H-bonded complexes containing 1,3,4-Oxadiazole derivatives. Mesomorphic behaviour, Photophysical Properties and Chiral Photoinduction.

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Electronic Supplementary Information (ESI)

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1. Experimental Details

1.1 General

NMR experiments

NMR experiments were performed on Bruker Avance spectrometers operating at 400.13 MHz and 500.13 for ^{1}H and 100.61and 125.75 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 maximun strength in sixteen spaced steps with a duration (δ) of 2.6 to 4 ms. Data were acquired in dichloromethane 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 (Nikon) with crossed polarizers and connected to a Mettler FP82 hot stage and a Mettler FP90 central processor.

Differential scanning calorimeter (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 Limdemann 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.

Circular Dichroism (CD)

CD spectra were recorded in a Jasco J-810. Neat samples were prepared by casting a tetrahydrofurane 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:

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

where ϕ_{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.

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

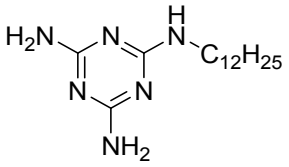
The relationship between the density (ρ) of the complexes **M-XX** and **M-XA** in the mesophase and the number of the molecules in the unit cell (*Z*) is given by the following equation:

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

Where M is the molar mass (g/mol) of the pure compound or of the complex, N is the Avogadro number, and V the unit cell volume (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. It is assumed that the density of the complexes should not be far from 1 g/cm^3.

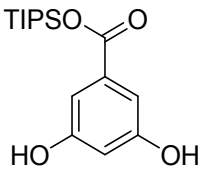
1.2 Synthesis

Dodecyl-1,3,5-triazine-2,4,6-triamine (M);



A mixture of 6-chloro-1,3,5-triazine-2,4-diamine (20.6 mmol), Na_2CO_3 (20.6 mmol), 1-dodecilamine (20.6 mmol) and 100mL dioxane was stirred under reflux for 6 h. After cooling, the reaction mixture was poured into 100mL of cold water. The precipitate was filtered off and the white solid dried on desiccator. The product was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (9:1) mixture and recrystallized from ethanol to give the compound. **Yield:** 75%. **IR** (KBr): 3467, 3336, 3176, 2918, 2848, 1667, 1639, 1560, 1443, 1302, 815cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 5.39, (s, 2H, -N*H*$_2$), 5.27 (s, 2H, -N*H*$_2$), 5.21 (t, J = 5.5 Hz, 1H, -N*H*-), 3.29 (q, *J* = 6.6 Hz, 2H, -C*H*$_2$NH-), 1.50 (m, 2H, -C*H*$_2$CH$_2$NH-), 1.24 (m, 18H, -C*H*$_2$-), 0.80 (t, *J* = 7.0 Hz, 3H, -C*H*$_3$). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 167.4, 166.8, 166.5, 40.7, 31.9, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 26.9, 22.7, 14.1. **ESI-MS** *m/z* = 296.0 $[M]^+$. **Elemental analysis:** (Requires for $C_{15}H_{30}N_6$: C, 61.19; H, 10.27; N, 28.54% found C, 61.11; H, 10.16; N, 28.03%). TGA: 211°C.

Triisopropylsilyl 3,5-dihydroxybenzoate (6);



The 3,5-dihydroxybenzóic acid (6.3 mmol) was dissolved in 20mL of DMSO and morpholine (8.4 mmol). The solution was allowed to stir for 5 min and triisopropylsilyl chloride (TIPSCl) (7.2 mmol) was added via syringe slowly upon rigorous stirring. The

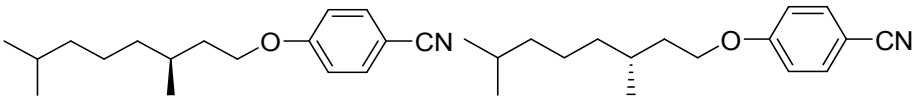
mixture was stirred for 15 min at room temperature. The reaction mixture was diluted with 50 mL of hexane/ethyl acetate mixture (1:1) and DMSO was removed upon several extractions with water. The organic phase was dried with anhydrous sodium sulfate and evaporated. The oil product was purified by flash chromatography on silica gel eluting with CH_2Cl_2/THF (95:5) mixture to give the product as white solid.

Yield: 83%. **m.p.**: 139°C. **IR** (KBr): 3300-3000 (OH), 2944, 2891, 1684, 1608, 1345, 1261, 1153, 1001, 883, 777, 687cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.18 (d, *J* = 2.2 Hz, 2H, Ar-*H*), 6.60 (t, *J* = 2.2 Hz, 1H, Ar-*H*), 5.90 (s, 2H, O*H*), 1.41 (q, *J* = 7.6 Hz, 3H, -C*H*$(CH_3)_2$), 1.13 (d, *J* = 7.6 Hz, 18H, -C*H*$_3$ TIPS). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 157.0, 133.3, 109.6, 107.7, 17.8, 12.0. **ESI-MS** *m/z*= 334.1 $[M+Na]^+$.

(S) and (R) -1-bromo-3,7-dimethyloctane;

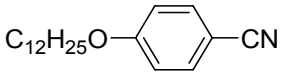
To a solution of (*S*)-8-bromo-2,6-dimethyloct-2-ene or (*R*)-8-bromo-2,6-dimethyloct-2-ene (25 mmol) in EtOAc (15 ml) was added the Adam's catalyst, PtO_2 (0.176 mmol). H_2 gas was bubbled through the solution slowly for about 30 min and the reaction was left under H_2 atmosphere for 24h. The suspension was filtered through Celite, washed with diethyl ether and the solvent was removed under vacuum. The product was a colorless transparent oil. The proceed was the same to the compound (R)-1-bromo-3,7-dimethyloctane. **Yield:** 99%, m.p.: oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 3.04 (m, 2H, -C*H*$_2$Br), 1,86 (m, 1H, -C*H*-$(CH_3)_2$), 1.64 (m, 2H, -C*H*$_2$CH$_2$Br), 1,52(m, 1H, -C*H*-$(CH_2)_2$-(CH_3)), 1.31-1.22 (m, 3H, -C*H*$_2$-), 1.16-1.10 (m, 3H, -C*H*$_2$-), 0.89 (d, *J* = 7.0 Hz, 3H, -C*H*$_3$), 0.87 (d, *J* = 6.4 Hz, 6H, -$(CH_3)_2$). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 40.0, 39.1, 36.7, 32.1, 31.6, 27.9, 24.5, 22.6, 22.5, 18.9.

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, OCH_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.

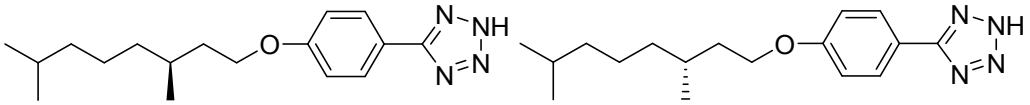
4-(dodecyloxy)benzonitrile (1c).



Synthetic procedure analogue to **1a**, **1b**. **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, OCH_2-), 1,72 (q, *J* = 6.5 Hz, 2H, OCH_2CH_2-), 1.37 (m, 2H, $OCH_2CH_2CH_2$-), 1.19 (m, 16H, -CH_2-), 0.80

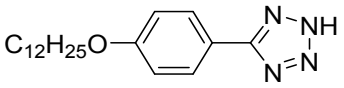
(t, *J* = 7.0 Hz, 3H, -C*H*$_3$). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 162.4, 133.8, 119.3, 115.1, 103.6, 68.4, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 28.9, 22.6, 14.1.

5-[4-((S)-3,7-dimethyloctyloxy)phenyl]tetrazole (2a) and 5-[4-((R)-3,7-dimethyloctyloxy)phenyl]tetrazole (2b).



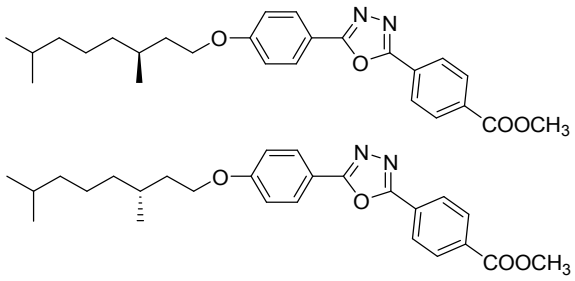
1a or **1b** (10.4 mmol), NaN_3 (31.3 mmol), NH_4Cl (31.3 mmol), and dimethylformamide (50 mL) were stirred at 110 °C for 12 h. The suspension was then poured into 350 mL of water/ice, after that the solution was acidification with concentrated HCl until pH~1. The crude product was collected by suction 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-d6) 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, OC*H*$_2$-), 1.86-1.78 (m, 1H, -C*H*-$(CH_3)_2$), 1.66-1.55 (m, 2H, OCH_2CH_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-d6) 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).



Synthetic procedure analogue to **2a**, **2b**. **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-d6) δ: 11.50 (s, 1H, HN-), 7.90 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 6.92 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 3.94 (t, *J* = 6.4 Hz, 2H, OCH_2-), 1.71 (m, 2H, OCH_2CH_2-), 1.38 (m, 2H, $OCH_2CH_2CH_2$-), 1.17 (m, 16H, -CH_2-), 0.79 (t, *J* = 6.5 Hz, 3H, -CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$ and DMSO-d6) 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 $[M]^+$.

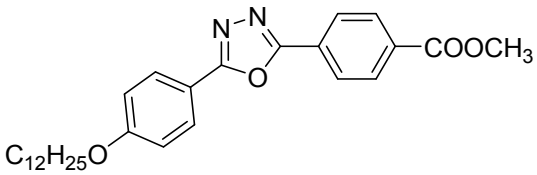
Methyl 4-{5-[4-((S)-3,7-dimethyloctyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoate (4a) and Methyl 4-{5-[4-((R)-3,7-dimethyloctyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoate (4b).



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; **2a** or **2b** (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 $[M+Na]^+$.

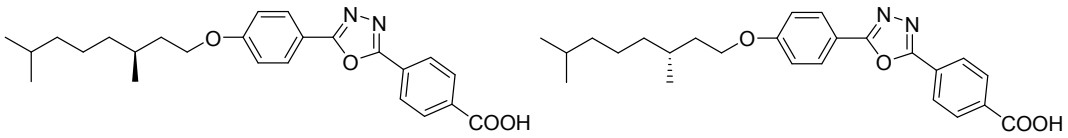
Methyl 4-{5-[4-(dodecyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoate (4c).



Synthetic procedure analogue to **4a**, **4b**. **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, OC*H*$_2$-), 3.96 (s, 3H, COC*H*$_3$), 1.82 (q, *J* = 6.4 Hz, 2H, -OCH_2C*H*$_2$), 1.47 (m, 2H, -OCH_2CH_2C*H*$_2$), 1.26 (m, 16H, -C*H*$_2$), 0.88 (t, *J* = 7.2 Hz, 3H, -C*H*$_3$). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 166.2, 164.5, 162.2, 130.2, 128.8, 127.9, 126.7,

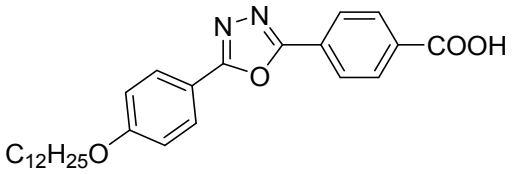
115.8, 115.0, 81.7, 68.3, 52.4, 31.9, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 29.1, 26.0, 22.7, 14.1. **MALDI-MS** *m/z* = 465.3 $[M]^+$.

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).



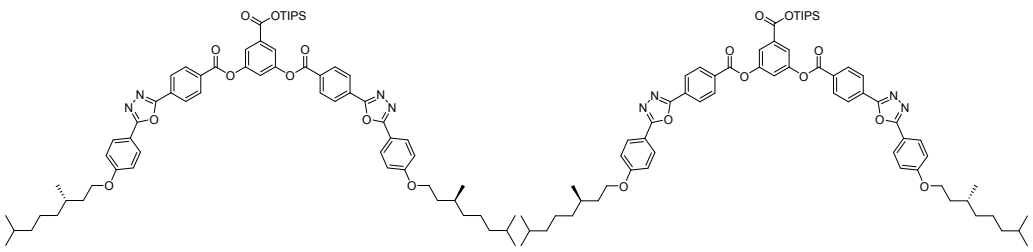
In a round bottom flask the compound **4a** or **4b** (5 mmol) and KOH (10 mmol) in mixture of EtOH:H_2O (7:3, 60 mL) were refluxed under stirring for 2h. After cooling, the resulting solution was acidified with HCl 5M until pH~1. The crude precipitate was filtered-off, washed with water and recrystallized 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-d6) δ: 8.11 (m, 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-d6) 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).



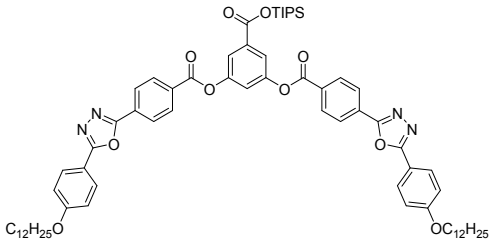
Synthetic procedure analogue to **5a**, **5b**. **Yield:** 99%, m.p.: 253°C. **IR** (KBr): 2954, 2920, 2848, 1683(C=O), 1613, 1496, 1384, 1250, 739cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$ and DMSO-d6) δ: 8.11 (m, 4H, Ar-*H*), 7.98 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 6.99 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 3.98 (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-d6) 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]$^{+}$.

