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Supporting Information

Amphotropic azobenzene derivatives with oligooxyethylene and glycerol based polar groups

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Content

1. Methods

A Mettler heating stage (FP 82 HT) was used for polarizing optical microscopy (POM, Optiphot 2, Nikon) and DSCs were recorded with a DSC-7 calorimeter (PerkinElmer) at 10 K min^{-1}. Lyotropic samples were sealed with the UV curable adhesive NOA71 to prevent solvent evaporation and examined with the BHS Olympus polarizing equipped with an LTS350 Linkam hot stage.

A Hamamatsu LC6 Hg/Xe lamp combined with suitable filting was used as the UV irradiation source. A YK-34 UV light meter (0-20.0 mW cm^{-2}) was used to measure the light densities of the UV irradiation.

For temperature dependent measurements of the layer spacing, the Anton Paar small angle scattering system SAXSess including a CCD detector was used. The X-ray diffraction patterns of aligned or partially aligned samples were recorded with a 2D detector (HI-STAR, Siemens). Ni filtered and pinhole collimated Cu-K$_\alpha$ radiation was used. The exposure time was normally 60 min. The sample to detector distance was 8.8 cm and 26.9 cm for the wide angle and small angle measurements, respectively. Alignment was achieved upon slow cooling (rate: 1 K·min^{-1} – 0.1 K·min^{-1}) of a small droplet of the sample on a glass plate and takes place at the sample–glass or at the sample–air interface, with domains fiber-like disordered around an axis perpendicular to the interface. The aligned samples were held on a temperature-controlled heating stage.

High-resolution small-angle powder diffraction experiments were recorded on Beamline BL16B1 at Shanghai Synchrotron Radiation Facility, SSRF. Samples were held in evacuated 1 mm capillaries. A modified Linkam hot stage with a thermal stability within 0.2 ºC was used, with a hole for the capillary drilled through the silver heating block and mica windows attached to it on each side. A MarCCD detector was used. q calibration and linearization were verified using several orders of layer reflections from silver behemate and a series of n-alkanes. The measurement of the positions and intensities of the diffraction peaks is carried out using Galactic PeakSolve^{TM} program, where experimental diffractograms are fitted using Gaussian shaped peaks. The diffraction peaks are indexed on the basis of their peak positions, and the lattice parameters and the plane groups are subsequently determined. Once the diffraction intensities are measured and the corresponding plane group determined, 2-d electron density maps can be reconstructed, on the basis of the general formula

$$E(xy) = \Sigma_{hkl} F(hk) \exp[i2\pi(hx+ky)] \qquad \text{(Eqn. 1)}$$

Here $F(hk)$ is the structure factor of a diffraction peak with index (hk). It is normally a complex number and the experimentally observed diffraction intensity

$$I(hk) = \mathrm{K}\cdot F(hk)\cdot F^*(hk) = \mathrm{K}\cdot|F(hk)|^2 \qquad \text{(Eqn. 2)}$$

Here K is a constant related to the sample volume, incident beam intensity etc. In this paper we are only interested in the relative electron densities, hence this constant is simply taken to be 1. Thus the electron density

$$E(xy) = \Sigma_{hk} \mathrm{sqrt}[I(hk)] \exp[i2\pi(hx+ky) + \phi_{hk}] \qquad \text{(Eqn. 3)}$$

As the observed diffraction intensity $I(hk)$ is only related to the amplitude of the structure factor $|F(hk)|$, the information about the phase of $F(hk)$, ϕ_{hk}, can not be determined directly from experiment. However, the problem is much simplified when the structure of the ordered phase is centrosymmetric, and hence the structure factor $F(hk)$ is always real and ϕ_{hk} is either 0 or π.

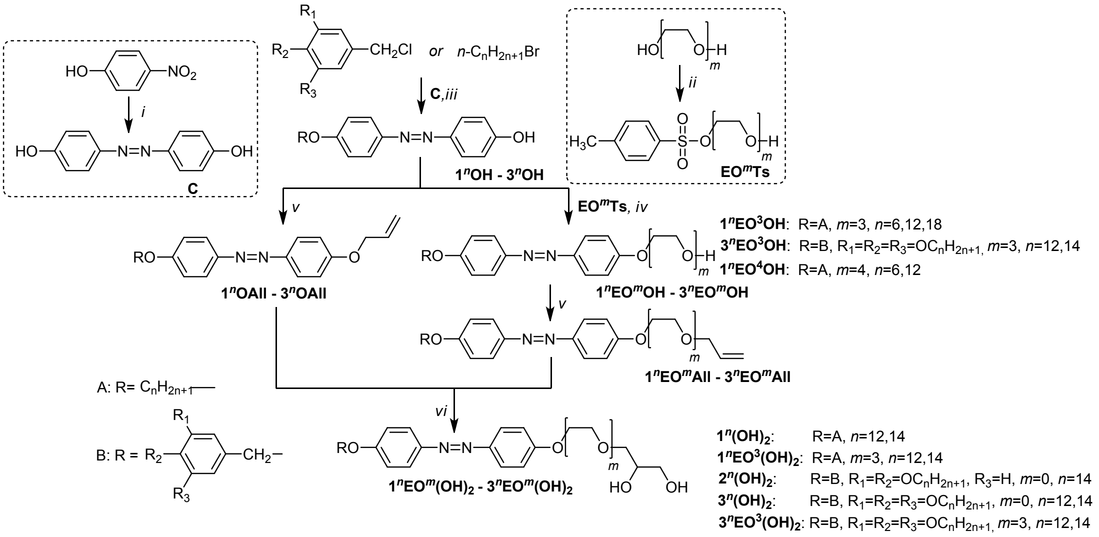
This makes it possible for a trial-and-error approach, where candidate electron density maps are reconstructed for all possible phase combinations, and the "correct" phase combination is then selected on the merit of the maps, helped by prior physical and chemical knowledge of the system. This is especially useful for the study of nanostructures, where normally only a limited number of diffraction peaks are observed.

GISAXS experiments were carried out on BL14B1 at Shanghai Synchrotron Radiation Facility, SSRF. Thin films were prepared from the melt on a silicon wafer. The thin film coated 5 x 5 mm^2 Si plates were placed on top of a custom built heater, which was then mounted on a six-circle goniometer. A MarCCD 165 detector at ESRF was used. The sample enclosure and the beam pipe were flushed with helium.

2. Materials synthesis and analytical data

Synthesis of the materials was performed as outlined in Scheme 1. Reactions requiring an inert gas atmosphere were conducted under argon and the glassware was oven-dried (140 °C). Commercially available chemicals were used as received. The alkoxybenzyl chlorides were prepared according to literature procedures.[1]Column chromatography was performed with silica gel 60 (230-400 mesh) from Merck.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker–DRX-500 spectrometer with tetramethylsilane (TMS) as the internal standard. High resolution MS (HR-MS) data were recorded on a Finnigan MAT 90 spectrometer at an ionization potential of 70 eV. Field-desorption (FD) mass spectra were recorded on a VG ZAB 2-SE-FPD spectrometer. Elemental analysis was performed using an Elementar VARIO EL elemental analyzer.



Scheme S1. Synthesis of compounds **1-3**. *Reagents and conditions*: *i*) KOH, H_2O, 195-200 °C, 5 h; *ii*) TsCl, CH_2Cl_2, Et_3N, 0 °C - 25 °C; *iii*) K_2CO_3, DMF, 90 °C, 12 h; *iv*) CH_3CN, K_2CO_3, 70 °C, 24 h; *v*) allyl bromide, NaH, THF, 70 °C, 12 h; *vi*) OsO_4, NMMNO, H_2O, acetone, 25 °C, 24 h.

2.1 Azobenzene-4,4-diol C[2]

A mixture of KOH (25 g, 380 mmol), *p*-nitrophenol (5 g, 36 mmol), and water (10 mL) was heated to 120 °C and left to stand for 1 h. When the temperature slowly rose to 195-200 °C, the reaction vigorously started to give a brown viscous liquid with a large number of bubbles developing. After the reaction was completed, products were dissolved in water. The dark-red solution was acidified to pH = 3 with concentrated HCl and extracted with ethyl acetate. Combined ethyl acetate extracts were dried over Na_2SO_4 overnight. Ethyl acetate was removed to dryness under reduced pressure. Residue was recrystallized from 50% (v/v) ethanol aqueous solution to give yellow crystals of azobenzene-4,4-diol, 2.0 g, 43% yield. m.p.: 168-170 °C. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 9.24 (s, 2 H, 2 O**H**), 7.77-7.76 (d, 4 H, J = 8.4 Hz, 4 Ar**H**), 6.95-6.93 (d, 4 H, J = 8.6 Hz, 4 Ar**H**).

2.2 General procedure for compounds EO*m*Ts[3]

4-Methylbenzene-1-sulfonyl chloride (2.3 g, 12 mmol) and triethylene glycol or tetraethylene glycol (60 mmol) were dissolved in dry CH_2Cl_2 (20 mL) and dry triethylamine (25 mL) under a nitrogen atmosphere. The mixture was stirred for 3 h at 0 °C, then stirred overnight at 25 °C. After the reaction was complete (TLC), ethyl acetate (50 mL) was added, the mixture was washed with H_2O (3×20 mL), and dried over anhydrous Na_2SO_4. The solvent was evaporated in *vacuo*. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10:1). NMRs of compounds **EO*m*Ts** correspond to those given in reference[4]

2.3 General procedure for compounds 1*n*OH - 3*n*OH

The mixture of K_2CO_3 (3 mmol), the *n*-bromoalkane (1 mmol) or 3,4,5-trialkoxylbenzylchloride (1 mmol) and **C** (1 mmol) were dissolved in dry DMF (20 mL), then heated to 90 °C and stirred for 12 h. After the reaction was complete (TLC), the mixture was cooled to room temperature, water (50 mL) and Et_2O (100 mL) were added to the mixture. The organic layer was separated and washed with H_2O (2 x 20 mL), dried over $MgSO_4$, then the solvent was removed in *vacuo*. The residue was purified by chromatography (petroleum ether: ethyl acetate = 5:1).

