Supporting Information

Tetrahedral Liquid-Crystalline Networks: An A15-Like Frank–Kasper Phase Based on Rod-Packing

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1. Methods

**Polarizing Optical Microscopy** - Transition temperatures were measured using a Mettler FP-82 HT hot stage and control unit in conjunction with a Leica DMRXP polarizing microscope. Textures of the liquid crystalline mesophases were recorded with Leica MC120 HD camera.

**Differential Scanning Calorimetry** - Transition enthalpies were determined as obtained from DSC-thermograms which were recorded on a Perkin-Elmer DSC-7 (heating and cooling rate: 10 K/min).

**In-house X-ray Scattering** - X-ray investigations on powder-like samples were carried out at Cu-Kα line (λ = 1.54 Å) using standard Coolidge tube source with a Ni-filter. Samples were prepared in the isotropic state on a glass plate. The sample was cooled (rate: 5 K·min⁻¹) to the measuring temperature. The samples were held on a temperature-controlled heating stage and the diffraction patterns were recorded with a 2D detector (Vantec 500, Bruker); exposure time was 15-30 min. For the WAXS measurement the distance between the sample and the detector defined to be 9.0 cm; for SAXS measurement the distance is 26.8 cm. As result XRD pattern is obtained which is transformed in a 1D plot by using GADDS over the full-range.

**Synchrotron small-angle X-ray scattering and electron density reconstruction** – High-resolution small angle X-ray scattering experiments were performed at BL16B1 at Shanghai Synchrotron Radiation Facility, SSRF. Powder samples were held in φ1mm capillary, and a Linkam hot stage with thermal stability within 0.2 °C was used with a hole for φ1mm capillaries drilled through the silver heating block and mica windows attached on both sides. A MarCCD165 detector was used for recording diffraction patterns and then integrated into 1D plots. The q-calibration was verified using silver behenate and n-alkanes. The diffractograms were fitted by Gaussian distributions to acquire diffraction positions and intensities. Then the peaks were indexed based on their positions.
and the lattice parameter along with plane/space symmetry were determined. Based on the symmetry and indexes, the integrated intensities were corrected by multiplicities and Lorentz factors, and together were used for reconstructing electron density maps via the general formula:

\[ \rho(\text{xyz}) = \sum_{hkl} F(hkl) \exp[2\pi i (hx + ky + lz)] \]  

(Eqn. S1)

where \( F(hkl) \) is the structure factor of each diffraction peak with index \((hkl)\), which is related to the intensity by:

\[ I(hkl) = K \cdot F(hkl) \cdot F^*(hkl) = K \cdot |F(hkl)|^2 \]  

(Eqn. S2)

where \( K \) is a constant related to the experiment, and here is safely taken to be 1 since only the relative electron density is concerned. Hence, the electron density is:

\[ \rho(\text{xyz}) = \sum_{hkl} \sqrt{I(hkl)} \exp[2\pi i (hx + ky + lz) + \phi_{hkl}] \]  

(Eqn. S3)

and in 2D case:

\[ \rho(\text{xy}) = \sum_{hk} \sqrt{I(hk)} \exp[2\pi i (hx + ky) + \phi_{hk}] \]  

(Eqn. S4)

In Equation S3 and S4, only the phases cannot be determined directly from the experiment. Here for our compounds, all the symmetry groups are centrosymmetric, leading the phases to be either 0 or \( \pi \). Since only limited diffraction peaks were detected for liquid crystalline self-assembled structures, it is possible to adopt a trail-and-error approach where all possible candidate phase combinations are listed and the best-fitted one was chosen based on prior physical and chemical knowledge of the system. For detailed discussions see Section 3.1.

**Simulation of the X-ray scattering** – Since the structure factors and electron density distribution are Fourier pairs, it is convenient to perform Fourier Transform of the electron density to acquire the diffraction intensities and phases, which is complementary to the reconstruction of electron density maps. Due to the complexity of the structure, numerical methods have been adopted in three steps. First, the electron density was distributed based on the packing of molecules. Then Fast Fourier Transform was performed, and intensities and phases are collected. Finally, comparison with experimental results are made for verifications. For details, see Section 3.2.
2. Additional Experimental Data

2.1 Phases transitions, DSC traces and POM textures

Table S1. Phase transitions and lattice parameters of the LC phases of compounds 1-3.

| Comp. | m | n | Phase transitions $T/\degree C$, [$\Delta H$/kJ·mol$^{-1}$] | $a$/nm ($T/\degree C$) |
|-------|---|---|----------------------------------------------------------|------------------------|
| 1     | 8 | 18| $H$: Cr 98 [60.3] Col$_{hex}$/p$_{6mm}$ 146 [4.6] Iso   | $a_{hex} = 4.21$ (120) |
|       |   |   | $K$: Iso 143 [-4.7] Col$_{hex}$/p$_{6mm}$ 45 [-8.9] Cr   |                        |
| 2a    | 2 | 20| $H$: Cr 120 [66.3] Col$_{hex}$/p$_{6mm}$ 126 [2.5] Iso | $a_{hex} = 4.16$ (120) |
|       |   |   | $K$: Iso 123 [-2.5] Col$_{hex}$/p$_{6mm}$ 73 [-9.1] Cr  |                        |
| 2b    | 4 | 20| $H$: Cr 76 [40.1] Col$_{hex}$/p$_{6mm}$ 121 [2.3] Cub/Pm$\bar{3}$n 131 [0.5] Iso | $a_{cub} = 8.62$ (130) |
|       |   |   | $K$: Iso 119 [-0.1] Cub/Pm$\bar{3}$n 116 [-2.1] Col$_{hex}$/p$_{6mm}$ 48 [-24.9] Cr | $a_{hex} = 4.14$ (100) |
| 2c    | 6 | 20| $H$: Cr 86 [48.0] Col$_{hex}$/p$_{6mm}$ 123 [2.4] Cub/Pm$\bar{3}$n 133 [0.4] Iso | $a_{cub} = 8.75$ (124) |
|       |   |   | $C$: Iso 129 [-b] Cub/Pm$\bar{3}$n 121 [-2.1] Col$_{hex}$/p$_{6mm}$ 51 [-13.4] Cr | $a_{hex} = 4.16$ (100) |
| 3a    | 2 | 22| $H$: Cr 118 [72.2] Iso                                  | $a_{hex} = 4.16$ (103) |
|       |   |   | $K$: Iso 106 [-2.3] Col$_{hex}$/p$_{6mm}$ 81 [-40.6] Cr |                        |
| 3b    | 4 | 22| $H$: Cr 92 [68.5] Col$_{hex}$/p$_{6mm}$ 101 [2.4] Cub/Pm$\bar{3}$n 125 [0.5] Iso | $a_{cub} = 8.65$ (104) |
|       |   |   | $C$: Iso 123 [-c] Cub/Pm$\bar{3}$n 94 [-2.5] Col$_{hex}$/p$_{6mm}$ 58 [-21.1] Cr | $a_{hex} = 4.16$ (80)  |
| 3c    | 6 | 22| $H$: Cr 114 [146.3] Cub/Pm$\bar{3}$n 132 [0.7] Iso     | $a_{cub} = 8.62$ (114) |
|       |   |   | $K$: Iso 132 [-d] Cub/Pm$\bar{3}$n 99 [-3.3] Col$_{hex}$/p$_{6mm}$ 66 [-14.1] Cr | $a_{hex} = 4.16$ (90)  |
| 3d$^c$| 8 | 22| $H$: Cr 118 [113.5] Cub/Pm$\bar{3}$n 138 [0.7] Iso     | $a_{hex} = 4.17$ (120) |
|       |   |   | $K$: Iso 135 [-0.4] Cub/Pm$\bar{3}$n 108 [-34.2] Col$_{hex}$/p$_{6mm}$ 76 [-11.4] Cr |                        |

$^a$ Heating and cooling rate at 10 K·min$^{-1}$, peak temperatures. Abbreviations: Cr = crystalline solid state; Iso = isotropic liquid; Col$_{hex}$/p$_{6mm}$ = hexagonal columnar phase representing a 2D triangular tiling (see Fig. 4b); Cub/Pm$\bar{3}$n = cubic phase with space group Pm$\bar{3}$n with a 3D tetrahedral tiling (see Fig. 4c); M1, M2 = unknown birefringent mesophases. $^b$ Very broad transition, therefore enthalpy not observable; compounds 1a-c have been reported previously. $^c$ The synthesis of 3d has been reported in ref.$^{51}$
Figure S1. DSC traces of compounds 1-3 recorded at 10 K·min⁻¹.
Figure S2. Polarizing optical microscopy of the Col\textsubscript{hex} and Cub/Pm\textbar n phases. a) Spherulitic textures of the Col\textsubscript{hex}/p6mm phase of 2a at 90 °C (thin sample), the inset shows the texture with additional λ-retarder palate indicating negative sign of the birefringence. The black dotted line indicates the indicatrix slow axis. b-d) LC phases of 2c, a) Col\textsubscript{hex} phase at 120 °C, c) Col\textsubscript{hex}-to-Cub transition at 123 °C on heating and d) Cub-to-Col\textsubscript{hex} transition at 121 °C on cooling; the domain structure of the texture of the Col\textsubscript{hex} phase is not retained upon Col\textsubscript{hex} \rightarrow Cub/ Pm\textbar n \rightarrow Col\textsubscript{hex} phase transition, \textit{i.e.} the textures in b) is different from d), because the columns can develop in any direction from the once formed cubic phase.
2.2 Additional SAXS and WAXS diffractograms

Figure S3. SAXS diffractograms of Cub/Pm\(\bar{3}n\) phases of compounds 2 and 3 at indicated temperatures.
Figure S4. SAXS diffractograms of Colhex/p6mm phases of compounds 1-3 at indicated temperatures.
Figure S5. WAXS diffractograms of Cub/Pm$\bar{3}$n phases of compounds 2 and 3 at the indicated temperatures.
Figure S6. WAXS diffractograms of Col_{hex}/p6mm phases of compounds 1-3 at the indicated temperatures.
Table S2. Experimental and calculated $d$-spacings of the Cub/$Pm\bar{3}n$ phase of compound 2b at 130 ºC (domain-like pattern).

| (hkl) | $d_{obs.}$ - spacing (nm) | $d_{cal.}$ - spacing (nm) | Intensity | Phase |
|-------|--------------------------|---------------------------|-----------|-------|
| (200) | 4.31                     | 4.32                      | /         | /     |
| (210) | 3.86                     | 3.86                      | /         | /     |
| (211) | 3.53                     | 3.53                      | /         | /     |
| (310) | 2.74                     | 2.73                      | /         | /     |
| (410) | 2.10                     | 2.10                      | /         | /     |
| (421) | 1.88                     | 1.89                      | /         | /     |

$a_{cub} = 8.62$ nm

Table S3. Experimental and calculated $d$-spacings, relative integrated intensities, and phases used in reconstruction of the EDs for the Cub/$Pm\bar{3}n$ phase of compound 2c at 124 ºC. All intensities are corrected by Lorentz factor and multiplicities.

| (hkl) | $d_{obs.}$ - spacing (nm) | $d_{cal.}$ - spacing (nm) | Intensity | Phase |
|-------|--------------------------|---------------------------|-----------|-------|
| (110) | 6.12                     | 6.14                      | 0.4       | $\pi$ |
| (200) | 4.34                     | 4.35                      | 91.7      | 0     |
| (210) | 3.89                     | 3.89                      | 100.0     | 0     |
| (211) | 3.55                     | 3.55                      | 77.9      | 0     |
| (220) | 3.06                     | 3.07                      | 1.0       | $\pi$ |
| (310) | 2.74                     | 2.75                      | 0.8       | 0     |
| (222) | 2.49                     | 2.51                      | 3.5       | $\pi$ |
| (321) | 2.32                     | 2.32                      | 0.6       | $\pi$ |
| (410) | 2.10                     | 2.11                      | 2.7       | 0     |
| (330) | 2.04                     | 2.05                      | 1.2       | $\pi$ |
| (411) |                          |                           | 0.6       | $\pi$ |
| (420) | 1.94                     | 1.94                      | 4.1       | 0     |
| (421) | 1.89                     | 1.90                      | 3.6       | 0     |
| (332) | 1.85                     | 1.85                      | 1.1       | 0     |
| (422) | 1.77                     | 1.77                      | 0.7       | 0     |

$a_{cub} = 8.69$ nm
Table S4. Experimental and calculated $d$-spacings, relative integrated intensities, and phases used in reconstruction of the EDs for the Cub/$Pm\bar{3}n$ phase of compound 3b at 104 °C. All intensities are corrected by Lorentz factor and multiplicities.

| $(hkl)$ | $d_{obs.}$ - spacing (nm) | $d_{cal.}$ - spacing (nm) | Intensity | Phase |
|---------|--------------------------|--------------------------|-----------|-------|
| (110)   | 6.12                     | 6.12                     | 0.7       | $\pi$ |
| (200)   | 4.33                     | 4.33                     | 66.8      | 0     |
| (210)   | 3.87                     | 3.87                     | 100.0     | 0     |
| (211)   | 3.54                     | 3.53                     | 67.0      | 0     |
| (220)   | 3.06                     | 3.06                     | 1.1       | $\pi$ |
| (310)   | 2.74                     | 2.74                     | 1.7       | 0     |
| (222)   | 2.50                     | 2.50                     | 1.3       | $\pi$ |
| (320)   | 2.40                     | 2.40                     | 0.2       | $\pi$ |
| (321)   | 2.31                     | 2.31                     | 0.8       | $\pi$ |
| (400)   | 2.16                     | 2.16                     | 1.3       | 0     |
| (410)   | 2.10                     | 2.10                     | 2.2       | 0     |
| (330)   | 2.04                     | 2.04                     | 1.0       | $\pi$ |
| (411)   |                          |                          | 0.5       | $\pi$ |
| (420)   | 1.94                     | 1.93                     | 4.8       | 0     |
| (421)   | 1.89                     | 1.89                     | 4.0       | 0     |
| (332)   | 1.85                     | 1.84                     | 1.1       | 0     |
| (422)   | 1.77                     | 1.77                     | 2.4       | 0     |
| (520)   | 1.61                     | 1.61                     | 0.5       | 0     |
| (432)   |                          |                          | 0.3       | 0     |
| (521)   | 1.58                     | 1.58                     | 0.1       | $\pi$ |
| (440)   | 1.53                     | 1.53                     | 0.4       | $\pi$ |
| (530)   | 1.48                     | 1.48                     | 0.1       | $\pi$ |
| (433)   | 1.48                     | 1.48                     | 0.1       | $\pi$ |

