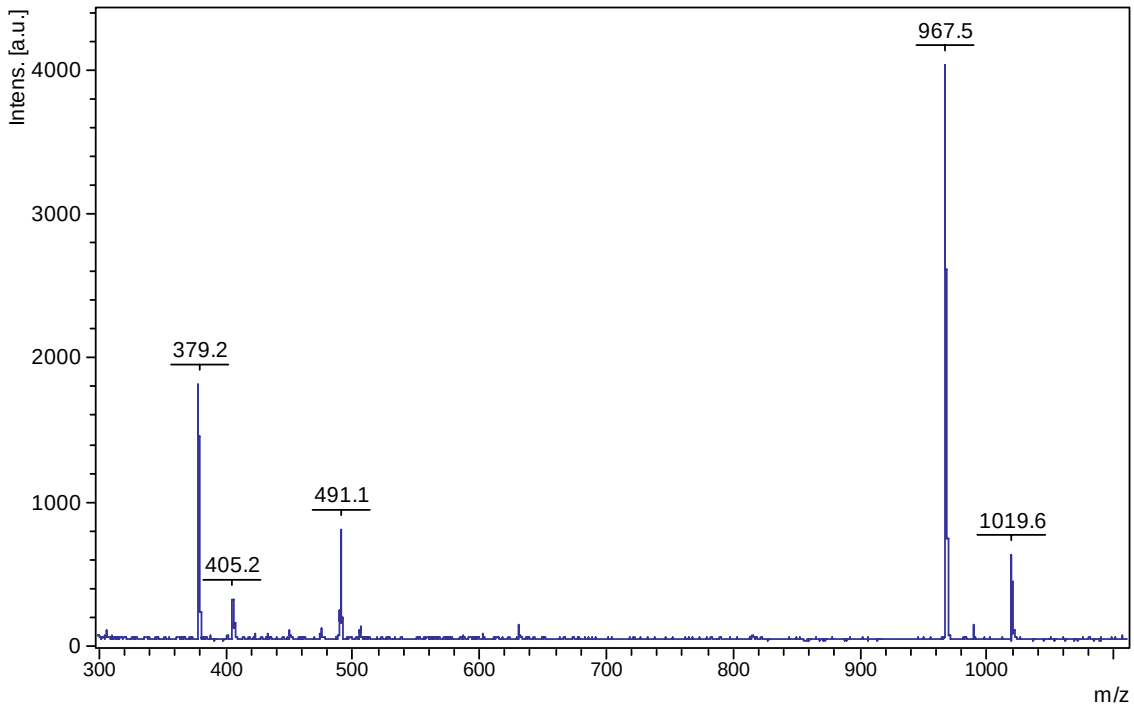


Figure SI1. IR spectra of the Melamine, the acid **X12E12** and their 1:3 complex **M-X12E12**.