1^6OH: yellow crystals (yield: 56 %). m.p.: 88 °C. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.86-7.82 (dd, J = 8.0, 8.5 Hz, 4 H, 4 Ar**H**), 6.99-6.98 (dd, J = 8.2, 8.2 Hz, 4 H, 4 Ar**H**), 5.26 (s, 1 H, O**H**), 4.04-4.02 (t, J = 6.1 Hz, 2 H, ArOC**H**$_2$), 1.83-1.80 (t, J = 7.4 Hz, 2 H, ArOCH$_2$C**H**$_2$), 1.48-1.46 (m, 2 H, ArOCH$_2$CH$_2$C**H**$_2$), 1.40-1.26 (m, 4 H, 2 C**H**$_2$), 0.92-0.89 (m, 3 H, C**H**$_3$).

1^{12}OH: yellow crystals (yield: 53 %). m.p.: 102 °C. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.86-7.82 (dd, J = 9.1, 8.6 Hz, 4 H, 4 Ar**H**), 6.99-6.92 (dd, J = 8.8, 8.3 Hz, 4 H, 4 Ar**H**), 5.21 (s, 1 H, O**H**), 4.04-4.02 (t, J = 6.2 Hz, 2 H, ArOC**H**$_2$), 1.89-1.80 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.48-1.46 (m, 2 H, ArOCH$_2$CH$_2$C**H**$_2$), 1.40-1.26 (m, 16 H, 8 C**H**$_2$), 0.89-0.87 (t, J = 6.4 Hz, 3H, C**H**$_3$).

1^{14}OH: yellow crystals (yield: 57 %). m.p.: 104 °C. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.85-7.80 (dd, J = 8.9, 8.6 Hz， 4 H, 4 Ar**H**), 7.03-6.97 (dd, J = 8.9, 8.9 Hz, 4 H, 4 Ar**H**), 5.52 (s, 1H, O**H**), 4.04-4.01 (t, J = 6.5 Hz, 2 H, ArOC**H**$_2$), 1.83-1.78 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.49-1.44 (m, 2 H, ArOCH$_2$CH$_2$C**H**$_2$), 1.36-1.35 (m, 20 H, 10 C**H**$_2$), 0.90-0.87 (t, J = 7.2 Hz, 3 H, C**H**$_3$).

1^{18}OH: yellow crystals (yield: 57 %). m.p.: 110 °C. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.87-7.82 (dd, J = 8.8, 8.7 Hz, 4 H, 4 Ar**H**), 7.00-6.92 (dd, J = 8.8, 8.6 Hz, 4 H, 4 Ar**H**), 5.17 (s, 1 H, O**H**), 4.05-4.02 (t, J = 6.5 Hz, 2 H, ArOC**H**$_2$), 1.84-1.79 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.48-1.45 (m, 2H, ArOCH$_2$CH$_2$C**H**$_2$), 1.36-1.26 (m, 28 H, 14 C**H**$_2$), 0.90-0.87 (t, J = 6.8 Hz, 3 H, C**H**$_3$).

2^{14}OH: yellow crystals (yield: 60 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.89-7.82 (m, 4 H, 4 Ar**H**), 7.08-6.99 (d, J = 9.0 Hz, 2 H, 2 Ar**H**), 6.98-6.90 (m, 3 H, 3 Ar**H**), 6.84-

6.80 (m, 2 H, 2 Ar**H**), 5.22 (s, 1 H, O**H**), 5.04 (s, 2 H, ArC**H**$_2$), 4.05-3.96 (m, 4 H, 2 ArOC**H**$_2$), 1.86-1.76 (m, 4 H, 2 ArOCH$_2$C**H**$_2$), 1.49-1.44 (m, 4 H, 2 ArOCH$_2$CH$_2$C**H**$_2$), 1.42-1.15 (m, 40 H, 20 C**H**$_2$), 0.90-0.88 (t, J = 6.9 Hz, 6 H, 2 C**H**$_3$).

3^{12}OH: yellow crystals (yield: 49 %). m.p.: 56 °C. ^{1}H-NMR (CDCl$_3$, 500 MHz) δ: 7.88-7.82 (dd, J = 8.5, 8.4 Hz, 4 H, 4 Ar**H**), 7.08-7.06 (d, J = 8.6 Hz, 2 H, 2 Ar**H**), 6.94-6.93 (d, J = 8.2 Hz, 2 H, 2 Ar**H**), 6.64 (s, 2 H, 2 Ar**H**), 5.50 (s, 1 H, O**H**), 5.02 (s, 2 H, ArC**H**$_2$), 4.03-3.94 (m, 6 H, 3 ArOC**H**$_2$), 1.81-1.72 (m, 6 H, 3 ArOCH$_2$C**H**$_2$), 1.48-1.43 (m, 6 H, 3ArOCH$_2$CH$_2$C**H**$_2$), 1.38-1.21 (m, 48 H, 24 C**H**$_2$), 0.89-0.86 (t, J = 6.9 Hz, 9 H, 3 C**H**$_3$).

3^{14}OH: yellow crystals (yield: 47 %). m.p.: 49 °C. ^{1}H-NMR (CDCl$_3$, 500 MHz) δ: 7.88-7.82 (dd, J = 8.7, 8.7 Hz, 4 H, 4 Ar**H**), 7.08-7.06 (d, J = 8.8 Hz, 2 H, 2 Ar**H**), 6.93-6.92 (d, J = 8.6 Hz, 2 H, 2 Ar**H**), 6.64 (s, 2 H, 2 Ar**H**), 5.42 (s, 1 H, O**H**), 5.02 (s, 2 H, ArC**H**$_2$), 4.00-3.95 (m, 6 H, 3 ArO**CH**$_2$), 1.81-1.73 (m, 6 H, 3 ArOCH$_2$C**H**$_2$), 1.47-1.45 (m, 2 H, ArOCH$_2$CH$_2$C**H**$_2$), 1.38-1.25 (m, 60 H, 30 C**H**$_2$), 0.89-0.86 (t, J = 6.8 Hz, 9 H, 3 C**H**$_3$).

2.4 General procedure for compounds 1^{n}EO^{m}OH - 3^{n}EO^{m}OH

A mixture of K$_2$CO$_3$ (0.414 g, 3 mmol), compounds of **1^{n}OH** or **3^{n}OH** (1 mmol) and triethylene glycol mono-4-methylbenzenesulfonate (1 mmol) or tetraethylene glycol mono-4-methylbenzenesulfonate (1 mmol) were dissolved in dry CH$_3$CN (20 mL) then heated to 70 °C and stirred for 12 h. After the reaction was complete (TLC), the mixture was cooled to room temperature, water (50 mL) and Et$_2$O (100 mL) were added to the mixture. The organic layer was separated and washed with H$_2$O (2 x 20 mL), dried over anhydrous MgSO$_4$, then the solvent was removed in *vacuo*. The residue was purified by chromatography (petroleum ether : ethyl acetate = 5 : 1).

1^{6}EO^{3}OH: yellow crystals (yield: 86 %). m.p.: 102 °C. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.87-7.85 (d, J = 8.7 Hz, 4 H, 4 Ar**H**), 7.02-6.97 (dd, J = 8.9, 8.8 Hz, 4 H, 4 Ar**H**), 4.21-4.19 (t, J = 4.5 Hz, 2 H, $ArOC\mathbf{H}_2CH_2O$), 4.03-4.00 (t, J = 6.5 Hz, 2 H, $ArOC\mathbf{H}_2$), 3.90-3.88 (t, J = 4.3 Hz, 2 H, $ArOCH_2C\mathbf{H}_2O$), 3.75-3.70 (m, 6 H, 3 $OC\mathbf{H}_2$), 3.63-3.61 (t, J = 4.5 Hz, 2 H, $C\mathbf{H}_2OH$), 2.61 (s, 1 H, O**H**), 1.83-1.78 (m, 2 H, $ArOCH_2C\mathbf{H}_2$), 1.48-1.46 (m, 2 H, $ArOCH_2CH_2C\mathbf{H}_2$), 1.37-1.34 (m, 4 H, 2 $C\mathbf{H}_2$), 0.92-0.90 (m, 3 H, $C\mathbf{H}_3$); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ: 161.7, 161.0, 147.7, 147.3, 124.8, 124.7, 115.2, 115.1, 72.9, 71.3, 70.8, 70.1, 68.7, 68.1, 62.2, 32.0, 29.6, 26.0, 23.0, 14.4 (multi carbons in alkyl chain); Elemental analysis calcd (%) for $C_{24}H_{34}N_2O_5$ (430.54): C 66.95, H 7.96, N 6.51; Found: C 67.01, H 7.99, N 6.49.

