Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

The Rhombic Honeycomb – A New Mode of Self-Assembly in Liquid Crystalline Soft Matter

Azhar Saeed,[a] Marco Poppe,[b] Matthias B. Wagner,[b] Sebastian Hauche,[b] Christian Anders,[b] Yu Cao,[a,c] Lei Zhang,[c] Carsten Tschierske*[b] and Feng Liu*[a]

[a] Shaanxi International Research Center for Soft Matter, State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, P. R. China. E-mail: feng.liu@xjtu.edu.cn

[b] Institute of Chemistry, Martin-Luther University Halle-Wittenberg, Kurt-Mothes Str. 2, D-06120 Halle/Saale, Germany. E-mail: carsten.tschierske@chemie.uni-halle.de

[c] MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, School of Physics, Xi'an Jiaotong University, Xi'an 710049, P. R. China

1. Experimental Section

1.1 Polarizing Optical Microscopy (POM)

Optical textures of all compounds were characterized by polarizing optical microscopy (Olympus BX51-P) with the combination of a heating stage (Linkam LTS420E) and controller (T95-HS). Optical investigations were carried out under equilibrium conditions between two glass slides that were used without further treatment. A full wavelength retardation plate was used to determine the sign of birefringence.

1.2 DSC measurements

Transition enthalpies were determined as obtained from differential scanning calorimetry (DSC) which were recorded on a TA DSC250 and DSC-8000 (Perkin Elmer) with heating and cooling rates of 10 K/min, peak temperatures are given.

1.3 Synchrotron-based X-ray Diffraction

High-resolution small-angle and wide-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 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 Pilatus 2M detector was used. q Calibration and linearization were verified using several orders of layer reflections from silver behenate and a series of n-alkanes. Experimental diffractograms are fitted using Gaussian-shaped peaks to determine the positions and intensities of the diffraction peaks. The diffraction peaks are indexed on the basis of their peak positions, and the lattice parameters and the space groups are subsequently determined. Once the diffraction intensities are measured, and the corresponding plane group determined, 2D electron density maps can be reconstructed based on the general formula

$$E(xy) = \sum_{hk} F(hk) \exp[i2\pi(hx+ky)] \quad (1)$$

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 is

$$I(hk) = K \cdot F(hk) \cdot F^*(hk) = K \cdot |F(hk)|^2 \quad (2)$$

Here K is a constant related to the sample volume, incident beam intensity etc. If the constant is equal to 1, then the electron density is

$$E(xy) = \sum_{hk} \mathrm{sqrt}[I(hk)] \exp[i2\pi(hx+ky) + \Phi_{hk}] \quad (3)$$

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}, cannot 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.

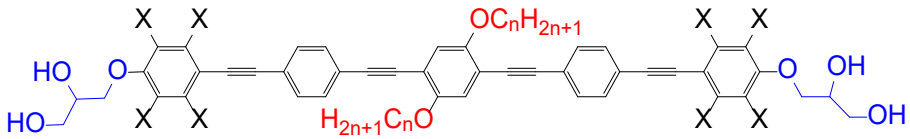
This makes it possible for a trial-and-error approach, where candidate electron density maps are reconstructed for all possible phase combinations. The "correct" phase combination is then selected on the merit of the maps, helped by prior physical and chemical knowledge of the system. This is especially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

1.4 Grazing Incident Small Angle X-ray Scattering

GISAXS experiments were performed at beamline BL16B1, Shanghai Synchrotron Radiation Facility (SSRF). Surface aligned samples were prepared by shearing the sample on a 10 × 10 mm^2 silica wafer. A Kohzu stage was used for heating and motions, and a MarCCD 165 was used for recording the scatterings.

2. Additional Data

Table S1. Phase transitions of the non-fluorinated (**H/*n***) and fluorinated (**F/*n***) compounds. The values for **H/18** and **F/18** were taken from ref.[S1]



H/*n* (X = H) **F/*n*** (X = F)