(S)-5-[(triisopropylsilyloxy)carbonyl]-1,3-phenylene bis(4-{5-[4-((S)-3,7-dimethyloctyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoate) (7a) and (R)-5-[(triisopropylsilyloxy)carbonyl]-1,3-phenylene bis(4-{5-[4-((R)-3,7-dimethyloctyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoate) (7b).



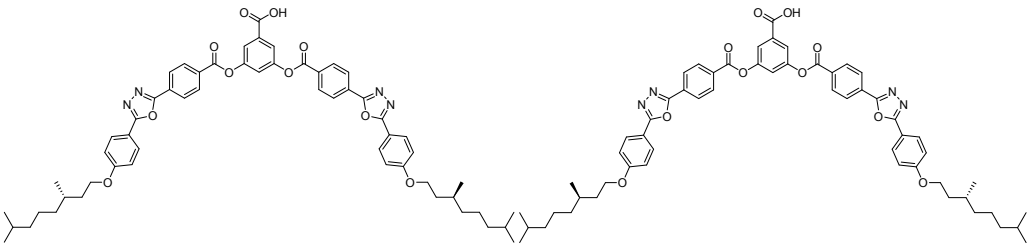
A mixture of the corresponding benzoic acid **3a** or **3b** (2.4 mmol), triisopropylsilyl 3,5-dihydroxybenzoate (1.0 mmol) and (N,N-dimethylamino)pyridinium-4-toluenesulfonate (DPTS) (2.4 mmol) in dichloromethane (50 ml) was stirred under argon atmosphere. The solution was cooled in an ice bath until 0°C. Subsequently N,N'-dicyclohexylcarbodiimide (2.4 mmol) solubilized in dichloromethane was added . The mixture was stirred at room temperature for 24h. 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. **Yield:** 68%, m.p.: 134°C. **IR** (KBr): 2955, 2920, 2866, 1740(C=O), 1702(C=O TIPS), 1615, 1496, 1306, 1251(C_{Ar}-O), 1129, 1070, 1013, 836, 740, 712 cm^{-1}. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ: 8.37 (d, *J* = 8.6 Hz, 4H, Ar-*H*), 8.3 (d, *J* = 8.6 Hz, 4H, Ar-*H*), 8.10 (d, *J* = 9.0 Hz, 4H, Ar-*H*), 7.90 (d, *J* = 2.0 Hz, 2H, Ar-*H*), 7.50 (t, *J* = 2.0 Hz, 1H, Ar-*H*), 7.05 (d, *J* = 9.0 Hz, 4H, Ar-*H*), 4.09 (m, 4H, OCH_2-), 1.92-1.84 (m, 2H, -C*H*$(CH_3)_2$), 1.73-1.61 (m, 6H, OCH_2CH_2-), 1.58-1.51 (m, 3H, -C*H*-$(CH_2)_2$-(CH_3)), 1.49-1.40 (m, 6H, -CH_2-), 1.37-1.26 (m, 6H, -CH_2-), 1.16 (d, *J* = 7.6 Hz, 18H, -CH_3 TIPS), 0.97 (d, *J* = 6.4 Hz, 6H, -CH_3), 0.88 (d, *J* = 6.6Hz, 12H, -$(CH_3)_2$). **^{13}C NMR** (100 MHz, CD_2Cl_2) δ: 165.2, 164.4, 163.7, 162.2, 151.0, 138.6, 134.1, 131.3, 130.9, 128.9, 128.8, 126.9, 120.9, 115.7, 115.0, 66.6, 39.2, 37.2, 36.0, 29.8, 27.9, 24.6, 22.7, 22.6, 19.6, 17.8, 12.0. **MALDI-MS** *m/z*= 1141.5 $[M+Na]^+$.

5-[(triisopropylsilyloxy)carbonyl]-1,3-phenylene bis(4-{5-[4-(dodecyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoate) (7c).



Synthetic procedure analogue to **7a** and **7b**. **Yield:** 90%, m.p.: 123°C. **IR** (KBr): 2922, 2852, 1745(C=O), 1705(C=O TIPS), 1611, 1496, 1305, 1254(C_{Ar}-O), 1131, 1070, 1013, 739, 710 cm^{-1}. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ: 8.46 (d, *J* = 8.4 Hz, 4H, Ar-*H*), 8.37 (d, *J* = 8.4 Hz, 4H, Ar-*H*), 8.16 (d, *J* = 8.4 Hz, 4H, Ar-*H*), 7.98 (d, *J* = 2.0 Hz, 2H, Ar-*H*), 7.58 (t, *J* = 2.0 Hz, 1H, Ar-*H*), 7.14 (d, *J* = 8.4 Hz, 4H, Ar-*H*), 4.13 (t, *J* = 6.8 Hz, 4H, OCH_2-), 1.90 (q, *J* = 7.0 Hz, 4H, -OCH_2CH_2-), 1.56 (m, 4H, -$OCH_2CH_2CH_2$-), 1.53 (m, 3H, -$CH(CH_3)_2$), 1.34 (m, 32H, -CH_2-), 1.24 (d, *J* = 7.0 Hz, 18H, -CH_3 TIPS), 0.96 (t, *J* = 6.8 Hz, 6H, -CH_3). **^{13}C NMR** (100 MHz, CD_2Cl_2) δ: 164.8, 163.9, 163.4, 162.8, 161.9, 150.8, 133.8, 130.9, 130.5, 128.5, 128.3, 126.4, 120.5, 119.8, 115.4, 114.7, 68.0, 31.5, 29.3, 29.2, 29.2, 29.1, 28.9, 28.9, 28.7, 25.5, 22.3, 17.2, 13.5, 11.7. **MALDI-MS** *m/z* = 1197.6 $[M+Na]^+$.

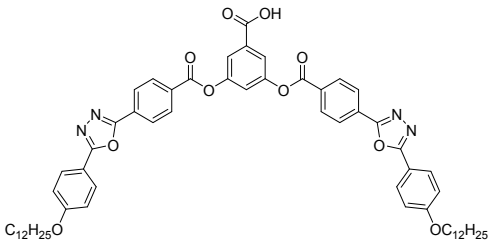
3,5-bis(4-{5-[4-((S)-3,7-dimethyloctyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoyloxy)benzoic acid (8a) and 3,5-bis(4-{5-[4-((R)-3,7-dimethyloctyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoyloxy)benzoic acid (8b).



The compound **7a** or **7b** (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 **8a** or **8b** as a white solid. **Yield:** 88 %, m.p.: 199°C. **IR** (KBr): 3300-2400 (COO-H), 2922, 2852, 1740 (C=O), 1698, 1608, 1511, 1496, 1254 (C_{Ar}-O), 1161, 1133, 1058, 1058, 1014 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.35 (d, *J* = 8.4 Hz, 4H, Ar-*H*), 8.27 (d, *J* = 8.4 Hz, 4H, Ar-*H*), 8.08 (d, *J* = 8.8 Hz, 4H, Ar-*H*), 7.97 (d, *J* = 2.0 Hz, 2H, Ar-*H*), 7.54 (t, *J* = 2.0 Hz, 1H, Ar-*H*), 7.02 (d, *J* = 8.8 Hz, 4H, Ar-*H*), 4.08 (m, 4H, OCH_2-), 1.90-1.82 (m, 2H, -C*H*$(CH_3)_2$), 1.70-1.59 (m, 6H, OCH_2CH_2-), 1.57-1.48 (m, 2H, -C*H*-$(CH_2)_2$-(CH_3)), 1.39-1.25 (m, 6H, -CH_2-), 1.19-1.15 (m, 6H, -CH_2-), 0.96 (d, *J* = 6.8 Hz, 6H, -CH_3), 0.87 (d, *J* = 6.8Hz, 12H, -(CH_3)$_2$). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 165.2, 163.6, 163.0, 162.3, 151.1, 131.2, 130.9, 128.9, 128.7, 126.9, 121.1, 120.8, 115.6, 115.1, 66.6, 39.2, 37.2, 36.0, 29.8, 27.9, 24.6, 22.7, 22.6, 19.6. **MALDI-MS** *m/z* = 963.7 $[M]^+$.

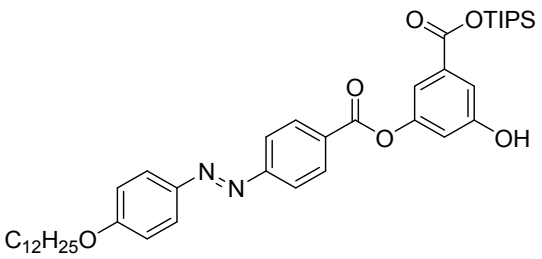
Elemental analysis: Requires for $C_{57}H_{62}N_4O_{10}$: C, 71.08; H, 6.49; N, 5.82% found: C, 70.89; H, 6.55; N, 5.78%).

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



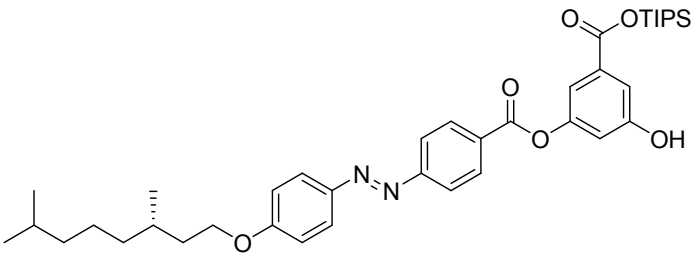
Synthetic procedure analogue to **8a** and **8b**. **Yield:** 74%, m.p.: 199°C. **IR** (KBr): 3200-2300 (COO-H), 2921, 2851, 1742 (C=O), 1698, 1610, 1496, 1469, 1254 (C_{Ar}-O), 1176, 1131, 1073, 1014, 739, 709 cm^{-1}. **^{1}H NMR** (400 MHz, CD_2Cl_2 and DMSO-d6) δ: 8.22 (d, *J* = 8.8 Hz, 4H, Ar-*H*), 8.15 (d, J = 8.8 Hz, 4H, Ar-*H*), 7.94 (d, *J* = 8.8 Hz, 4H, Ar-*H*), 7.76 (d, *J* = 2.0 Hz, 2H, Ar-*H*), 7.34 (t, *J* = 2.0 Hz, 1H, Ar-*H*), 6.90 (d, *J* = 8.8 Hz, 4H, Ar-*H*), 3.91 (t, *J* = 6.0 Hz, 4H, OC*H*$_2$-), 1.68 (q, *J* = 6.0 Hz, 4H, OCH$_2$C*H*$_2$-), 1.33 (m, 4H, OCH$_2$CH$_2$C*H*$_2$-), 1.21 (m, 32H, -C*H*$_2$-), 0.73 (t, *J* = 7.0 Hz, 6H, -C*H*$_3$). **^{13}C NMR** (100 MHz, CD_2Cl_2 and DMSO-d6) δ: 169.3, 166.1, 164.8, 163.3, 162.7, 161.9, 150.6, 130.9, 130.5, 128.4, 128.3, 126.5, 120.4, 119.5, 115.2, 114.7, 67.9, 31.5, 29.2, 29.2, 29.1, 29.1, 28.9, 28.9, 28.7, 25.6, 22.2, 13.7. **MALDI-MS** *m/z* = 1019.8 $[M]^+$. **Elemental analysis:** (Requires for $C_{61}H_{70}N_4O_{10}$: C, 71.88; H, 6.92; N, 5.50% found: C, 72.01; H, 7.09; N, 5.42%).

Triisopropylsilyl 3-[(4-{[4-(dodecyloxy)phenyl]diazenyl}benzoyl)oxy]-5-hydroxybenzoate (9a).



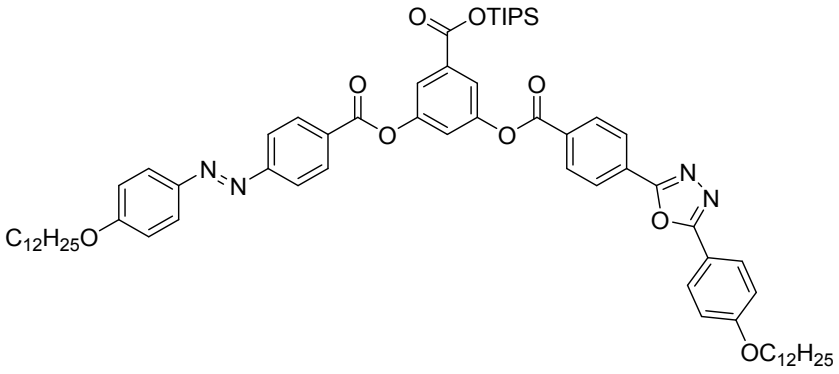
Synthetic procedure described in ref 7b (F. Vera *et al*., *J. Mater. Chem*, 2012, **22**, 18025). **Yield:** 39 %. **IR** (KBr): 3500-3100 (OH), 2954, 2920, 2848, 1734 (C=O), 1679 (C=O TIPS), 1496, 1384, 1255, 739 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.33 (d, *J* = 8.6 Hz, 2H, Ar-*H*), 7.98 (d, *J* = 8.6 Hz, 2H, Ar-*H*), 7.96 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 7.49 (dd, *J* = 2.2 Hz; 1.4 Hz, 1H, Ar-*H*), 7.48 (dd, *J* = 2.2 Hz, 1.4 Hz, 1H, Ar-*H*), 7.03 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 7.0 (dd, *J* = 2.2 Hz, *J* = 2.2 Hz, 1H, Ar-*H*), 4.07 (t, *J* = 6.6 Hz, 2H, OCH_2-), 1.84-1.79 (q, *J* = 6.6 Hz, 2H, OCH_2CH_2-), 1.51-1.38 (m, 5H, $OCH_2CH_2CH_2$- and -C*H*-), 1.28 (m, 16H, -CH_2-), 1.15 (d, *J* = 7.4 Hz, 18H, -CH_3 TIPS), 0.89 (t, *J* = 6.6 Hz, 3H, -CH_3). **MALDI-MS** *m/z* = 703.4 $[M+Na]^+$.