$d_{cub} = 8.65$ nm
Table S5. Experimental and calculated $d$-spacings, relative integrated intensities, and phases used in reconstruction of the EDs for the Cub/$Pm\bar{3}n$ phase of compound 3e at 114 °C. All intensities are corrected by Lorentz factor and multiplicities.

| (hkl) | $d_{\text{obs.}}$ - spacings (nm) | $d_{\text{cal.}}$ - spacings (nm) | Intensity | Phase |
|-------|----------------------------------|----------------------------------|-----------|-------|
| (110) | 6.09                             | 6.10                             | 0.5       | $\pi$ |
| (200) | 4.31                             | 4.31                             | 68.9      | 0     |
| (210) | 3.85                             | 3.85                             | 100.0     | 0     |
| (211) | 3.52                             | 3.52                             | 67.1      | 0     |
| (220) | 3.05                             | 3.05                             | 0.9       | $\pi$ |
| (310) | 2.73                             | 2.73                             | 1.5       | 0     |
| (222) | 2.49                             | 2.49                             | 1.5       | $\pi$ |
| (320) | 2.39                             | 2.39                             | 0.1       | $\pi$ |
| (321) | 2.30                             | 2.30                             | 0.6       | $\pi$ |
| (400) | 2.15                             | 2.16                             | 2.6       | 0     |
| (410) | 2.09                             | 2.09                             | 2.7       | 0     |
| (330) | 2.03                             | 2.03                             | 2.1       | $\pi$ |
| (411) | 2.03                             | 2.03                             | 1.1       | $\pi$ |
| (420) | 1.93                             | 1.93                             | 6.6       | 0     |
| (421) | 1.88                             | 1.88                             | 5.5       | 0     |
| (332) | 1.84                             | 1.84                             | 1.6       | 0     |
| (422) | 1.76                             | 1.76                             | 3.3       | 0     |
| (430) | 1.72                             | 1.72                             | 0.3       | 0     |
| (432) | 1.60                             | 1.60                             | 0.5       | 0     |
| (520) | 1.57                             | 1.57                             | 0.1       | $\pi$ |
| (521) | 1.57                             | 1.57                             | 0.4       | $\pi$ |
| (440) | 1.52                             | 1.52                             | 0.2       | $\pi$ |
| (530) | 1.48                             | 1.48                             | 0.2       | $\pi$ |
| (433) | 1.48                             | 1.48                             |           |       |

$d_{\text{cub}} = 8.62$ nm
**Table S6.** Experimental and calculated $d$-spacings, relative integrated intensities, and phases used in reconstruction of the EDs for the Cub/$Pm3n$ phase of compound 3d$^{81}$ at 130 ºC. All intensities are corrected by Lorentz factor and multiplicities.

| (hkl) | $d_{obs.}$- spacings (nm) | $d_{cal.}$- spacings (nm) | Intensity | Phase |
|-------|--------------------------|---------------------------|-----------|-------|
| (110) | 6.05 | 6.07 | 0.5 | $\pi$ |
| (200) | 4.29 | 4.30 | 64.0 | 0 |
| (210) | 3.84 | 3.84 | 100.0 | 0 |
| (211) | 3.51 | 3.51 | 64.0 | 0 |
| (220) | 3.04 | 3.04 | 0.6 | $\pi$ |
| (310) | 2.72 | 2.72 | 1.5 | 0 |
| (222) | 2.48 | 2.48 | 2.3 | $\pi$ |
| (320) | 2.39 | 2.38 | 0.2 | $\pi$ |
| (321) | 2.30 | 2.30 | 0.9 | $\pi$ |
| (400) | 2.15 | 2.15 | 4.1 | 0 |
| (410) | 2.09 | 2.08 | 3.5 | 0 |
| (330) | 2.03 | 2.02 | 3.7 | $\pi$ |
| (411) | | | 0.0 | $\pi$ |
| (420) | 1.92 | 1.92 | 9.4 | 0 |
| (421) | 1.88 | 1.87 | 8.8 | 0 |
| (332) | 1.84 | 1.83 | 2.4 | 0 |
| (422) | 1.76 | 1.75 | 4.7 | 0 |
| (430) | 1.72 | 1.72 | 0.5 | 0 |
| (432) | 1.60 | 1.60 | 0.8 | 0 |
| (520) | | | 0.0 | 0 |
| (521) | 1.57 | 1.57 | 0.2 | $\pi$ |
| (440) | 1.52 | 1.52 | 0.6 | $\pi$ |
| (530) | 1.48 | 1.47 | 0.2 | $\pi$ |
| (433) | | | 0.2 | $\pi$ |

$a_{cub} = 8.59$ nm
Table S7. Experimental and calculated $d$-spacings, relative integrated intensities, and phases used in reconstruction of electron densities for the Col$_{\text{hex}}$/$p6mm$ phase of compound 1-3 at given temperatures. All intensities are corrected by Lorentz factor and multiplicities.

| Comp. | $T$ (°C) | $(hk)$ | $d_{\text{obs}}$ (nm) | $d_{\text{cal}}$ (nm) | Intensity | Phase | $a_{\text{hex}}$ (nm) |
|-------|----------|--------|------------------------|------------------------|-----------|-------|----------------------|
| 1     | 120      | (10)   | 3.65                   | 3.65                   | 100       | 0     | 4.21                 |
|       |          | (20)   | 1.83                   | 1.82                   | 55.5      | 0     |                      |
| 2a    | 120      | (10)   | 3.60                   | 3.60                   | 100       | 0     | 4.16                 |
|       |          | (20)   | 1.80                   | 1.80                   | 50.3      | 0     |                      |
|       |          | (21)   | 1.36                   | 1.36                   | 0.2       | $\pi$ |                      |
| 2b    | 100      | (10)   | 3.61                   | 3.60                   | 100.0     | 0     | 4.16                 |
|       |          | (20)   | 1.80                   | 1.80                   | 85.9      | 0     |                      |
|       |          | (21)   | 1.36                   | 1.36                   | 0.8       | $\pi$ |                      |
| 2c    | 100      | (10)   | 3.65                   | 3.65                   | 77.2      | 0     | 4.21                 |
|       |          | (11)   | 2.11                   | 2.11                   | 0.1       | $\pi$ |                      |
|       |          | (20)   | 1.82                   | 1.82                   | 100.0     | 0     |                      |
|       |          | (21)   | 1.38                   | 1.38                   | 0.9       | $\pi$ |                      |
| 3a    | 103      | (10)   | 3.60                   | 3.60                   | 100.0     | 0     | 4.16                 |
|       |          | (11)   | 2.08                   | 2.08                   | 0.3       | $\pi$ |                      |
|       |          | (20)   | 1.80                   | 1.80                   | 57.9      | 0     |                      |
|       |          | (21)   | 1.36                   | 1.36                   | 0.3       | $\pi$ |                      |
| 3b    | 80       | (10)   | 3.60                   | 3.60                   | 99.4      | 0     | 4.16                 |
|       |          | (20)   | 1.80                   | 1.80                   | 100.0     | 0     |                      |
|       |          | (21)   | 1.36                   | 1.36                   | 0.9       | $\pi$ |                      |
| 3c    | 90       | (10)   | 3.61                   | 3.60                   | 68.1      | 0     | 4.16                 |
|       |          | (20)   | 1.80                   | 1.80                   | 100.0     | 0     |                      |
|       |          | (21)   | 1.36                   | 1.36                   | 0.8       | $\pi$ |                      |
## 2.3 Structural parameters

### Table S8. Structural data for Cub/Pm\(3n\) phase of compounds 2 and 3.

| Comp. | \(T\) [°C] | \(a_{\text{cub}}\) [nm] | \(V_{\text{cell}}\) [nm\(^3\)] | \(V_{\text{mol}}\) [nm\(^3\)] | \(n_{\text{cell,cr}}\) | \(n_{\text{cell,liq}}\) | \(n_{\text{cell,LC}}\) | \(n_{\text{bundle}}\) |
|-------|-------------|-----------------|-----------------|-----------------|---------------|-----------------|-----------------|-----------------|
| 2b    | 120         | 8.62            | 641             | 2.16            | 296           | 233             | 264             | 4.9             |
| 2c    | 124         | 8.69            | 656             | 2.26            | 290           | 228             | 259             | 4.8             |
| 3b    | 104         | 8.65            | 647             | 2.26            | 286           | 225             | 256             | 4.7             |
| 3c    | 114         | 8.62            | 641             | 2.36            | 271           | 213             | 242             | 4.5             |

\(T\) indicates that the temperature is in the Cub/Pm\(3n\) phase range, \(V_{\text{cell}}\) = volume of the unit cell, calculated according to \(V_{\text{cell}} = a_{\text{cub}}^3\). \(V_{\text{mol}}\) = volume of the molecule as determined by the crystal volume increments. \(n_{\text{cell,cr}}\) = number of molecules per unit cell in the crystalline state, calculated according to \(n_{\text{cell,cr}} = V_{\text{cell}}/V_{\text{mol}}\) (average packing coefficient in the crystal is \(k = 0.7\)). \(n_{\text{cell,liq}}\) = number of molecules in the unit cell of an isotropic liquid with an average packing coefficient \(k = 0.55\), calculated according to \(n_{\text{cell,liq}} = 0.55/0.7\). \(n_{\text{cell,LC}}\) = number of molecules in the unit cell in the LC state as estimated from the average of \(n_{\text{cell,cr}}\) and \(n_{\text{cell,liq}}\). \(n_{\text{bundle}}\) = number of molecules per bundle in the cubic organization as \(n_{\text{bundle}} = n_{\text{cell,LC}}/54\).

### Table S9. Structural data for Colhex/p6mm phase of compounds 1-3.

| Comp. | \(T\) [°C] | \(a_{\text{hex}}\) [nm] | \(h\) [nm] | \(V_{\text{cell}}\) [nm\(^3\)] | \(V_{\text{mol}}\) [nm\(^3\)] | \(n_{\text{cell,cr}}\) | \(n_{\text{cell,LC}}\) | \(n_{\text{wall}}\) |
|-------|-------------|-----------------|-------|-----------------|-----------------|---------------|-----------------|-------------|
| 1     | 120         | 4.21            | 0.46  | 7.06            | 2.26            | 3.12          | 2.79            | 0.93        |
| 2a    | 125         | 4.13            | 0.46  | 6.89            | 2.06            | 3.34          | 2.98            | 0.99        |
| 2b    | 100         | 4.16            | 0.45  | 6.74            | 2.16            | 3.12          | 2.78            | 0.93        |
| 2c    | 100         | 4.21            | 0.46  | 7.06            | 2.26            | 3.12          | 2.79            | 0.93        |
| 3a    | 103         | 4.16            | 0.47  | 7.04            | 2.16            | 3.26          | 2.91            | 0.97        |
| 3b    | 80          | 4.16            | 0.45  | 6.74            | 2.26            | 2.98          | 2.66            | 0.89        |
| 3c    | 90          | 4.16            | 0.45  | 6.74            | 2.36            | 2.86          | 2.55            | 0.85        |
| 3d\(^\text{S1}\) | 100       | 4.17            | 0.46  | 6.93            | 2.46            | 2.82          | 2.51            | 0.84        |

\(T\) indicates that the temperature is in the Colhex/p6mm phase range, \(V_{\text{cell}} = \frac{3}{2} a_{\text{hex}}^2 h\) where \(h\) represents the height of the unit cell and is extracted from the maximum of the WAXS diffraction. \(n_{\text{wall}}\) = number of molecules in the cross section of the honeycomb walls as \(n_{\text{wall}} = n_{\text{cell,LC}}/3\); the values being a bit smaller than one molecule indicate a defective triangular honeycombs with some triangular honeycombs fused locally to rhombic cells. Therefore, \(n_{\text{wall}}\) decreases with chain elongation and thermal expansion. This is in line with the easy break down of this honeycomb and its transition to the tetrahedral packing (Pm\(3n\)-12/14 phase) by rising temperature.
3. Determination of the structures

Since all the compounds show a similar diffractogram, compound 3b is chosen as an example to illustrate the determination of the hexagonal columnar and cubic LC structure, including the reconstruction of the electron density map and for the cubic phase also by simulation of the intensities.

3.1 Hexagonal columnar phase

![Figure S7](image)

**Figure S7.** (a) The electron density map of hexagonal columnar phase of 3b. (b-e) shows the duality between VT and DT for the hexagonal columnar \( p6mm \) phases.

The SAXS pattern of the columnar phases (Fig. S4 and Table S7) show SAXS peaks with a ratio of their reciprocal spacings of \( 1: \sqrt{3}: 2: \sqrt{7} \) which can be indexed to a 2D hexagonal lattice. The LC state is confirmed by the diffuse WAXS scattering with maxima at \( ~0.45 \) nm (Fig. S6). The calculated lattice parameters are around 4.14 - 4.21 nm, corresponding to the molecular length of \( L_{\text{mol}} = 4.0-4.4 \) nm (depending on the glycerol conformations), in line with the formation of triangular honeycomb LCs which is additionally confirmed by the negative birefringence of the textures as observed between crossed polarizers with additional \( \lambda \)-retarder plate (see Fig. S2a). The negative birefringence indicates that the main intramolecular \( \pi \)-conjugation pathway along the rods is perpendicular or only
slightly tilted with respect to the column long axis, in line with a honeycomb LC.

Additional confirmation of the triangular honeycomb comes from the electron density map in Figure S7a. The phase choice is the same as previously used for related compounds. A point to note is that the electron density of aromatic rods is much lower than the polar groups and is quite close to aliphatic side chains. A slightly enhanced electron density in the middle of the aromatic cores (light blue) is due to the ether oxygens of the side chains. The model of the molecular organization in the triangular honeycomb is shown in Fig S7e (the triangular prismatic cells are filled by the side chains).

Figure S7b-d compares different types of \( p6mm \) phases observed in LC soft matter systems; the hexagonal honeycomb in (c) represents the VT of the commonly observed hexagonal packing of columns (b), while the triangular honeycomb (d, e) is its topological dual which is the DT of the hexagonal honeycomb in (c).