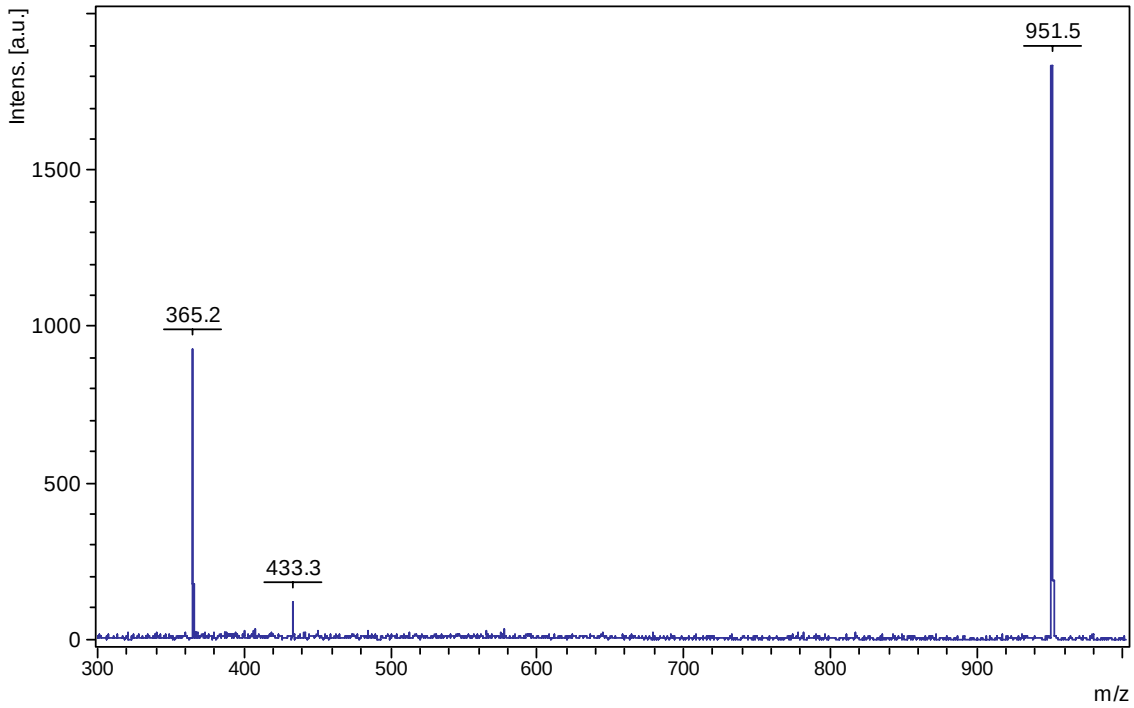
1.3. MALDI-TOF Spectra



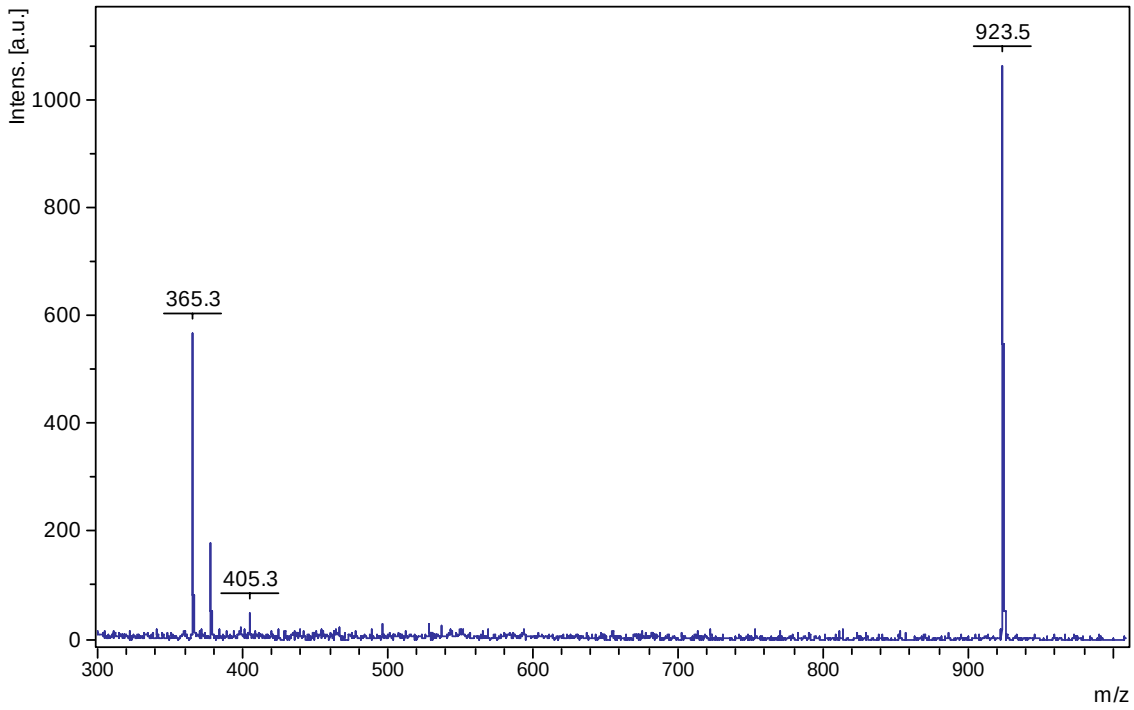
(a)



(b)



(c)



(d)

Figure SI2. MALDI-TOF spectra of (a) **X12E12**, (b) **X(S)10*E12**, (c) **X(R)10*E12**, (d) **X12E(S)10***.

1.4. DOSY experiments

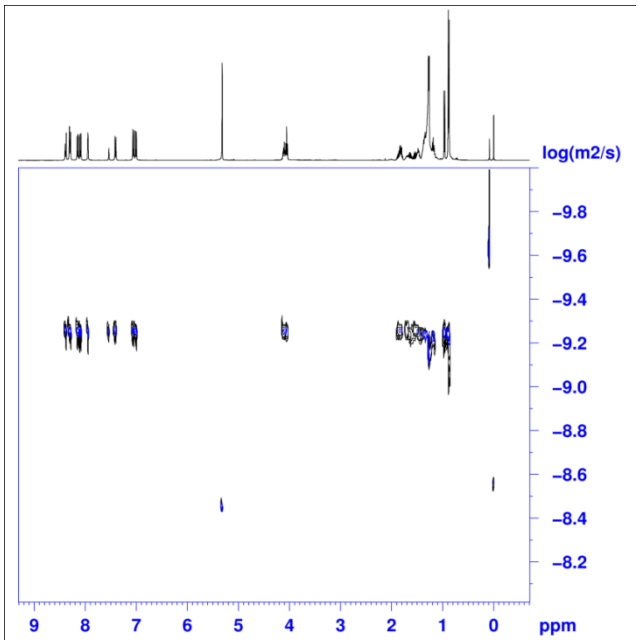


Figure SI3. 2D spectrum, in CD_2Cl_2, representing chemical shifts versus diffusion coefficients (logarithmic scale) for the acid **X12E(S)10*.**

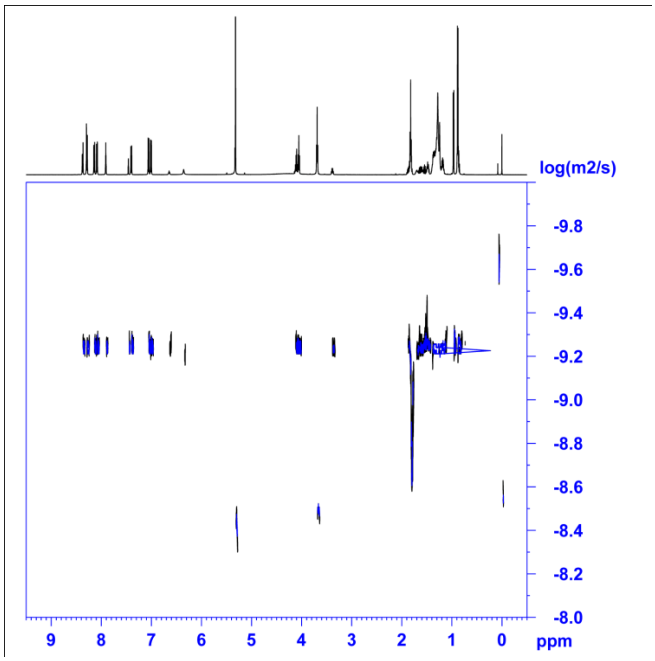


Figure SI4. 2D spectrum, in CD_2Cl_2, representing chemical shifts versus diffusion coefficients (logarithmic scale) for the complex **M-X12E(S)10*.**