(S)-Triisopropylsilyl 3-{[4-({4-[(3,7-dimethyloctyl)oxy]phenyl}diazenyl)benzoyl]oxy}-5-hydroxybenzoate (9b).



Synthetic procedure described in ref 7b (F. Vera *et al*., *J. Mater. Chem*, 2012, **22**, 18025). **Yield:** 41%. **IR** (KBr): 3500-3100 (OH), 2950, 2846, 1730 (C=O), 1677 (C=O TIPS), 1496, 1382, 1254, 738cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.32 (d, *J* = 8.6 Hz, 2H, Ar-*H*), 7.98 (d, *J* = 8.6 Hz, 2H, Ar-*H*), 7.96 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 7.49 (dd, *J* = 2.2 Hz; 1.4 Hz, 1H, Ar-*H*), 7.46 (dd, *J* = 2.2 Hz, 1.4 Hz, 1H, Ar-*H*), 7.03 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 6.99 (dd, *J* = 2.2 Hz, *J* = 2.2 Hz, 1H, Ar-*H*), 5.49 (s, 1H, O*H*), 4.09 (m, 2H, OCH_2), 1.87 (m, 1H, -C*H*-), 1.76-1.48 (m, 6H, -CH_2-), 1.46-1.24 (m, 6H, -CH_2-), 1.21-1.06 (d, *J* = 7.6, 18H, -CH_3 TIPS), 0.97 (d, *J* = 6.4 Hz, 3H, -CH_3), 0.88 (d, *J* = 6.8 Hz, 6H, -(CH_3)$_2$). **MALDI-MS** *m/z* = 675.5 [M]$^+$.

Triisopropylsilyl 3-[(4-{5-[4-(dodecyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoyl)oxy]-5-[(4-{[4-(dodecyloxy)phenyl]diazenyl}benzoyl)oxy]benzoate (10a).

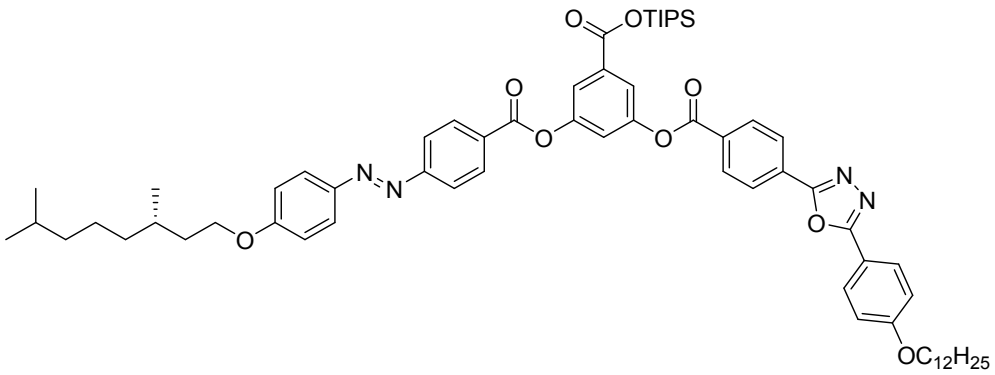


A mixture of the corresponding phenol **9 (a, b, or c**) (1.0 mmol) and the corresponding benzoic acid **5** (**a, b, c**) (1.2 mmol), and (N,N-dimethylamino)pyridinium-4-toluenesulfonate (DPTS) (2.4 mmol) in dichloromethane (50 ml) was stirred under argon atmosphere. The solution was cooled in an ice bath until 0°C. Subsequently N,N'-dicyclohexylcarbodiimide (1.2 mmol) solubilized in dichloromethane was added . The mixture was stirred at room temperature for 24h. 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.

Yield: 94%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.37 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 8.34 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 8.29 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 8.09 (d, *J* = 9.2 Hz, 2H, Ar-*H*), 7.98 (d, *J* = 7.0 Hz, 2H, Ar-*H*), 7.96 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.88 (d, *J* = 2.4 Hz, 2H, Ar-*H*), 7.49 (t, *J* = 2.0 Hz, 1H, Ar-*H*), 7.04 (d, *J* = 5.6 Hz, 2H, Ar-*H*), 7.02 (d, *J* = 5.6 Hz, 2H, Ar-*H*), 4.05 (m, 4H, OCH_2-), 1.83 (q, *J* = 7.2 Hz, 4H, OCH_2CH_2-), 1.51-1.44 (m, 7H, $OCH_2CH_2CH_2$- and -CH-), 1.27 (m, 32H, -CH_2-), 1.16 (d, *J* = 7.6 Hz, 18H, -CH_3 TIPS), 0.88 (t, *J* = 7.2 Hz, 6H, -CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 165.3, 164.4, 163.7, 163.1, 162.5, 162.3, 156.0, 151.2, 151.0, 146.8, 134.1, 131.3, 130.9, 129.7,

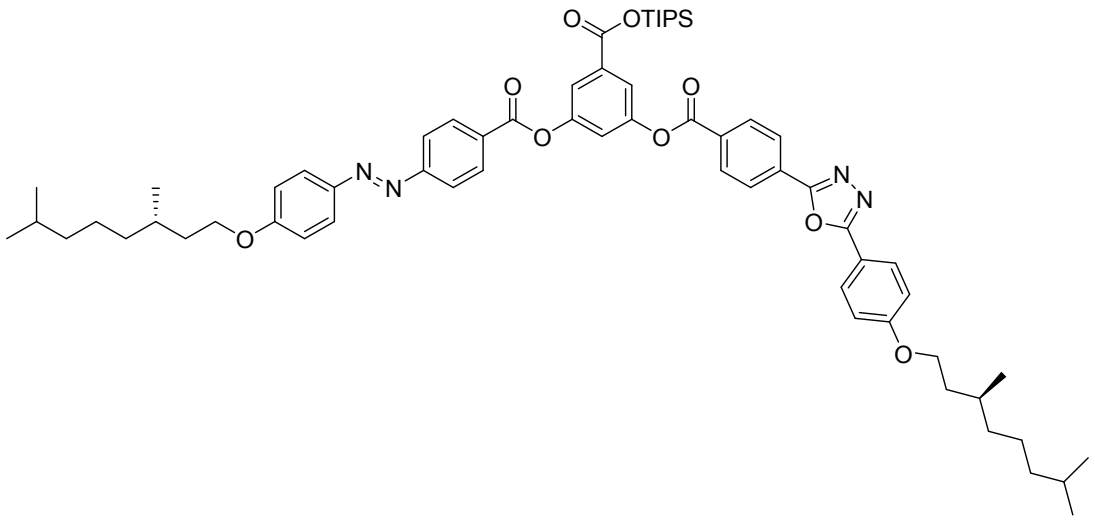
128.8, 128.7, 126.9, 125.3, 122.6, 115.7, 115.0, 114.8, 68.4, 68.3, 31.9, 29.6, 29.6, 29.5, 29.5, 29.2, 29.1, 26.0, 22.7, 17.8, 14.1, 12.0. **MALDI-MS** *m/z* = 1001.4 $[M+Na]^+$.

(S,)-Triisopropylsilyl 3-{[4-({4-[(3,7-dimethyloctyl)oxy]phenyl} diazenyl)benzoyl]oxy}-5-[(4-{5-[4-(dodecyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoyl)oxy]benzoate (10b).



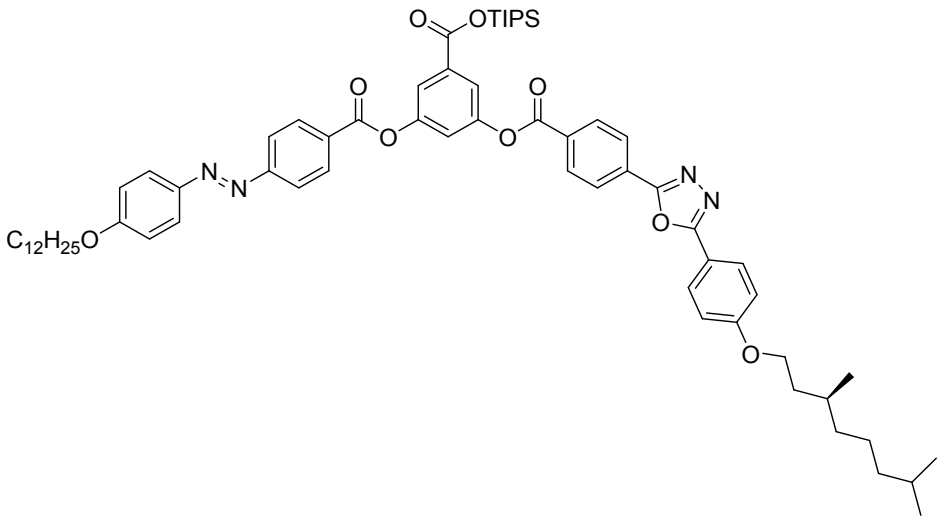
Yield: 94%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.37 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 8.34 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 8.29 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 8.09 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 7.99 (d, *J* = 6.0 Hz, 2H, Ar-*H*), 7.97 (d, *J* = 6.8 Hz, 2H, Ar-*H*), 7.88 (d, *J* = 2.4 Hz, 2H, Ar-*H*), 7.49 (t, *J* = 2.4 Hz, 1H, Ar-*H*), 7.04 (d, *J* = 4.4 Hz, 2H, Ar-*H*), 7.02 (d, *J* = 4.0 Hz, 2H, Ar-*H*), 4.09 (m, 2H, OCH_2-), 4.05 (m, 2H, OCH_2-), 1.91-1.77 (m, 3H, -CH_2-and-C*H*), 1.75-1.59 (m, 3H, -CH_2-) 1.54-1.41 (m, 5H, -CH_2- and CH_{TIPS}), 1.39-1.23 (m, 19H, -CH_2-), 1.16 (d, *J* = 7.6 Hz, 21H, -C$H_{3\ \text{TIPS}}$), 0.97 (d, *J* = 6.4 Hz, 3H, -CH_3) 0.88 (d, *J* = 6.8 Hz, 9H, -(CH_3) and -(CH_3)$_2$). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 165.2, 164.4, 164.2, 163.7, 163.2, 162.5, 162.3, 156.0, 151.3, 151.0, 146.8, 134.1, 131.3, 130.9, 129.7, 128.9, 128.8, 126.9, 125.3, 122.6, 121.1, 120.8, 120.4, 115.7, 115.0, 114.8, 68.3, 66.8, 53.4, 39.2, 37.2, 36.0, 31.9, 29.8, 29.7, 29.6, 29.5, 29.5, 29.4, 29.3, 29.1, 27.8, 26.0, 24.6, 22.7, 22.6, 19.6, 17.8, 14.1, 12.0. **MALDI-MS** *m/z* = 1107.7 $[M]^+$.

Triisopropylsilyl 3-{[4-(5-{4-[((S)-3,7-dimethyloctyl)oxy]phenyl}-1,3,4-oxadiazol-2-yl)benzoyl]oxy}-5-{[4-((E)-{4-[((S)-3,7-dimethyloctyl)oxy]phenyl}diazenyl)benzoyl]oxy}benzoate (10d).