1^{12}EO^{3}OH: yellow crystals (yield: 93 %). m.p.: 112 °C. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.87-7.85 (d, J = 8.8 Hz, 4 H, 4 Ar**H**), 7.02-6.97 (dd, J = 8.8, 8.8 Hz, 4 H, 4 Ar**H**), 4.22-4.20 (t, J = 4.9 Hz, 2 H, $ArOC\mathbf{H}_2CH_2O$), 4.04-4.01 (t, J = 6.6 Hz, 2 H, $ArOC\mathbf{H}_2$), 3.91-3.89 (t, J = 4.6 Hz, 2 H, $ArOCH_2C\mathbf{H}_2O$), 3.76-3.70 (m, 6 H, 3 $OC\mathbf{H}_2$), 3.63-3.62 (t, J = 4.3 Hz, 2 H, $C\mathbf{H}_2OH$), 1.84-1.78 (m, 2 H, $ArOCH_2C\mathbf{H}_2$), 1.50-1.44 (m, 2 H, $ArOCH_2CH_2C\mathbf{H}_2$), 1.36-1.22 (m, 16 H, 8 $C\mathbf{H}_2$), 0.89-0.87 (t, J = 7.0 Hz, 3 H, $C\mathbf{H}_3$); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ: 161.7, 161.1, 147.7, 147.4, 124.7, 124.6, 115.2, 115.1, 72.9, 71.3, 70.8, 70.1, 68.8, 68.1, 62.2, 32.3, 30.0, 29.9, 29.8, 29.6, 26.4, 23.1, 14.5 (multi carbons in alkyl chain); Elemental analysis calcd (%) for $C_{30}H_{46}N_2O_5$ (514.70): C 70.01, H 9.01, N 5.44; Found: C 69.96, H 9.04, N 5.42.

1^{18}EO^{3}OH: yellow crystals (yield: 85 %). m.p.: 114 °C. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.87-7.85 (d, J = 8.9 Hz, 4 H, 4 Ar**H**), 7.03-6.97 (dd, J = 8.9, 9.0 Hz, 4 H, 4 Ar**H**), 4.22-4.21 (t, J = 4.5 Hz, 2 H, $ArOC\mathbf{H}_2CH_2O$), 4.04-4.03 (t, J = 6.5 Hz, 2 H, $ArOC\mathbf{H}_2$), 3.91-3.90 (t, J = 4.6 Hz, 2 H, $ArOCH_2C\mathbf{H}_2O$), 3.76-3.70 (m, 6 H, 3 $OC\mathbf{H}_2$), 3.64-3.62 (t, J = 4.8 Hz, 2 H, $C\mathbf{H}_2OH$), 2.44 (s, 1 H, O**H**), 1.84-1.78 (m, 2 H, $ArOCH_2C\mathbf{H}_2$), 1.49-1.44 (m, 2 H, $ArOCH_2CH_2C\mathbf{H}_2$), 1.38-1.22 (m, 28 H, 14 $C\mathbf{H}_2$), 0.89-0.87 (t, J = 6.6 Hz, 3 H, $C\mathbf{H}_3$); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ: 161.7, 161.1, 147.7, 147.3, 124.7, 124.6, 115.2, 115.1, 72.9, 71.3, 70.8, 70.1, 68.7, 68.1, 62.2, 32.3, 30.0, 29.9, 29.8, 29.62, 26.4, 23.1, 14.5 (multi carbons in alkyl chain); Elemental analysis calcd (%) for $C_{36}H_{58}N_2O_5$ (598.86): C 72.20, H 9.76, N 4.68; Found: C 72.25, H 9.73, N 4.69.

3^{12}EO^{3}OH: yellow crystals (yield: 89 %). mp: 74 °C. ^{1}H-NMR ($CDCl_3$, 500 MHz) *δ*: 7.88-7.86 (m, 4 H, 4 Ar**H**), 7.09-7.07 (dd, *J* = 8.7, 8.7 Hz, 4 H, 4 Ar**H**), 6.64 (s, 2 H, 2 Ar**H**), 5.03 (s, 2 H, ArC**H**$_2$), 4.24 (s, 2 H, ArOC**H**$_2$CH$_2$O), 4.00-3.92 (m, 8 H, ArOCH$_2$C**H**$_2$O, 3 ArOC**H**$_2$CH$_2$), 3.76-3.73 (m, 6 H, 3 OC**H**$_2$), 3.66-3.64 (m, 2 H, C**H**$_2$OH), 1.87-1.81 (m, 6 H, 3 ArOCH$_2$C**H**$_2$), 1.46-1.44 (m, 6 H, 3 ArOCH$_2$CH$_2$C**H**$_2$), 1.37-1.21 (m, 48 H, 24 C**H**$_2$), 0.88-0.86 (m, 9 H, 3 C**H**$_3$); ^{13}C-NMR ($CDCl_3$, 125 MHz) *δ*: 161.2, 153.8, 147.7, 138.6, 131.8, 124.8, 115.5, 115.2, 106.7, 73.9, 72.9, 71.3, 71.1, 70.8, 70.1, 69.6, 68.1, 62.2, 32.3, 30.8, 30.1, 29.8, 26.5, 23.1, 14.5 (multi carbons in alkyl chain); Elemental analysis calcd (%) for $C_{61}H_{100}N_2O_8$ (989.46): C 74.05, H 10.19, N 2.83; Found: C 74.10, H 10.22, N 2.82.

3^{14}EO^{3}OH: yellow crystals (yield: 87 %). mp: 79 °C. ^{1}H-NMR ($CDCl_3$, 500 MHz) *δ*: 7.87-7.86 (m, 4 H, 4 Ar**H**), 7.08-7.01 (dd, *J* = 8.4, 8.5 Hz, 4 H, 4 Ar**H**), 6.64 (s, 2 H, 2 Ar**H**), 5.02 (s, 2 H, ArC**H**$_2$), 4.22-4.20 (m, 2 H, ArOC**H**$_2$CH$_2$O), 3.98-3.91 (m, 8 H, ArOCH$_2$C**H**$_2$O, 3 ArOC**H**$_2$CH$_2$), 3.76-3.73 (m, 6 H, 3 OC**H**$_2$), 3.64-3.62 (m, 2 H, C**H**$_2$OH), 1.80-1.73 (m, 6 H, 3 ArOCH$_2$C**H**$_2$), 1.47-1.45 (m, 6 H, 3 ArOCH$_2$CH$_2$C**H**$_2$), 1.38-1.21 (m, 60 H, 30 C**H**$_2$), 0.88-0.86 (m, 9 H, 3 C**H**$_3$); ^{13}C-NMR ($CDCl_3$, 125 MHz) *δ*: 161.2, 153.7, 147.7, 138.6, 131.8, 124.8, 115.5, 115.2, 106.7, 73.8, 72.9, 71.3, 71.1, 70.8, 70.1, 69.6, 68.1, 62.2, 32.3, 30.8, 30.1, 29.8, 26.5, 23.1, 14.5 (multi carbons in alkyl chain); Elemental analysis calcd (%) for $C_{67}H_{112}N_2O_8$ (1073.61): C 74.95, H 10.51, N 2.61; Found: C 74.89, H 10.53, N 2.62.

1^{6}EO^{4}OH: yellow crystals (yield: 78 %). m.p.: 104°C. ^{1}H-NMR ($CDCl_3$, 500 MHz) *δ*: 7.87-7.85 (m, 4 H, 4 Ar**H**), 7.02-6.97 (dd, *J* = 8.7, 8.8 Hz, 4 H, 4 Ar**H**), 4.20-4.19 (m, 2 H, ArOC**H**$_2$CH$_2$O), 4.03-4.00 (t, *J* = 6.5 Hz, 2 H, ArOC**H**$_2$), 3.90-3.88 (m, 2 H, ArOCH$_2$C**H**$_2$O), 3.74-3.70 (m, 10 H, 5 OC**H**$_2$), 3.63-3.61 (t, *J* = 4.3 Hz, 2 H, C**H**$_2$OH), 2.56 (s, 1 H, O**H**), 1.82-1.78 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.48-1.46 (m, 2 H, ArOCH$_2$CH$_2$C**H**$_2$), 1.38-1.23 (m, 4 H, 2 C**H**$_2$), 0.92-0.90 (m, 3 H, C**H**$_3$); ^{13}C-NMR (CDCl$_3$, 125 MHz) *δ*: 161.7, 161.1, 147.7, 147.3, 124.8, 124.7, 115.2, 115.1, 72.9, 71.3, 70.8, 70.1, 68.8, 68.1, 62.2, 32.0, 30.1, 29.6, 26.1, 23.0, 14.4 (multi carbons in alkyl chain); Elemental analysis calcd (%) for $C_{26}H_{38}N_2O_6$ (474.59): C 65.80, H 8.07, N 5.90; Found: C 65.75, H 8.10, N 5.88.

1^{12}EO^{4}OH: yellow crystals (yield: 93 %). m.p.: 112 °C. ^{1}H-NMR (CDCl$_3$, 500 MHz) *δ*: 7.87-7.85 (m, 4 H, 4 Ar**H**), 7.02-6.97 (dd, *J* = 8.7, 8.8 Hz, 4 H, 4 Ar**H**), 4.20-4.18 (m, 2 H, ArOC**H**$_2$CH$_2$O), 4.03-4.00 (t, *J* = 6.4 Hz, 2 H, ArOC**H**$_2$), 3.90-3.88 (t, *J* = 4.0 Hz, 2 H, ArOCH$_2$C**H**$_2$O), 3.74-3.70 (m, 10 H, 5 OC**H**$_2$), 3.63-3.61 (t, *J* = 4.0 Hz, 2 H, C**H**$_2$OH), 2.67 (s, 1 H, O**H**), 1.82-1.78 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.46-1.43 (m, 2 H, ArOCH$_2$CH$_2$C**H**$_2$), 1.38-1.22 (m, 16 H, 8 C**H**$_2$), 0.89-0.87 (t, *J* = 6.2 Hz, 3 H, C**H**$_3$); ^{13}C-NMR (CDCl$_3$, 125 MHz) *δ*: 161.7, 161.0, 147.6, 147.2, 124.8, 124.7, 115.2, 115.1, 72.9, 71.3, 70.8, 70.0, 68.7, 68.0, 62.2, 32.4, 30.1, 30.0, 29.8, 29.6, 26.5, 23.2, 14.6 (multi carbons in alkyl chain); Elemental analysis calcd (%) for $C_{32}H_{50}N_2O_6$ (558.75): C 68.79, H 9.02, N 5.01; Found: C 68.85, H 9.03, N 5.00.