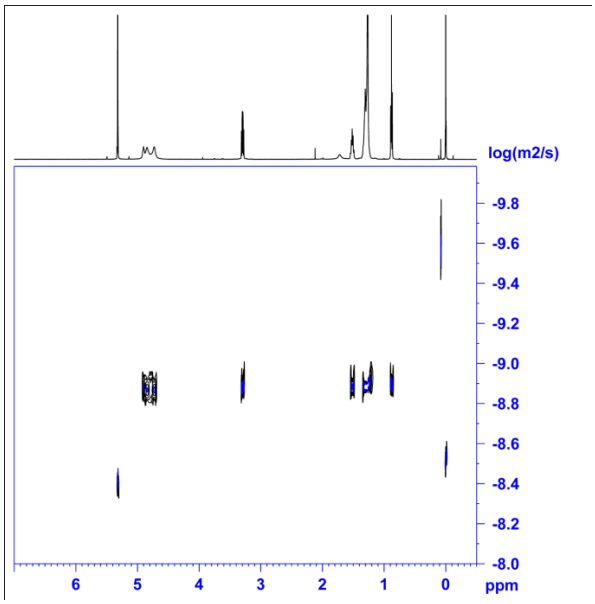
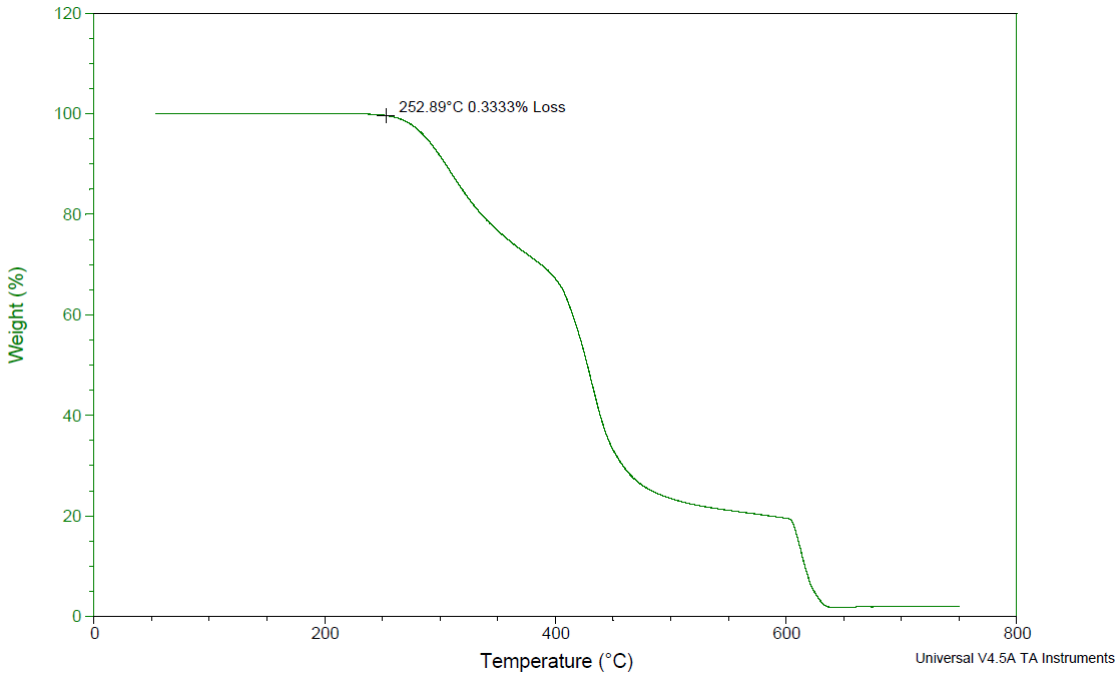


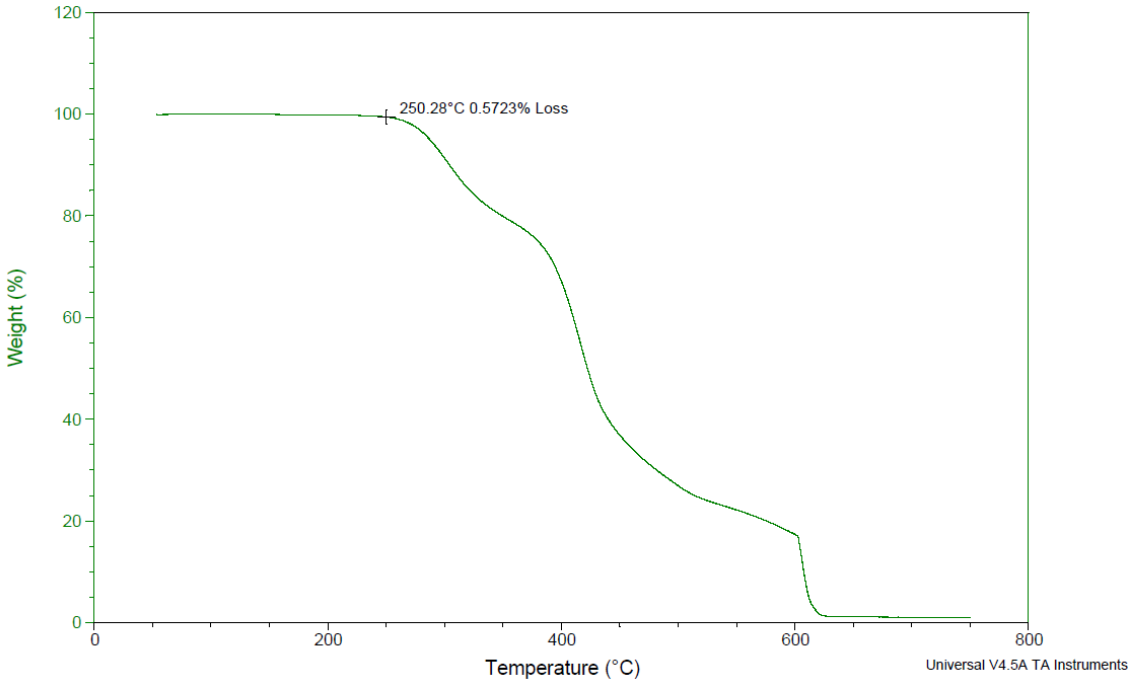
Figure SI5. 2D spectrum, in CD_2Cl_2, representing chemical shifts versus diffusion coefficients (logarithmic scale) for the melamine (**M).**

1.5. TGA curves

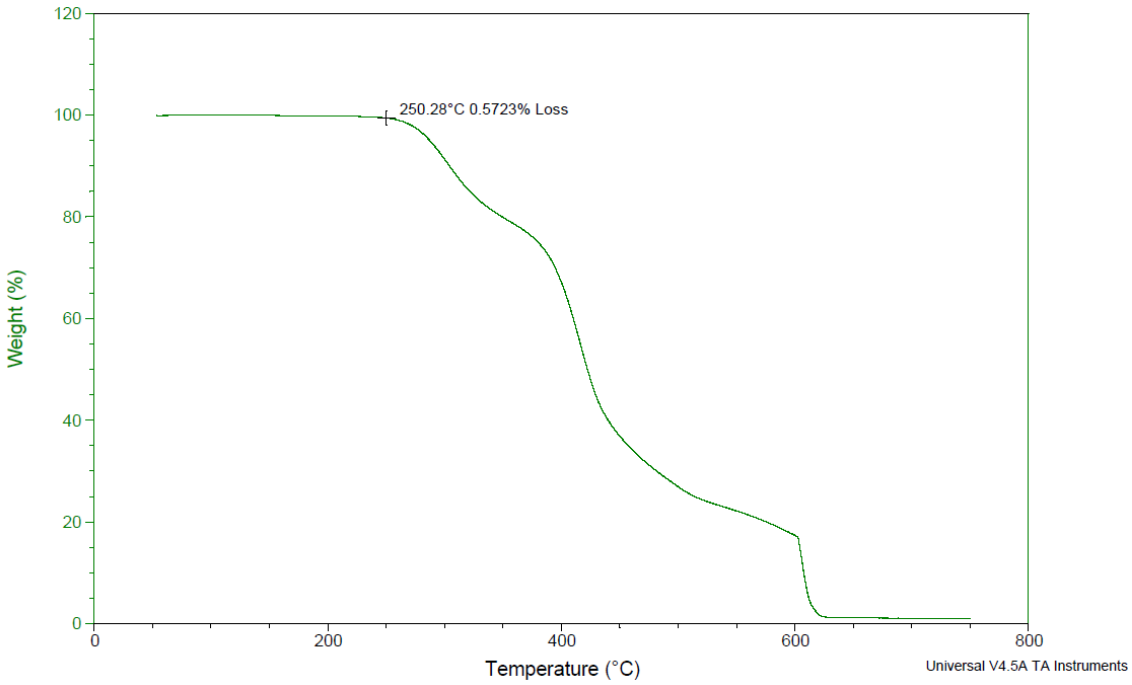
(a)