Comp.	Phase Transitions (T/°C [ΔH/kJmol^{-1}])
H/18	H: Cr 158 [69.4] Iso C: Iso 156 [-3.1] Col$_{hex}$/*p6mm* 149 [-65.4] Cr
H/20	H: Cr$_1$ 122 [51.4] Cr$_2$ 145 [17.0] Iso C: Iso 143 [-2.1] Col$_{hex}$/*p6mm* 108 [-49.7] Cr
H/22	H: Cr$_1$ 94 [36.4] Cr$_2$ 119 [61.6] Cr$_3$ 127 [35.1] Col$_{hex}$/*p6mm* 134 [1.7] Iso [a] C: Iso 132 [-1.5] Col$_{hex}$/*p6mm* 109 [-1.2] Col$_{rec}$/c2*mm* 97 [b] [-47.1] Cr
H/24	H: Cr$_1$ 113 [49.4] Cr$_2$ 123 [1.5] Cr$_3$ 127 [4.13] Iso C: Iso 119 [-2.5] Col$_{rec}$/*c2mm* 91 [-58.1] Cr
H/26	H: Cr 115 [53.2] Iso C: Iso 112 [-2.7] Col$_{rec}$/*c2mm* 87 [-60.6] Cr
H/28	H: Cr 119 [58.9] Col$_{squ}$/*p4mm* 125 [3.2] Iso C: Iso 120 [-3.3] Col$_{squ}$/*p4mm* 92 [-68.9] Cr
H/30	H: Cr 118 [64.4] Iso C: Iso 113 [-3.24] Col$_{squ}$/*p4mm* 81 [-71.0] Cr
H/32	H: Cr 116 [57.8] Iso C: Iso 107 [-2.9] Col$_{squ}$/*p4mm* 82 [-65.0] Cr
F/18	H: Cr 138 [60.9] Col$_{hex}$/*p6mm* 160 [3.8] Iso C: Iso 159 [-3.6] Col$_{hex}$/*p6mm* 125 [-2.9] Cub$_{bi}$/*Ia*$\bar{3}$*d* 113 [-61.3] Cr
F/20	H: Cr 87 [38.3] Col$_{rec}$/*c2mm* 114 [5.1] Col$_{hex}$/*p6mm* 150 [3.4] Iso C: Iso 147 [-3.1] Col$_{hex}$/*p6mm* 112 [-4.6] Col$_{rec}$/*c2mm* 70 [-38.9] Cr
F/22	H: Cr 106 [88.5] Col$_{rec}$/*c2mm* 122 [0.6] Col$_{hex}$/*p6mm* 143 [2.4] Iso C: Iso 140 [-1.9] Col$_{hex}$/*p6mm* 121 [-0.4] Col$_{rec}$/*c2mm* 65 [-76.3] Cr
F/24	H: Cr$_1$ 91 [117.4] Cr$_2$ 109 [103] Col$_{rec}$/*c2mm* 137 [3.3] Iso C: Iso 134 [-3.3] Col$_{rec}$/*c2mm* 69 [-92.3] Cr
F/28	H: Cr 79 [81.7] Col$_{rec}$/*c2mm* 131 [4.5] Iso C: Iso 127 [-4.3] Col$_{rec}$/*c2mm* 59 [-76.8] Cr
F/30	H: Cr 83 [92.7] Col$_{rec}$/*c2mm* 121 [3.0] Iso C: Iso 116 [-2.1] Col$_{rec}$/*c2mm* 62 [-85.3] Cr
F/32	H: Cr 108 [35.5] Col$_{squ}$/*p4mm* 138 [2.0] Iso C: Iso 134 [-2.0] Col$_{squ}$/*p4mm* 78 [-35.3] Cr

[a] Data from first heating scan; [b] during XRD investigation crystallization already starts at 124°C.

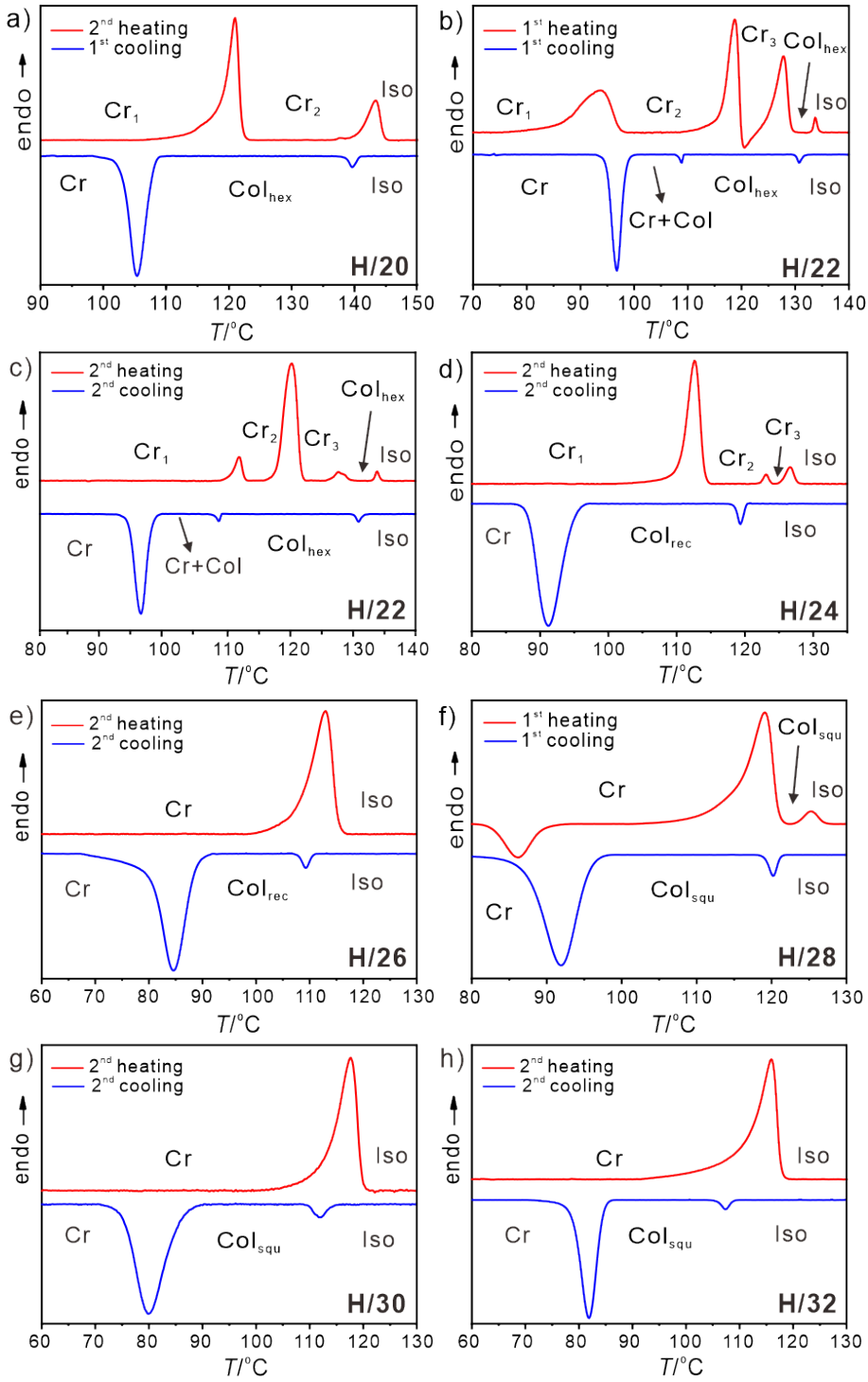


Figure S1. DSC heating and cooling traces of compounds **H/*n***, recorded at 10 K min^{-1}.