### 3.2 Reconstruction of electron density map of cubic phase

As the cubic space group \( Pm\overline{3}n \) is centrosymmetric, the phase of each Bragg peak is constrained to be either 0 or \( \pi \). For cubic phase here, there exist more than 20 peaks, meaning that it is impossible to enumerate and compare all the possible \( >2^{20} \) phase combinations. However, since the strong peaks dominate the main features and peaks with high-order indexes show subtle information, the phase combination is determined step by step, i.e. fixing strongest peaks first to demonstrate the main feature and adding weak peaks after to the final structure.

First, since the diffraction peaks (200), (210) and (211) are much stronger than the rest peaks, they will determine the main features of the electron density map. While the electron density distribution of the aromatic cores is inevitably affected by the polar groups and the aliphatic groups due to the high mobility of the molecules, the polar groups are relatively isolated, which is adopted as a criterion to choose the proper phase
combination. When the aggregation of the polar groups is settled, the aromatic cores should be corrected between the polar groups with aliphatic chains forming the continuum. Another criterion is the electron density histogram. A larger narrow peak should appear at low-electron-density region corresponding to the uniform electron density distribution of fluid aliphatic chains, which is a natural feature of the liquid crystals as confirmed by WAXS (see Figure S5). The 8 possible phase combinations and corresponding histograms are collected in Figure S8. Apparently, phase combinations 0π0, 0ππ, 0π0 and πππ are a simple shift of phase combinations 000, 00π, π00 and π0π respectively. The histogram of phase combinations π0π and πππ does not meet the requirement as the peak locates at the high-electron-density region. For phase combination 00π (0ππ), an interlocking model with columns along the principle axes is proposed. To form such a structure, there exists two possible arrangements of the molecules. Firstly, the rod-like cores form bundles with linear 2-way junctions (see structure Pm3n-2 in Table S13). However, there exist only 6 bundles in a unit cell leading the number of molecules in a single bundle to be ~42, which is impossible for such molecules with two bulk chains at opposite sides. Otherwise, the cores only forms columns with rods sliding along the columns. However, this arrangement would weaken the hydrogen bonds between the sticking ending groups and lead to the mixture of the aromatic and polar groups, which are not favored for stability of the structure. Thus, the crossed column model is not likely to be the case. Then the remaining phase combinations, 000 (0π0) and π00 (ππ0), are quite similar with the same model where polar groups from sphere-like micelles connected with aromatic bundles. Since the junctions are 12- and 14-fold, the volume should be close to the ratio 14/12. Furthermore, the electron density histogram of 000 (0π0) is more proper for describing the uniformity of the aliphatic chains. Consequently, 000 is chosen as phases for further discussions.
Figure S8. The structure of 8 possible phase combinations using the 3 strongest peaks.

It is unlikely for such a polyphilic molecule to organize in spherical micelles with the rod-like cores in the centers. Since the glycerol groups form spheroidic aggregates occupying the (0, 0, 0) and (0.25, 0.5, 0) and equivalent points, the aromatic rods should connect them with aliphatic chains being the continuum. Previous study showed that similar X-shaped molecules formed bundles with the number of molecules in a single bundle being ~6. As the number of molecules in a unit cell is 257, the bundles in a unit cell should be 257/6 ≈ 43 or larger. Here a model of 54 bundles is adopted with all the glycerol groups connected. Then the number of molecules in a single bundle is ~4.7, which is smaller than in previous reports of low valency network phases. This model is supported by the electron density map with additional 5 strong peaks, (310), (410), (420), (421) and (422) added. Among the 32 cases, phase combination 00000 was chosen according to the model and the histogram (Figure S9). The electron density map and histogram support the model that all the glycerol aggregations are connected by the aromatic bundles. In the histogram, the electron density of the aliphatic parts is nearly uniform. The electron density of the
aromatic segment changes gradually by partial mixing with the high-electron-density glycerols and low-electron-density aliphatic chains, in line with the aromatic bundles connecting the glycerol aggregations in the continuum of the aliphatic chains. The glycerol groups form micellar aggregates including the hydrogen bonds. However, since the proper space filling in the polar spheres requires some longitudinal shift of the rods along the bundles, the electron density in the spheroids is affected by these aromatic segments. Thus, in the ED histogram, the ED in the spheroids shows a change from lower in the periphery to higher in the centers.

Figure S9  Electron density map of the Cub/Pm\(^{\bar{3}}\)n phase of compound 2b a) reconstructed by 8 strong peaks with phase combination 00000000 and b) corresponding histogram.

Since the main feature of the structure is determined by the strong XRD peaks, the phase selections of the remaining peaks will give only subtle modifications. Then, the rest phases are acquired by simulation using the geometric model constructed from the ED map in Fig. S9.

3.3 Simulation of diffraction intensities

The simulation starts with construction of a geometric model composed of spheroids of the glycerols and rods involving the OPE cores. While the 12-fold junctions are nearly spherical since the bundles attached are identical, the 14-fold junctions are represented by oblate ellipsoids according to symmetry constraints and packing models of molecules.
As shown in Figure S10, there exist two limiting cases for the molecules in the bundles: 1) the molecules are staggered to reach the junction center and 2) the molecules are centered in the bundles without staggering and in this case the ends of the glycerols cannot reach the centers of the spheres at the junctions, even if fully stretched. Both cases are possible and cannot be distinguished. Thus, a mean value of the two extreme case is chosen to estimate the ratio of long to short axis. The core length (aromatic + polar) is about ~4.4nm which is nearly half the lattice parameter. Thus, the core length is set to be 0.50 and the aromatic length is about \(\frac{3.10}{8.65}=0.36\) (black lines), leading the polar length to be about 0.07 (purple lines). In Fig S10a, the points for ending of polar groups are (0.32, 0.50, 0), (0.2187, 0.4374, 0) and (0.2214, 0.4714, 0.0572), and in Fig. S10b are (0.32, 0.50, 0), (0.2055, 0.4110, 0) and (0.1985, 0.4485, 0.1030). Taking the mean values, (0.32, 0.50, 0), (0.2121, 0.4242, 0) and (0.2100, 0.4600, 0.0801) into estimation, the least-square ratio of long axis to short axis is ~1.46.

**Figure S10.** Two extreme cases of molecular packing modes in bundles attached to 14-fold junctions.

Based on the volume fraction of polar groups 0.096 and the volume of 14-fold junction is \(~14/12\) times the volume of 12-fold junction, the radius of 12-fold junction is 0.137 and the half axes of 14-fold junctions are 0.112 and 0.163. The electron density of the polar group is 450 e/nm\(^3\).
Then considering the aromatic groups, they should form cylinders connecting the junctions. The volume fraction of aromatic groups is about 0.275 and electron density is \( \sim 395 \text{ e/nm}^3 \). Then the radius of bundles is estimated to be about 0.073 for 54 bundles.

The remaining space is filled with aliphatic segments (including the ether oxygens) with
an electron density 328. After the model was constructed, a 128*128*128 grid is adopted to distribute the electron density (Figure S13). Then FFTS3 is performed with intensities and phases collected in Table S9 and Fig 3 in the main text.

Figure S13. Electron density distribution in a unit cell based on the ellipsoids-cylinders model
Table S10. Comparison between experimental (compound 3b) and simulated intensities and phases.

| (hkl) | $I$-exp. | $I$-simu. | Phases |
|-------|----------|----------|--------|
| (110) | 0.7      | 1.2      | $\pi$  |
| (200) | 66.8     | 91.7     | 0      |
| (210) | 100.0    | 100.0    | 0      |
| (211) | 67.0     | 87.6     | 0      |
| (220) | 1.1      | 6.2      | $\pi$  |
| (310) | 1.7      | 3.2      | 0      |
| (222) | 1.3      | 0.6      | $\pi$  |
| (320) | 0.2      | 0.02     | $\pi$  |
| (321) | 0.8      | 0.7      | $\pi$  |
| (400) | 1.3      | 2.3      | 0      |
| (410) | 2.2      | 11.5     | 0      |
| (330) | 1.0      | 1.2      | $\pi$  |
| (411) | 0.5      | 0.02     | $\pi$  |
| (420) | 4.8      | 8.6      | 0      |
| (421) | 4.0      | 8.1      | 0      |
| (332) | 1.1      | 0.5      | 0      |
| (422) | 2.4      | 12.2     | 0      |
| (520) | 0.5      | 3.5      | 0      |
| (432) | 0.3      | 4.4      | 0      |
| (521) | 0.1      | 1.9      | $\pi$  |
| (440) | 0.4      | 6.7      | $\pi$  |
| (530) | 0.1      | 8.4      | $\pi$  |
| (433) | 0.1      | 3.6      | $\pi$  |

The simulated diffraction shows a similar intensity distribution to experiments. The main deviation can be deduced by comparing the electron density maps reconstructed from
both intensities (Figure S14). Judging from the histograms, the electron density of the aromatic segments varies a lot for experimental and simulated results. The electron density of the bundles in Fig S14b is higher than in Fig S14a, and it changes much slower in Fig S14d than Fig S14c. This is reasonable as in simulation the electron density of aromatic parts is set to be a constant, whereas in the real case the bundles can adjust themselves to fit the space filling, leading to a looser and less ordered packing of aromatic rods with a smoother ED gradient. The same argument holds for the boundaries between the polar spheroids and the rods (see above). In summary, the simulation supports the proposed bundled structure of the cubic phase.

**Figure S14.** Comparisons between electron density maps reconstructed by a) experimental (compound 3b) and b) simulated intensities, and corresponding electron density histograms for c) experimental and d) simulated results.
3.4. Discussion of alternative phase structures

A possible alternative crossed column structure of the $Pm\bar{3}n$ phase formed by three sets of non-interconnected $90^\circ$ crossed columns per unit cell (structure B1 in Table S11$^{54-55}$) could be excluded based on the reconstructed ED maps (Fig. 3b) and as it would require too many ($251/6\approx42$) molecules in the cross section of each column (see Table S13 and discussion in Section 3.2).

A structure where the rod-like molecules organize into bundles forming the spheres by rotational disorder and the chains wrapped around these almost spherical aggregates, as known for some hexacatenar compounds with alkyl chains fixed to both ends of the rod-like core,$^{56}$ can also be excluded based on the ED maps and molecular packing considerations.
4. Detailed structures of the tetrahedral bundled A15 cubic phase

4.1 Delaunay triangulation (tetrahedrization) in Cub/Pm\(\bar{3}m\) phase

A Delaunay triangulation (tetrahedrization) can be obtained by connecting the adjacent points which share the common Voronoi edge (plane). In return, a Voronoi vertex is a circumcenter of a Delaunay tetrahedron. Thus, for Cub/Pm\(\bar{3}m\) phase with (0, 0, 0), (0.5, 0, 0.25) and equivalent points occupied, there exist three kinds of Delaunay edges connecting the adjacent points and three kinds of Delaunay tetrahedrons filling the whole space, corresponding to two kinds of Voronoi polyhedrons (see Figure 1 in main text).

The lattice parameter of the cubic phase is set to be 1 for simplicity. The length and the volume information are collected in Tables S11 and S12.

| Table S11. Structure information of the three kinds of bundles in a unit cell. |
|-----------------------------|---------------------|---------------------|---------------------|
| Type | B1 | B2 | B3 |
| Structure | ![Structure Image] | ![Structure Image] | ![Structure Image] |
| Length | 0.50 | 0.56 | 0.61 |
| Number /unit cell | 6 | 24 | 24 |
| Adjacent Triangles | 6 | 5 | 5 |
| \(n_{\text{mol}}\) | ~ 5 |


Table S12. Structure information of the three kinds of tetrahedrons in a unit cell.

| Type    | T1                  | T2                  | T3                  |
|---------|---------------------|---------------------|---------------------|
| Structure | ![Structure T1](image) | ![Structure T2](image) | ![Structure T3](image) |
| Edge Lengths (numbers) | 0.56 (3) | 0.50 (1) | 0.50 (2) |
|          | 0.61 (3) | 0.56 (3) | 0.61 (4) |
| Volume   | 0.0234 | 0.0208 | 0.0208 |
| Triangular Area (numbers) | 0.1432 (3) | 0.1250 (1) | 0.1398 (4) |
|          | 0.1624 (1) | 0.1432 (2) | 0.1398 (1) |
| Sum of Area | 0.5920 | 0.5512 | 0.5590 |
| Number /unit cell | 16 | 24 | 6 |
| L-D*       | 0.3608 | 0.3494 | 0.3536 |

* L-D refers to the distance from the circumscribed sphere center to junctions.

4.2 Derivation of the Weaire-Phelan “minimal surface”

Previous bundled cubic phases based on G-, P-, D- and I-WP type minimal surfaces all have the boundary derived by the shift and the shrinkage of the TPMS (Triply Periodic Minimal Surface). There exist similarities and differences for Weaire-Phelan surface corresponding to Voronoi polyhedrons since it is self-intersected. When the Weaire-Phelan surface shrinks, each original junction will split into several new junctions. Connecting these new junctions with lines parallel to the Delaunay edges leads to pentagonal and hexagonal prisms, which join all the polyhedrons together to form a new surface that, in our case, can be regarded as the materials dividing surface separating the cores and the side chains (see Figure S15. For a continuous change, see the document WP_surface.gif). Furthermore, the limitation of the shrinkage leads exactly to the
Delaunay tetrahedrons, which is the dual tessellation of the Voronoi tessellation with Weaire-Phalen surface. The junctions in G-, D-, P- and I-WP phase are 3-fold, 4-fold, 6-fold and 8-fold respectively. Here in A15 phase, the junctions are 12-fold and 14-fold, which are the highest so far.

Figure S15. a) Weaire-Phelan “minimal surface” enclosed into irregular dodecahedrons (blue) and tetrakaidecahedrons (yellow). b) Shrinkage of W-P surface with the original junctions connected leads to the new surface which separates the bundles from the continuum. c) The final shrinkage of the W-P minimal surface leads to the tetrahedral networks corresponding to Delaunay triangulation.