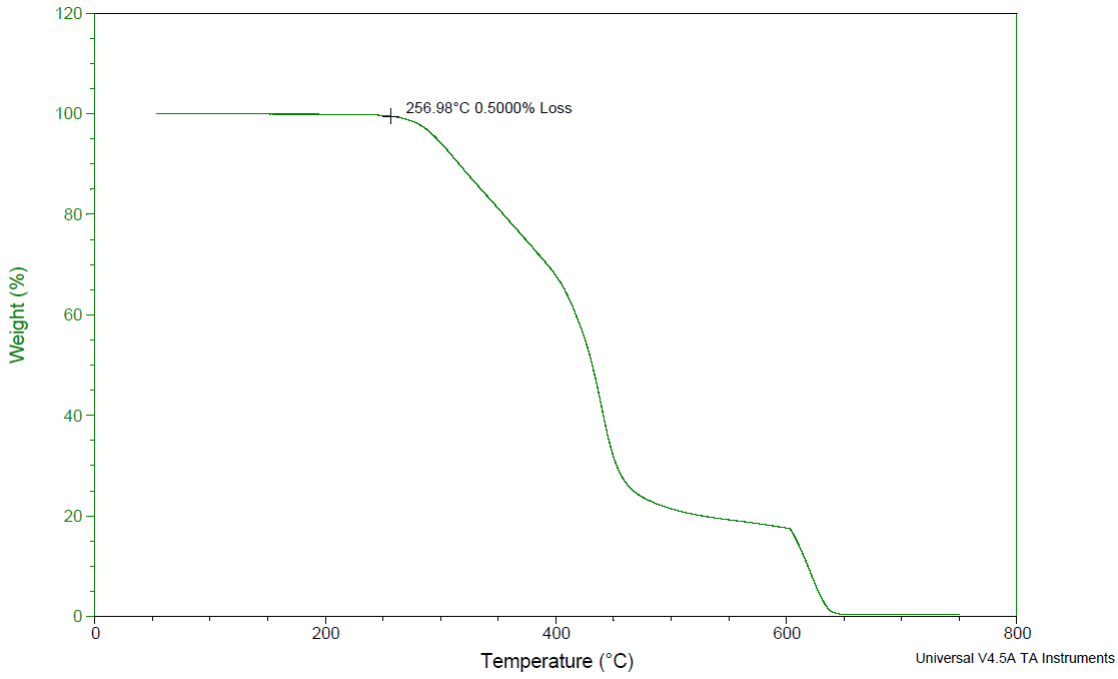
(b)


250.28°C 0.5723% Loss
Weight (%)
Temperature (°C)
Universal V4.5A TA Instruments

(c)


250.28°C 0.5723% Loss
Weight (%)
Temperature (°C)
Universal V4.5A TA Instruments

(d)



(e)