2.5 General procedure for compounds 1^{n}OAll - 3^{n}OAll and 1^{n}EO^{m}All-3^{n}EO^{m}All

The mixture of NaH (3 mmol), the compounds **1^{n}OH - 3^{n}OH** or **1^{n}EO^{m}OH - 3^{n}EO^{m}OH** (1 mmol) and allyl bromide (1.1 mmol) were dissolved in dry THF (20 mL) then heated to 70 °C and stirred for 6 h. After the reaction was complete (TLC), water (50 mL) and Et$_2$O (100 mL) were added to the mixture. The organic layer was separated and washed with H$_2$O (2 x 20 mL), dried over MgSO$_4$, then the solvent was removed in *vacuo*. The residue was purified by chromatography (petroleum ether: ethyl acetate = 15:1).

1^{12}OAll: yellow crystals (yield: 98 %). mp: 92 °C. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.87-7.85 (m, 4 H, 4 Ar**H**), 7.05-6.98 (m, 4H, 4 Ar**H**), 6.12-6.04 (m, 1 H, C**H** = CH_2), 5.47-5.46 (d, J = 1.3 Hz, 1 H, CH = C$\mathbf{H_2}$), 5.31-5.31 (d, J = 1.2 Hz, 1 H, CH = C$\mathbf{H_2}$), 4.62-4.61 (d, J = 5.2 Hz, 2 H, ArOC$\mathbf{H_2}$CH), 4.04-4.02 (m, 2 H, ArOC$\mathbf{H_2}$$CH_2$), 1.84-1.78 (m, 2 H, Ar$OCH_2C\mathbf{H_2}$), 1.50-1.44 (m, 2 H, Ar$OCH_2CH_2C\mathbf{H_2}$), 1.36-1.27 (m, 16 H, 8 C$\mathbf{H_2}$), 0.90-0.87 (t, J = 7.2 Hz, 3 H, C$\mathbf{H_3}$).

1^{14}OAll: yellow crystals (yield: 100 %). mp: 95 °C. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.87-7.85 (m, 4 H, 4 Ar**H**), 7.02-6.95 (m, 4 H, 4 Ar**H**), 6.11-6.05 (m, 1 H, C**H** = CH_2), 5.47-5.43 (d, J = 17.3 Hz, 1 H, CH = C$\mathbf{H_2}$), 5.34-5.31 (d, J = 10.4 Hz, 1 H, CH = C$\mathbf{H_2}$), 4.62-4.61 (d, J = 5.0 Hz, 2 H, ArOC$\mathbf{H_2}$CH), 4.04-4.02 (m, J = 6.5 Hz, 2 H, ArOC$\mathbf{H_2}$$CH_2$), 1.83-1.80 (m, 2 H, Ar$OCH_2C\mathbf{H_2}$), 1.47-1.27 (m, 22 H, 11 C$\mathbf{H_2}$), 0.90-0.87 (t, J = 7.0 Hz, 3 H, C$\mathbf{H_3}$).

2^{14}OAll: yellow crystals (yield: 89 %). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.88-7.85 (m, 4 H, 4 Ar**H**), 7.08-7.00 (m, 4 H, 4 Ar**H**), 6.89-6.87 (m, 3 H, 3 Ar**H**), 6.10-6.01 (m, 1 H, C**H** = CH_2), 5.48-5.30 (d, 2 H, CH = C$\mathbf{H_2}$), 5.04 (s, 2 H, ArC$\mathbf{H_2}$O), 4.63-4.60 (m, 2 H, ArOC$\mathbf{H_2}$CH = CH_2), 4.03-3.98 (d, J = 3.0 Hz, 4 H, 2 ArOC$\mathbf{H_2}$), 1.81-1.73 (m, 4 H, 2 ArOCH_2C$\mathbf{H_2}$), 1.50-1.43 (m, 4 H, 2 ArOCH_2CH_2C$\mathbf{H_2}$), 1.41-1.15 (m, 40 H, 20 C$\mathbf{H_2}$), 0.90-0.85 (t, J = 6.0 Hz, 6 H, 2 C$\mathbf{H_3}$).

3^{12}OAll: yellow crystals (yield: 99 %). mp: 58 °C. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.88-7.86 (m, 4 H, 4 Ar**H**), 7.08-7.06 (d, J = 8.8 Hz, 2 H, 2 Ar**H**), 7.02-7.01 (d, J = 8.7 Hz, 2 H, 2 Ar**H**), 6.64 (s, 2 H, 2 Ar**H**), 6.10-6.05 (m, 1 H, C**H** = CH_2), 5.46-5.43 (d, J = 17.1 Hz, 1 H, CH = C$\mathbf{H_2}$), 5.33-5.31 (d, J = 10.3 Hz, 1 H, CH = C$\mathbf{H_2}$), 5.02 (s, 2 H, ArC$\mathbf{H_2}$), 4.62-4.61(d, J = 4.8 Hz, 2 H, ArOC$\mathbf{H_2}$CH), 3.99-3.94 (m, 6 H, 3 ArOC$\mathbf{H_2}$$CH_2$), 1.81-1.73 (m, 6 H, 3 ArOCH_2C$\mathbf{H_2}$), 1.46 (s, 6 H, 3 ArOCH_2CH_2C$\mathbf{H_2}$), 1.26 (m, 48 H, 24 C$\mathbf{H_2}$), 0.89-0.86 (t, J = 6.6 Hz, 9 H, 3 C$\mathbf{H_3}$).

3^{14}OAll: yellow crystals (yield: 98 %). mp: 68 °C. ^{1}H-NMR ($CDCl_3$, 500 MHz) *δ*: 7.88-7.86 (m, 4 H, 4 Ar**H**), 7.08-7.06 (d, *J* = 8.5 Hz, 2 H, 2 Ar**H**), 7.02-7.01 (d, *J* = 8.6 Hz, 2 H, 2 Ar**H**), 6.63 (s, 2 H, 2 Ar**H**), 6.10-6.05 (m, 1 H, C**H** = CH$_2$), 5.47-5.43 (d, *J* = 17.4 Hz, 1 H, CH = C$\mathbf{H}_2$), 5.34-5.31 (d, *J* = 10.8 Hz, 1 H, CH = C$\mathbf{H}_2$), 5.02 (s, 2 H, ArC$\mathbf{H}_2$), 4.62-4.61 (d, *J* = 4.0 Hz, 2 H, ArOC$\mathbf{H}_2$CH), 3.99-3.94 (m, 6 H, 3 ArOC$\mathbf{H}_2$CH$_2$), 1.81-1.73 (m, 6 H, 3 ArOCH$_2$C$\mathbf{H}_2$), 1.46 (s, 6 H, 3 ArOCH$_2$CH$_2$C$\mathbf{H}_2$), 1.26 (m, 60 H, 30 C$\mathbf{H}_2$), 0.89-0.87 (t, *J* = 6.3 Hz, 9 H, 3 C$\mathbf{H}_3$).

1^{12}EO^{3}All: yellow crystals (yield: 93 %). mp: 71 °C. ^{1}H-NMR ($CDCl_3$, 500 MHz) *δ*: 7.87-7.85 (m, 4 H, 4 Ar**H**), 7.02-6.98 (m, 4 H, 4 Ar**H**), 5.95-5.88 (m, 1 H, C**H** = CH$_2$), 5.29-5.26 (d, *J* = 15.9 Hz, 2 H, CH = C$\mathbf{H}_2$), 5.19-5.16 (d, *J* = 10.3 Hz, 2 H, CH = C$\mathbf{H}_2$), 4.22-4.20 (t, *J* = 4.8 Hz, 2 H, ArOC$\mathbf{H}_2$CH$_2$O), 4.04-3.98 (m, 4 H, ArOCH$_2$C$\mathbf{H}_2$O, C$\mathbf{H}_2$CH), 3.91-3.89 (t, *J* = 4.6 Hz, 2 H, ArOCH$_2$C$\mathbf{H}_2$O), 3.71-3.60 (m, 8 H, 4 OC$\mathbf{H}_2$), 1.84-1.78 (m, 2 H, ArOCH$_2$C$\mathbf{H}_2$), 1.36-1.35 (m, 2 H, ArOCH$_2$CH$_2$C$\mathbf{H}_2$), 1.26 (m, 16 H, 8 C$\mathbf{H}_2$), 0.89-0.87 (t, *J* = 7.1 Hz, 3 H, C$\mathbf{H}_3$).