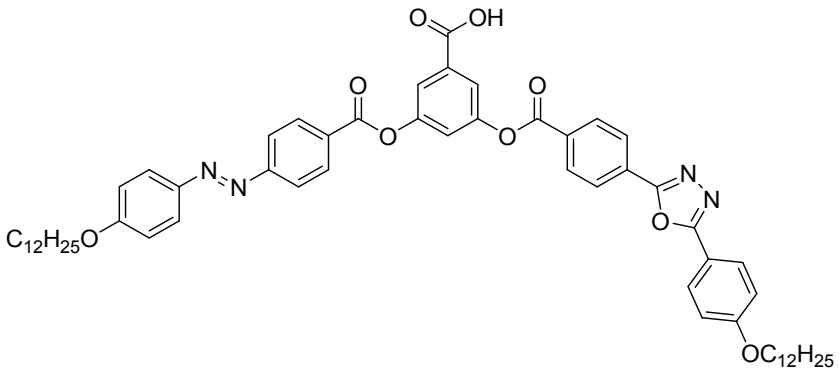
Yield: 85%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.37 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 8.34 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 8.30 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 8.09 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 7.99 (d, *J* = 6.0 Hz, 2H, Ar-*H*), 7.96 (d, *J* = 6.4 Hz, 2H, Ar-*H*), 7.88 (d, *J* = 3.2 Hz, 2H, Ar-*H*), 7.49 (t, *J* = 3.0 Hz, 1H, Ar-*H*), 7.05 (d, *J* = 5.6 Hz, 2H, Ar-*H*), 7.02 (d, *J* = 5.6 Hz, 2H, Ar-*H*), 4.09 (m, 4H, OCH_2-), 1.86 (q, *J* = 6.0 Hz, 2H, C*H*-(CH_3)$_2$), 1.75-1.58 (m, 4H, -OCH$_2$CH_2), 1.57-1.47 (m, 2H, -CH_2-C*H*(CH$_3$)-), 1.39-1.23 (m, 6H, -CH_2-), 1.22-1.10 (m, 6H, -CH_2-), 1.16 (d, *J* = 9.6 Hz, 21H, -CH_2 and -C$H_{3\ TIPS}$), 0,97 (d, *J* = 8.4 Hz, 6H, -CH_3), 0.88 (d, *J* = 8.8 Hz, 12H, -(CH_3)$_2$). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 165.2, 164.4, 164.1, 163.7, 163.1, 162.5, 162.2, 155.9, 151.2, 151.0, 146.8, 134.1, 131.3, 130.9, 129.7, 128.9, 128.8, 126.9, 125.3, 122.6, 121.1, 120.8, 120.4, 115.7, 115.0, 114.8, 66.8, 66.6, 39.2, 37.2, 36.0, 36.0, 29.8, 27.9, 24.6, 22.7, 22.6, 19.6, 17.8, 12.0. **MALDI-MS** *m/z* = 1079.7 $[M]^+$.

(S)-triisopropylsilyl 3-{[4-(5-{4-[(3,7-dimethyloctyl)oxy]phenyl}-1,3,4-oxadiazol-2-yl)benzoyl]oxy}-5-[(4-{[4-(dodecyloxy)phenyl]diazenyl}benzoyl)oxy]benzoate (10e).



Yield: 77%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 8.35 (m, 6H, Ar-*H*), 8.10 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 7.99 (d, *J* = 6.0 Hz, 2H, Ar-*H*), 7.96 (d, *J* = 6.0 Hz, 2H, Ar-*H*), 7.88 (d, *J* = 2.1 Hz, 2H, Ar-*H*), 7.49 (t, *J* = 2.1 Hz, 1H, Ar-*H*), 7.05 (d, *J* = 5.7 Hz, 2H, Ar-*H*), 7.02 (d, *J* = 5.7 Hz, 2H, Ar-*H*), 4.08 (m, 4H, OCH_2-), 1.91-1.77 (m, 3H, -CH_2- and -C*H*), 1.75-1.59 (m, 3H, -CH_2-), 1.54-1.41 (m, 5H, -CH_2- and C*H* $_{TIPS}$), 1.39-1.23 (m, 19H, -CH_2-), 1.16 (d, *J* = 7.5 Hz, 21H, -C$H_{3\ TIPS}$), 0.97 (d, *J* = 6.3 Hz, 3H, -CH_3), 0.88 (d, *J* = 6.6 Hz, 9H, -(CH_3) and -(CH_3)$_2$). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 165.3, 164.4, 164.2, 163.7, 163.2, 162.5, 162.3, 156.0, 151.2, 151.0, 146.8, 134.1, 131.4, 131,3, 130.9, 129.7, 128.9, 128.7, 126.9, 125.3, 122.6, 121.1, 120.8, 120.4, 115.7, 115.1, 114.8, 68.4, 66.6, 39.2, 37.2, 36.0, 31.9, 29.8, 29.7, 29.6, 29.5, 29.5, 29.4, 29.3, 29.1, 27.9, 26.0, 24.6, 22.7, 22.6, 22.6, 19.6, 17.8, 14.1, 12.0. **MALDI-MS** *m/z* = 1129.7 $[M]^+$.

3-[(4-{5-[4-(dodecyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoyl)oxy]-5-[(4-{[4-(dodecyloxy)phenyl]diazenyl}benzoyl)oxy]benzoic acid (11a).

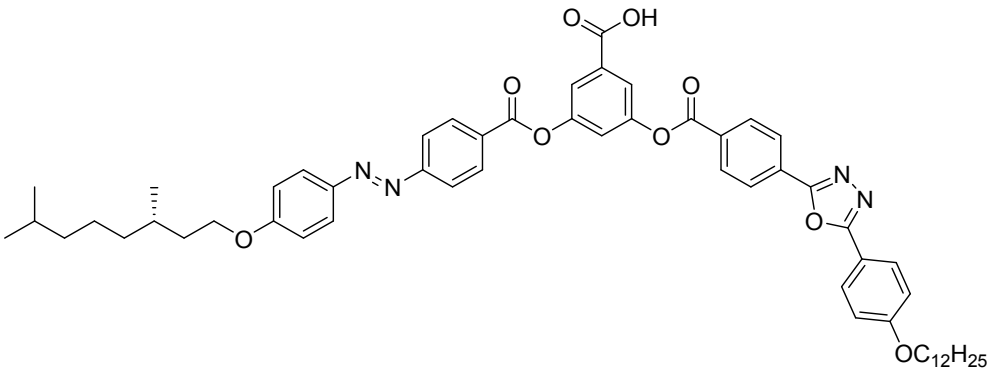


The compound **10 (a, b, c, d, e)** (1.0 mmol) was dissolved in 50 mL of dichloromethane and the solution was cooling to -78°C with a bath nitrogen and isopropyl alcohol. After 10 min tetra-n-butylammonium fluoride 1M (5.0 mmol) dissolved in THF was added via syringe upon rigorous stirring. The reaction 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 as a white solid.

Yield: 94%. m.p.: 178 °C. **IR** (KBr): 3200-2300 (COO-H), 2920, 2851, 1738(C=O), 1700, 1610, 1498, 1470, 1299, 1252 (C_{Ar}-O), 1135, 1072, 1011 cm^{-1}. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ: 8.32 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 8.29 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 8.24 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 8.03 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 7.94 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 7.91 (d, *J* = 9.2 Hz, 2H, Ar-*H*), 7.82 (d, *J* = 2.0 Hz, 2H, Ar-*H*), 7.42 (t, *J* = 2.4 Hz, 1H, Ar-*H*), 7.01 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 6.98 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 4.01 (m, 4H, OCH_2-), 1.77 (q, *J* = 6.8 Hz, 4H, OCH_2CH_2-), 1.45 (m, 4H, $OCH_2CH_2CH_2$-), 1.26 (m, 32H, -CH_2-), 0.83 (t, *J* = 6.8 Hz, 6H, -CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 165.9,

164.6, 163.5, 163.1, 162.5, 161.7, 155.3, 150.6, 150.4, 146.1, 133.1, 130.8, 130.7, 130.3, 129.1, 128.3, 128.1, 126.4, 124.8, 122.0, 120.3, 120.0, 119.4, 115.0, 114.6, 114.3, 67.9, 67.7, 31.1, 29.0, 29.0 28.9, 28.9, 28.7, 28.7, 28.6, 28.5, 25.4, 22.1, 13.6. **MALDI-MS** *m/z* = 1001.4 $[M + Na]^+$. **Elemental analysis:** (Requires for $C_{59}H_{70}N_4O_9$: C, 72.37; H, 7.21; N, 5.72 %; found: C, 72.28; H, 7.39; N, 5.44 %).

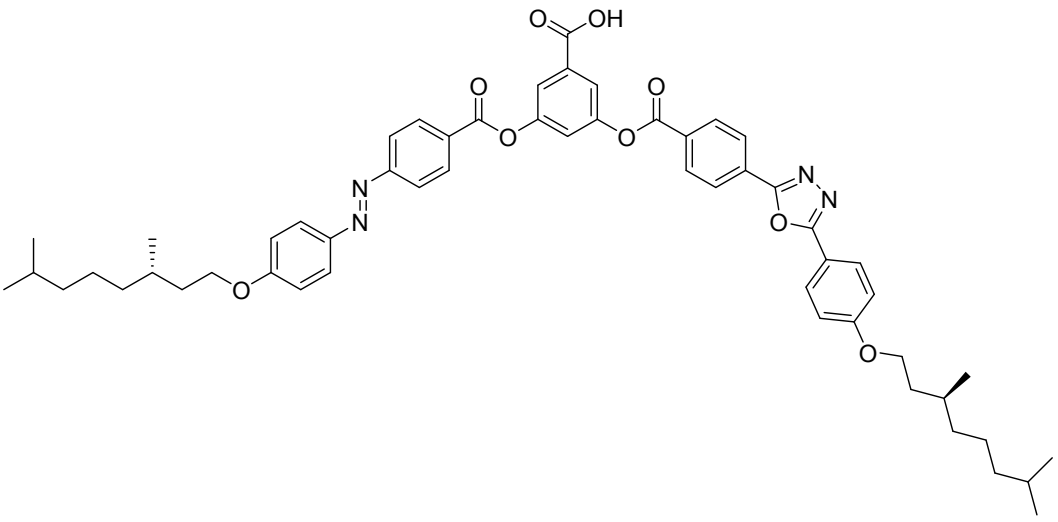
(S)-3-{[4-({4-[(3,7-dimethyloctyl)oxy]phenyl}diazenyl)benzoyl]oxy}-5-[(4-{5-[4-(dodecyloxy)phenyl]-1,3,4-oxadiazol-2-yl}benzoyl)oxy]benzoic acid (11b).



Yield: 73%. m.p. 183 °C. **IR** (KBr): 3200-2300 (COO-H), 2921, 2851, 1740(C=O), 1698, 1609, 1497, 1472, 1303, 1253 (C_{Ar}-O), 1134, 1068, 1011 cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 8.33 (m, 6H, Ar-*H*), 8.09 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 7.97 (m, 4H, Ar-*H*), 7.56 (t, *J* = 2.1 Hz, 1H, Ar-*H*), 7.05 (d, *J* = 3.6 Hz, 2H, Ar-*H*), 7.01 (d, *J* = 3.6 Hz, 2H, Ar-*H*), 4.10 (m, 2H, OCH_2-), 4.05 (t, *J* = 6.3 Hz, 2H, OCH_2-), 1.92-1.77 (m, 3H, -CH_2-and-C*H*), 1.75-1.59 (m, 3H, -CH_2-and-C*H*), 1.58-1.43 (m, 3H, -CH_2-), 1.42-1.21 (m, 19H, -CH_2-), 1.22-1.12 (m, 2H, -CH_2-), 0.97 (d, *J* = 8.8 Hz, 3H, -CH_3), 0.88 (m, 9H, -(CH_3) and -(CH_3)$_2$). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 168.7, 165.2, 164.1, 163.7, 163.1, 162.5, 162.3, 156.0, 151.4, 151.1, 146.8, 131.6, 131.3, 131.2, 130.9, 129.5, 128.9, 128.8, 126.9, 125.3, 122.6, 121.3, 121.2, 115.6, 115.0, 114.8, 68.3, 66.7, 39.2, 37.2, 36.0, 31.9, 29.8, 29.6, 29.6, 29.5, 29.5, 29.3, 29.1, 27.9, 25.9, 24.6, 22.7, 22.6, 19.6,

14.1. **MALDI-MS** *m/z* = 951.6 $[M]^+$. **Elemental analysis:** (Requires for $C_{57}H_{66}N_4O_9$: C, 71.98; H, 6.99; N, 5.89 % found: C, 71.74; H, 7.03; N, 5.67 %).

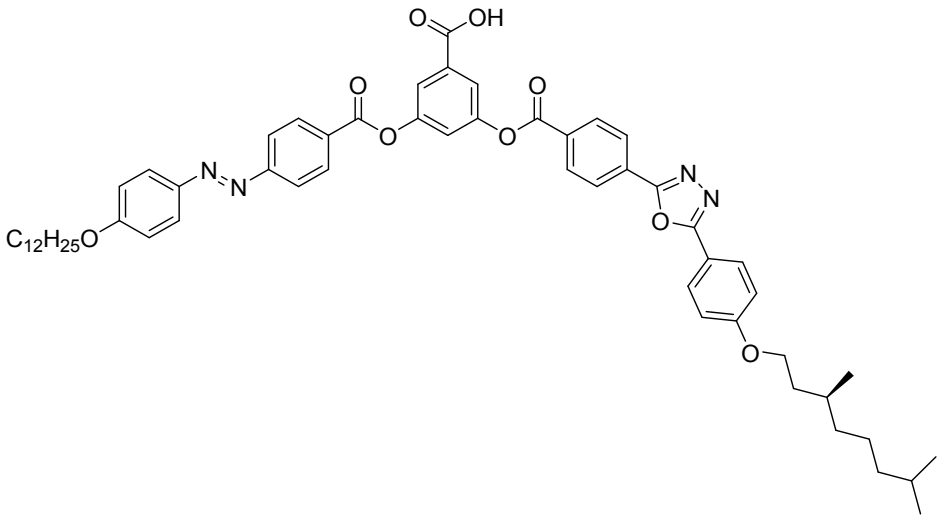
3-{[4-(5-{4-[((S)-3,7-dimethyloctyl)oxy]phenyl}-1,3,4-oxadiazol-2-yl)benzoyl]oxy}-5-{[4-(-{4-[((S)-3,7-dimethyloctyl)oxy]phenyl}diazenyl)benzoyl]oxy}benzoic acid (11d).