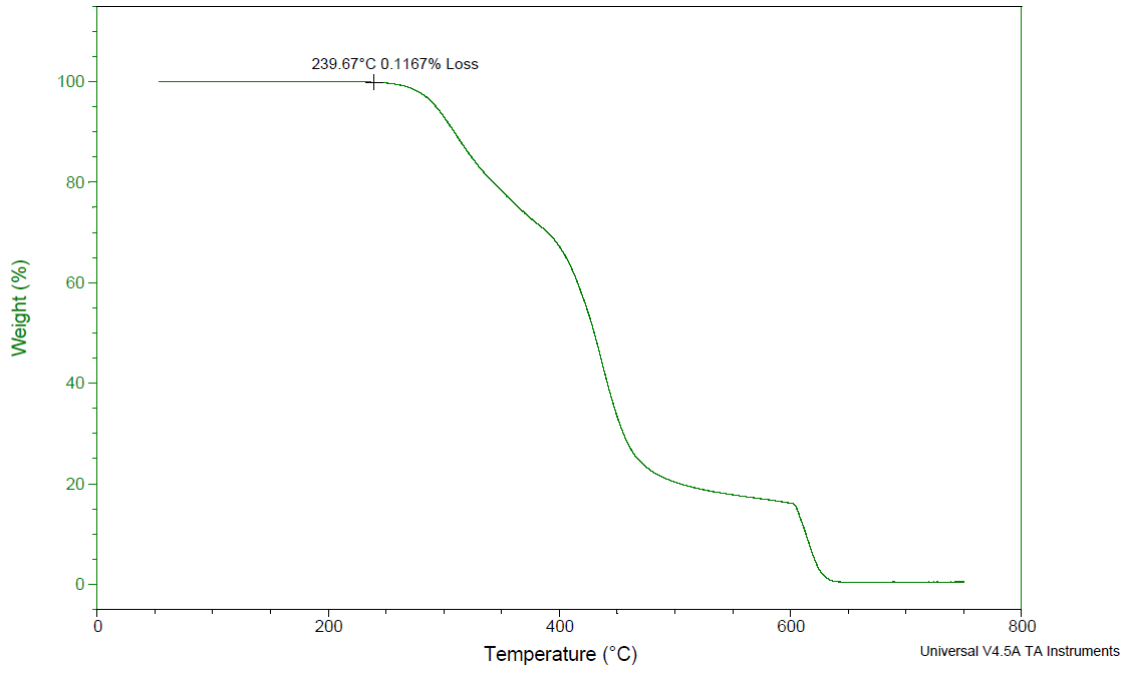
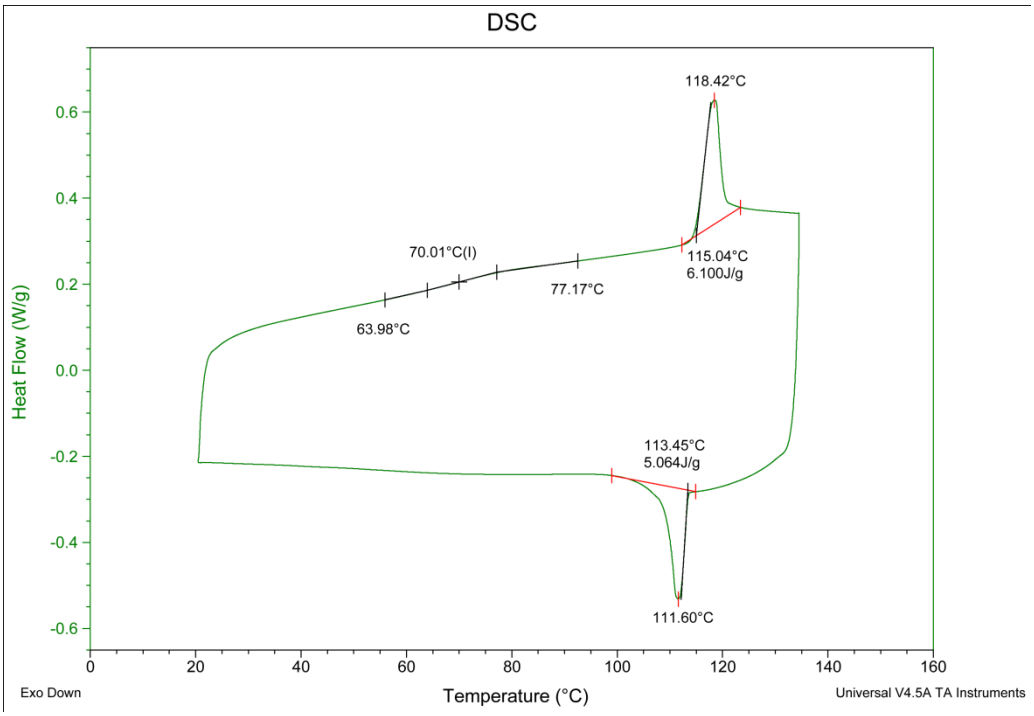
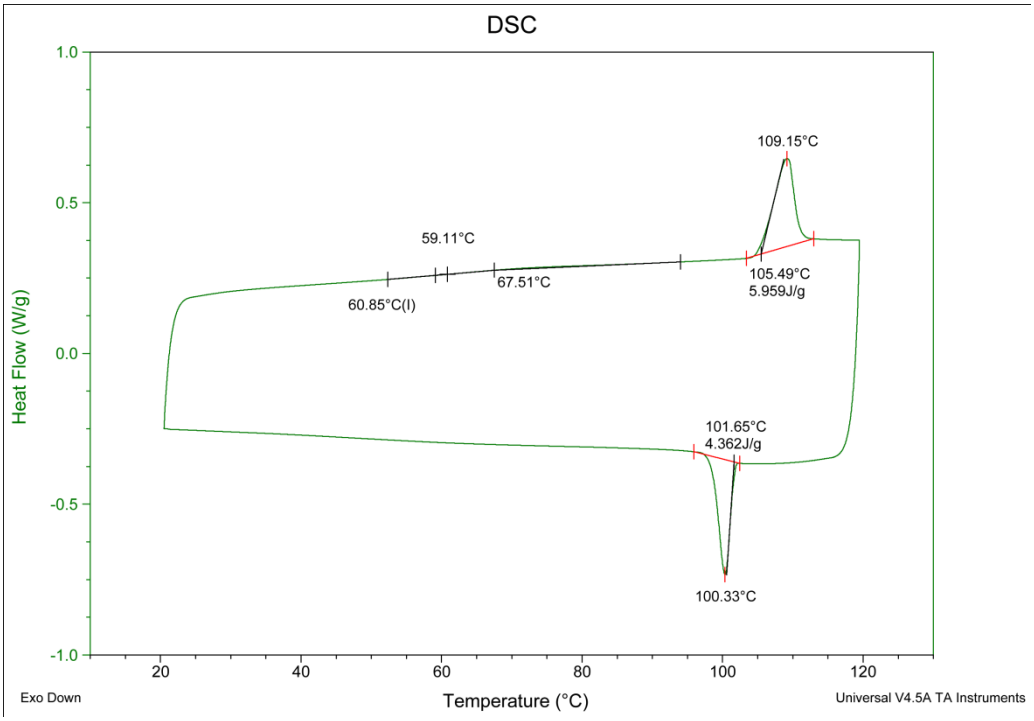


Figure SI6. TGA thermograms of (a) **X12E12**, (b) **X(S)10*E12**, (c) **X(R)10*E12**, (d) **X(S)10*E(S)10*,** (e) **X12E(S)10***.