1^{14}EO^{3}All: yellow crystals (yield: 97 %). mp: 73 °C. ^{1}H-NMR ($CDCl_3$, 500 MHz) *δ*: 7.86-7.85 (m, 4 H, 4 Ar**H**), 7.02-6.94 (m, 4 H, 4 Ar**H**), 5.94-5.89 (m, 1 H, C**H** = CH$_2$), 5.29-5.26 (d, *J* = 17.3 Hz, 2 H, CH = C$\mathbf{H}_2$), 5.19-5.16 (d, *J* = 10.3 Hz, 2 H, CH = C$\mathbf{H}_2$), 4.21-4.20 (t, *J* = 4.6 Hz, 2 H, ArOC$\mathbf{H}_2$CH$_2$O), 4.13-3.95 (m, 4 H, ArOC$\mathbf{H}_2$CH$_2$, C$\mathbf{H}_2$CH), 3.90-3.89 (t, *J* = 4.5 Hz, 2 H, ArOCH$_2$C$\mathbf{H}_2$O), 3.71-3.67 (m, 8 H, 4 OC$\mathbf{H}_2$), 1.82-1.80 (m, 2 H, ArOCH$_2$C$\mathbf{H}_2$), 1.47-1.44 (m, 2 H, ArOCH$_2$CH$_2$C$\mathbf{H}_2$), 1.26 (s, 20 H, 10 C$\mathbf{H}_2$), 0.89-0.87 (t, *J* = 7.0 Hz, 3 H, C$\mathbf{H}_3$).

3^{12}EO^{3}All: yellow crystals (yield: 92 %). mp: 46 °C. ^{1}H-NMR ($CDCl_3$, 500 MHz) *δ*: 7.88-7.85 (m, 4 H, 4 Ar**H**), 7.07-7.06 (d, *J* = 8.8 Hz, 2 H, 2 Ar**H**), 7.02-7.00(d, *J* = 8.8 Hz, 2 H, 2 Ar**H**), 6.63(s, 2 H, 2 Ar**H**), 5.95-5.85 (m, 1 H, C**H** = CH$_2$), 5.29-5.25 (d, *J* = 17.5 Hz, 2 H, CH = C$\mathbf{H}_2$), 5.18-5.16 (d, *J* = 10.3 Hz, 2 H, CH = C$\mathbf{H}_2$), 5.01 (s, 2 H, ArC$\mathbf{H}_2$), 4.20 (s, 2 H, ArOC$\mathbf{H}_2$CH$_2$O), 4.03-3.89 (m, 6 H, 3 ArOC$\mathbf{H}_2$CH$_2$), 3.75-3.66

(m, 2 H, $ArOCH_2C\mathbf{H}_2O$), 3.61-3.60 (m, 8 H, 4 $OC\mathbf{H}_2$), 1.81-1.74 (m, 6 H, 3 $ArOCH_2C\mathbf{H}_2$), 1.46 (s, 6 H, $3ArOCH_2CH_2C\mathbf{H}_2$), 1.26 (m, 48 H, 24 $C\mathbf{H}_2$), 0.89-0.87 (t, *J* = 6.3 Hz, 9 H, 3 $C\mathbf{H}_3$).

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$3^{14}EO^3All$: yellow crystals (yield: 97 %). mp: 53 °C. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.88-7.85 (m, 4 H, 4 Ar**H**), 7.08-7.06 (d, *J* = 8.9 Hz, 2 H, 2 Ar**H**), 7.02-7.01 (d, *J* = 8.8 Hz, 2 H, 2 Ar**H**), 6.63 (s, 2 H, 2 Ar**H**), 5.92-5.91 (m, 1 H, C**H** = CH_2), 5.29-5.26 (d, *J* = 17.1 Hz, 2 H, CH = $C\mathbf{H}_2$), 5.19-5.16 (d, *J* = 10.6 Hz, 2 H, CH = $C\mathbf{H}_2$), 5.02 (s, 2 H, $ArC\mathbf{H}_2$), 4.22-4.20 (t, *J* = 4.6 Hz, 2 H, $ArOC\mathbf{H}_2CH_2O$), 4.03-3.89 (m, 6 H, 3 $ArOC\mathbf{H}_2CH_2$), 3.76-3.67 (m, 2 H, $ArOCH_2C\mathbf{H}_2O$), 3.62-3.60 (m, 8 H, 4 $OC\mathbf{H}_2$), 1.81-1.73 (m, 6 H, 3 $ArOCH_2C\mathbf{H}_2$), 1.46 (s, 6 H, 3 $ArOCH_2CH_2C\mathbf{H}_2$), 1.26 (m, 60 H, 30 $C\mathbf{H}_2$), 0.89-0.87 (t, *J* = 6.3 Hz, 9 H, 3 $C\mathbf{H}_3$).

2.6 General procedure for oxidation of $1^nEO^m(OH)_2$ - $3^nEO^m(OH)_2$

1^nOAll - 3^nOAll or 1^nEO^mAll - 3^nEO^mAll (1 mmol) and NMMNO (0.6 mL, 60 % solution in water) were dissolved in acetone. Osmium tetroxide (0.7 mL, 0.004 M solution in *tert*-butanol) was added, and the solution was stirred for 24 h at RT. After the reaction was complete (TLC), saturated solution of Na_2SO_3 (5 mL) was added, and the mixture was stirred for 30 min at RT. The mixture was filtered. Ethyl acetate (30 mL) and 10% H_2SO_4 (5 mL) were added into the liquid and the organic layer was separated, washed with saturated solution of $NaHCO_3$ (50 mL) and H_2O (50 mL), dried over anhydrous Na_2SO_4, and the solvent was evaporated in *vacuo*. The residue was purified by chromatography (petroleum ether: ethyl acetate = 3:1).

$1^{12}(OH)_2$: yellow crystals (yield: 88 %). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.53-7.51 (m, 4 H, 4 Ar**H**), 6.73-6.67 (dd, *J* = 8.9, 8.9 Hz, 4 H, 4 Ar**H**), 3.83-3.72 (m, 4 H, $ArOC\mathbf{H}_2CH$, $ArOC\mathbf{H}_2CH_2$), 3.44-3.35 (m, 3 H, C**H**OH, $C\mathbf{H}_2OH$), 1.53-1.47 (m, 2 H, ArOCH$_2$C**H$_2$**), 1.20-1.14 (m, 2 H, ArOCH$_2$CH$_2$C**H$_2$**), 1.06-0.86 (m, 16 H, 8 C**H**$_2$), 0.59-0.56 (t, *J* = 7.0 Hz, 9 H, 3 C**H**$_3$). ^{13}C-NMR (CDCl$_3$, DMSO, 125 MHz) δ: 161.4, 161.2, 147.2, 147.0, 124.4(2C), 124.4(2C), 115.1(2C),114.9(2C), 70.6, 69.9, 68.5, 63.6, 32.00, 30.0, 29.9, 29.7, 29.6, 29.4, 29.4, 29.3, 26.1, 22.7, 14.2(multi carbons in alkyl chain). Elemental analysis calcd (%) for $C_{27}H_{40}N_2O_4$ (456.62): C 71.02, H 8.83, N 6.13; Found: C 70.96, H 8.81, N 6.14.

1^{14}(OH)$_2$: yellow crystals (yield: 90 %). 110 °C. ^{1}H-NMR (CDCl$_3$, 500 MHz) δ: 7.86-7.81 (m, 4 H, 4 Ar**H**), 7.12-7.03 (m, 4 H, 4 Ar**H**), 4.14-3.98 (m, 4 H, ArOC**H**$_2$CH, ArOC**H$_2$**CH$_2$), 3.86-3.49 (m, 3 H, C**H**OH, C**H**$_2$OH), 1.76-1.74 (m, 2 H, ArOCH$_2$C**H$_2$**), 1.45-1.41 (m, 2 H, ArOCH$_2$CH$_2$C**H$_2$**), 1.34-1.25 (m, 20 H, 10 C**H**$_2$), 0.87-0.85 (t, *J* = 7.0 Hz, 3 H, C**H**$_3$). ^{13}C-NMR(DMSO, 125 MHz) δ: 162.0, 161.8, 147.2 (2 C), 125.1 (2 C), 124.9 (2 C), 116.0 (2 C), 115.9 (2 C), 71.1, 80.9, 68.9, 63.6, 32.1, 29.8 (3 C), 29.7 (3 C), 29.5 (3 C), 26.3, 22.9, 14.7 (multi carbons in alkyl chain). Elemental analysis calcd (%) for $C_{29}H_{44}N_2O_4$ (484.67): C 71.87, H 9.15, N 5.78; Found: C 71.98, H 9.12, N 5.80.

2^{14}(OH)$_2$: yellow crystals (yield: 86 %). ^{1}H-NMR (CDCl$_3$, 300 MHz) δ: 7.89-7.86 (m, 4 H, 4 Ar**H**), 7.09-6.95 (m, 6 H, 6 Ar**H**), 6.90-6.87 (d, *J* = 9.0 Hz, 1 H, Ar**H**), 5.04 (s, 2 H, ArC**H**$_2$O), 4.13-4.07 (m, 3 H, ArOC**H$_2$**C**H**OH), 4.03-4.01 (m, 4 H, 2 ArOC**H$_2$**CH$_2$CH$_2$), 3.98-3.74 (m, 2 H, CH(OH)C**H$_2$**OH), 2.59 (s, 1 H, CH$_2$CH(O**H**)CH$_2$(OH), 2.04 (s, 1 H, CH$_2$CH(OH)CH$_2$(O**H**), 1.86-1.76 (m, 4 H, 2 ArOCH$_2$C**H$_2$**), 1.48-1.42 (m, 4 H, 2 ArOCH$_2$CH$_2$C**H$_2$**), 1.41-1.13 (m, 40 H, 20 C**H**$_2$), 0.90-0.85 (t, *J* = 6.0 Hz, 6 H, 2 C**H**$_3$). ^{13}C-NMR (DMSO, 75 MHz) δ: 161.0, 160.5, 149.1 (2 C), 129.1 (2 C), 124.1 (2 C), 120.5 (2 C), 115.2 (2 C), 115.0 (2 C), 114.1 (2C), 110.1, 102.5, 71.1, 80.9, 68.9, 63.6, 32.1, 29.8 (3 C), 29.7 (3 C), 29.5 (3 C), 26.3, 22.9, 14.7 (multi carbons in alkyl chain). Elemental analysis calcd (%) for $C_{50}H_{78}N_2O_6$ (803.16): C 74.77, H 9.79, N 3.49; Found: C 74.91, H 9.77, N 3.50.