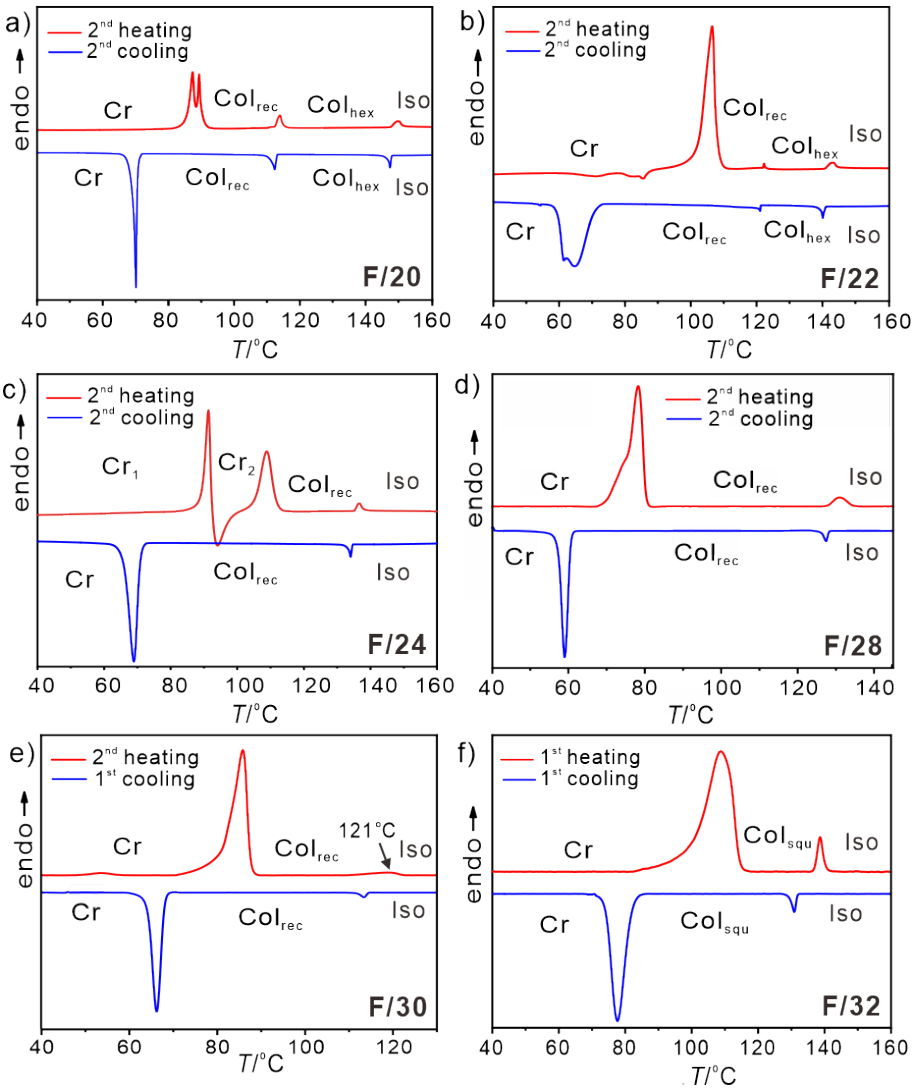


Figure S2. DSC heating and cooling traces of compounds **F/*n***, recorded at 10 K min^{-1}.