4.3 Comparison between the A15 phase and other cubic phases

For comparison with different structures, both molecular length and volume must be verified. To be consistent to Tables S11 and S12, the lattice parameter of the A15 phase is 1 with the molecular length being 0.5 and molecular volume being $1/250 = 0.004$ (average number of molecules in a unit cell is $\sim 250$). Then, the lattice parameters of different cubic phases are determined by the molecular length and the number of molecules in a single bundle is estimated.
Table S13. Structure information for different cubic phases ($n_{\text{bundle}}$ = number of bundles in a unit cell; $n_{\text{molecules}}$ = number of molecules in a single bundle).

| Structure | Symmetry | Unit cell | $a_{\text{cub}}$ | $n_{\text{bundle}}$ | $n_{\text{molecules}}$ |
|-----------|----------|-----------|------------------|---------------------|-------------------------|
| DP        | $Im\overline{3}m$ | ![Diagram](Image) | 0.50             | 6                   | 5.2                     |
| SP        | $Pm\overline{3}m$ | ![Diagram](Image) | 0.50             | 3                   | 10.4                    |
| DD        | $Pn\overline{3}m$ | ![Diagram](Image) | 0.58             | 4                   | 12.0                    |
| SD        | $Fd\overline{3}m$ | ![Diagram](Image) | 1.15             | 16                  | 24.1                    |
| DG        | $Ia\overline{3}d$ | ![Diagram](Image) | 1.41             | 24                  | 29.5                    |
| SG        | $I4_132$ | ![Diagram](Image) | 1.41             | 12                  | 58.9                    |
| BCC - 8   | $Im\overline{3}m$ | ![Diagram](Image) | 0.58             | 8                   | 6.0                     |
| $Pm\overline{3}n$ - 2 | $Pm\overline{3}n$ | ![Diagram](Image) | 1                 | 6                   | 41.7                    |
| Structure    | Symbol   | h | k | l | Density |
|--------------|----------|---|---|---|---------|
| $Pm\bar{3}n$-12/14 | $Pm\bar{3}n$ | 1 | 54 | 4.6 |
| $Im\bar{3}m$-14 | $Im\bar{3}m$ | 0.58 | 14 | 3.4 |
5. Additional Discussion

5.1 dV/dr Diagrams

The average radial distribution of volume, dV/dr ~ r curves, is used for describing how the lateral chains fill a unit cell during self-assembly. In the previous studies, it has been employed to describe the phase transitions of dendritic and polyphilic molecules. For structures filled by networks, the term r represents the distance to the network and the term V indicates volume enclosed within the distance r. Numerical method has been applied to estimate the dV/dr curves using the following algorithm.

- First, a unit cell (or a single tetrahedron) is divided into 100*100*100 small cells and the distances of each points to the nearest edge are calculated.
- Second, for a specific distance r, a contour surface with value r is estimated composed of small triangular elements.
- Third, the area of the contour surface S is collected as the sum of areas of the small triangles. Then the area is attributed to the limitation of the dV/dr differentiation.
- Finally, different S ~ r curves, i.e. dV/dr ~ r curves, are collected for comparisons, of which some curves are normalized (i.e. divided by the whole volume) to represent the average space filling of a single molecule in a unit cell.

To illustrate the discrepancy of the three kinds bundles in a unit cell, the dV/dr curves of each bundle is estimated and a comparison with 3D bundled hexagonal phase (taking the bundle length to be 0.5, then V = πr^2*0.5 and dV/dr = πr) is made (Figure S16). As shown in Figure S16, the dV/dr increases at first with different gradient due to the different lengths of the bundles. After a certainly value where different bundles begin to converge, the growth starts to slow down and then decreases until finally to zero, which stand for the furthest distances to the edges. The differences between the bundles make it more flexible for molecules to adopt a suitable packing during the self-assembly.
Figure S16. The $dV/dr$ curves of all 3 different types of bundles in a unit cell of the Cub/$Pm\bar{3}n$ phase, compared with a longitudinal rod-bundle phase with hexagonal lattice.

The final $dV/dr$ curve of a whole unit cell equals to average of the $dV/dr$ curves of each bundle, i.e. $(dV/dr_1*6 + dV/dr_2*24 + dV/dr_3*24)/54$.

In Figure S17, the unnormalized $dV/dr$ curves of the cubic phases collected in Figure 4 in the main text (normalized curves, i.e. $dV/dr$ is divided by the volume of a single molecule) are shown.

Figure S17. Unnormalized $dV/dr$ curves of selected cubic phases. As a complement to Figure 4 in the main text, here the number of molecules in each bundle is assumed to be identical, thus showing general trends of the development of the different morphologies depending on side-chain volume distribution at constant rod-length.
5.2 Voronoi tessellations and Delaunay triangulations

The phase transition from ordinary hexagonal (inverted) columnar LC phases (polar or rigid cores in a fluid continuum) to micellar cubic phases upon alkyl chain expansion is associated with a transition of their Voronoi cells from honeycombs to polyhedra. The triangular honeycomb, representing the Delaunay triangulation of this Col_{hex} phase, leads to the triangular honeycomb, transforming to the network of rod-bundles, being the Delaunay triangulation of the micellar cubic phase with $Pm\bar{3}n$ lattice. (Figure S18).

**Figure S18.** Duality between Voronoi tessellation and Delaunay triangulation for hexagonal phase and cubic phase with the same phase sequence.
6. Synthesis and analytical data

6.1 General

Diethylmalonate and \( n \)-bromohexane was used as obtained from VEB Laborchemie Apolda. \( n \)-Bromoeicosane was used as obtained from Sigma-Aldrich. \( n \)-Bromodocosane was used as obtained from ABCR. 3-[4-(4-Ethynylphenylethynyl)phenyl]-1,2-\( O \)-isopropylidenepropane-1,2-diol\(^{S7}\) (10), 1,4-dihydroxy-2,5-diiodobenzene\(^{S8}\) (3), diethyl 2-ethylmalonate\(^{S9}\) (4a), diethyl 2-butylmalonate\(^{S10}\) (4b), diethyl 2-hexylmalonate\(^{S11}\) (4c), were synthesized according to the procedures given in the references. The synthesis of compound 3d has been reported in ref.\(^{S1}\)

The purity was checked by thin-layer chromatography (TLC, silica gel 60 F254, Merck). Column chromatography was performed with silica gel 60 (0.063-0.2, Merck), flash chromatography with silica gel 60 (0.040-0.063, Merck). Triethylamine was distilled from \( \text{CaH}_2 \) and stored over molecular sieve. DMF was stored over molecular sieve.

\(^1\text{H}, \ ^{13}\text{C}\)-NMR spectra (Varian Unity 500 and Varian Unity 400 spectrometers) were recorded in \( \text{CDCl}_3 \) or pyridine-\( d_5 \) solutions, with tetramethylsilane as internal standard). All measurements were operated at 27 °C.

Elemental analyses were performed using a Leco CHNS-932 elemental analyzer. Mass spectra were recorded with a Bruker HR-ESI-TOF. The measurements were performed in THF (1 mg/mL) with 0.1 mg/mL \( \text{LiCl} \).

6.2 Synthesis of the 1,4-dialkoxy-2,5-diiodohydroquinone derivatives 9

Scheme S1. Synthesis of the 1,4-dialkoxy-2,5-diiodohydroquinone derivatives 9.
6.2.1 Synthesis of the branched alkyl bromides (8)

6.2.1.1 General procedures

**P1: Substitution of diethyl malonates**\(^{\text{S12}}\) The reaction was carried out under an argon atmosphere. Sodium hydride (1.3 equ per each acidic proton, 60% in mineral oil) was slowly suspended in DMF (abs., 5 mL per mmol) and the mixture was cooled to 0 °C. Diethyl malonate (1 equ.) and the appropriate \(n\)-bromoalkane (1.5 equ each substitution) in DMF (2 mL per mmol) was added one after another and the mixture was stirred at room temperature for 3 h. After reaction water (250 mL) was added and the mixture was extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with sat. aqu. LiCl, water and brine. After drying over anhydrous Na\(_2\)SO\(_4\) the solvent was removed under reduced pressure. The residue was purified by column chromatography.

**P2: Dealkoxydecarbonylation**\(^{\text{S12}}\) A mixture of the 2,2’-dialkylmalonate (1 equ), LiCl (1.3 equ) and water (1.3 equ) in DMSO (3 mL per mmol) was stirred at reflux for 24 h. After cooling to room temperature water (150 mL) was added. The mixture was extracted with diethyl ether (3 × 50 mL) and the combined organic layers were washed with water (3 × 50 mL). After drying over anhydrous Na\(_2\)SO\(_4\) the solvent was removed under reduced pressure. The residue was purified by column chromatography.

**P3: Reduction with LiAlH\(_4\)**\(^{\text{S13}}\) The reaction was carried out under an argon atmosphere. LiAlH\(_4\) (2.3 equ) was slowly suspended in dry diethyl ether (10 mL per mmol). 2,2’-dialkylmalonate (1 equ) was dissolved in dry diethyl ether (5 mL per mmol) and added dropwise to the suspension. The mixture was heated to reflux for 6 h. After completion of the reaction water was added dropwise with stirring until the excess of LiAlH\(_4\) was destroyed. The precipitate was dissolved by adding H\(_2\)SO\(_4\) (10%, 50 mL) dropwise. The mixture was extracted with diethyl ether (3 × 50 mL) and the combined organic layers were washed with sat. aqu. Na\(_2\)S\(_2\)O\(_3\), water and brine. After drying over anhydrous
Na₂SO₄ the solvent was removed under reduced pressure and the residue purified by column chromatography.

**P4: Bromination with HBr**

The obtained branched alcohol (1 equ), Bu₄NHSO₄ (tip of a spatula) and conc. H₂SO₄ (1 mL) was suspended in HBr (48%, 30 mL) and heated to reflux for 24 h. After cooling to room temperature, the mixture was extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with water and brine and dried over anhydrous Na₂SO₄. After removal of the solvent the residue was purified by column chromatography.

6.2.1.2 1-Bromo-2-octyleicosane (8a)

**Dimethyl 2-octyl-2′-octadecylmalonate (5a):** Synthesized according to P1 from dimethyl 2-octylmalonate 4a (7.00 g, 28.7 mmol), 1-bromo-octadecane (12.42 g, 37.3 mmol), sodium hydride (1.50 g, 37.3 mmol) in DMF (100 mL). Purification by column chromatography (eluent: CHCl₃/n-hexane = 1:1). Colourless liquid, yield: 11.65 g (82%), C₃₁H₆₀O₄, \( M = 496.45 \text{ g/mol}, \ ¹H-NMR \ (400 \text{ MHz, CDCl₃}) \ δ \ 3.70 \text{ (s, 6H, –OC₃H₃)}, \ 1.91 – 1.81 \text{ (m, 4H, –C₃H₂–)}, \ 1.45 – 1.06 \text{ (m, 44H, –C₃H₂–)}, \ 0.88 \text{ (t, } ³J = 6.8 \text{ Hz, 3H, –CH₃)}, \ 0.87 \text{ (t, } ³J_{H,H} = 6.9 \text{ Hz, 3H, –CH₃}) \text{ ppm.}

**Methyl 2-octyleicosanoate (6a):** Synthesized according to P2 from 5a (11.65 g, 23.5 mmol), lithiumchloride (1.30 g, 30.5 mmol), H₂O (0.55 g, 30.5 mmol) in DMSO (50 mL). Purification by column chromatography (eluent: CHCl₃/n-hexane = 1:1). Colourless liquid, yield: 8.88 g (86%), C₂₉H₅₈O₂, \( M = 438.44 \text{ g/mol}, \ ¹H-NMR \ (400 \text{ MHz, CDCl₃}) \ δ \ 3.66 \text{ (s, 3H, –OC₃H₃)}, \ 2.39 – 2.28 \text{ (m, 1H, –C₃H–)}, \ 1.66 – 1.11 \text{ (m, 48H, –C₃H₂–)}, \ 0.88 \text{ (t, } ³J = 6.8 \text{ Hz, 3H, –CH₃)}, \ 0.87 \text{ (t, } ³J_{H,H} = 6.9 \text{ Hz, 3H, –CH₃}) \text{ ppm.}

**2-Octyleicosan-1-ol (7a):** Synthesized according to P3 from 6a (8.88 g, 20.3 mmol), lithiumaluminiumhydride (1.00 g, 26.4 mmol) in dry Et₂O (100 mL). Purification by column chromatography (eluent: CHCl₃). Colourless solid, yield: 7.16 g (86%), C₂₈H₅₈O₃.
$M = 410.45 \text{ g/mol, mp. 38 } ^\circ\text{C, } ^1\text{H-NMR (400 MHz, CDCl}_3\text{)} \delta 3.53 (d, 3J_{HH} = 5.5 \text{ Hz, 2H, } -\text{CH}_2-\text{OH}), 1.53 - 1.38 (m, 1H, } -\text{CH}--), 1.36 - 1.17 (m, 49H, } -\text{CH}_2--, -\text{OH} ), 0.88 (t, 3J_{HH} = 6.8 \text{ Hz, 6H, } -\text{CH}_3) \text{ ppm.}

1-Bromo-2-octyleicosane (8a): Synthesized according to P4 from 7a (7.16 g, 17.6 mmol), HBr (48%, 30 mL), H$_2$SO$_4$ (1 mL) and Bu$_4$NHSO$_3$ (tip of spatula). Purification by column chromatography (eluent: n-hexane). Colourless liquid, yield: 4.29 g (52%), C$_{28}$H$_{57}$Br, $M = 472.36 \text{ g/mol, } ^1\text{H-NMR (400 MHz, CDCl}_3\text{)} \delta 3.44 (d, 3J_{HH} = 4.8 \text{ Hz, 2H, } -\text{CH}_2-\text{Br}), 1.65 - 1.57 (m, 1H, } -\text{CH}--), 1.42 - 1.15 (m, 48H, } -\text{CH}_2--), 0.88 (t, 3J_{HH} = 6.9 \text{ Hz, 3H, } -\text{CH}_3), 0.88 (t, 3J_{HH} = 6.9 \text{ Hz, 3H, } -\text{CH}_3) \text{ ppm.}

6.2.1.3 1-Bromo-2-ethylidyicosane (8b)

Diethyl 2-ethyl-2'-eicosylmalonate (5b): Synthesized according to P1 from diethyl 2-ethylmalonate 4a (7.00 g, 37.2 mmol), 1-bromoeicosane (13.40 g, 37.2 mmol), sodium hydride (1.93 g, 48.4 mmol) in DMF (100 mL). Purification by column chromatography (eluent: CHCl$_3$/n-hexane = 1:1). Colourless solid, yield: 15.90 g (91%), C$_{29}$H$_{56}$O$_4$, $M = 468.42 \text{ g/mol, } ^1\text{H-NMR (400 MHz, CDCl}_3\text{)} \delta 4.17 (q, 3J_{HH} = 7.1 \text{ Hz, 4H, } -\text{OCH}_2--), 1.89 - 1.81 (m, 4H, } -\text{CH}--), 1.35 - 1.07 (m, 52H, } -\text{CH}_2--), 0.87 (t, 3J_{HH} = 6.8 \text{ Hz, 3H, } -\text{CH}_3), 0.81 (t, 3J_{HH} = 7.5 \text{ Hz, 3H, } -\text{CH}_3) \text{ ppm.}

Ethyl 2-ethylidyicosanoate (6b): Synthesized according to P2 from 5b (15.87 g, 33.9 mmol), lithiumchloride (1.87 g, 44.0 mmol), H$_2$O (0.79 g, 44.0 mmol) in DMSO (100 mL). Purification by column chromatography (eluent: CHCl$_3$/n-hexane = 1:1). Colourless solid, yield: 7.43 g (56%), C$_{26}$H$_{52}$O$_2$, $M = 396.40 \text{ g/mol, mp. 28 } ^\circ\text{C, } ^1\text{H-NMR (400 MHz, CDCl}_3\text{)} \delta 4.14 (q, 3J_{HH} = 14.1, 7.0 \text{ Hz, 2H), 2.29 - 2.19 (m, 1H), 1.66 - 1.05 (m, 43H), 0.88 (t, 3J_{HH} = 7.4 \text{ Hz, 3H), 0.88 (t, 3J_{HH} = 6.8 Hz, 3H) ppm.}

2-Ethylidyicosan-1-ol (7b): Synthesized according to P3 from 6b (7.43 g, 18.9 mmol), lithiumaluminiumhydride (0.93 g, 24.5 mmol) in dry Et$_2$O (100 mL). Purification by
column chromatography (eluent: CHCl₃). Colourless solid, yield: 4.00 g (61%), C₂₄H₅₀O, M = 354.39 g/mol, mp. 49 °C, ¹H-NMR (400 MHz, CDCl₃) δ 3.55 (d, 3JH,H = 5.1 Hz, 2H, –CH₂–OH), 1.60 – 1.18 (m, 42H, –CH₂–, –CH₂–, –OH), 0.96 – 0.83 (m, 6H, –CH₃) ppm.