$3^{12}(OH)_2$: yellow crystals (yield: 92 %). ^{1}H-NMR (CDCl$_3$, 500 MHz) δ: 8.14-8.11 (dd, J = 6.0, 6.2 Hz, 4 H, 4 Ar**H**), 7.33-7.31 (d, J = 8.9 Hz, 2 H, 2 Ar**H**), 7.25-7.23 (d, J = 8.8 Hz, 2 H, 2 Ar**H**), 6.89 (s, 2 H, 2 Ar**H**), 5.26 (s, 2 H, ArC**H**$_2$), 4.37-4.21 (m, 6 H, 3 ArOC**H**$_2$CH$_2$), 4.09-4.01 (m, 3 H, C**H**OHC**H**$_2$OH), 2.07-1.99 (m, 6 H, 3 ArOCH$_2$C**H$_2$**), 1.73-1.71 (m, 6 H, 3 ArOCH$_2$CH$_2$C**H$_2$**), 1.52 (s, 48 H, 24 C**H**$_2$), 1.15-1.13 (t, J = 6.9 Hz, 9 H, 3 C**H**$_3$).^{13}C-NMR (CDCl$_3$, 125 MHz) δ: 161.3, 160.8, 153.8 (2 C), 147.8, 147.6, 138.5, 131.9, 124.8 (4 C), 115.5 (2 C), 115.2 (2 C), 106.7 (2 C), 73.9, 71.1, 70.8, 69.8, 69.6 (2 C), 64.0, 32.3 (3 C), 30.1 (6 C), 30.1 (6 C), 29.8 (6 C), 26.5 (3 C), 23.5 (3 C), 23.1 (3 C), 14.5 (3C)(multi carbons in alkyl chain). Elemental analysis calcd (%) for $C_{58}H_{94}N_2O_7$ (931.38): C 74.79, H 10.17, N 3.01; Found: C 74.92, H 10.15, N 3.00.

$3^{14}(OH)_2$: yellow crystals (yield: 88 %). ^{1}H-NMR (CDCl$_3$, 500 MHz) δ: 7.88-7.86 (d, 4 H, J = 8.3 Hz, 4 Ar**H**), 7.08-7.06 (d, 2 H, J = 8.0 Hz, 2 Ar**H**), 7.01-6.99 (d, 2 H, J = 8.1 Hz, 2 Ar**H**), 6.63 (s, 2 H, 2 Ar**H**), 5.01 (s, 2 H, ArC**H**$_2$), 4.11-3.96 (m, 6 H, 3 ArOC**H**$_2$CH$_2$), 3.87-3.77 (m, 3 H, C**H**OH, C**H**$_2$OH), 1.79-1.67 (m, 6 H, 3 ArOCH$_2$C**H$_2$**), 1.46 (s, 6 H, 3 ArOCH$_2$CH$_2$C**H$_2$**), 1.26 (s, 60 H, 30 C**H**$_2$), 0.88 (s, 9 H, 3 C**H**$_3$). ^{13}C-NMR (CDCl$_3$, 125 MHz) δ: 161.3, 160.8, 153.8 (2 C), 147.9, 147.6, 138.6, 131.8, 124.8(4C), 115.5(2C), 115.2(2C), 106.7(2C), 73.9, 71.1, 70.8, 69.9, 69.7 (2 C), 64.0, 32.3 (3 C), 30.1 (9 C), 29.8 (9 C), 29.8 (9 C), 26.5 (3 C), 23.1 (3 C), 14.5 (3 C) (multi carbons in alkyl chain). Elemental analysis calcd (%) for $C_{64}H_{106}N_2O_7$ (1015.54): C 75.69, H 10.52, N 2.76; Found: C 75.58, H 10.50, N 2.77.

$1^{12}EO^3(OH)_2$: yellow crystals (yield: 93 %). ^{1}H-NMR (CDCl$_3$, 500 MHz) δ: 7.84-7.82 (m, 4 H, 4 Ar**H**), 7.14-7.09 (m, 4 H, 4 Ar**H**), 4.66-4.65 (t, J = 5.1 Hz, 2 H, ArOC**H$_2$**CH$_2$O), 4.51-4.49 (t, J = 5.6 Hz, 2 H, ArOC**H$_2$**CH$_2$), 4.07-4.05 (m, 4 H, ArOCH$_2$C**H$_2$**O, C**H**$_2$OH), 3.62-3.28 (m, 11 H, 5 OC**H**$_2$, CH$_2$C**H**), 2.64 (s, 2 H, 2 O**H**), 1.77-1.73 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.44-1.41 (t, J = 6.8 Hz, 2 H, ArOCH$_2$CH$_2$C**H$_2$**,),1.32-1.25 (m, 16 H, 8 C**H**$_2$), 0.87-0.84 (t, J = 7.0 Hz, 3 H, C**H**$_3$).

^{13}C-NMR (DMSO, 125 MHz) *δ*: 161.8, 161.6, 147.1, 147.0, 125.0 (2 C), 125.0 (2 C), 115.9 (2 C), 115.8 (2 C), 73.6, 71.43, 71.0, 70.8, 71.0(2C), 69.7, 68.8, 68.5, 64.0, 32.2, 29.9 (2 C), 29.8 (2 C), 29.6 (2 C), 29.5, 26.3, 22.9, 14.8 (multi carbons in alkyl chain). Elemental analysis calcd (%) for $C_{33}H_{52}N_2O_7$ (588.78): C 67.32, H 8.90, N 4.76; Found: C 67.44, H 8.88, N 4.77.

1^{14}EO^{3}(OH)$_{2}$: yellow crystals (yield: 87%). ^{1}H-NMR (CDCl$_3$, 500 MHz) *δ*: 7.87-7.85(d, *J* = 8.9 Hz, 4 H, 4Ar**H**),7.02-6.93(m, 4 H, 4Ar**H**), 4.22-4.20(t, *J* = 4.5 Hz, 2 H, ArOC**H**$_2$CH$_2$O), 4.03-4.01(t, *J* = 6.5 Hz, 2 H, ArOC**H**$_2$CH$_2$), 3.89-3.86(m, 4 H, ArOCH$_2$C**H**$_2$O, C**H**$_2$OH), 3.75-3.41(m, 11 H, 5OC**H**$_2$, CH$_2$C**H**), 2.62(s, 1 H, CH$_2$CH(O**H**)CH$_2$(OH), 2.16(s, 1 H, CH$_2$CH(OH)CH$_2$(O**H**)), 1.83-1.78(m, 2 H, ArOCH$_2$C**H$_2$**), 1.47-1.44(t, 2 H, ArOCH$_2$CH$_2$C**H$_2$**), 1.36-1.26(m, 20 H, 10C**H**$_2$), 0.89-0.87(t, *J* = 7.2 Hz, 3 H, C**H**$_3$).^{13}C-NMR (CDCl$_3$, 125 MHz) *δ*: 161.7, 161.1, 147.7, 147.3, 124.7(2C), 12 4.7(2C), 115.3(2C), 115.1(2C), 73.4,71.2, 71.1, 71.0, 70.1(2C), 68.8, 68.4, 68.1, 64.3, 32.3, 30.1(3C), 30.0(2C), 29.8(2C), 29.6(2C), 26.4, 23.1, 14.48. Elemental analysis calcd (%) for $C_{35}H_{56}N_2O_7$ (616.83): C 68.15, H 9.15, N 4.54; Found: C 68.24, H 9.12, N 4.53.

3^{12}EO^{3}(OH)$_{2}$: yellow crystals (yield: 92 %). ^{1}H-NMR (CDCl$_3$, 500 MHz) *δ*: 7.88-7.86 (m, 4 H, 4 Ar**H**), 7.08-7.06 (d, *J* = 8.8 Hz, 2 H, 2 Ar**H**), 7.03-7.01 (d, *J* = 8.8 Hz, 2 H, 2 Ar**H**), 6.63 (s, 2 H, 2 Ar**H**), 5.02 (s, 2 H, ArC**H**$_2$), 4.21-4.21 (t, *J* = 4.3 Hz, 2 H, ArOC**H**$_2$CH$_2$O), 3.99-3.94 (m, 6 H, 3 ArOC**H**$_2$CH$_2$), 3.88-3.86 (m, 4 H, ArOCH$_2$C**H**$_2$O, C**H**$_2$OH), 3.74-3.56 (m, 11 H, 5 OC**H**$_2$, CH$_2$C**H**), 2.59 (s, 2 H, 2 O**H**), 1.81-1.73 (m, 6 H, 3 ArOCH$_2$C**H$_2$**), 1.46 (s, 6 H, 3 ArOCH$_2$CH$_2$C**H$_2$**), 1.26 (m, 48 H, 24 C**H**$_2$), 0.89-0.86 (t, *J* = 6.8 Hz, 9 H, 3 C**H**$_3$). ^{13}C-NMR (CDCl$_3$, 125 MHz) *δ*: 161.2 (2 C), 153.8 (2 C), 147.7 (2 C), 138.6, 131.8, 124.8 (4 C), 115.5 (2 C), 115.3 (2 C), 106.7 (2 C), 73.9, 73.4, 71.3 (2 C), 71.1 (2 C), 71.0 (2 C), 70.1, 69.6 (2 C), 68.1, 64.3, 32.3 (3 C), 30.8 (3 C), 30.1 (6 C), 30.1 (6 C), 29.8 (6 C), 26.5 (3 C), 23.1 (3 C), 14.5

(3 C) (multi carbons in alkyl chain). Elemental analysis calcd (%) for $C_{64}H_{106}N_2O_{10}$ (1063.53): C 72.28, H 10.05, N 2.63; Found: C 72.18, H 10.08, N 2.62.