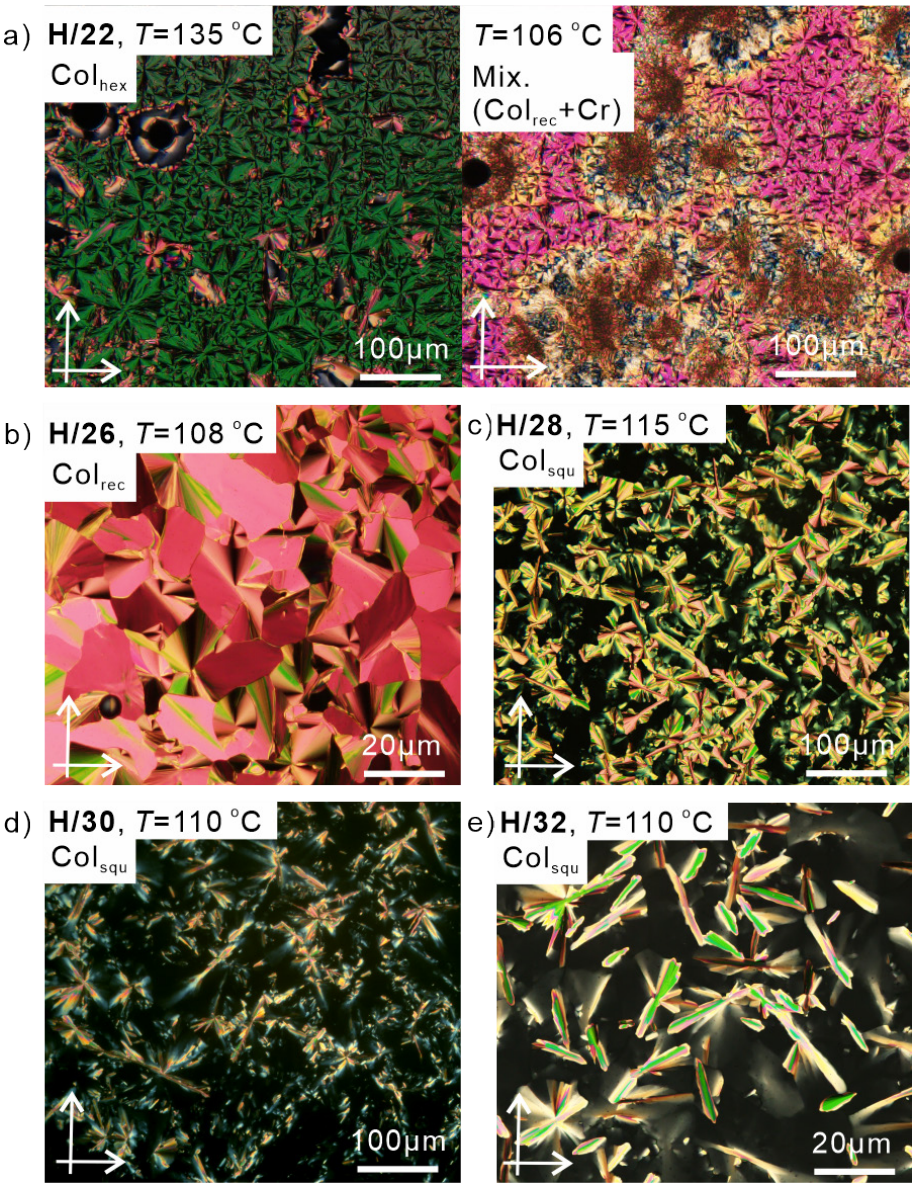


Figure S3. Selected textures of compounds (a) **H/22**; (b) **H/26**; (c) **H/28**; (d) **H/30**; and (e) **H/32** as observed between crossed polarizers.

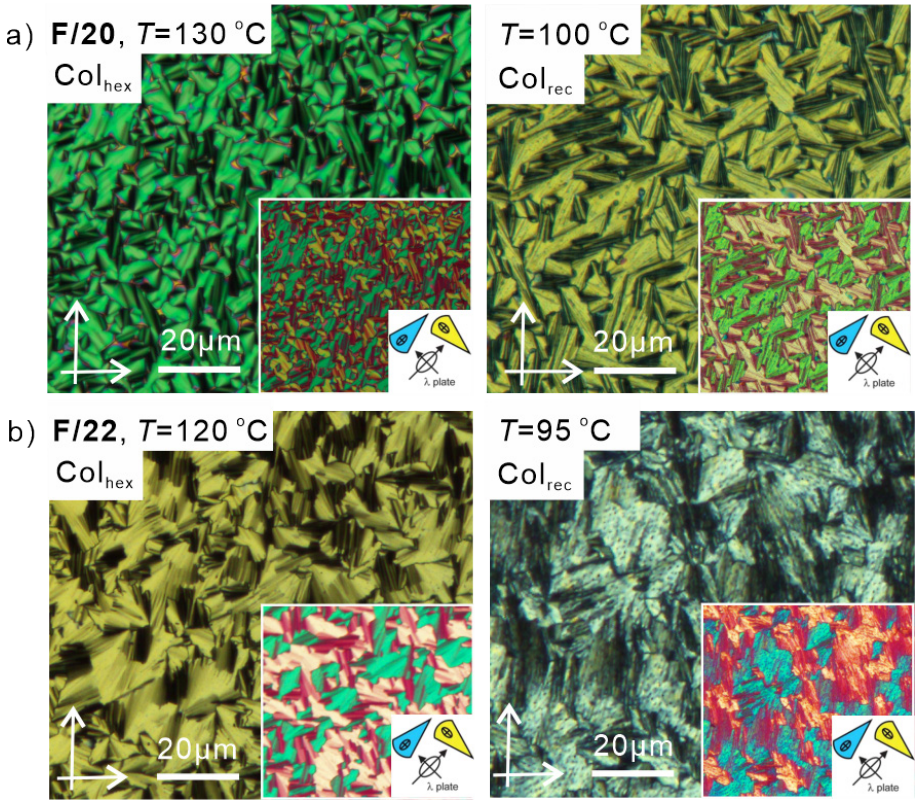


Figure S4. Representative textures of hexagonal and rectangular phases of compound (a) **F/20**; and (b) **F/22**; were obtained on cooling from an isotropic liquid. The inset figures show the texture with an additional λ-retarder plate. The orientations of the low and high index axes of the indicatrix are shown in the inset. A blue shift occurs in the main indicatrix direction when the orientation of the π-conjugation pathway is almost parallel to the high index axis of the retarder plate, whereas a yellow shift occurs when the π-conjugation pathway is perpendicular to the high index axis.