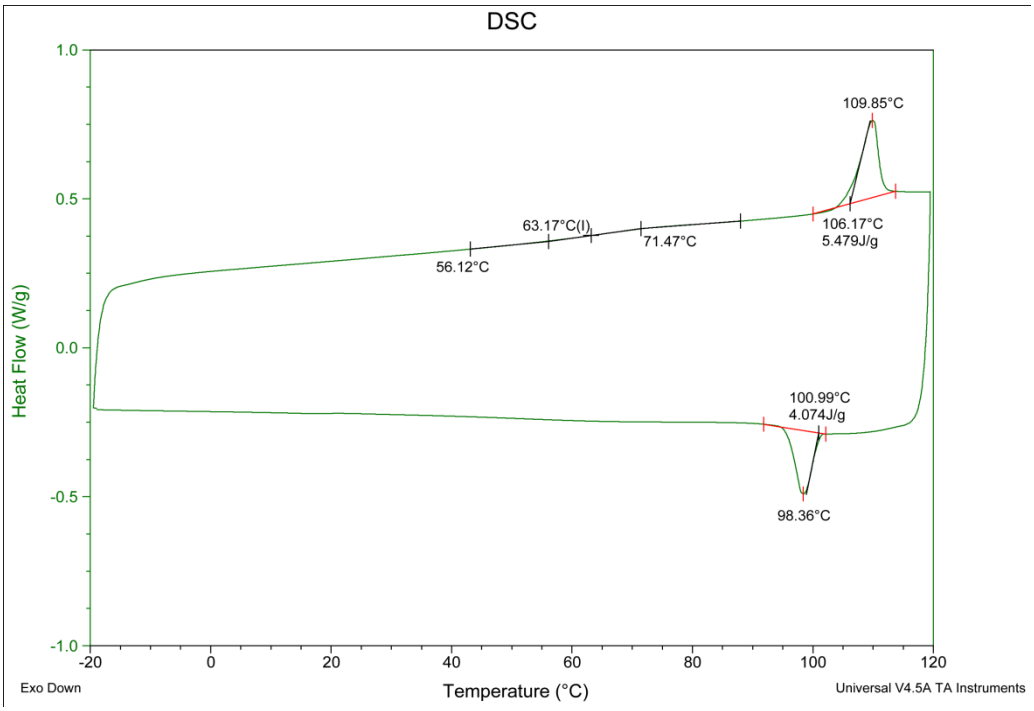
1.6. DSC thermograms



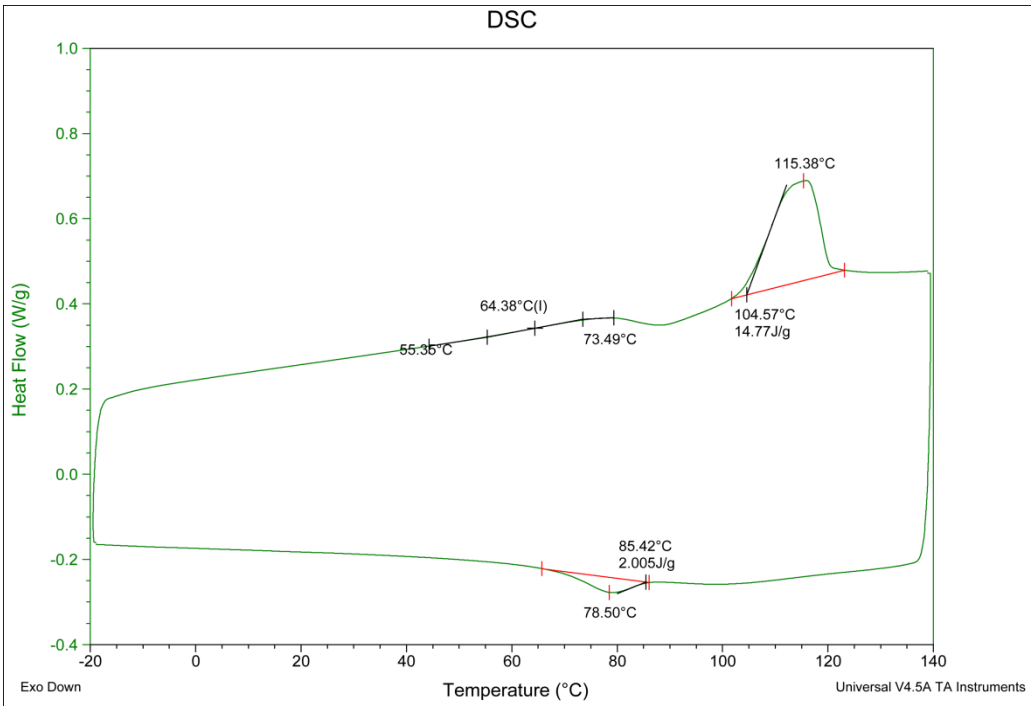
(a)



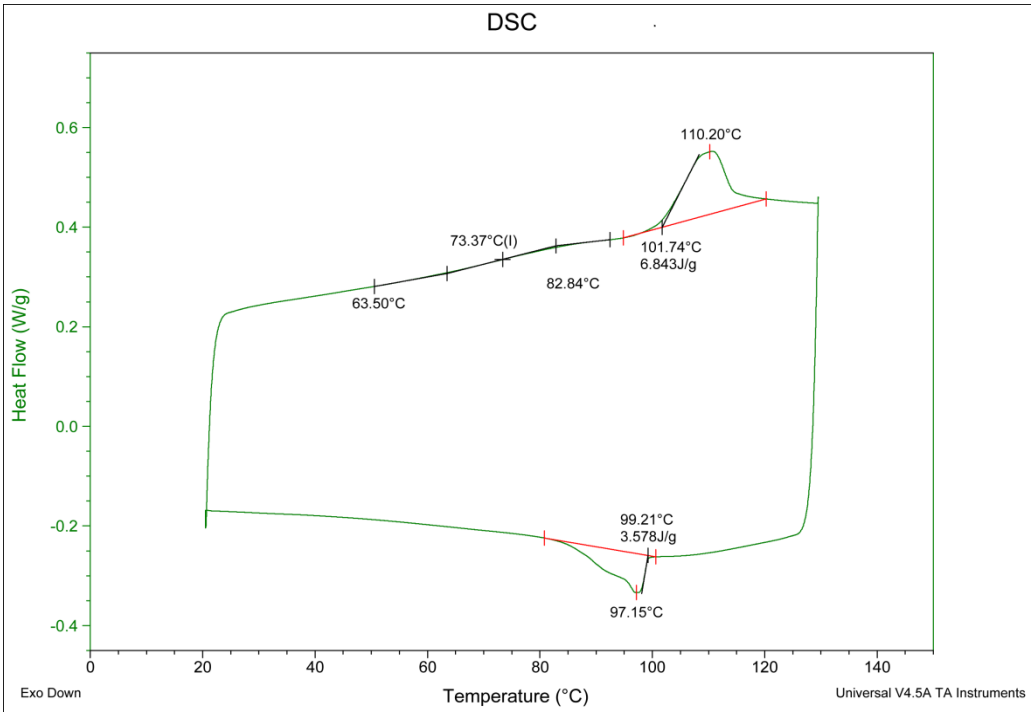
(b)


DSC
109.85°C
63.17°C(I)
71.47°C
106.17°C
5.479J/g
56.12°C
100.99°C
4.074J/g
98.36°C
Heat Flow (W/g)
Exo Down
Temperature (°C)
Universal V4.5A TA Instruments

(c)


DSC
115.38°C
64.38°C(I)
73.49°C
104.57°C
14.77J/g
55.35°C
85.42°C
2.005J/g
78.50°C
Heat Flow (W/g)
Exo Down
Temperature (°C)
Universal V4.5A TA Instruments

(d)



(e)

Figure SI7. DSC thermograms of (a) **X12E12**, (b) **X(S)10*E12**, (c) **X(R)10*E12**, (d) **X(S)10*E(S)10*,** (e) **X12E(S)10***. All the thermograms display the second heating-cooling cycle, which was recorded at a rate of 10 ºC/min.