1-Bromo-2-ethylsuccosane (8b): Synthesized according to P4 from 7b (4.00 g, 11.4 mmol), HBr (48%, 30 mL), H₂SO₄ (1 mL) and Bu₄NHSO₃ (tip of spatula). Purification by column chromatography (eluent: n-hexane). Colourless solid, yield: 3.86 g (81%), C₂₄H₄₉Br, M = 416.30 g/mol, mp. 32 °C, ¹H-NMR (500 MHz, CDCl₃) δ 3.49 – 3.41 (m, 2H, –CH₂–Br), 1.58 – 1.45 (m, 1H, –CH–), 1.43 – 1.20 (m, 40H, –CH₂–), 0.89 (t, 3JH,H = 7.4 Hz, 3H, –CH₃), 0.88 (t, 3JH,H = 7.0 Hz, 3H, –CH₃) ppm.

6.2.1.4 1-Bromo-2-butyldocosan (8c)

Diethyl 2-butyld-2′-eicosylmalonate (5c): Synthesized according to P1 from diethyl 2-butyldomalonate 4b (7.00 g, 32.4 mmol), 1-bromoeicosane (15.20 g, 42.4 mmol), sodium hydride (1.68 g, 42.4 mmol) in DMF (100 mL). Purification by column chromatography (eluent: CHCl₃/n-hexane = 1:1). Colourless solid, yield: 15.08 g (94%), C₃₁H₆₀O₄, M = 496.45 g/mol, mp. 35 °C, ¹H-NMR (500 MHz, CDCl₃) δ 4.17 (q, 3JH,H = 7.1 Hz, 4H, –OCH₂–), 1.90 – 1.82 (m, 4H, –CH₂–), 1.43 – 1.07 (m, 46H, –CH₂–, –CH₃), 0.91 – 0.86 (m, 3JH,H = 7.2 Hz, 6H, –CH₃) ppm.

Ethyl 2-butyldocosanoate (6c): Synthesized according to P2 from 5c (15.09 g, 30.4 mmol), lithiumchloride (1.67 g, 39.6 mmol), H₂O (0.71 g, 39.6 mmol) in DMSO (50 mL). Purification by column chromatography (eluent: CHCl₃/n-hexane = 1:1). Colourless liquid, yield: 6.12 g (47%), C₂₈H₅₆O₂, M = 424.43 g/mol, ¹H-NMR (400 MHz, CDCl₃) δ 4.13 (q, 3JH,H = 6.8 Hz, 2H, –OCH₂–), 2.35 – 2.25 (m, 1H, –CH–), 1.67 – 1.03 (m, 47H, –CH₂–, –CH₃), 0.92 – 0.85 (m, 6H, –CH₃) ppm.

2-Butyldocosan-1-ol (7c): Synthesized according to P3 from 6c (6.12 g, 14.4 mmol), lithiumaluminiumhydride (0.71 g, 18.8 mmol) in dry Et₂O (100 mL). Purification by
column chromatography (eluent: CHCl₃). Colourless solid, yield: 4.94 g (90%), C₂₆H₄₄O, M = 382.42 g/mol, mp. 52 °C, ¹H-NMR (400 MHz, CDCl₃) δ 3.54 (d, ³Jₗ,ₗ = 5.5 Hz, 2H, –CH₂–OH), 1.57 – 1.08 (m, 46H, –CH–, –CH₂–, –OH), 0.93 – 0.85 (m, 6H, –CH₃) ppm.

1-Bromo-2-butyldocosane (8c): Synthesized according to P₄ from 7c (4.94 g, 12.9 mmol), HBr (48%, 30 mL), H₂SO₄ (1 mL) and Bu₄NHSO₃ (tip of spatula). Purification by column chromatography (eluent: n-hexane). Colourless solid, yield: 3.64 g (63%), C₂₆H₅₃Br, M = 444.33 g/mol, mp. 38 °C, ¹H-NMR (400 MHz, CDCl₃) δ 3.44 (d, ³Jₗ,ₗ = 4.8 Hz, 2H, –CH₂–Br), 1.65 – 1.58 (m, 1H, –CH–), 1.42 – 1.07 (m, 44H, –CH₂–), 0.90 (t, ³Jₗ,ₗ = 6.9 Hz, 3H, –CH₃)) ppm.

6.2.1.5 1-Bromo-2-hexyldocosane (8d)

Diethyl 2-hexyl-2’-eicosylmalonate (5d): Synthesized according to P₁ from diethyl 2-hexylmalonate 4c (10.60 g, 43.4 mmol), 1-bromoeicosane (18.82 g, 52.1 mmol), sodium hydride (1.04 g, 43.4 mmol) in DMF (100 mL). Purification by column chromatography (eluent: CHCl₃/n-hexane = 1:1). Colourless liquid, yield: 20.3 g (89%), C₃₃H₆₄O₄, M = 524.86 g/mol, ¹H-NMR (400 MHz, CDCl₃) δ 4.16 (q, ³Jₗ,ₗ = 7.1 Hz, 4H, –CH₂–), 1.89 – 1.81 (m, 4H, –CH₂–), 1.35 – 1.07 (m, 50H, –CH₂–), 0.87 (t, ³Jₗ,ₗ = 6.8 Hz, 6H, –CH₃) ppm.

Ethyl 2-hexyldocosanoate (6d): Synthesized according to P₂ from 5d (20.30 g, 38.7 mmol), lithiumchloride (5.33 g, 0.12 mmol), H₂O (0.70 g, 38.7 mmol) in DMSO (100 mL). Purification by column chromatography (eluent: CHCl₃/n-hexane = 1:1). Colourless liquid, yield: 8.60 g (49%), C₃₀H₆₀O₂, M = 452.80 g/mol, mp. 30 °C, ¹H-NMR (400 MHz, CDCl₃) δ 4.13 (q, ³Jₗ,ₗ = 7.1 Hz, 2H, –CH₂–), 2.34 – 2.22 (m, 1H, –CH–), 1.50 – 1.18 (m, 51H, –CH₂–), 0.87 (t, ³Jₗ,ₗ = 6.8 Hz, 6H, –CH₃) ppm.

2-Hexyldocosan-1-ol (7d): Synthesized according to P₃ from 6d (8.60 g, 19.0 mmol),
lithiumaluminiumhydride \((2.16 \text{ g, } 57.0 \text{ mmol})\) in dry Et\(_2\)O (100 mL). Purification by column chromatography (eluent: CHCl\(_3\)). Colourless solid, yield: 7.00 g (90\%), \(\text{C}_{28}\text{H}_{58}\text{O}\), \(M = 410.76 \text{ g/mol}\), mp. 41 °C, \(^1\text{H-NMR} (400 \text{ MHz, CDCl}_3) \delta 3.53 \text{ (d, } ^3J_{H,H} = 5.5 \text{ Hz, 2H, –CH}_2\text{–OH}), 1.50 – 1.41 \text{ (m, 1H, –CH–), 1.39 – 1.19 \text{ (m, 48H, –CH}_2\text{–}), 0.88 \text{ (t, } ^3J_{H,H} = 6.8 \text{ Hz, 6H, –CH}_3\text{)} \text{ ppm.}

**1-Bromo-2-hexyldocosane (8d):** Synthesized according to P4 from 7d (7.00 g, 17.0 mmol), HBr (48\%, 50 mL), H\(_2\text{SO}_4\) (1 mL) and Bu\(_4\text{NHSO}_3\) (tip of spatula). Purification by column chromatography (eluent: \(n\)-hexane). Colourless solid, yield: 5.20 g (64\%), \(\text{C}_{28}\text{H}_{57}\text{Br}\), \(M = 473.66 \text{ g/mol}\), mp. 36 °C, \(^1\text{H-NMR} (400 \text{ MHz, CDCl}_3) \delta 3.44 \text{ (d, } ^3J_{H,H} = 4.8 \text{ Hz, 2H, –CH}_2\text{–Br), 1.64 – 1.55 \text{ (m, 1H, –CH–), 1.47 – 1.18 \text{ (m, 48H, –CH}_2\text{–), 0.88 \text{ (t, } ^3J_{H,H} = 6.9 \text{ Hz, 6H, –CH}_3\text{)} \text{ ppm.}

6.2.1.6 **1-Bromo-2-ethytetrascosane (8e)**

**Diethyl 2-ethyl-2-docosylmalonate (5e):** Synthesized according to P1 from diethyl 2-ethylmalonate 4a (7.00 g, 37.2 mmol), 1-bromodocosane (18.80 g, 48.4 mmol), sodium hydride (1.93 g, 48.4 mmol) in DMF (100 mL). Purification by column chromatography (eluent: CHCl\(_3\)/\(n\)-hexane = 1:1). Colourless solid, yield: 13.00 g (70\%), \(\text{C}_{31}\text{H}_{60}\text{O}_4\), \(M = 496.45 \text{ g/mol}\), mp. 41 °C, \(^1\text{H-NMR} (400 \text{ MHz, CDCl}_3) \delta 4.17 \text{ (q, } ^3J_{H,H} = 7.1 \text{ Hz, 4H, –OC}_2\text{H–), 1.89 – 1.82 \text{ (m, 4H, –CH}_2\text{–), 1.48 – 1.05 \text{ (m, 46H, –CH}_2\text{–, –CH}_3\text{), 0.88 \text{ (t, } ^3J_{H,H} = 6.8 \text{ Hz, 3H, –CH}_3\text{), 0.81 \text{ (t, } ^3J_{H,H} = 7.6 \text{ Hz, 3H, –CH}_3\text{)} \text{ ppm.}

**Ethyl 2-ethyltetrascanoate (6e):** Synthesized according to P2 from 5e (13.00 g, 26.2 mmol), lithiumchloride (1.45 g, 34.1 mmol), H\(_2\text{O} \) (0.61 g, 34.1 mmol) in DMSO (50 mL). Purification by column chromatography (eluent: CHCl\(_3\)/\(n\)-hexane = 1:1). Colourless solid, yield: 2.32 g (21\%), \(\text{C}_{28}\text{H}_{56}\text{O}_2\), \(M = 424.43 \text{ g/mol}\), mp. 67 °C, \(^1\text{H-NMR} (400 \text{ MHz, CDCl}_3) \delta 4.14 \text{ (q, } ^3J_{H,H} = 7.1 \text{ Hz, 2H, –OCH}_2\text{–), 2.29 – 2.18 \text{ (m, 1H, –CH–), 1.67 – 1.08
2-Ethyltetracosanol (7e): Synthesized according to P3 from 6e (2.32 g, 5.5 mmol), lithiumaluminiumhydride (0.27 g, 7.1 mmol) in dry Et₂O (100 mL). Purification by column chromatography (eluent: CHCl₃). Colourless solid, yield: 1.60 g (77%), C₂₆H₅₄O, M = 382.42 g/mol, mp. 73 °C, ¹H-NMR (400 MHz, CDCl₃) δ 3.55 (d, J₃H,H = 5.1 Hz, 2H, –C₃H₂–OH), 1.48 – 1.18 (m, 46H, –C₆H–, –C₃H₂–, –O₂H), 0.95 – 0.83 (m, 6H, –C₃H₃) ppm.

1-Bromo-2-ethyltetracosane (8e): Synthesized according to P4 from 7e (1.60 g, 4.2 mmol), HBr (48%, 20 mL), H₂SO₄ (1 mL) and Bu₄NHSO₃ (tip of spatula). Purification by column chromatography (eluent: n-hexane). Colourless solid, yield: 1.18 g (64%), C₂₆H₅₃Br, M = 444.33 g/mol, mp. 47 °C, ¹H-NMR (400 MHz, CDCl₃) δ 3.46 (d, J₃H,H = 2.5 Hz, 2H, –C₃H₂–Br), 1.59 – 1.49 (m, 1H, –C₆H–), 1.32 – 1.18 (m, 44H, –C₆H₂–), 0.89 (t, J₃H,H = 7.4 Hz, 6H, –CH₃), 0.88 (t, J₃H,H = 6.8 Hz, 6H, –CH₃) ppm.