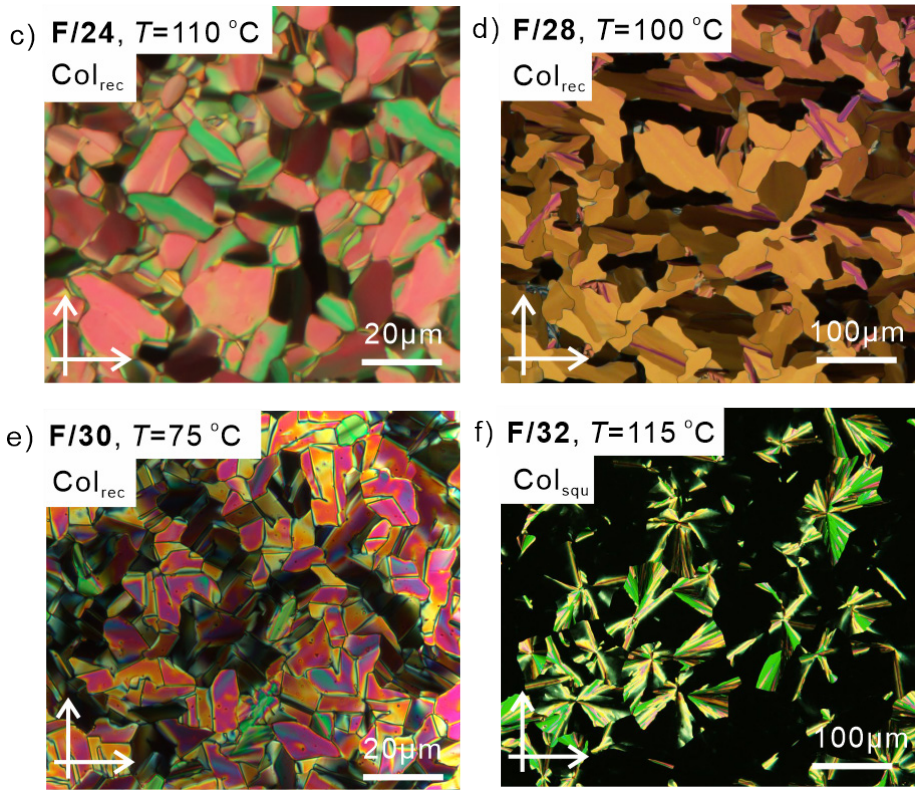


Figure S4 (continued). Selected textures of compounds (c) **F/24**; (d) **F/28**; (e) **F/30** and (f) **F/32** as observed between crossed polarizers.