1.7. X-ray Diffraction

Table SI1. X-ray diffraction data for the mesophases of the complexes **M-XE**.

Compound [3:1]	Mesophase	Parameters	d_{obs}(Å)	d_{calc}(Å)	(hk)
M-X12E12	Col_r	**a** = 81,6 Å	56.0	56.0	11
		b = 77,0 Å	38.5	38.5	02
			34.3	34.8	12
			21.7	21.7	23
M-X(S)10*E12	Col_r	**a =** 77,6 Å	55.5	55.45	11
		b = 79,2 Å	39.6	39.6	02
			36.5	35.3	12
			21.8	21.7	32
			17.4	17.4	42
			12.9	12.5	26
M-X(R)10*E12	Col_r	**a** = 77.0 Å	54.8	54.8	11
		b = 77.8 Å	38.9	38.9	02
			34.4	34.5	12
			21.5	21.4	32
			18.5	18.7	41
			15.1	15.1	51
			13,036	12.30	26
M-X(S)10*E(S)10*	Col_h	**a** = 48.1 Å	41.6	41.6	10
		h = 3.4 Å	24.1	24.0	11
			20.6	20.8	20
			15.5	15.7	21
M-X12E(S)10*	Col_r	**a** = 77.0 Å	54.8	54.8	11
		b = 77.8 Å	38.9	38.9	02
			32.9	34.7	12
			21.2	21.4	32
			14.8	15.1	51
			12.8	12.3	26

Col_r: rectangular columnar mesophase; a, b: rectangular lattice constants; d_{obs}: observed spacing; d_{calc}: calculated spacing; h k: Miller indexes of the 2D-lattice.

1.8. Job´s plot and titration NMR experiments

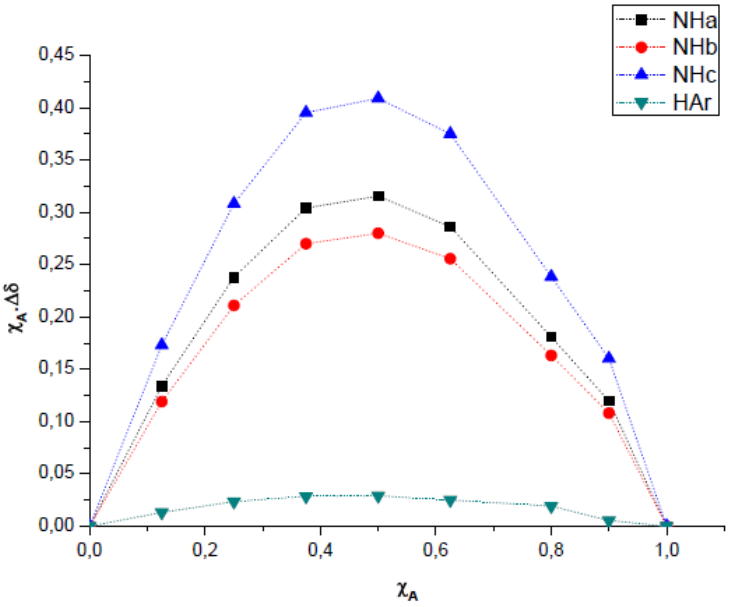


Figure SI8. Job´s plot to determine the stoichiometry of the **M-X12E(S)10***complex. The sum of concentration was kept to be 8.2 mM (CD_2Cl_2, 298K)

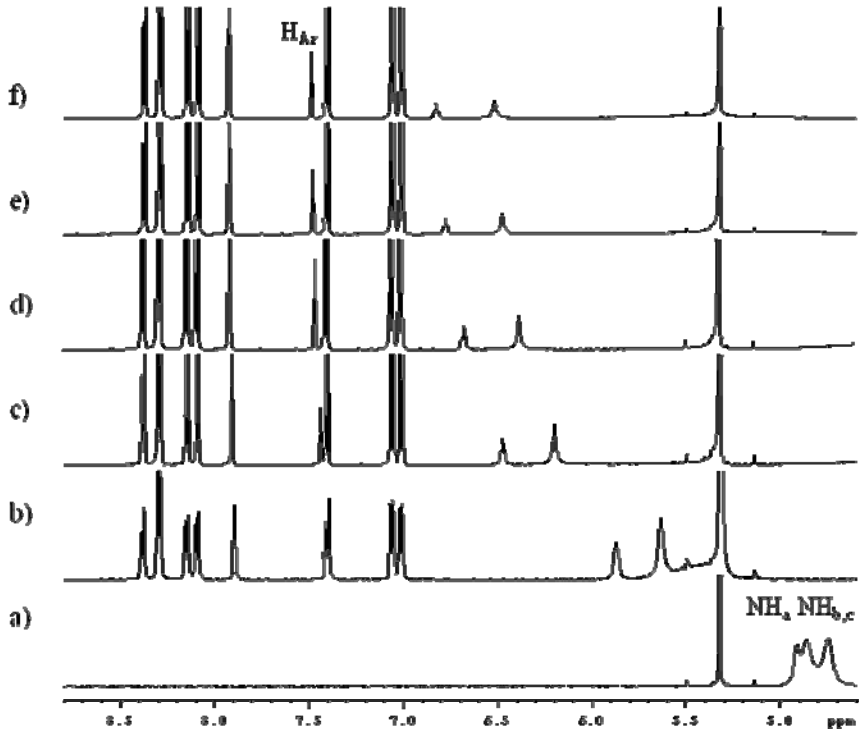


Figure SI9. ^{1}H NMR spectra (CD_2Cl_2, 298K) recorded for the complex **M-X12E(S)10*** formed by a) melamine **M** (2.55mM) with b) 2.55 mM, c) 5.11 mM, d) 7.65 mM, e) 10.2 mM and f) 12.75 mM of acid **X12E(S)10*.**