6.2.1.7 1-Bromo-2-butyltetracosane (8f)

Diethyl 2-butyl-2′-docosylmalonate (5f): Synthesized according to P1 from diethyl 2-butylmalonate 4b (8.50 g, 39.4 mmol), 1-bromodocosane (20.0 g, 51.4 mmol), sodium hydride (2.36 g, 59.1 mmol) in DMF (100 mL). Purification by column chromatography (eluent: CHCl₃/n-hexane = 1:1). Colourless solid, yield: 13.26 g (64%), C₃₃H₆₄O₄, M = 524.48 g/mol, mp. 39 °C, ¹H-NMR (400 MHz, CDCl₃) δ 4.17 (q, J₃H,H = 7.2 Hz, 4H, –OCH₂–), 1.92 – 1.81 (m, 4H, –CH₂–), 1.65 – 1.05 (m, 50H, –CH₂–, –CH₃), 0.89 (t, J₃H,H = 7.3 Hz, 3H, –CH₃), 0.88 (t, J₃H,H = 6.9 Hz, 3H, –CH₃) ppm.

Ethyl 2-butyltetraicosanoate (6f): Synthesized according to P2 from 5f (13.26 g, 25.3 mmol), lithiumchloride (1.39 g, 32.9 mmol), H₂O (0.59 g, 32.9 mmol) in DMSO (50 mL). Purification by column chromatography (eluent: CHCl₃/n-hexane = 1:1). Colourless
solid, yield: 9.88 g (86%), C_{30}H_{60}O_{2}, M = 452.46 g/mol, mp. 36 °C, $^1$H-NMR (400 MHz, CDCl$_3$) δ 4.17 (q, $^3$J$_{H,H}$ = 7.2 Hz, 2H, –OC$_2$H$_2$–), 2.35 – 2.25 (m, 1H, –CH–), 1.67 – 1.02 (m, 53H, –CH$_2$–, –CH$_3$), 0.89 (t, $^3$J$_{H,H}$ = 7.3 Hz, 3H, –CH$_3$), 0.88 (t, $^3$J$_{H,H}$ = 6.9 Hz, 3H, –CH$_3$) ppm.

2-Butyltetracosanol (7f): Synthesized according to P3 from 6f (9.88 g, 21.8 mmol), lithiumaluminiumhydride (1.10 g, 28.4 mmol) in dry Et$_2$O (100 mL). Purification by column chromatography (eluent: CHCl$_3$). Colourless solid, yield: 1.80 g (20%), C$_{28}$H$_{58}$O, M = 410.45 g/mol, mp. 61 °C, $^1$H-NMR (400 MHz, CDCl$_3$) δ 3.54 (d, $^3$J$_{H,H}$ = 5.5 Hz, 2H, –C$_2$H$_2$–OH), 1.50 – 1.18 (m, 50H, –C$_2$H–, –C$_2$H$_2$–, –O–H), 0.95 – 0.84 (m, 6H, –CH$_3$) ppm.

1-Bromo-2-butyltetracosane (8f): Synthesized according to P4 from 7e (1.80 g, 4.4 mmol), HBr (48%, 30 mL), H$_2$SO$_4$ (1 mL) and Bu$_4$NHSO$_3$ (tip of spatula). Purification by column chromatography (eluent: n-hexane). Colourless solid, yield: 1.60 g (77%), C$_{28}$H$_{57}$Br, M = 472.36 g/mol, mp. 43 °C, $^1$H-NMR (400 MHz, CDCl$_3$) δ 3.44 (d, $^3$J$_{H,H}$ = 4.8 Hz, 2H, –CH$_2$–Br), 1.64 – 1.58 (m, 1H, –CH–), 1.43– 1.17 (m, 48H, –CH$_2$–), 0.90 (t, $^3$J$_{H,H}$ = 6.9 Hz, 3H, –CH$_3$), 0.88 (t, $^3$J$_{H,H}$ = 6.9 Hz, 3H, –CH$_3$) ppm.

6.2.1.8 1-Bromo-2-hexyltetracosane (8g)

Diethyl 2-hexyl-2′-docosylmalonate (5g): Synthesized according to P1 from diethyl 2-hexylmalonate 4c (6.70 g, 27.5 mmol), 1-bromodocosane (13.90 g, 35.7 mmol), sodium hydride (2.20 g, 55.0 mmol) in DMF (100 mL). Purification by column chromatography (eluent: CHCl$_3$/n-hexane = 1:1). Colourless solid, yield: 4.86 g (32%), C$_{35}$H$_{68}$O$_4$, M = 552.51 g/mol, mp. 35 °C, $^1$H-NMR (500 MHz, CDCl$_3$) δ 4.18 (q, $^3$J$_{H,H}$ = 7.1 Hz, 4H, –OCH$_2$–), 1.94 – 1.81 (m, 4H, –CH$_2$–), 1.39 – 1.10 (m, 54H, –CH$_2$–, –CH$_3$), 0.89 (t, $^3$J$_{H,H}$ = 6.9 Hz, 3H, –CH$_3$), 0.89 (t, $^3$J$_{H,H}$ = 6.8 Hz, 3H, –CH$_3$) ppm.
**Ethyl 2-hexyltetracosanoate (6g):** Synthesized according to P2 from 5g (4.86 g, 8.8 mmol), lithiumchloride (0.48 g, 11.4 mmol), H$_2$O (0.21 g, 11.4 mmol) in DMSO (100 mL). Purification by column chromatography (eluent: CHCl$_3$/n-hexane = 1:1). Colourless solid, yield: 3.70 g (88%), C$_{32}$H$_{64}$O$_2$, $M = 480.49$ g/mol, mp. 40 °C, $^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 4.15 (q, $^3J_{H,H} = 7.1$ Hz, 2H, –OC$_2$H$_2$–), 2.35 – 2.27 (m, 1H, –CH–), 1.67 – 1.16 (m, 55H, –CH$_2$–, –CH$_3$), 0.89 (t, $^3J_{H,H} = 6.9$ Hz, 3H, –CH$_3$), 0.89 (t, $^3J_{H,H} = 7.0$ Hz, 3H, –CH$_3$) ppm.

**2-Hexyltetracosan-1-ol (7g):** Synthesized according to P3 from 6g (3.70 g, 7.7 mmol), lithiumaluminiumhydride (0.58 g, 15.4 mmol) in dry Et$_2$O (100 mL). Purification by column chromatography (eluent: CHCl$_3$). Colourless solid, yield: 2.09 g (62%), C$_{30}$H$_{62}$O, $M = 438.48$ g/mol, mp. 42 °C, $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 3.54 (t, $^3J_{H,H} = 5.3$ Hz, 2H, –CH$_2$–OH), 1.51 – 1.42 (m, 1H, –CH–), 1.37 – 1.19 (m, 52H, –CH$_2$–), 1.13 (t, $^3J_{H,H} = 5.2$ Hz, 1H, –OH), 0.88 (t, $^3J_{H,H} = 6.8$ Hz, 3H, –CH$_3$), 0.88 (t, $^3J_{H,H} = 6.9$ Hz, 3H, –CH$_3$) ppm.

**1-Bromo-2-hexyltetracosane (8g):** Synthesized according to P4 from 7g (2.09 g, 4.8 mmol), HBr (48%, 30 mL), H$_2$SO$_4$ (1 mL) and Bu$_4$NHSO$_3$ (tip of spatula). Purification by column chromatography (eluent: n-hexane). Colourless solid, yield: 1.84 g (77%), C$_{30}$H$_{61}$Br, $M = 500.40$ g/mol, mp. 42 °C, $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 3.44 (d, $^3J_{H,H} = 4.8$ Hz, 2H, –CH$_2$–Br), 1.66 – 1.56 (m, 1H, –CH–), 1.42 – 1.18 (m, 52H, –CH$_2$–), 0.89 (t, $^3J_{H,H} = 6.7$ Hz, 3H, –CH$_3$), 0.88 (t, $^3J_{H,H} = 6.9$ Hz, 3H, –CH$_3$) ppm.

**6.2.2 1,4-Dialkoxy-2,5-diiodobenzenes (9)**

A mixture of 1,4-dihydroxy-2,5-diiodobenzene (1 equ.), the appropriate bromoalkene 8 (2.5 equ.), K$_2$CO$_3$ (5 equ.) and Bu$_4$NI (tip of a spatula) in anhydrous DMF (5 mL per mmol) was stirred at 120 °C for 12 h. After cooling to room temperature, the reaction was poured into water (50 mL) and the aqueous layer was extracted with Et$_2$O (3x50 mL). The combined organic layers were washed with saturated aqu. LiCl, water and brine.
After drying over anhydrous Na$_2$SO$_4$, filtration and evaporation of the solvent, the crude product was purified by column chromatography.

1,4-Bis(2-octyleicosyl-1-oxy)-2,5-diiodobenzene (9a): Synthesized according to P5 from 1,4-diiodohydroquinone (0.50 g, 1.4 mmol), 8a (1.37 g, 2.9 mmol), potassium carbonate (1.00 g, 7.0 mmol), Bu$_4$NI (tip of spatula) in DMF (50 mL). Purification by column chromatography (eluent: $n$-hexane). Colourless solid, yield: 0.06 g (5%), C$_{62}$H$_{116}$I$_2$O$_2$, $M = 1146.71$ g/mol, mp. 45 °C, $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.15 (s, 2H, Ar–H), 3.80 (d, $3J_{H,H} = 5.4$ Hz, 4H, –OC$_2$H$_2$–), 1.83 – 1.72 (m, 2H, –CH$_2$–), 1.57 – 1.11 (m, 96H, –CH$_2$–), 0.88 (t, $3J_{H,H} = 6.8$ Hz, 12H, –CH$_3$) ppm.

1,4-Bis(2-ethyldocosyl-1-oxy)-2,5-diiodobenzene (9b): Synthesized according to P5 from 1,4-diiodohydroquinone (0.50 g, 1.4 mmol), 8b (1.21 g, 2.9 mmol), potassium carbonate (2.28 g, 7.0 mmol), Bu$_4$NI (tip of spatula) in DMF (50 mL). Purification by column chromatography (eluent: $n$-hexane). Colourless solid, yield: 0.33 g (23%), C$_{54}$H$_{100}$I$_2$O$_2$, $M = 1034.58$ g/mol, mp. 61 °C, $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.16 (s, 2H, Ar–H), 3.81 (d, $3J_{H,H} = 5.5$ Hz, 4H, –OCH$_2$–), 1.79 – 1.68 (m, 2H, –CH–), 1.62 – 1.16 (m, 80H, –CH$_2$–), 0.93 (t, $3J_{H,H} = 7.5$ Hz, 6H, –CH$_3$), 0.88 (t, $3J_{H,H} = 6.8$ Hz, 6H, –CH$_3$) ppm.

1,4-Bis(2-butyldocosyl-1-oxy)-2,5-diiodobenzene (9c): Synthesized according to P5 from 1,4-diiodohydroquinone (0.70 g, 1.9 mmol), 8c (1.80 g, 4.0 mmol), potassium carbonate (3.10 g, 9.5 mmol), Bu$_4$NI (tip of spatula) in DMF (50 mL). Purification by column chromatography (eluent: $n$-hexane). Colourless solid, yield: 0.14 g (7%), C$_{58}$H$_{108}$I$_2$O$_2$, $M = 1090.64$ g/mol, mp. 58 °C, $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.15 (s, 2H, Ar–H), 3.80 (d, $3J_{H,H} = 5.4$ Hz, 4H, –OCH$_2$–), 1.83 – 1.73 (m, 2H, –CH–), 1.45 – 1.15 (m, 88H, –CH$_2$–), 0.94 – 0.85 (m, 12H, –CH$_3$) ppm.

1,4-Bis(2-hexyldocosyl-1-oxy)-1,5-diiodobenzene (9d): Synthesized according to P5
from 1,4-diiodohydroquinone (0.20 g, 0.6 mmol), 8d (0.6 g, 1.3 mmol), potassium carbonate (0.80 g, 6.1 mmol), Bu₄NI (tip of spatula) in DMF (50 mL). Purification by column chromatography (eluent: *n*-hexane). Colourless solid, yield: 0.50 g (71%), C₆₂H₁₁₆I₂O₂, M = 1147.39 g/mol, mp. 58 °C, ¹H-NMR (400 MHz, CDCl₃) δ 7.15 (s, 2H, Ar–H), 3.80 (d, 3JH,H = 5.4 Hz, 4H, –OCH₂–), 1.83 – 1.73 (m, 2H, –CH–), 1.45 – 1.19 (m, 96H, –CH₂–), 0.88 (t, 3JH,H = 6.8 Hz, 12H, –CH₃).  

1,4-Bis(2-ethyltetracosyl-1-oxy)-2,5-diiodobenzene (9e): Synthesized according to P5 from 1,4-diiodohydroquinone (0.46 g, 1.26 mmol), 8e (1.18 g, 2.7 mmol), caesium carbonate (2.10 g, 6.4 mmol), Bu₄NI (tip of spatula) in DMF (50 mL). Purification by column chromatography (eluent: *n*-hexane). Colourless solid, yield: 0.12 g (9%), C₅₈H₁₀₈I₂O₂, M = 1090.64 g/mol, mp. 62 °C, ¹H-NMR (400 MHz, CDCl₃) δ 7.16 (s, 2H, Ar–H), 3.81 (d, 3JH,H = 5.4 Hz, 4H, –OCH₂–), 1.78 – 1.67 (m, 2H, –CH–), 1.58 – 1.20 (m, 88H, –CH₂–), 0.93 (t, 3JH,H = 7.5 Hz, 6H, –CH₃), 0.88 (t, 3JH,H = 6.8 Hz, 6H, –CH₃) ppm.  

1,4-Bis(2-butyrtetracosyl-1-oxy)-2,5-diiodobenzene (9f): Synthesized according to P5 from 1,4-diiodohydroquinone (0.58 g, 1.6 mmol), 8f (1.60 g, 3.4 mmol), potassium carbonate (1.10 g, 8.0 mmol), Bu₄NI (tip of spatula) in DMF (50 mL). Purification by column chromatography (eluent: *n*-hexane). Colourless solid, yield: 0.15 g (8%), C₆₂H₁₁₆I₂O₂, M = 1146.71 g/mol, mp. 62 °C, ¹H-NMR (400 MHz, CDCl₃) δ 7.15 (s, 2H, Ar–H), 3.80 (d, 3JH,H = 5.4 Hz, 4H, –OCH₂–), 1.83 – 1.73 (m, 2H, –CH–), 1.57 – 1.19 (m, 96H, –CH₂–), 0.94 – 0.85 (m, 12H, –CH₃) ppm.  