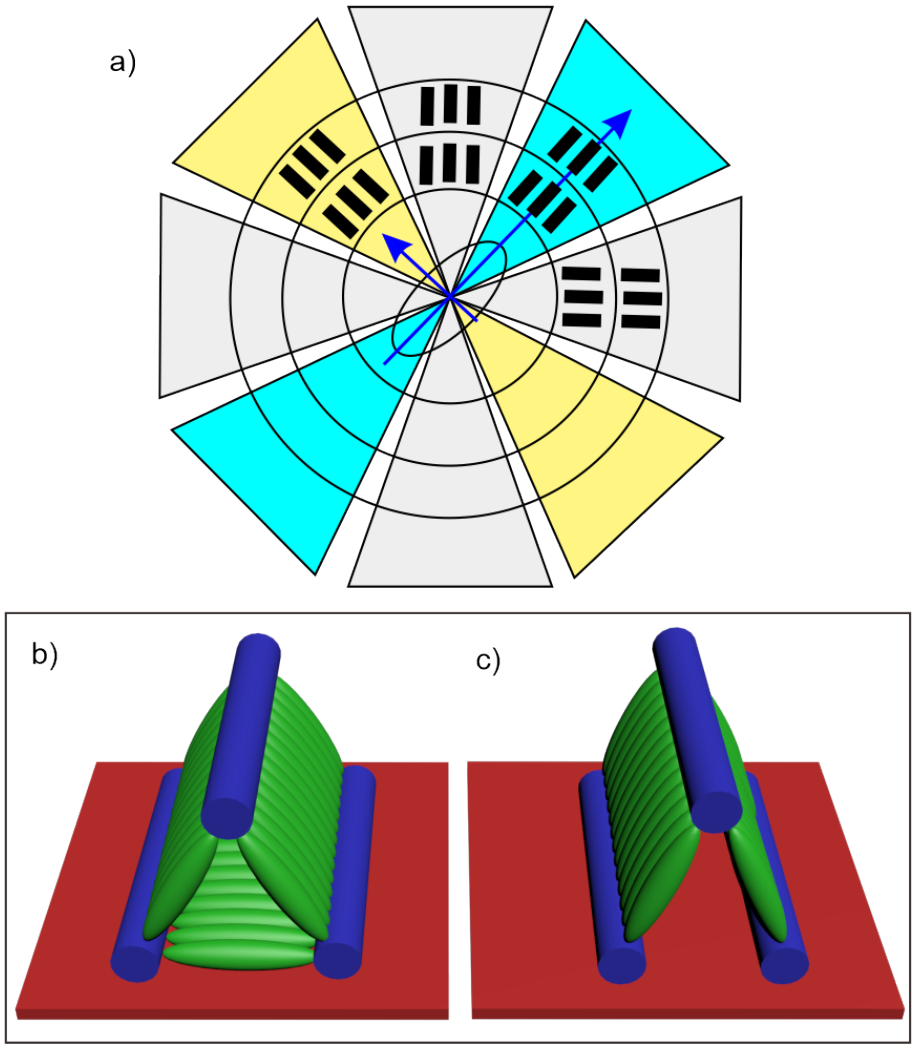


Figure S5. (a) Experiments with λ-retarder plate; the direction of polarizer and analyzer is horizontal and vertical, respectively, and the high index indicatrix axis is 45° SW to NE. The light beam is perpendicular to the substrate. In the honeycomb LC phases the orientation of the π-conjugated rods is usually perpendicular to the long axes of the prismatic cells (columns). If the molecules in the walls are non-tilted (with respect to the normal to the column long axis) the orientation of the π-conjugated aromatic cores is almost parallel to the high index axis of the retarder plate (indicatrix shown in blue), leading to a blue shift in the main indicatrix direction, thus indicating negative birefringence (major π-conjugation pathway is perpendicular to the column long axis). (b, c) The main alignments of the columnar phase including the triangular structure without the breaking of molecules (left) and with the breaking of molecules (right) is parallel to surface.

Investigation with a λ-retarder plate (Figure S4a, b) indicate that all columnar phases are optically negative, confirming the alignment of the π-conjugated cores on average perpendicular to the column long axis.

In optical investigations the transition from the triangular to the rhombic honeycomb is indicated by an emerging birefringence in homeotropic aligned areas of the uniaxial Col_{hex} phase (columns perpendicular to the substrates and parallel to the viewing direction) due to the emerging phase biaxiality. Simultaneously, in planar aligned areas with the columns parallel to the substrate surfaces the birefringence of the spherulitic texture significantly decreases at the Col_{hex}-Col_{rec} transition (yellow to gray, see Figure S4a, b), due to the removal of the walls separating pairs of triangles (Figure S5c). Obviously, the alignment of the rods in the remaining walls is preferentially with their long axes almost perpendicular to the surfaces (to achieve maximal density of the glycerol columns on the polar surfaces) and therefore the walls arranged parallel to the surfaces are removed (see Figure S13 for models). This preferred alignment becomes less dominant for compounds with longer alkyl chains having wider rhombus, and thus, for these compounds the jump in birefringence becomes smaller. Simultaneously, increased filling of the prismatic cells by longer alkyl chains enhances the stiffness of the honeycombs and therefore mosaic textures become dominant for the *c*2*mm* and *p*4*mm* phases of all compounds with longer chains (Figure S4 (**continued**)).