Yield: 89%. m.p. 181 °C. **IR** (KBr): 3200-2300 (COO-H), 2952, 2926, 2867, 1743 (C=O), 1698, 1608, 1495, 1470, 1298, 1253 (C_{Ar}-O), 1173, 1134, 1069, 1011, 836 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.37 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 8.34 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 8.30 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 8.10 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 7.98 (d, *J* = 6.8 Hz, 2H, Ar-*H*), 7.96 (m, 4H, Ar-*H*), 7.55 (t, *J* = 2.4 Hz, 1H, Ar-*H*), 7.04 (d, *J* = 6.8 Hz, 2H, Ar-*H*), 7.02 (d, *J* = 6.4 Hz, 2H, Ar-*H*), 4.09 (m, 4H, OCH_2-), 1.88 (q, *J* = 5.6 Hz, 2H, C*H*-(CH_3)$_2$), 1.75-1.58 (m, 4H, -OCH_2CH_2), 1.57-1.47 (m, 2H, -CH_2-C*H*(CH_3)-), 1.39-1.23 (m, 6H, -CH_2-), 1.22-1.10 (m, 6H, -CH_2-), 0.97 (d, *J* = 6.4 Hz, 6H, -CH_3), 0.88 (d, *J* = 6.4 Hz, 12H, -(CH_3)$_2$). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 168.6, 165.3, 164.1, 163.7, 163.1, 162.5, 162.2, 156.0, 151.4, 151.1, 146.8, 131.6, 131.3, 131.2, 130.9,

129.5, 128.9, 128.8, 126.9, 125.3, 122.6, 121.3, 121.2, 121.0, 115.6, 115.1, 114.8, 66.8, 66.6, 39.2, 37.2, 36.0, 36.0, 29.8, 27.9, 24.6, 22.7, 22.6, 19.6, **MALDI-MS** *m/z* = 923.5 $[M]^+$. **Elemental analysis:** (Requires for $C_{55}H_{62}N_4O_9$: C, 71.56; H, 6.77; N, 6.07 %: found C, 71.08; H, 6.81; N, 6.03 %).

(S)-3-{[4-(5-{4-[(3,7-dimethyloctyl)oxy]phenyl}-1,3,4-oxadiazol-2-yl)benzoyl]oxy}-5-[(4-{[4-(dodecyloxy)phenyl]diazenyl}benzoyl)oxy]benzoic acid (11e).



Yield: 78%. m.p. 196 °C. **IR** (KBr): 3200-2300 (COO-H), 2923, 2852, 1743 (C=O), 1698, 1599, 1497, 1468, 1298, 1253 (C_{Ar}-O), 1176, 1133, 1069, 1011, 836 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.37 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 8.34 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 8.30 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 8.10 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 7.99 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.96 (m, 4H, Ar-*H*), 7.55 (t, *J* = 2.0 Hz, 1H, Ar-*H*), 7.04 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.02 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 4.09 (m, 2H, OCH_2-), 4.05 (t, *J* = 6.8 Hz, 2H, OCH_2-), 1.77 (m, 3H, -CH_2- and -C*H*), 1.74-1.59 (m, 3H, -CH_2- and -C*H*), 1.58-1.43 (m, 3H, -CH_2-), 1.41-1.21 (m, 19H, -CH_2-), 1.22-1.12 (m, 2H, -CH_2-), 0.96 (d, *J* = 6.4 Hz, 3H, -CH_3), 0.87 (m, 9H, -(CH_3) and -(CH_3)$_2$). **^{13}C NMR** (100 MHz, $CDCl_3$) δ:

168.5, 165.3, 164.1, 163.7, 163.2, 162.6, 162.3, 156.1, 151.4, 151.2, 146.8, 131.7, 131.4, 131.3, 131.1, 129.6, 129.0, 128.9, 128.8, 127.0, 125.4, 122.7, 121.2, 121.0, 115.7, 115.1, 114.9, 114.8, 68.5, 66.7, 53.5, 39.2, 37.3, 36.0, 31.9, 29.8, 29.7, 29.7, 29.6, 29.4, 29.4, 29.2, 28.0, 26.0, 24.7, 22.7, 22.6, 19.7, 14.2. **MALDI-MS** *m/z* = 973.4 $[M+Na]^+$. **Elemental analysis:** (Requires for $C_{57}H_{66}N_4O_9$: C, 71.98; H, 6.99; N, 5.89 %: found C, 71.36; H, 7.09; N. 5,80 %).

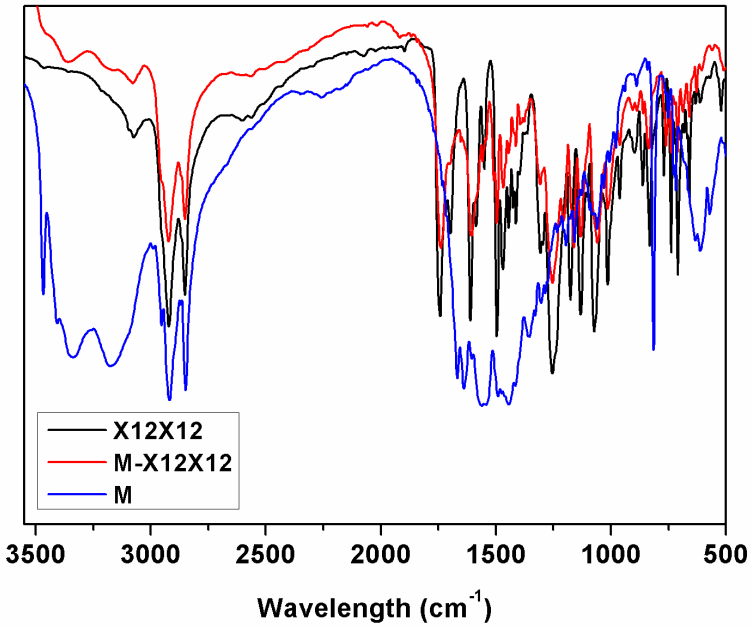


Figure S1: IR spectra of the melamine **M**, the acid **X12X12** and the complex **M-X12X12**.

1.3. NMR experiments

The chemical structures of the acids and the complexes were confirmed by one-dimensional ^{1}H and ^{13}C NMR spectroscopy and by two-dimensional ^{1}H-^{1}H COSY, DOSY, ^{1}H-^{13}C HSQC, and ^{1}H-^{13}C HMBC experiments.

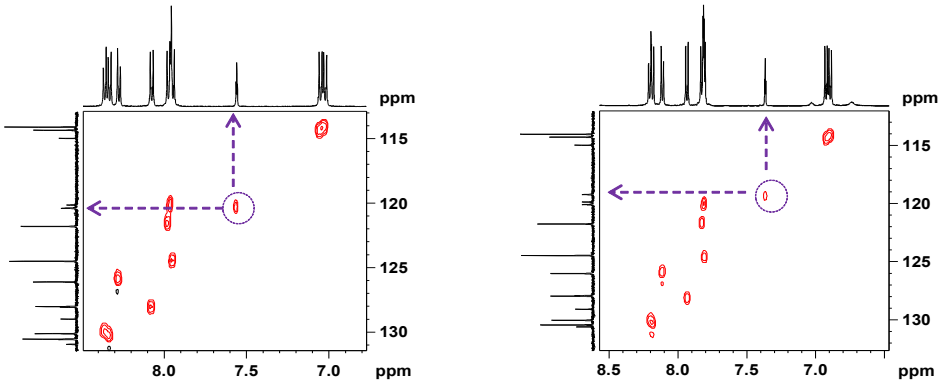


Figure S2. ^{1}H-^{13}C HSQC spectrum for the acid **X(S)10*A(S)10*** and its complex **M-X(S)10*A(S)10***. (500 MHz, CD_2Cl_2, 25 ºC).

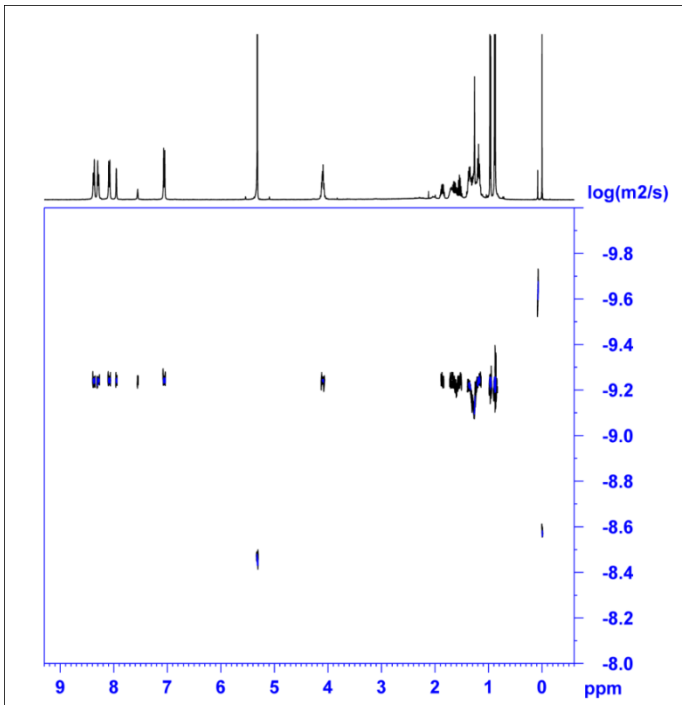


Figure S3. 2D spectrum, in CD_2Cl_2, representing chemical shifts versus diffusion coefficients (logarithmic scale) for the acid **X(S)10*X(S)10*.**

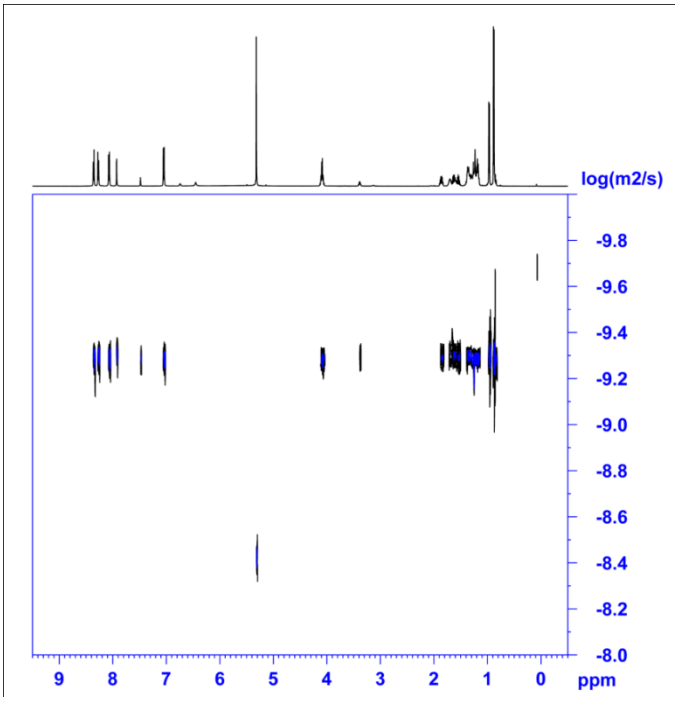


Figure S4. 2D spectrum, in CD_2Cl_2, representing chemical shifts versus diffusion coefficients (logarithmic scale) for the complex **M-X(S)10*X(S)10*.**

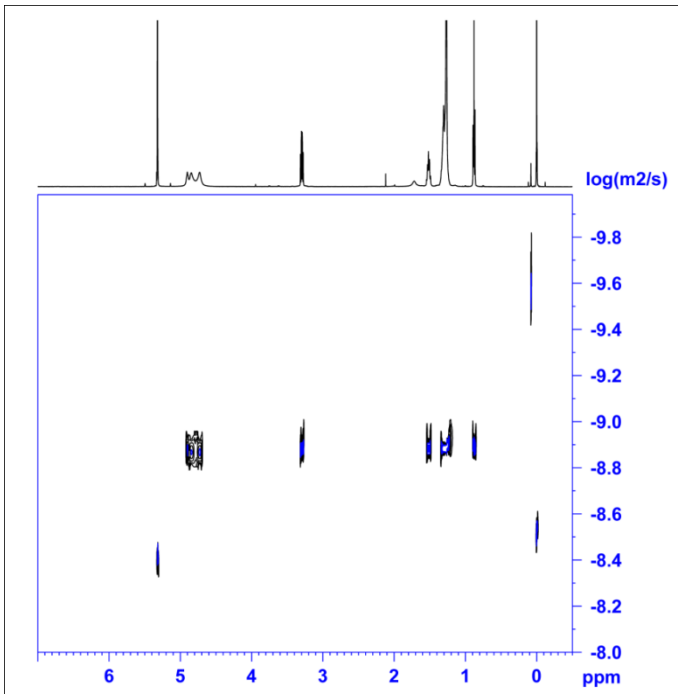


Figure S5. 2D spectrum, in CD_2Cl_2, representing chemical shifts versus diffusion coefficients (logarithmic scale) for the triazine (**M).**