1,4-Bis(2-hexyltetracosyl-1-oxy)-2,5-diiodobenzene (9g): Synthesized according to P5 from 1,4-diiodohydroquinone (0.64 g, 1.7 mmol), 8g (1.84 g, 3.7 mmol), potassium carbonate (1.17 g, 8.5 mmol), Bu₄NI (tip of spatula) in DMF (50 mL). Purification by column chromatography (eluent: *n*-hexane). Colourless solid, yield: 0.82 g (40%), C₆₆H₁₂₄I₂O₂, M = 1202.77 g/mol, mp. 51 °C, ¹H-NMR (500 MHz, CDCl₃) δ 7.16 (s, 2H,
6.3 Synthesis of compounds 1-3

A mixture of 1,4-dialkoxy-2,5-diiodobenzene 9 (1 equ.) and the acetylene 10 (2.1 equ.) was dissolved in purified Et₃N (5 mL per mmol). After degassing with argon for 30 min [Pd(PPh₃)₄] (3 mol%) and CuI (2 mol%) were added and the mixture was refluxed for 6 h. After removing the solvent the obtained residue was purified by column chromatography.

1,4-Bis(2-octyleicosyl-1-oxy)-2,5-bis{4-[4-(2,3-O-isopropylidene-2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (11a): Synthesized according to P8 from 9a (60 mg, 0.05 mmol), 10 (37 mg, 0.11 mmol), [Pd(PPh₃)₄] (1.7 mg, 0.002 mmol), CuI (0.2 mg, 0.001 mmol) in NEt₃ (50 mL). Purification by column chromatography (eluent: CHCl₃). Yellow solid, yield: 70 mg (90%), C₁₆₆H₃₅₄O₈, M = 1555.16 g/mol, mp. 97 °C, ¹H-NMR (400 MHz, CDCl₃) δ 7.54 – 7.43 (m, 12H, Ar–H), 7.00 (s, 2H, Ar–H), 6.93 – 6.87 (m, 4H, Ar–H), 4.53 – 4.45 (m, 2H, –OCH–), 4.18 (dd,
$^3J_{H,H} = 8.5$ Hz, $^2J_{H,H} = 6.4$ Hz, 2H, –OCH$_2$–), 4.08 (dd, $^3J_{H,H} = 9.5$ Hz, $^2J_{H,H} = 5.4$ Hz, 2H, –OCH$_2$–), 3.97 (dd, $^3J_{H,H} = 9.5$ Hz, $^2J_{H,H} = 5.9$ Hz, 2H, –OCH$_2$–), 3.94 – 3.88 (m, 6H, –OCH$_2$–), 1.90 – 1.80 (m, 2H, –CH–), 1.63 – 1.12 (m, 108H, –CH$_2$–, acetonide–CH$_3$), 0.87 (t, $^3J_{H,H} = 6.9$ Hz, 6H, –CH$_3$), 0.87 (t, $^3J_{H,H} = 6.9$ Hz, 7H, –CH$_3$) ppm.

1.4-Bis(2-ethyldocosyl-1-oxy)-2,5-bis{4-[4-(2,3-O-isopropylidene-2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (11b): Synthesized from 9b (148 mg, 0.14 mmol), 10 (100 mg, 0.30 mmol), [Pd(PPh$_3$)$_4$] (4.8 mg, 0.004 mmol), CuI (0.5 mg, 0.003 mmol) in NEt$_3$ (50 mL). Purification by column chromatography (eluent: CHCl$_3$). Yellow solid, yield: 180 mg (90%), C$_{98}$H$_{138}$O$_8$, $M = 1443.04$ g/mol, mp. 150 °C, $^1$H-NMR (500 MHz, CDCl$_3$) δ 7.53 – 7.43 (m, 12H, Ar–H), 7.00 (s, 2H, Ar–H), 6.94 – 6.87 (m, 4H, Ar–H), 4.52 – 4.45 (m, 2H, –OCH–), 4.18 (dd, $^3J_{H,H} = 8.5$ Hz, $^2J_{H,H} = 6.4$ Hz, 2H, –OCH$_2$–), 4.08 (dd, $^3J_{H,H} = 9.5$ Hz, $^2J_{H,H} = 5.4$ Hz, 2H, –OCH$_2$–), 3.97 (dd, $^3J_{H,H} = 9.5$ Hz, $^2J_{H,H} = 5.9$ Hz, 2H, –OCH$_2$–), 3.95 – 3.87 (m, 6H, –OCH$_2$–), 1.85 – 1.76 (m, 2H, –CH–), 1.68 – 1.10 (m, 92H, –CH$_2$–, acetonide–CH$_3$), 0.97 (t, $^3J_{H,H} = 7.5$ Hz, 6H, –CH$_3$), 0.88 (t, $^3J_{H,H} = 7.0$ Hz, 6H, –CH$_3$) ppm.

1,4-Bis(2-butyldocosyl-1-oxy)-2,5-bis{4-[4-(2,3-O-isopropylidene-2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (11c): Synthesized from 9c (140 mg, 0.13 mmol), 10 (90 mg, 0.27 mmol), [Pd(PPh$_3$)$_4$] (4.5 mg, 0.004 mmol), CuI (0.5 mg, 0.003 mmol) in NEt$_3$ (50 mL). Purification by column chromatography (eluent: CHCl$_3$). Yellow solid, yield: 180 mg (92%), C$_{102}$H$_{146}$O$_8$, $M = 1499.10$ g/mol, mp. 125 °C, $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.49 – 7.42 (m, 12H, Ar–H), 6.99 (s, 2H, Ar–H), 6.93 – 6.84 (m, 4H, Ar–H), 4.53 – 4.45 (m, 2H, –OCH–), 4.17 (dd, $^3J_{H,H} = 8.5$ Hz, $^2J_{H,H} = 6.4$ Hz, 2H, –OCH$_2$–), 4.08 (dd, $^3J_{H,H} = 9.5$ Hz, $^2J_{H,H} = 5.4$ Hz, 2H, –OCH$_2$–), 3.95 – 3.87 (m, 6H, –OCH$_2$–), 1.85 – 1.76 (m, 2H, –CH–), 1.68 – 1.10 (m, 92H, –CH$_2$–, acetonide–CH$_3$), 0.97 (t, $^3J_{H,H} = 7.5$ Hz, 6H, –CH$_3$), 0.88 (t, $^3J_{H,H} = 7.0$ Hz, 6H, –CH$_3$) ppm.
1,4-Bis(2-hexyldecyl-1-oxy)-2,5-bis{4-[4-(2,3-O-isopropylidene-2,3-dihydroxy-propyl-1-oxy)phenylethynyl]phenylethynyl}benzene (11d): Synthesized from 9d (500 mg, 0.45 mmol), 10 (300 mg, 0.90 mmol), [Pd(PPh3)4] (16 mg, 0.01 mmol), CuI (1.7 mg, 0.009 mmol) in NEt3 (50 mL). Purification by column chromatography (eluent: CHCl3). Yellow solid, yield: 600 mg (85%), C106H154O8, M = 1556.35 g/mol, mp. 114 °C, ¹H-NMR (400 MHz, CDCl3) δ 7.52 – 7.43 (m, 12H, Ar–H), 7.00 (s, 2H, Ar–H), 6.93 – 6.87 (m, 4H, Ar–H), 4.53 – 4.45 (m, 2H, –OCH–), 4.18 (dd, 3JH,H = 8.5 Hz, 3JH,H = 6.4 Hz, 2H, –OCH2–), 4.08 (dd, 3JH,H = 9.6 Hz, 3JH,H = 5.3 Hz, 2H, –OCH2–), 4.00 – 3.95 (m, 2H, –OCH2–), 3.94 – 3.88 (m, 6H, –OCH2–), 1.90 – 1.80 (m, 2H, –CH–), 1.47 (s, 6H, acetonide–CH3), 1.41 (s, 6H, acetonide–CH3), 1.39 – 1.17 (m, 96H, –CH2–), 0.88 (t, 3JH,H = 6.8 Hz, 12H, –CH3) ppm.

1,4-Bis(2-ethyltetradecyl-1-oxy)-2,5-bis{4-[4-(2,3-O-isopropylidene-2,3-dihydroxy-propyl-1-oxy)phenylethynyl]phenylethynyl}benzene (11e): Synthesized from 9e (100 mg, 0.09 mmol), 10 (64 mg, 0.19 mmol), [Pd(PPh3)4] (3.1 mg, 0.003 mmol), CuI (0.3 mg, 0.002 mmol) in NEt3 (50 mL). Purification by column chromatography (eluent: CHCl3). Yellow solid, yield: 120 mg (89%), C102H146O8, M = 1499.10 g/mol, mp. 143 °C, ¹H-NMR (500 MHz, CDCl3) δ 7.51 – 7.43 (m, 12H, Ar–H), 7.00 (s, 2H, Ar–H), 6.92 – 6.87 (m, 4H, Ar–H), 4.53 – 4.45 (m, 2H, –OCH–), 4.18 (dd, 3JH,H = 8.5 Hz, 3JH,H = 6.4 Hz, 2H, –OCH2–), 4.08 (dd, 3JH,H = 9.5 Hz, 3JH,H = 5.4 Hz, 2H, –OCH2–), 3.97 (dd, 3JH,H = 9.5 Hz, 3JH,H = 5.9 Hz, 2H, –OCH2–), 3.95 – 3.88 (m, 6H, –OCH2–), 1.86 – 1.76 (m, 2H, –CH–), 1.64 – 1.16 (m, 100H, –CH2–, acetonide–CH3), 0.97 (t, 3JH,H = 7.5 Hz, 6H, –CH3), 0.88 (t, 3JH,H = 7.0 Hz, 6H, –CH3) ppm.

1,4-Bis(2-butyltetradecyl-1-oxy)-2,5-bis{4-[4-(2,3-O-isopropylidene-2,3-dihydroxy-propyl-1-oxy)phenylethynyl]phenylethynyl}benzene (11f): Synthesized from 9f (140 mg, 0.12 mmol), 10 (85 mg, 0.26 mmol), [Pd(PPh3)4] (4.1 mg, 0.004 mmol), CuI (0.5 mg, 0.002 mmol) in NEt3 (50 mL). Purification by column chromatography (eluent: CHCl3). Yellow solid, yield: 150 mg (86%), C106H154O8, M = 1555.16 g/mol, mp. 104 °C, ¹H-
**NMR** (500 MHz, CDCl3) δ 7.51 – 7.44 (m, 12H, Ar–H), 7.00 (s, 2H, Ar–H), 6.92 – 6.88 (m, 4H, Ar–H), 4.52 – 4.45 (m, 2H, –OCH–), 4.21 – 4.15 (m, 2H, –OCH2–), 4.11 – 4.05 (m, 2H, –OCH2–), 4.01 – 3.94 (m, 2H, –OCH2–), 3.94 – 3.88 (m, 6H, –OCH2–), 1.88 – 1.83 (m, 2H, –CH–), 1.62 – 1.19 (m, 108H, –CH2–, acetonide–CH3), 0.92 – 0.85 (m, 12H, –CH3) ppm.

**1,4-Bis(2-hexyltetracosyl-1-oxy)-2,5-bis{4-[4-(2,3-O-isopropylidene-2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (11g):** Synthesized from 9g (204 mg, 0.17 mmol), 10 (120 mg, 0.36 mmol), [Pd(PPh3)4] (6.0 mg, 0.005 mmol), CuI (0.6 mg, 0.003 mmol) in NEt3 (50 mL). Purification by column chromatography (eluent: CHCl3). Yellow solid, yield: 240 mg (88%), C110H162O8, M = 1611.23 g/mol, mp. 108 °C, 1H-NMR (400 MHz, CDCl3) δ 7.52 – 7.38 (m, 12H, Ar–H), 7.00 (s, 2H, Ar–H), 6.95 – 6.86 (m, 4H, Ar–H), 4.53 – 4.44 (m, 2H, –OCH–), 4.21 – 4.14 (m, 2H, –OCH2–), 4.10 – 4.05 (m, 2H, –OCH2–), 4.00 – 3.86 (m, 8H, –OCH2–), 1.92 – 1.80 (m, 2H, –CH–), 1.74 – 1.07 (m, 116H, –CH2–, acetonide–CH3), 0.95 – 0.85 (m, 12H, –CH3) ppm.

**6.3.2 Synthesis and analytical data of compounds 1 - 3**
A mixture of the appropriate isopropylidene acetal 11 (1 equ.) and PPTS (tip of a spatula) was dissolved in THF/MeOH (1:1) and stirred at 50 °C for 12 h. After finishing the reaction the solvent was removed and the residue solved in DCM. The organic layer was washed with NaHCO3 solution (3 x 50 mL), water and brine. After drying over Na2SO4 the solvent was removed and the residue purified with column chromatography.

**1,4-Bis(2-octyleicosyl-1-oxy)-2,5-bis{4-[4-(2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (1):** Synthesized according to P9 from 11a (70 mg, 0.05 mmol), PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL each). Purification by column chromatography (eluent: CHCl3/MeOH 9:1) and following recrystallization. Yellow-greenish solid, yield: 36 mg (54%), C100H146O8, M = 1476 g/mol, 1H-NMR (400 MHz, pyridine-d5) δ 7.85 – 7.80 (m, 4H, Ar–H), 7.77 – 7.71 (m, 4H, Ar–H), 7.68 – 7.62
(m, 4H, Ar–H), 7.57 (s, 2H, Ar–H), 7.14 – 7.07 (m, 4H, Ar–H), 5.2 (broad, OH, H2O), 4.61 – 4.37 (m, 6H, –OCH–, –OCH2–), 4.27 – 4.19 (m, 4H, –OCH2–), 4.14 (d, $^3J_{H,H} = 5.4$ Hz, 4H, –OCH2–), 2.10 – 1.97 (m, 2H, –CH–), 1.84 – 1.17 (m, 96H, –C–), 0.90 (t, $^3J_{H,H} = 6.4$ Hz, 6H, –CH3), 0.89 (t, $^3J_{H,H} = 6.4$ Hz, 6H, –CH3) ppm. 13C-NMR (101 MHz, pyridine-d5) δ 160.05, 154.34 (CAr –O), 133.36, 131.80, 131.77 (CAr–H), 124.00, 123.5 (overlapped with py-d5), 117.04, 115.16, 114.97, 114.29 (CAr-H, quart. CAr); 95.24, 92.45, 88.92, 88.30 (–C≡C–); 72.37, 71.10, 70.85, 64.02 (–OCH–, –OCH2–); 4.09 (d, $^3J_{H,H} = 5.5$ Hz, 4H, –OCH2–), 1.97 – 1.85 (m, 2H, –CH–), 1.80 – 1.17 (m, 68H, –C–), 1.05 (t, $^3J_{H,H} = 7.4$ Hz, 6H, –CH3), 0.89 (t, $^3J_{H,H} = 6.7$ Hz, 6H, –CH3) ppm. 13C-NMR (101 MHz, pyridine-d5) δ 160.02, 154.29 (CAr–O), 133.33, 131.76, 131.74 (CAr–H), 123.94, 123.52, 116.98, 115.14, 114.94, 114.25 (CAr-H, quart. CAr); 95.19, 92.42, 88.87, 88.28 (–C≡C–); 71.92, 71.07, 70.81, 63.99 (–OCH–, –OCH2–); 39.80 (–CH–); 31.87, 31.18, 30.19, 29.78, 29.75, 29.74, 29.73, 29.72, 29.67, 29.36, 27.01, 24.21, 22.68 (–CH2–); 14.02, 11.29 (–CH3) ppm. Calc. for C100H146O8·H2O [%]: C 80.38, H 9.98; found C 80.24, H 9.94.