1.9. DC and Absorbance spectral

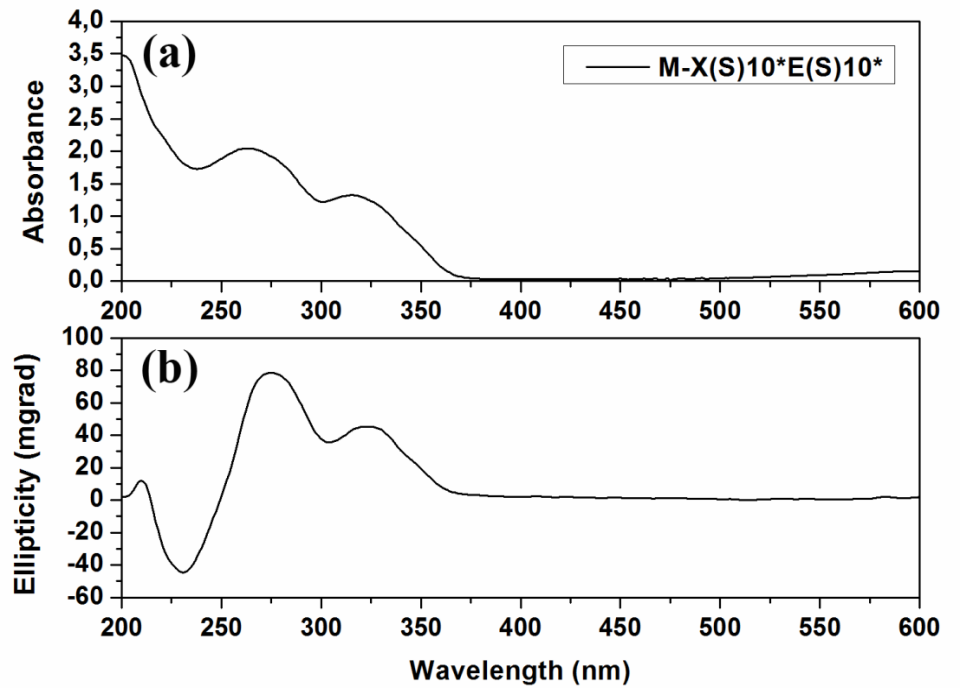


Figure SI10. Absorbance (a) and CD (b) spectra recorded on thin films in the mesophase (25°C) of the complex **M-X(S)10*E(S)10*** .

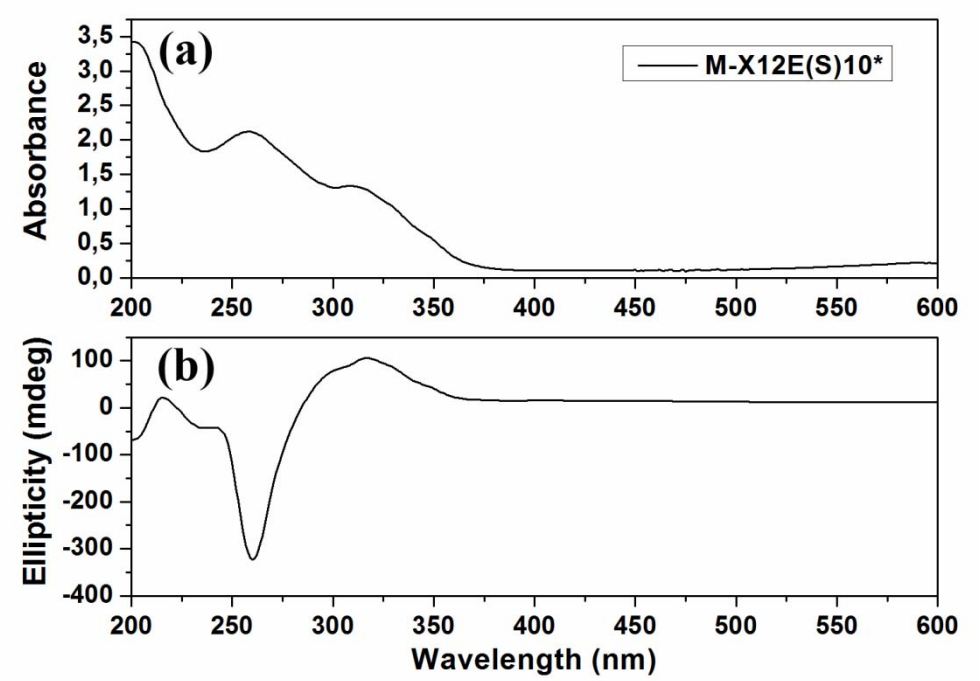


Figure SI11.Absorbance (a) and CD (b) spectra recorded on thin films in the mesophase (25°C) of the complex **M-X12E(S)10***.

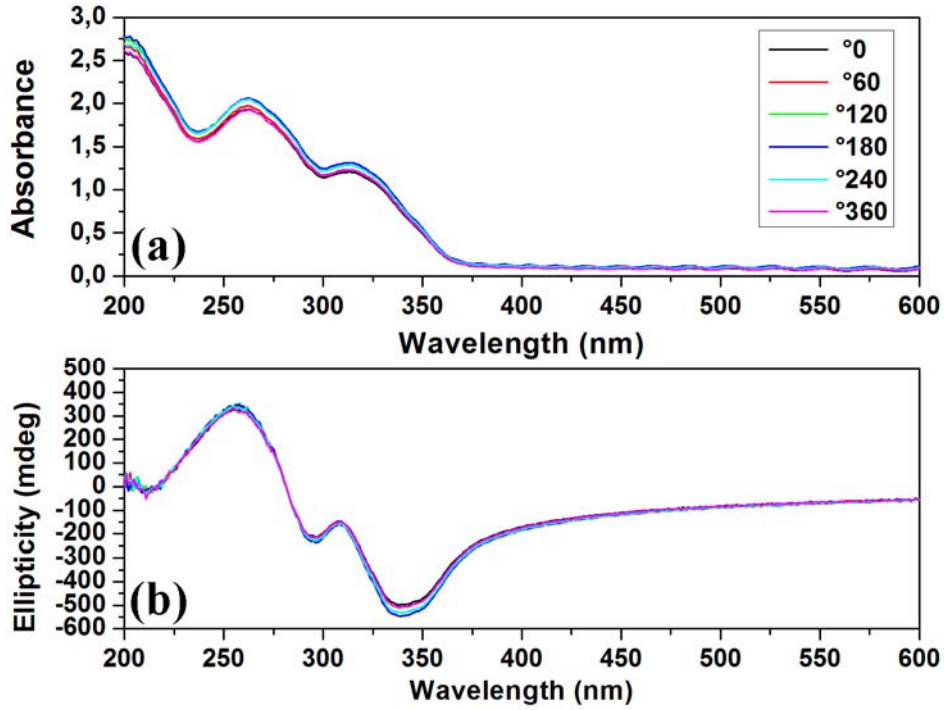


Figure SI12. Absorbance (a) and CD (b) spectra recorded on thin films in the mesophase (25°C) of the complex **M-X(S)10*E12** at six different orientations (in-plane) of the sample cells rotated by 60°.