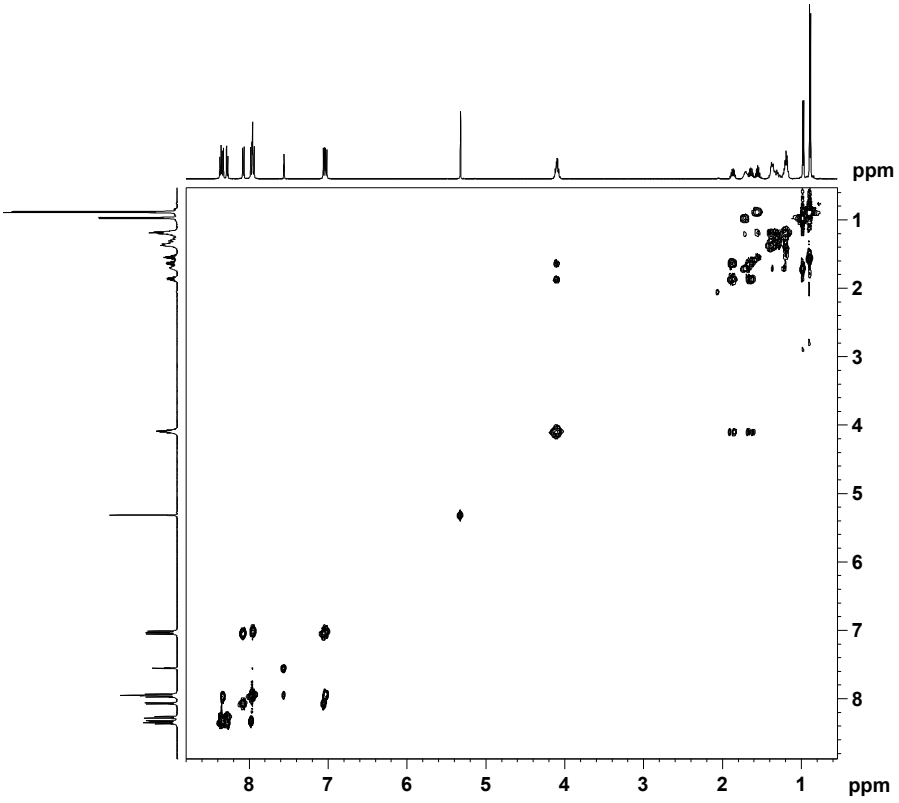


Figure S6. ^1H-^1H COSY spectrum for the acid **X(S)10*A(S)10***in CD_2Cl_2 at 25 ºC.

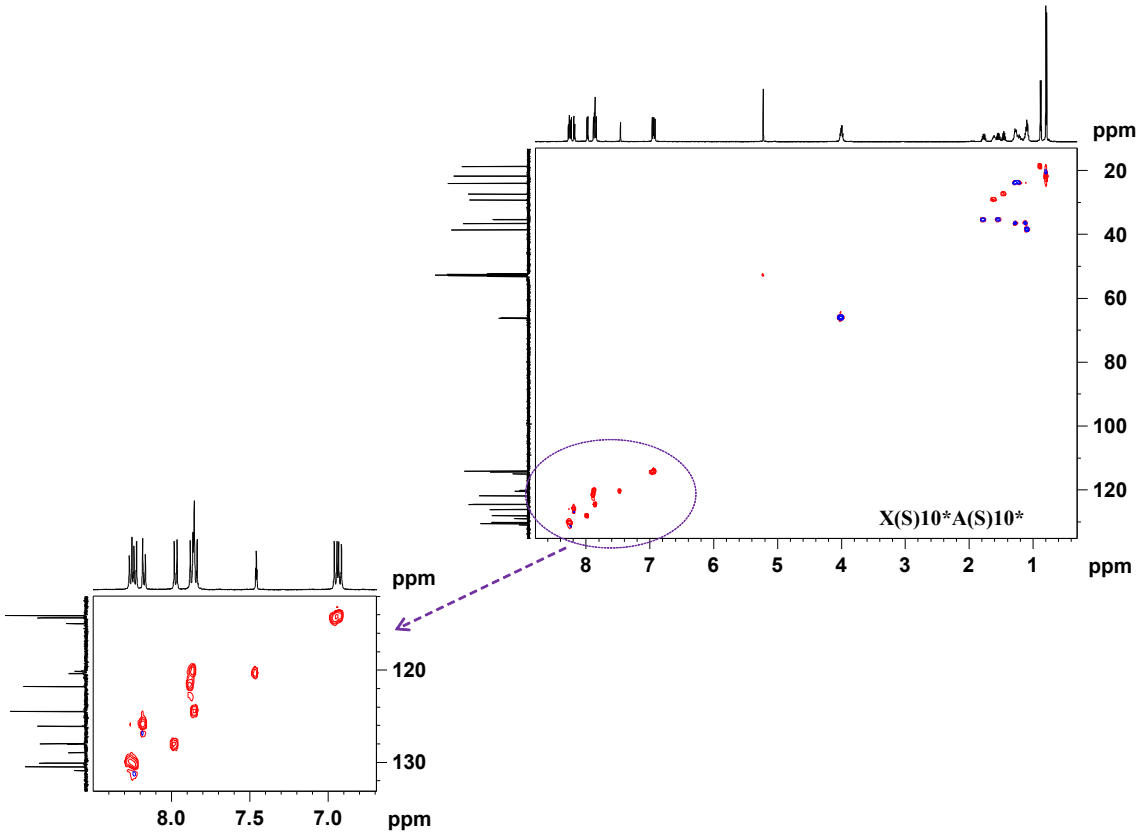


Figure S7. ^{1}H-^{13}C HSQC spectrum for the acid **X(S)10*A(S)10***in CD_2Cl_2 at 25 ºC.

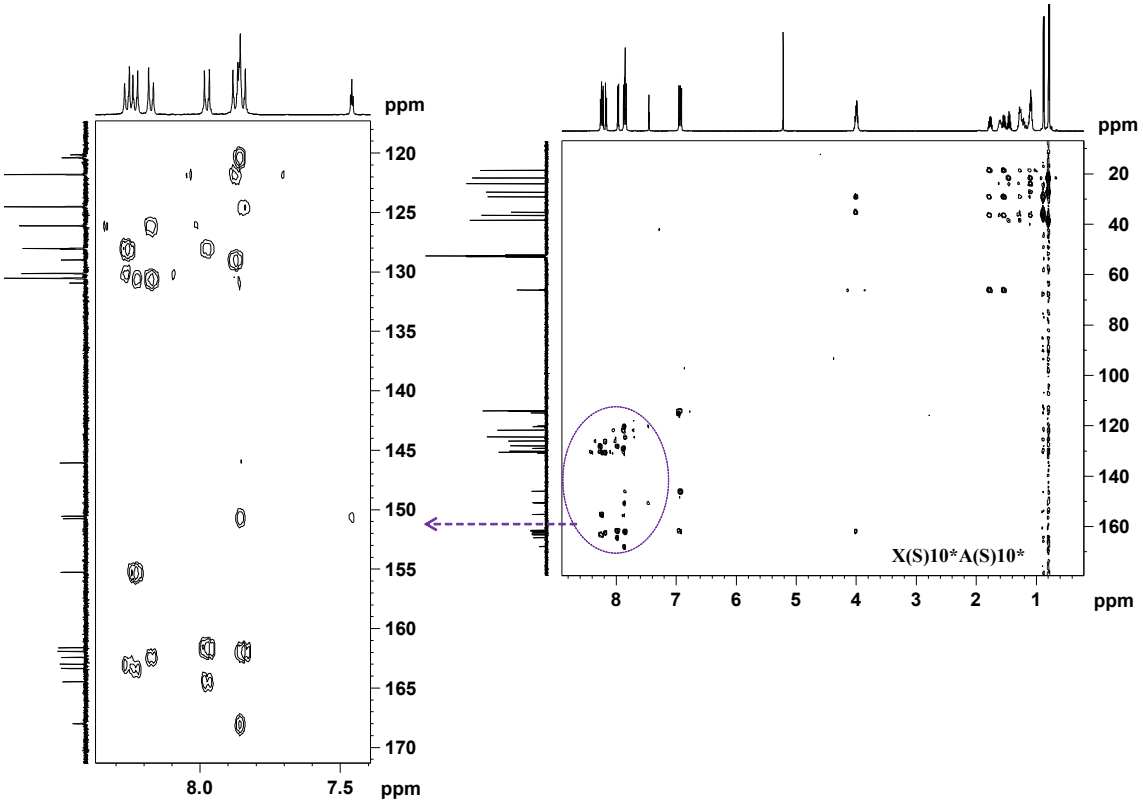


Figure S8. ^{1}H-^{13}C HMBC spectrum for the acid **X(S)10*A(S)10***in CD_2Cl_2 at 25 ºC.

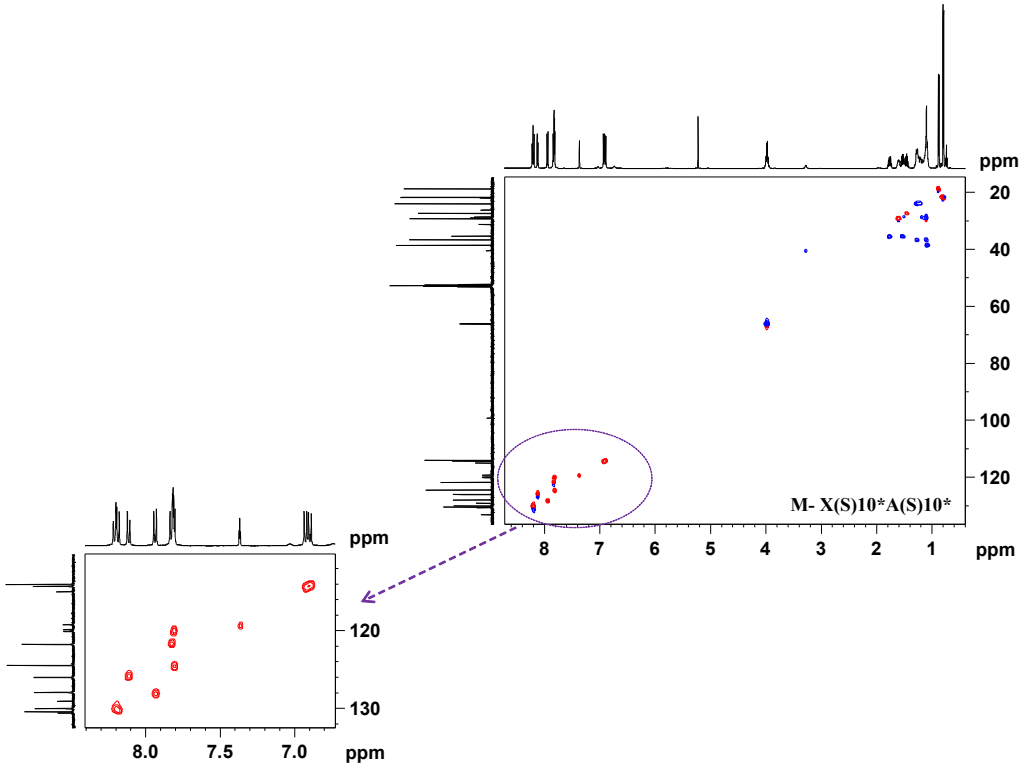


Figure S9. ^{1}H-^{13}C HSQC spectrum for the complex **M-X(S)10*A(S)10***in CD_2Cl_2 at 25 ºC.

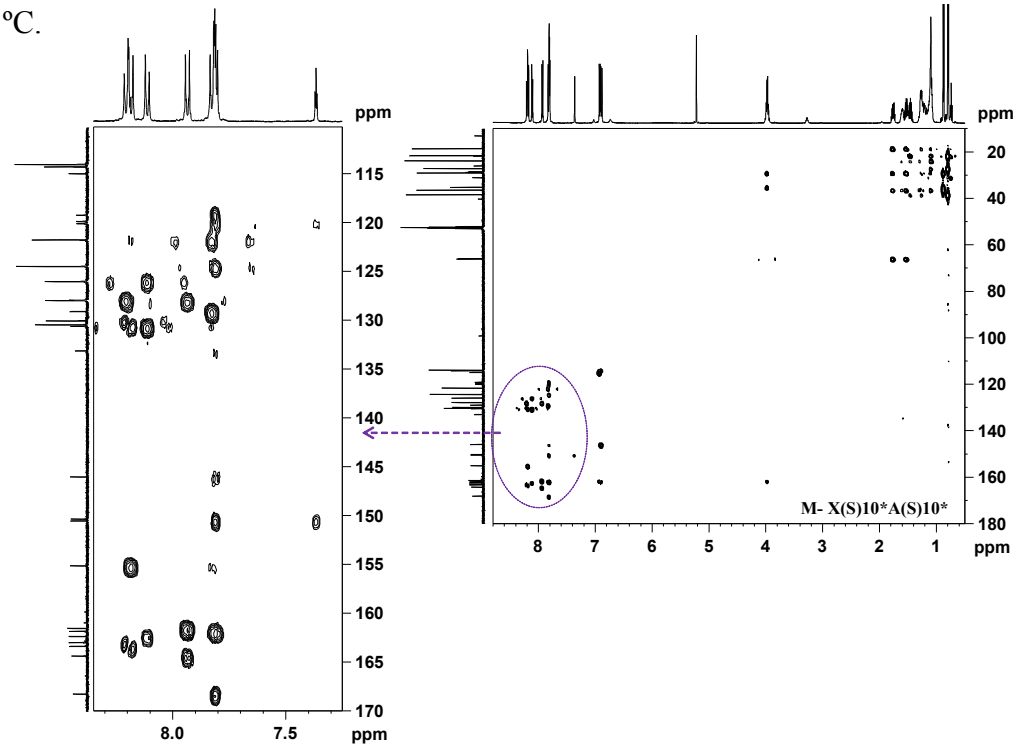
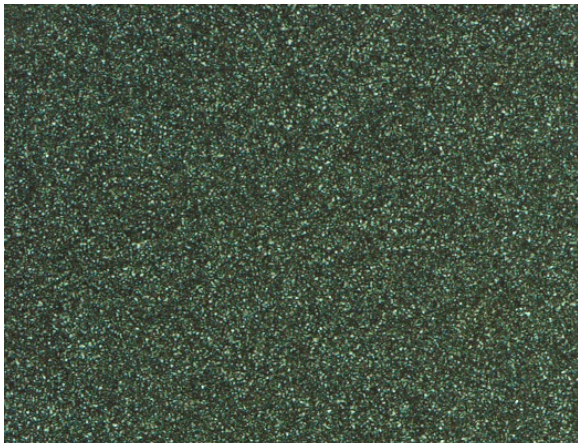
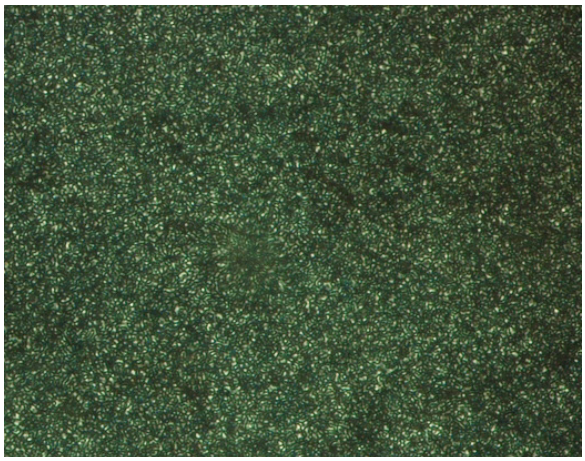