1,4-Bis(2-ethyldocosyl-1-oxy)-2,5-bis{4-[4-(2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (2a): Synthesized from 11b (180 mg, 0.12 mmol), PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL each). Purification by column chromatography (eluent: CHCl3/MeOH 9:1) and following recrystallization. Yellow-greenish solid, yield: 126 mg (77%), C 92H130O8, M = 1364 g/mol, 1H-NMR (400 MHz, pyridine-d5) δ 7.83 – 7.77 (m, 4H, Ar–H), 7.75 – 7.70 (m, 4H, Ar–H), 7.68 – 7.62 (m, 4H, Ar–H), 7.52 (s, 2H, Ar–H), 7.14 – 7.08 (m, 4H, Ar–H), 5.6 (broad, OH, H2O), 4.61 – 4.37 (m, 6H, –OCH–, –OCH2–), 4.27 – 4.19 (m, 4H, –OCH2–), 4.09 (d, $^3J_{H,H} = 5.5$ Hz, 4H, –OCH2–), 1.97 – 1.85 (m, 2H, –CH–), 1.80 – 1.17 (m, 68H, –C–), 1.05 (t, $^3J_{H,H} = 7.4$ Hz, 6H, –CH3), 0.89 (t, $^3J_{H,H} = 6.7$ Hz, 6H, –CH3) ppm. 13C-NMR (101 MHz, pyridine-d5) δ 160.02, 154.29 (CAr–O), 133.33, 131.76, 131.74 (CAr–H), 123.94, 123.52, 116.98, 115.14, 114.94, 114.25 (CAr-H, quart. CAr); 95.19, 92.42, 88.87, 88.28 (–C≡C–); 71.92, 71.07, 70.81, 63.99 (–OCH–, –OCH2–); 39.80 (–CH–); 31.87, 31.18, 30.19, 29.78, 29.75, 29.74, 29.73, 29.72, 29.67, 29.36, 27.01, 24.21, 22.68 (–CH2–); 14.02, 11.29 (–CH3) ppm. Calc. for C100H146O8·H2O [%]: C 80.38, H 9.98; found C 80.24, H 9.94.

1,4-Bis(2-butyldocosyl-1-oxy)-2,5-bis{4-[4-(2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (2b): Synthesized from 11c (180 mg, 0.12 mmol),
PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL each). Purification by column chromatography (eluent: CHCl₃/MeOH 9:1) and following recrystallization. Yellow-greenish solid, yield: 108 mg (63%), C₉₆H₁₃₈O₈, M = 1420 g/mol, $^{1}H$-NMR (400 MHz, pyridine-d₅) $\delta$ 7.84 – 7.79 (m, 4H, Ar–H), 7.75 – 7.71 (m, 4H, Ar–H), 7.68 – 7.63 (m, 4H, Ar–H), 7.55 (s, 2H, Ar–H), 7.14 – 7.09 (m, 4H, Ar–H), 4.9 (broad, OH, H₂O), 4.61 – 4.38 (m, 6H, –OC₃H₄–, –OC₃H₂–), 4.28 – 4.19 (m, 4H, –OC₃H₂–), 4.11 (d, $^3J_{H,H} = 5.5$ Hz, 4H, –OC₃H₂–), 2.06 – 1.93 (m, 2H, –C₃H–), 1.82 - 1.20 (m, 88H, –C₅H₂–), 0.94 (t, $^3J_{H,H} = 7.1$ Hz, 6H, –C₃H₃), 0.89 (t, $^3J_{H,H} = 6.8$ Hz, 6H, –CH₃) ppm. $^{13}$C-NMR (101 MHz, pyridine-d₅) $\delta$ 160.01, 154.27 (CAr–O); 133.32, 131.75, 131.73 (CAr-H); 123.94, 123.50, 116.97, 115.13, 114.92, 114.22 (CAr-H, quart. CAr); 95.19, 92.42, 88.87, 88.27 (–C≡C–); 72.30, 71.07, 70.81, 63.99 (–OCH₃, –OCH₂–); 38.30 (–CH₂–); 31.95, 31.85, 31.66, 31.36, 30.20, 29.76, 29.74, 29.72, 29.71, 29.65, 29.34, 29.20, 27.00, 23.15, 22.66 (–CH₂); 14.01, 14.00 (–CH₃) ppm. Calc. for C₉₆H₁₃₈O₈·H₂O [%]: C 80.18, H 9.81; found C 80.24, H 10.03.

1,4-Bis(2-hexyldocosyl-1-oxy)-2,5-bis{4-[4-(2,3-dihydroxypropyl-1-oxy)phenylethylnyl|phenylethynyl|benzene (2c):Synthesized from 11d (600 mg, 0.40 mmol), PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL each). Purification by column chromatography (eluent: CHCl₃/MeOH 9:1) and following recrystallization. Yellow-greenish solid, yield: 440 mg (78%), C₁₀₀H₁₄₆O₈, M = 1476 g/mol, $^{1}H$-NMR (500 MHz, pyridine-d₅) $\delta$ 7.82 – 7.78 (m, 4H, Ar–H), 7.74 – 7.70 (m, 4H, Ar–H), 7.66 – 7.61 (m, 4H, Ar–H), 7.55 (s, 2H, Ar–H), 7.12 – 7.07 (m, 4H, Ar–H), 5.4 (broad, OH, H₂O), 4.58-4.39 (m, 6H, –OCH₃, –OCH₂–), 4.24 – 4.18 (m, 4H, –OCH₂–), 4.11 (d, $^3J_{H,H} = 5.6$ Hz, 4H, –OCH₂–), 2.04 – 1.96 (m, 2H, –CH₂–), 1.81 – 1.18 (m, 96H, –CH₃), 0.87 (t, $^3J_{H,H} = 7.0$ Hz, 12H, –CH₃) ppm. $^{13}$C-NMR (126 MHz, pyridine-d₅) $\delta$ 160.05, 154.33 (CAr–O); 133.37, 131.81, 131.78 (CAr–H); 124.95, 123.50, 117.15, 115.19, 115.0, 114.30 (CAr-H, quart. CAr); 95.24, 92.46, 88.93, 88.31 (–C≡C–); 72.40, 71.11, 70.87, 64.03 (–OCH₃, –CH₂O–); 38.41 (–CH₂–); 31.90, 31.89, 31.74, 30.24, 29.87, 29.81, 29.76, 29.70, 29.39, 27.06, 25.59, 22.75, 22.71 (–CH₂–); 14.05 (–CH₃) ppm. Calc. for C₁₀₀H₁₄₆O₈ [%]: C 81.36, H 9.97; found C 81.62, H 9.91.
1,4-Bis(2-ethyltetraicosyl-1-oxy)-2,5-bis{4-[4-(2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (3a): Synthesized from 11e (120 mg, 0.08 mmol), PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL each). Purification by column chromatography (eluent: CHCl3/MeOH 9:1) and following recrystallization. Yellow-greenish solid, yield: 87 mg (77%), C_{96}H_{138}O_{8}, M = 1420 g/mol, \textbf{1H-NMR} (400 MHz, pyridine-d$_5$) δ 7.84 – 7.77 (m, 4H, Ar–H), 7.76 – 7.69 (m, 4H, Ar–H), 7.69 – 7.63 (m, 4H, Ar–H), 7.52 (s, 2H, Ar–H), 7.15 – 7.08 (m, 4H, Ar–H), 5.5 (broad, OH, H$_2$O), 4.62 – 4.38 (m, 6H, –OC$_H$–, –OC$_H$$_2$–), 4.28 – 4.18 (m, 4H, –OCH$_2$–), 4.09 (d, $^{3}J_{H,H} = 5.4$ Hz, 4H, –OCH$_2$–), 1.97 – 1.84 (m, 2H, –CH–), 1.81 – 1.17 (m, 88H, –CH$_2$–), 1.05 (t, $^{3}J_{H,H} = 7.4$ Hz, 6H, –CH$_3$), 0.89 (t, $^{3}J_{H,H} = 6.6$ Hz, 6H, –CH$_3$) ppm. \textbf{13C-NMR} (101 MHz, pyridine-d$_5$) δ 160.05, 154.31 (CAr–O); 133.36, 131.79, 131.77, (CAr–H); 123.95, 123.5 (overlapped by py-d$_5$), 117.01, 115.17, 114.97, 114.27 (CAr–H, quart. CAr); 95.22, 92.46, 88.90, 88.31 (–C≡C–); 71.94, 71.11, 70.85, 64.03 (–OCH–, –OCH$_2$–); 39.83 (–CH–); 31.89, 31.21, 30.22, 29.80, 29.78, 29.75, 29.69, 29.38, 27.03, 24.24, 22.70 (–CH$_2$–); 14.04, 11.31 (–CH$_3$) ppm. \textbf{HR-MS} (m/z): [M]+Cl–calc. for C$_{96}$H$_{138}$O$_8$Cl, 1454.009; found. 1454.001. Calc. for C$_{96}$H$_{138}$O$_8$.H$_2$O [%]: C 80.18, H 9.81; found C 80.00, H 9.65.

1,4-Bis(2-butyltetraicosyl-1-oxy)-2,5-bis{4-[4-(2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (3b): Synthesized from 11f (150 mg, 0.10 mmol), PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL each). Purification by column chromatography (eluent: CHCl3/MeOH 9:1) and following recrystallization. Yellow-greenish solid, yield: 112 mg (76%), C$_{100}$H$_{146}$O$_8$, M = 1476 g/mol, \textbf{1H-NMR} (400 MHz, pyridine-d$_5$) δ 7.86 – 7.78 (m, 4H, Ar–H), 7.76 – 7.70 (m, 4H, Ar–H), 7.69 – 7.62 (m, 4H, Ar–H), 7.55 (s, 2H, Ar–H), 7.15 – 7.08 (m, 4H, Ar–H), 4.9 (broad, OH, H$_2$O), 4.61 – 4.37 (m, 6H, –OCH–, –OCH$_2$–), 4.28 – 4.19 (m, 4H, –OCH$_2$–), 4.10 (d, $^{3}J_{H,H} = 5.5$ Hz, 4H, –OCH$_2$–), 2.05 – 1.94 (m, 2H, –CH–), 1.82 -1.17 (m, 96H, –CH$_2$–), 0.94 (t, $^{3}J_{H,H} = 7.1$ Hz, 6H, –CH$_3$), 0.89 (t, $^{3}J_{H,H} = 6.9$ Hz, 6H, –CH$_3$) ppm. \textbf{13C-NMR} (101 MHz, pyridine-d$_5$) δ 160.05, 154.31 (CAr–O); 133.36, 131.79, 131.77 (CAr–H); 123.95, 123.5 (overlapped by py-d$_5$), 117.01, 115.17, 114.97, 114.27 (CAr–H, quart. CAr); 95.22, 92.46, 88.90, 88.31 ($^{3}$C≡C–); 71.94, 71.11, 70.85, 64.03 (–OCH–, –OCH$_2$–); 39.83 (–CH–); 31.89, 31.21, 30.22, 29.80, 29.78, 29.75, 29.69, 29.38, 27.03, 24.24, 22.70 (–CH$_2$–); 14.04, 11.31 (–CH$_3$) ppm.
1,4-Bis(2-hexyltetracosyl-1-oxy)-2,5-bis{4-[4-(2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (3c): Synthesized from 11g (240 mg, 0.16 mmol), PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL each). Purification by column chromatography (eluent: CHCl3/MeOH 9:1) and following recrystallization. Yellow-greenish solid, yield: 163 mg (71%), C104H154O8, M = 1532 g/mol, 1H-NMR (400 MHz, pyridine-d5) δ 7.85 – 7.80 (m, 4H, Ar–H), 7.77 – 7.71 (m, 4H, Ar–H), 7.69 – 7.62 (m, 4H, Ar–H), 7.57 (s, 2H, Ar–H), 7.14 – 7.08 (m, 4H, Ar–H), 4.8 (broad, OH, H2O), 4.61 – 4.39 (m, 6H, –OC6H–, –OC6H2–), 4.27 – 4.19 (m, 4H, –OC6H2–), 4.13 (d, 3JH,H = 5.6 Hz, 4H, –OC6H2–), 2.07 – 1.95 (m, 2H, –CH–), 1.84 - 1.18 (m, 104H, –CH2–), 0.92 – 0.86 (m, 12H, –CH3) ppm. 13C-NMR (101 MHz, pyridine-d5) δ 160.07, 154.34 (CAr–O); 133.38, 131.82, 131.79 (CAr-H); 124.00, 123.55, 117.15, 115.18, 114.98, 114.28 (CAr-H, quart. CAr); 95.28, 92.48, 88.92, 88.30 (–C≡C–); 72.32, 71.12, 70.87, 64.04 (–OCH–, –OCH2–); 38.40 (–CH–); 31.90, 31.89, 31.74, 30.25, 29.88, 29.82, 29.79, 29.76, 29.70, 29.39, 27.06, 22.76, 22.72 (–CH2–); 14.06 (–CH3) ppm. HR-MS (m/z): [M]+Cl– calc. for C104H154O8Cl, 1566.133; found. 1566.128. Calc. for C104H154O8·H2O [%]: C 80.57, H 10.14; found C 80.44, H 10.04.
6.4 Representative NMR spectra

**Figure S19.** $^1$H-NMR spectrum of 2b (pyridine-d$_5$, 400 MHz).

**Figure S20.** $^{13}$C-NMR spectrum of 2b (pyridine-d$_5$, 101 MHz).
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