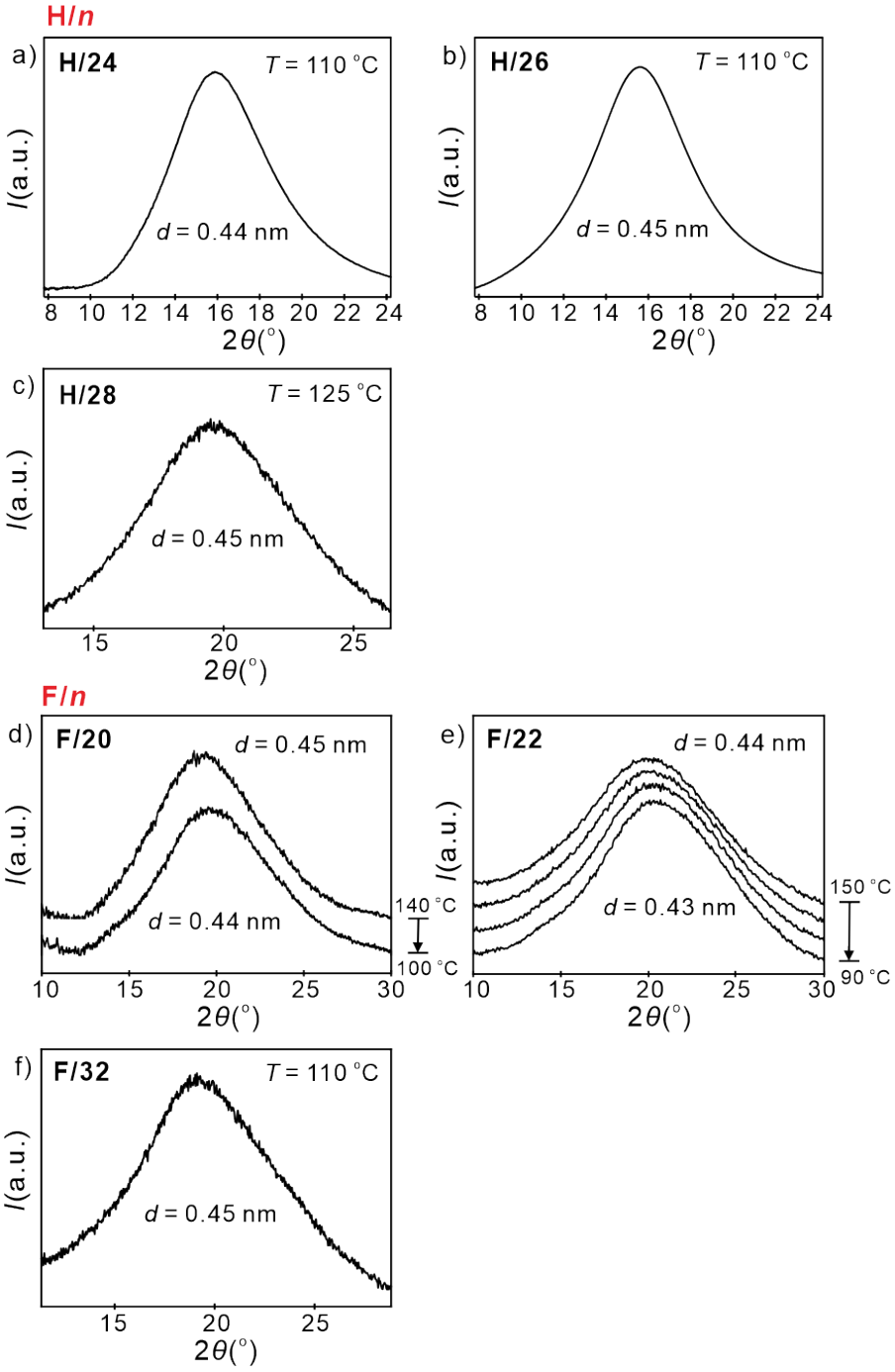


Figure S6. WAXS diffractograms of compound (a) **H/24**; (b) **H/26**; (c) **H/28**; (d) **F/20**; (e) **F/22**; and (f) **F/32**.

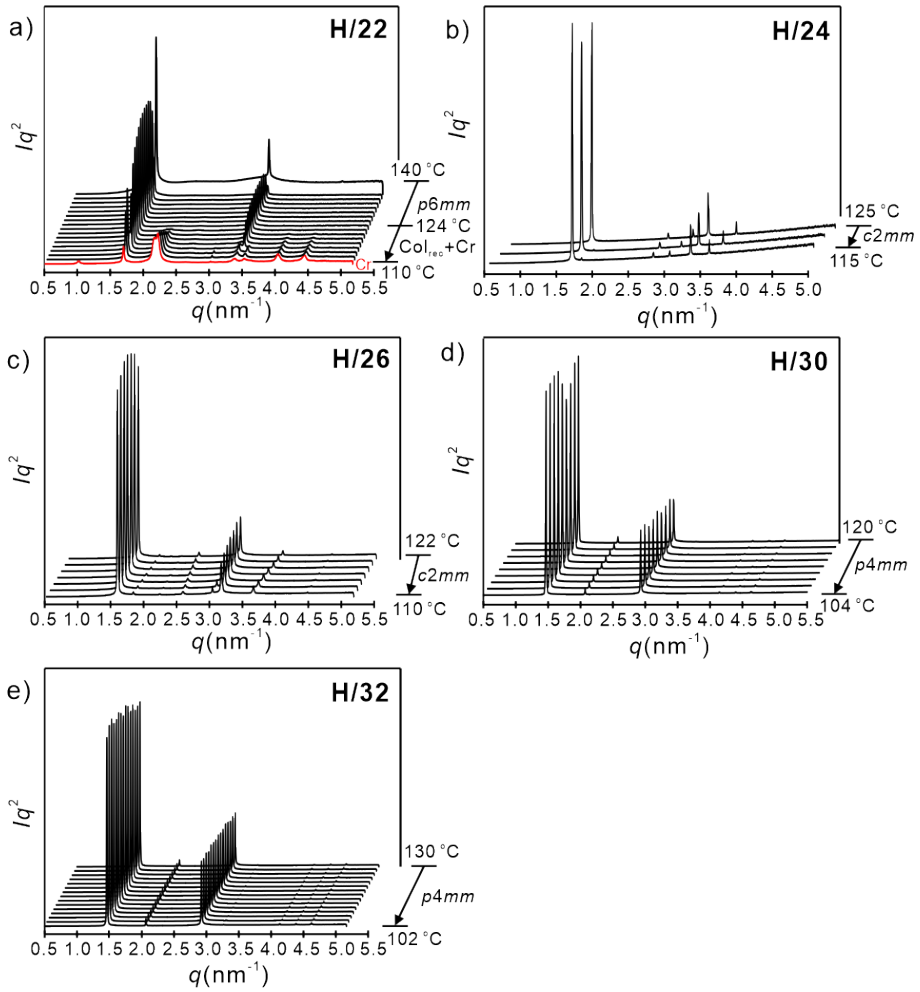


Figure S7. SAXS diffractograms of compound (continuous cooling) (a) **H/22**; (b) **H/24**; (c) **H/26**; (d) **H/30**; and (e) **H/32**.