$3^{14}EO^3(OH)_2$: yellow crystals (yield: 87 %). ^{1}H-NMR ($CDCl_3$, 500 MHz) *δ*: 7.87-7.85 (m, 4 H, 4 Ar**H**), 7.07-7.05 (d, *J* = 8.8 Hz, 2 H, 2 Ar**H**), 7.02-7.00 (d, *J* = 8.9 Hz, 2 H, 2 Ar**H**), 6.63 (s, 2 H, 2 Ar**H**), 5.01 (s, 2 H, ArC**H**$_2$), 4.22-4.20 (t, *J* = 4.7 Hz, 2 H, ArOC**H**$_2$CH$_2$O), 3.98-3.93 (m, 6 H, 3 ArOC**H$_2$**CH$_2$), 3.89-3.85 (m, 4 H, ArOCH$_2$C**H**$_2$O, C**H**$_2$OH), 3.74-3.53 (m, 11 H, 5 OC**H**$_2$, CH$_2$C**H**), 1.82-1.71 (m, 6 H, 3 ArOCH$_2$C**H$_2$**), 1.46 (s, 3 ArOCH$_2$CH$_2$C**H$_2$**), 1.6 (s, 60 H, 30 C**H**$_2$), 0.88-0.86 (t, *J* = 7.1 Hz, 9 H, 3C**H**$_3$).^{13}CNMR ($CDCl_3$, 125 MHz) *δ*: 161.2 (2 C), 153.8 (2 C), 147.7 (2 C), 138.6, 13 1.8, 124.8 (4 C), 115.5 (2 C), 115.3 (2 C), 106.7 (2 C), 73.9, 73.4, 71.2 (2 C), 71.1 (2 C), 71.0 (2 C), 70.1, 69.6 (2 C), 68.1, 64.3, 32.3 (3 C), 30.1 (9 C), 29.8 (9 C), 29.8 (9 C), 26.5 (3 C), 23.1 (3 C), 14.5 (3 C)(multi carbons in alkyl chain). Elemental analysis calcd (%) for $C_{70}H_{118}N_2O_{10}$ (1147.69): C 73.26, H 10.36, N 2.44; Found: C 73.18, H 10.33, N 2.43.

3. Additional data

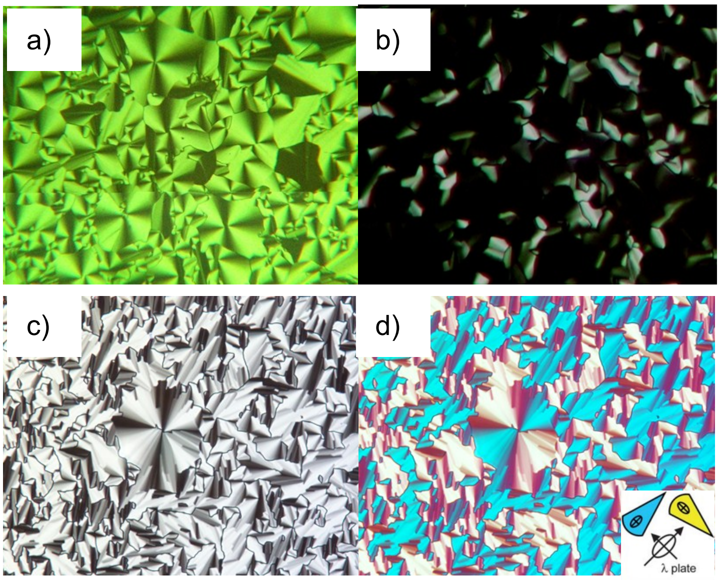
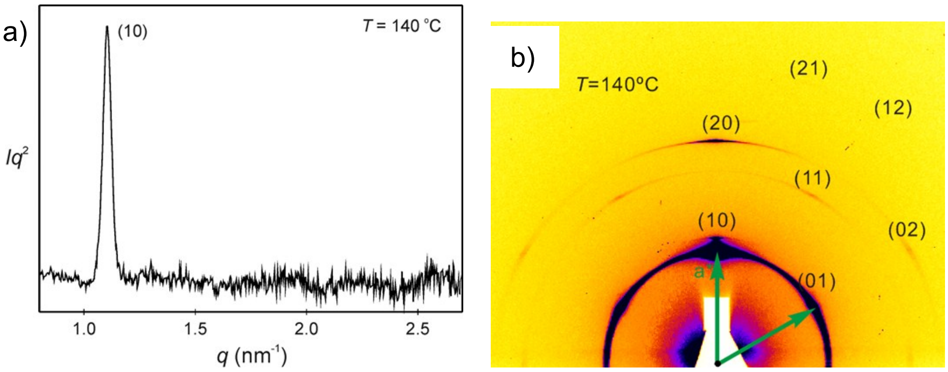


Figure S1. (a) Texture of the Col$_{hex}$ phase of compound **3^{12}EO^{3}OH** after cooling from the isotropic state at 65 °C, the alignment of the columns is parallel to the surfaces; (b) texture of the Col$_{hex}$ phase of compound **3^{12}EO^{3}(OH)$_2$** after cooling down from isotropic state to 106 °C, the dark areas result from the alignment of the columns perpendicular to the substrate surfaces; (c) texture of compound **3^{12}EO^{3}(OH)$_2$** after cooling from the isotropic liquid to 100 °C; (d) same texture, in (e) with additional λ-retarder plate.



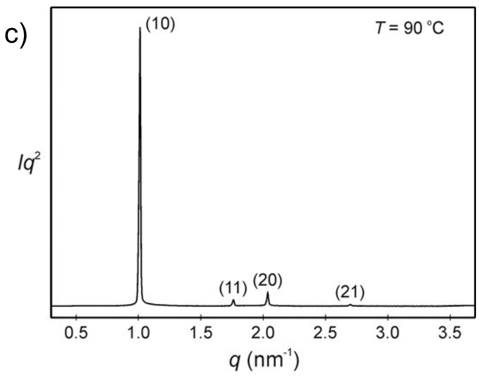


Figure S2. (a) SAXS diffraction pattern of $\mathrm{Col_{hex}}/p6mm$ phase of compound **$2^{14}(OH)_2$** at $T = 140$ ºC; (b) GISAX pattern of $\mathrm{Col_{hex}}/p6mm$ phase of compound **$2^{14}(OH)_2$** at $T = 140$ ºC; c) SAXS diffraction pattern of $\mathrm{Col_{hex}}/p6mm$ phase of compound **$3^{12}EO^3(OH)_2$** at 90 ºC

Table S.1 Experimental and calculated *d*-spacing of the observed SAXS reflection of the SmA phase of **$1^{12}(OH)_2$** at 169 ºC.

(*hk*)	$d_{\mathrm{obs.}}$ – spacing (nm)	$d_{\mathrm{cal.}}$ – spacing (nm)
(01)	5.14	5.16
(02)	2.59	2.58
diff	0.47	
$d = 5.16$ nm		

Table S2. Experimental and calculated *d*-spacing of the observed SAXS reflection of the SmC phase of **$1^{12}(OH)_2$** at 167 ºC.

(*hk*)	$d_{\mathrm{obs.}}$ – spacing (nm)	$d_{\mathrm{cal.}}$ – spacing (nm)
(01)	5.02	5.05
(02)	2.54	2.53
diff	0.47	
$d = 5.05$ nm		

Table S3. Experimental and calculated *d*-spacing of the observed SAXS reflection of the SmC phase in **$1^{12}EO^3OH$** at 105 ºC.

(*hk*)	$d_{\mathrm{obs.}}$ – spacing (nm)	$d_{\mathrm{cal.}}$ – spacing (nm)

(01)	5.57	5.57
(02)	2.80	2.79
diff	0.45	
d = 5.57 nm		

Table S4. Experimental and calculated *d*-spacing of the observed SAXS reflection of the Col$_{hex}$ /*p*6*mm* phase of **2^{14}(OH)$_2$** at 140 ºC.