Figure S10. ^{1}H-^{13}C HMBC spectrum for the complex **M-X(S)10*A(S)10***in CD_2Cl_2 at 25 ºC.

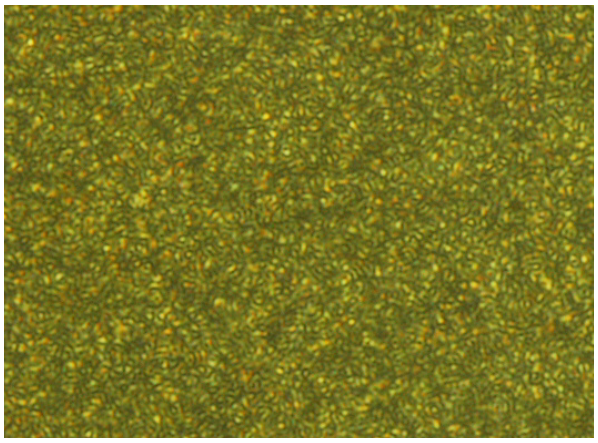
1.4. POM photographs and DSC thermograms



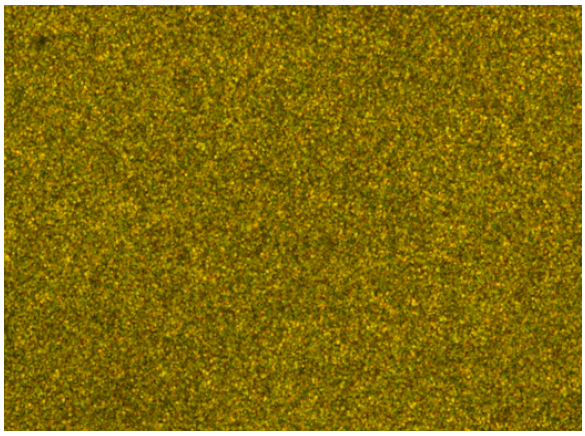
M-X(S)10*X(S)10* at r.t



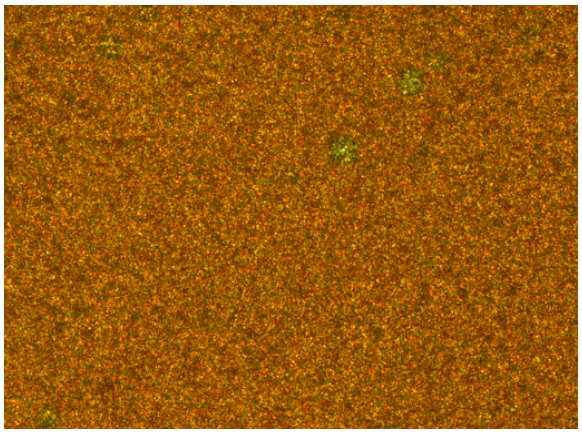
M-X(R)10*X(R)10* at 100ºC



M- X12A12 at r.t.

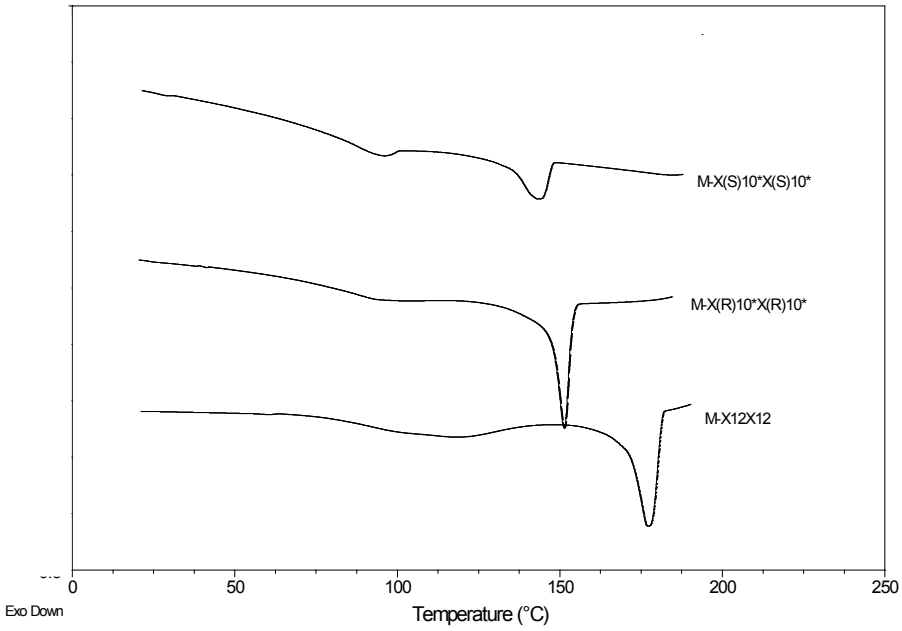


M- X(S)10*A(S)10* at r.t.

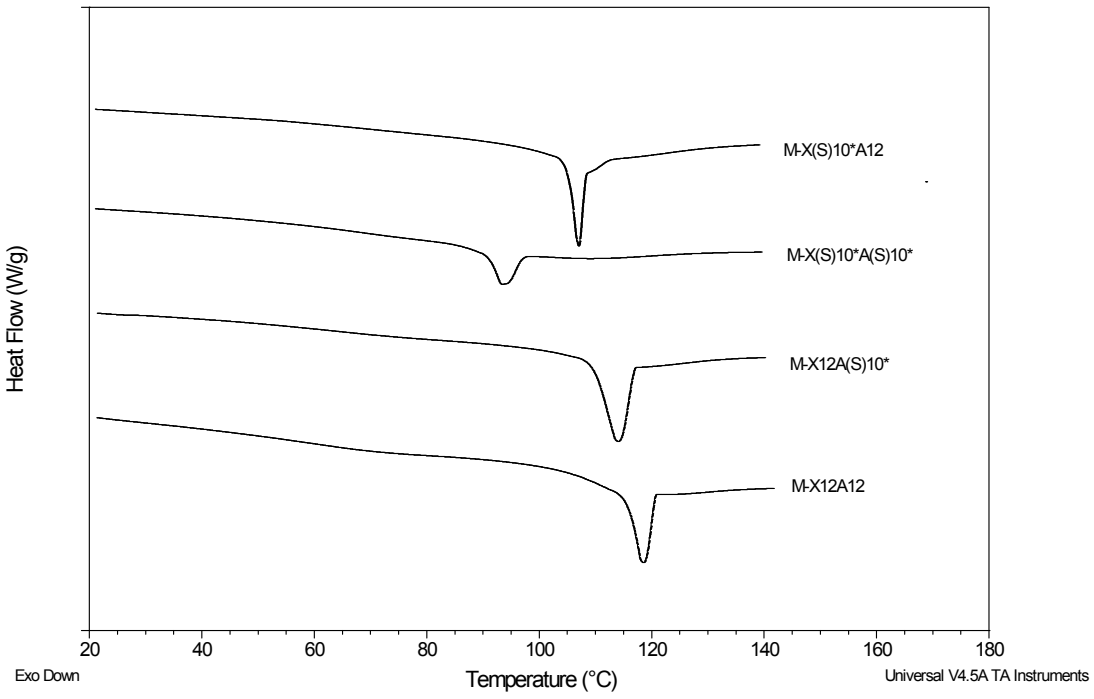


M-X(S)10*A12 at r.t.

Figure S11 . Polarized optical photographs of the complexes.



(a)



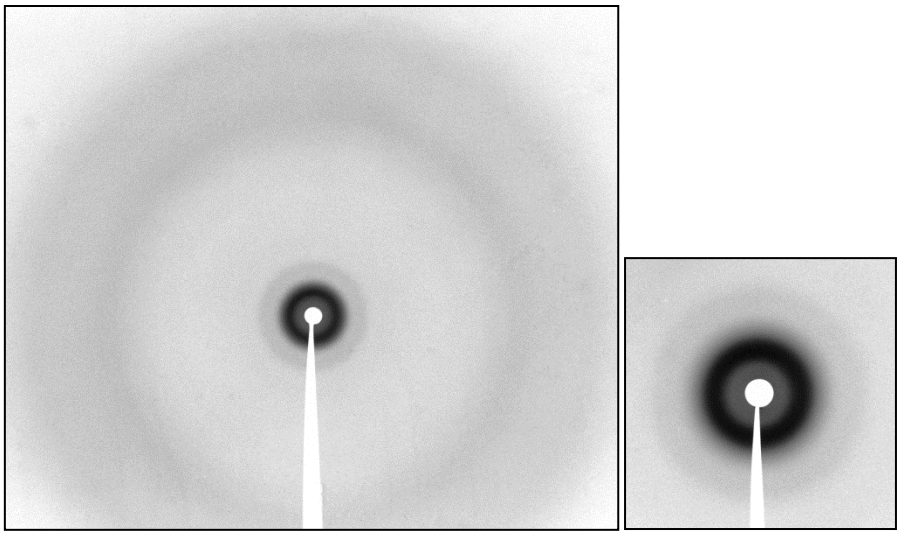
(b)

Figure S12. DSC thermograms of (a) **M-XX** (b) **M-XA** complexes on the second cooling scan at 10ºC/min.

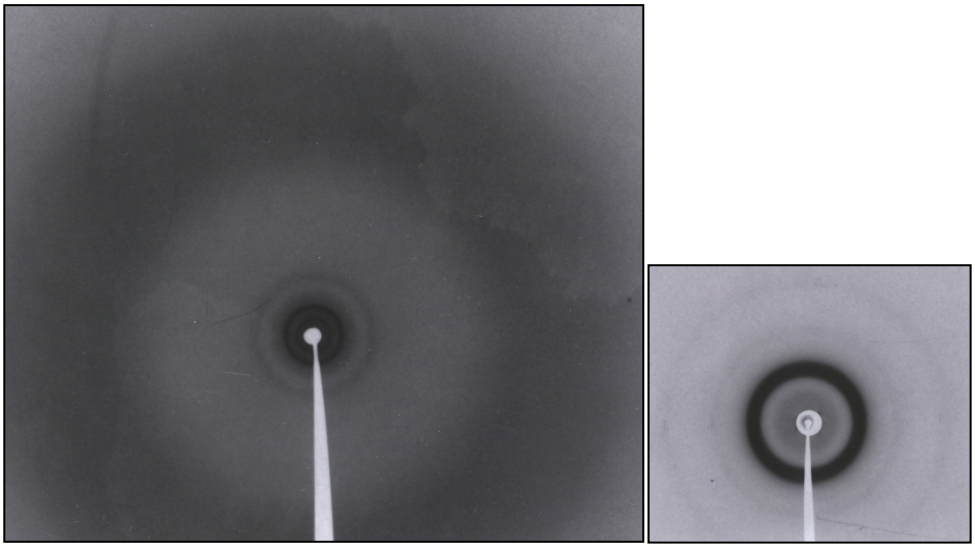
1.5. X-ray diffracton parameters and patterns

Complex [1:3]	Mesophase	Parameters	d_{obs}(Å)	d_{calc}(Å)	(*hk*)
M-X12X12	Col_h	**a** = 47.5 Å	41.1	41.1	10
		h = 3.5 Å	19.8	20.55	20
M-X(*S*)10*X(*S*)10*	Col_h	**a** = 50.2 Å	43.5	43.5	10
		h = 3.4 Å	25.1	25.1	11
			16.3	16.4	21
M-X(*R*)10*X(*R*)10*	Col_h	**a** = 49.7 Å	43.0	43.0	10
		h = 3.4 Å	25.3	24.8	11
			16.1	16. 3	21
M-X12A 12	Col_r	**a** = 98.6	61.6	61.6	11
		b = 78.9	39.5	39.45	02
			32.9	32.8	30
			23.5	23,5	41
			19.8	19.7	04
			16.0	16.1	61
			13.4	13.2	72
M-X12A(S)10*	Col_r	**a** = 78.6	55.0	55.0	11
		b = 77.0	38.5	38.5	02
			33.9	34.6	12
			21.7	21.7	32
			12.8	12.4	62
M-X(S)10*A(S)10*	Col_r	**a** = 96.1	56.9	56.9	11
		b =70.4	35.2	35.2	02
			21.8	22.1	23
			14.6	14.6	62
			12.4	12.8	72
M-X(S)10*A12	Col_r	**a** = 82.2	56.9	56.9	11
		b = 78.6	39.4	39.4	02
			35.2	35.5	21
			22.4	22.5	23
			13.2	12.5	26

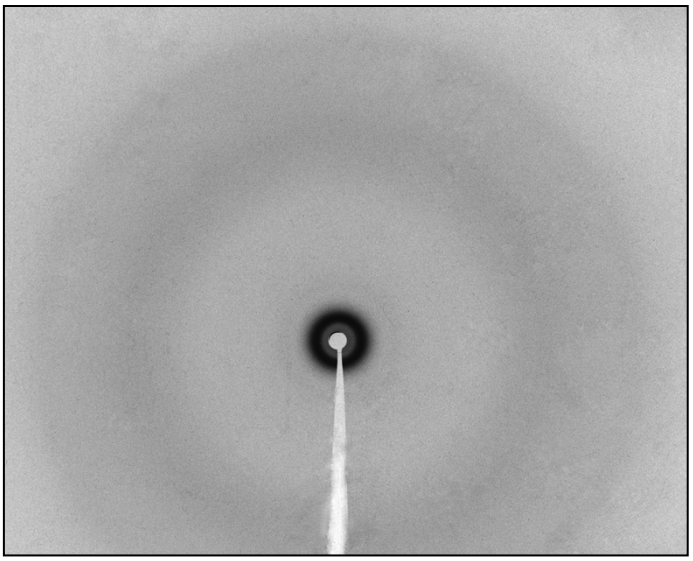
Table S1. Lattice Parameters Measured by X-ray Diffraction for the mesophases of **M-XX** and **M-XA.** All the experiments were carried out at room temperature.



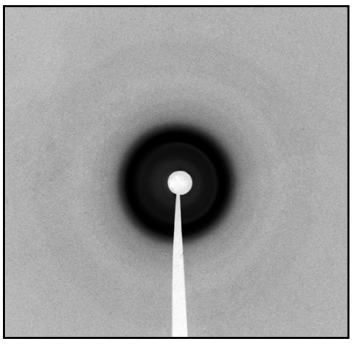
M-X12X12



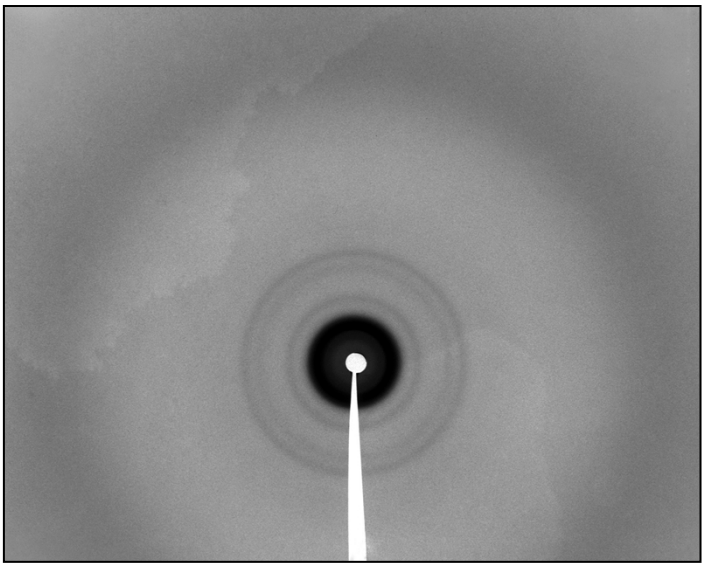
M-X(R)10*X(R)10*



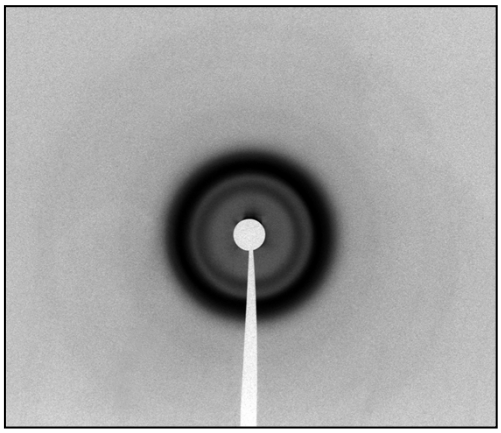
M-X(S)10*X(S)10*



M-X12A12



M-X(S)10*A(S)10*



M-X(S)10*A12

Figure S13. X-ray diffraction patterns of the complexes **M-XX** and **M-XA**.

1.6. Circular dichroism

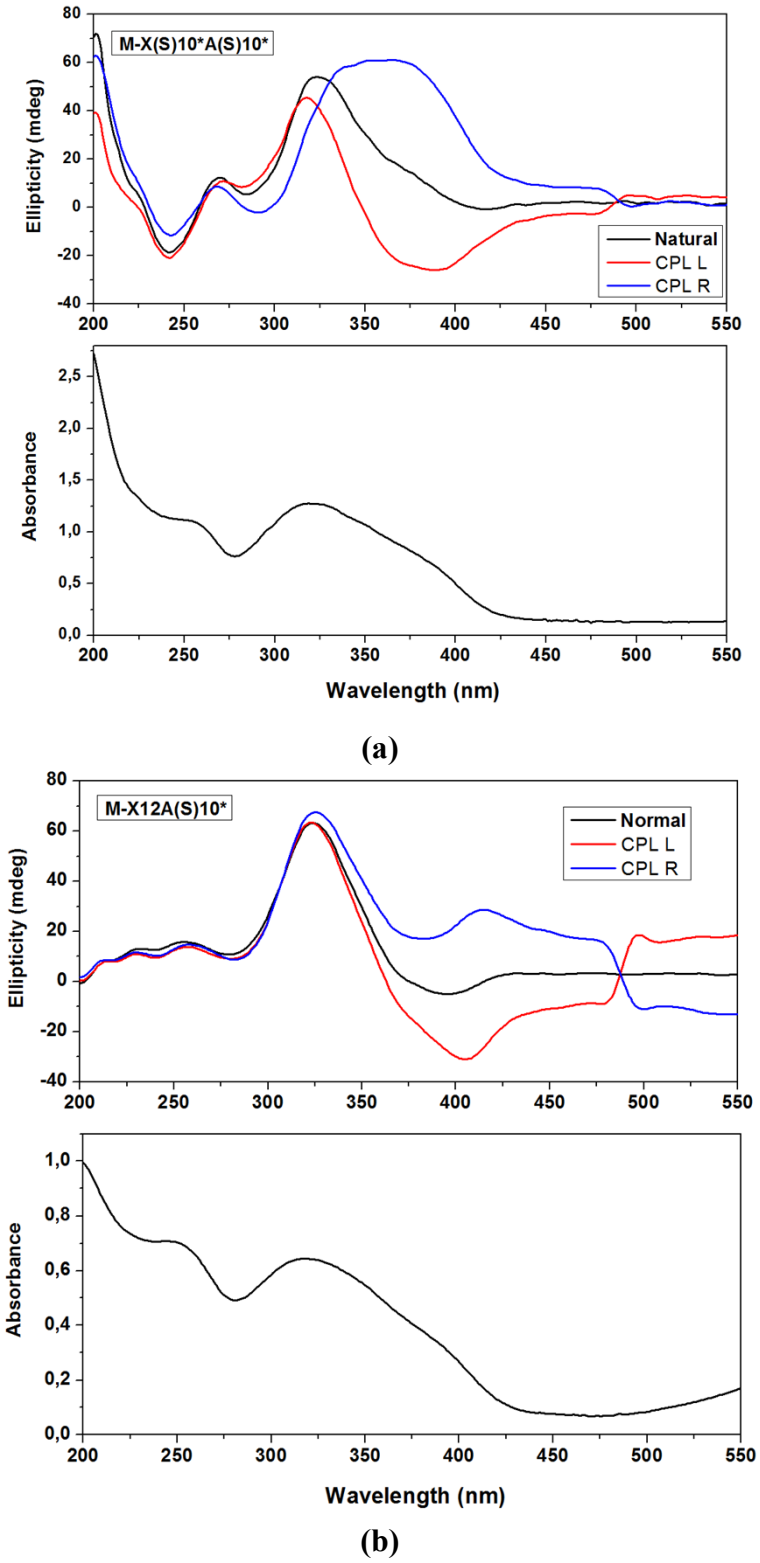
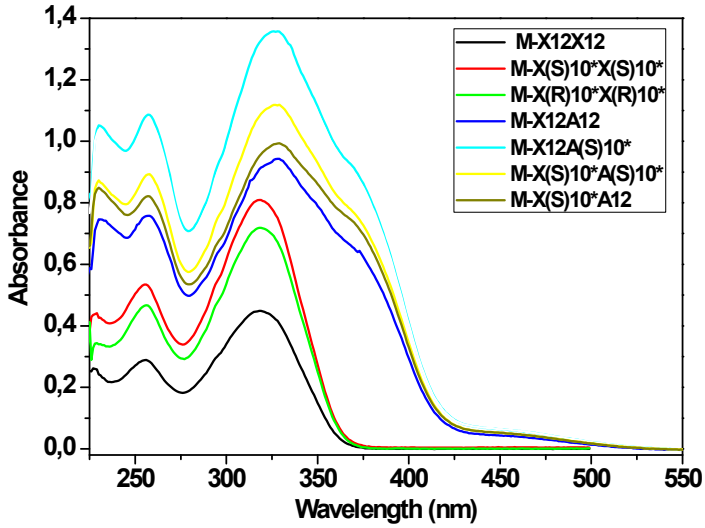
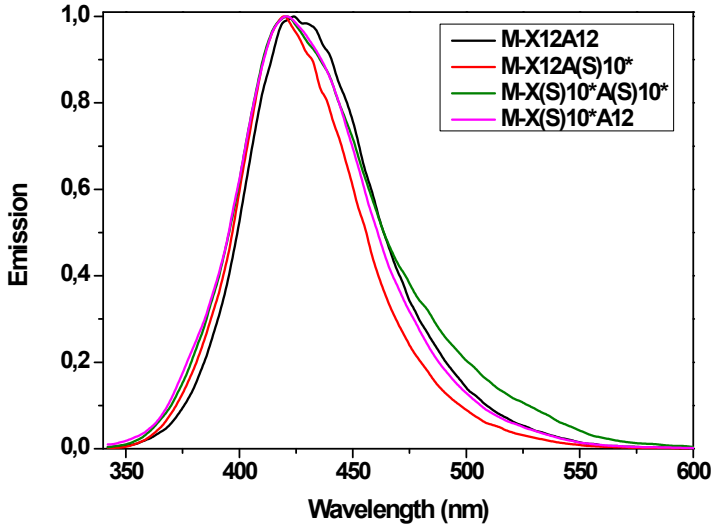


Figure S14. Circular dichroism spectra of **M-X(S)10*A(S)10*** (a), **M-X12A(S)10*** (b).

1.7. Absorbance and fluorescence spectra



(a)



(b)

Figure S15: Absorption spectra of **M-XX** and **M-XA (a)** and normalized emission spectra of **M-XA (b)** in solution.

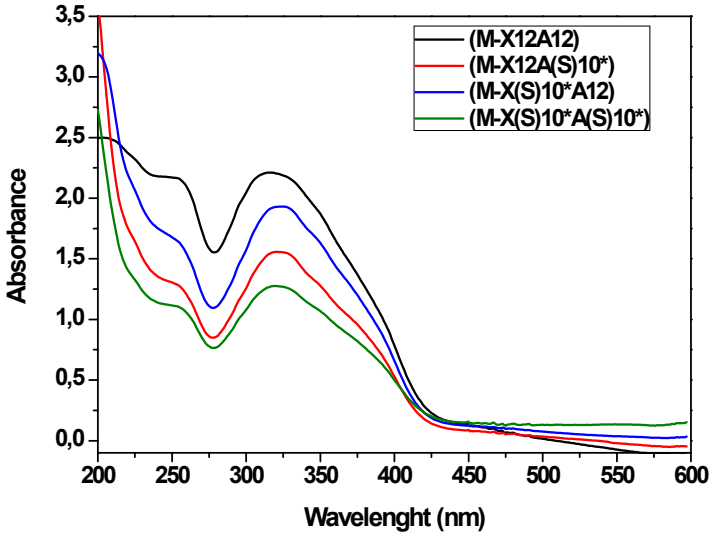


Figure S16: Absorption spectra of **M-XA** in film.