(*hk*)	$d_{obs.}$ – spacing (nm)	$d_{cal.}$ – spacing (nm)
(10)	5.76	5.76
a_{hex} = 6.65 nm		

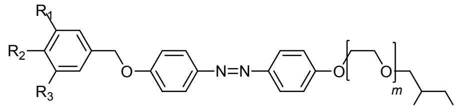
Table S5. Experimental and calculated *d*-spacing of the observed SAXS reflection of the hexagonal *p*6*mm* phase of **3^{12}EO^{3}(OH)$_2$** at 90 ºC. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$ – spacing (nm)	$d_{cal.}$ – spacing (nm)	*intensity*	*Phase*
(10)	6.21	6.21	100.0	0
(11)	3.59	3.59	2.6	π
(20)	3.10	3.11	5.3	π
(21)	2.34	2.35	0.4	π
a_{hex} = 7.17 nm				

Table S6. Experimental and calculated *d*-spacing of the observed SAXS reflection of the hexagonal *p*6*mm* phase of **3^{12}(OH)$_2$** at 90 ºC. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$ – spacing (nm)	$d_{cal.}$ – spacing (nm)	*intensity*	*Phase*
(10)	5.37	5.37	100.0	0
(11)	3.10	3.10	0.2	π
(20)	2.68	2.68	3.8	π
(21)	2.02	2.03	0.3	π
a_{hex} = 6.20 nm				

Table S7. Calculations of molecular volume (V_{mol}), volume of the (hypothetical) unit cells(V_{cell}) and number of molecules in these unit cells (n_{cell}).^{a}



$2^nEO^m(OH)_2$ - $3^nEO^m(OH)_2$

Comp	phase	a/nm (T/°C)	V_{cell} [nm^3]	V_{mol} [nm^3]	$n_{\text{cell,cryst}}$	$n_{\text{cell,liq}}$	n_{cell}
$2^{14}(OH)_2$	Col$_{\text{hex}}$/$p6mm$	6.65 (140)	17.2	1.19	14.5	11.4	13.0
$3^{12}(OH)_2$	Col$_{\text{hex}}$/$p6mm$	6.20 (90)	15.0	1.40	10.7	8.4	9.6
$3^{12}EO^3(OH)_2$	Col$_{\text{hex}}$/$p6mm$	7.17 (90)	20.0	1.58	12.7	9.9	11.3

^{a} V_{cell} = volume of the unit cell defined by the dimensions $a_{\text{hex}}^2 \times \sin(60°) \times 0.45$ nm for hexagonal phases and a_{cub}^3 for the cubic phases; V_{mol} = volume for a single molecule as calculated using the crystal volume increments[5] $n_{\text{cell,cryst}}$ = number of molecules in the unit cell, calculated according to $n_{\text{cell,cryst}} = V_{\text{cell}}/V_{\text{mol}}$ (average packing coefficient in the crystal is $k = 0.7$;[6] $n_{\text{cell,liq}}$ = number of molecules in the unit cell of an isotropic liquid with an average packing coefficient $k = 0.55$, calculated according to $n_{\text{cell,liq}} = 0.55/0.7 \times n_{\text{cell,cryst}}$; n_{cell} = in the LC phase estimated as the average of that in the $n_{\text{cell,cryst}}$ and $n_{\text{cell,liq}}$.

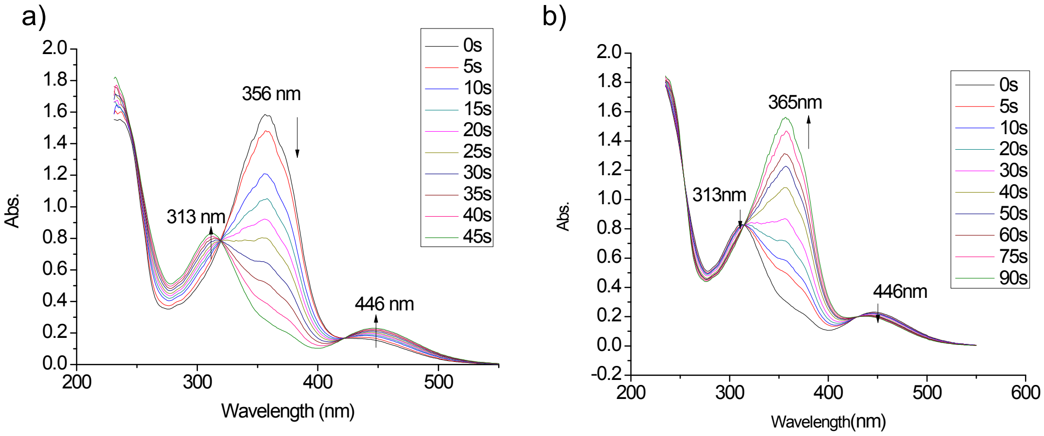


Figure S3. UV Spectra of **$3^{12}(OH)_2$** in CH_2Cl_2 solution, changing with the time: a) from trans- to cis-azobenzene under irradiation with 365 nm light); b) from cis- to trans-azobenzene under irradiation visible light.

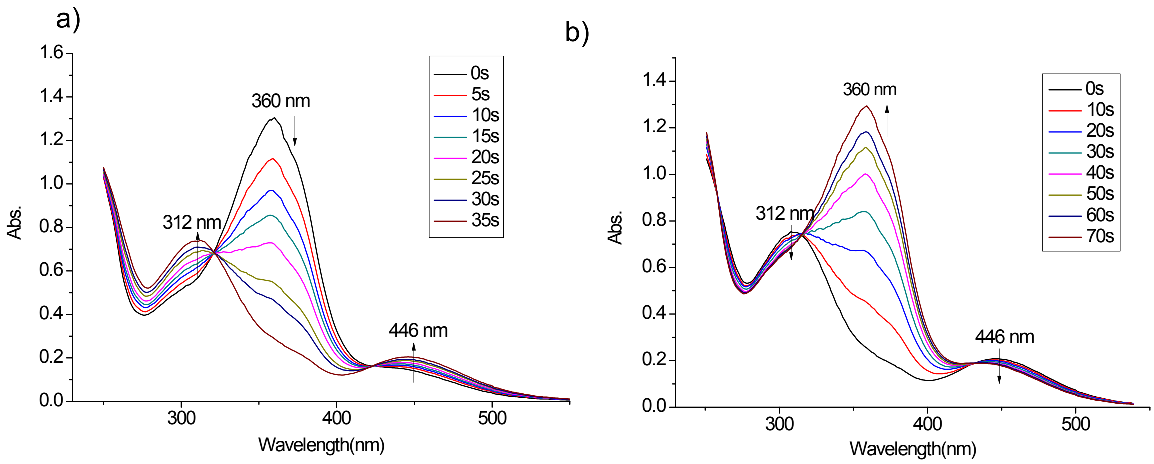


Figure. S4. UV Spectra of $\mathbf{1^{12}(OH)_2}$ in CH_2Cl_2 solution, changing with time a) from trans- to cis-azobenzene under irradiation with 365 nm light); b) from *cis*- to *trans*-azobenzene under irradiation with visible light.

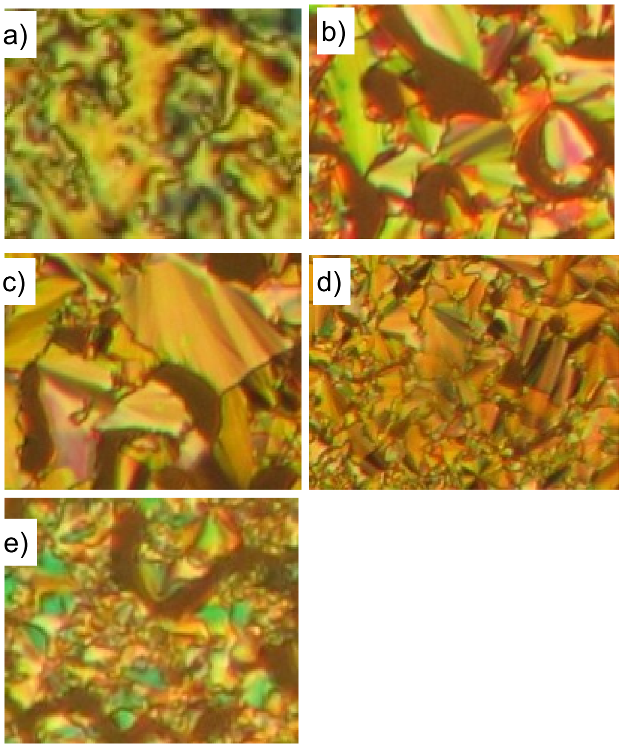


Figure S6. Textures of compound $\mathbf{1^{12}EO^{3}OH}$ at 98 °C. a) SmC schlieren texture before irradiation, b,c) SmA fan texture with some homeotropic areas as observed after irradiation with 365 nm (5mW cm^{-2}) b) for 20 s and c) for 60 s. d,e) Textures as observed after thermal annealing without irradiation d) for 30 minutes and e) for 60 minutes; optically isotropic areas in b) and c) represent areas with homeotropic alignment of the SmA phase, whereas those in e) represent areas of isotropic liquid coexisting with the reformed SmC phase, resulting from partial decomposition after prolonged thermal treatment.

4. References

[S1] [a] M. Müri, K.C. Schuermann, L.D. Cola, M. Mayor, *Eur. J. Org. Chem.*, 2009, **15**, 2562–2575; [b] M. Yoshio, T. Kagata, K. Hoshino, T. Mukai, H. Ohno, T. Kato, *J. Am. Chem. Soc.*, 2006, **128**, 5570–5577.

[S2] W. H. Wei, T. Tomohiro, M. Kodaka, and H. Okuno, *J. Org. Chem.*, 2000, **65**, 8979–8987.

[S3] R. Loska, A. Janiga, and D. Gryko, *Journal of Porphyrins and Phthalocyanines.*, 2013, **17**, 104–117.

[S4] J. Moreau and J. Marchand-Brynaert, *Eur. J. Org. Chem.*, 2011, **9**, 1641–1644.

[S5] A. Immirzi, B. Perini, *Acta Cryst. Sect. A.*, 1977, **33**, 216–218.

[S6] A. I. Kitaigorodsky, *Molekülkristalle*, Akademieverlag Berlin, 1979.