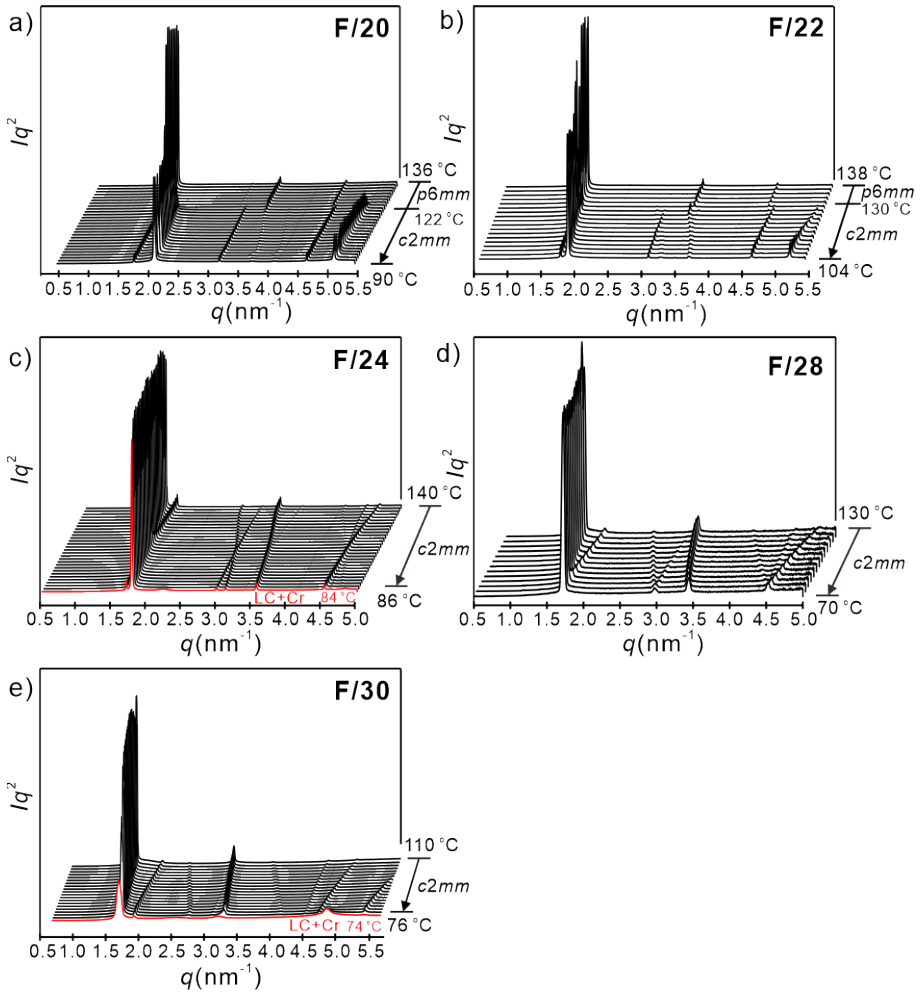


Figure S8. SAXS diffractograms of compound (continuous cooling) (a) **F/20**; (b) **F/22**; (c) **F/24**; (d) **F/28**; and (e) **F/30**.

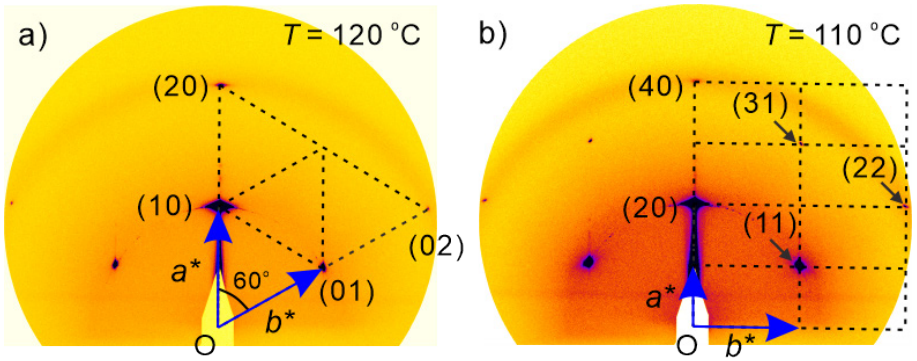


Figure S9. GISAXS patterns of (a) Col_{hex}/*p6mm* phase of **F/22** at T = 120 ºC; and (b) Col_{rec}/*c2mm* phase of **F/22** at T = 110 ºC.

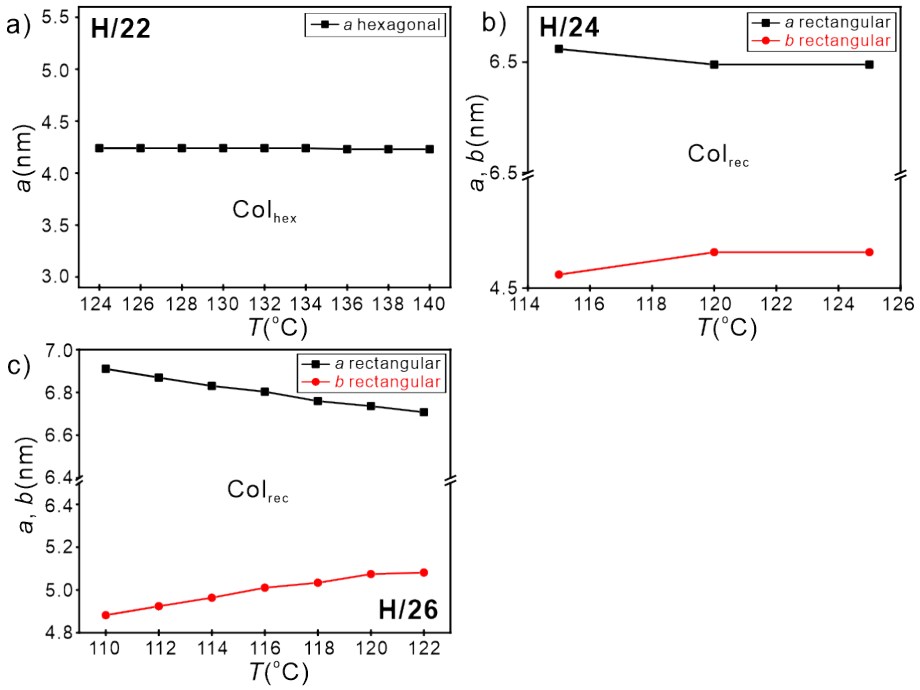


Figure S10. Temperature dependence of lattice parameters *a* and *b* for hexagonal and rectangular phases for compound (a) **H/22**; (b) **H/24**; and (c) **H/26**.

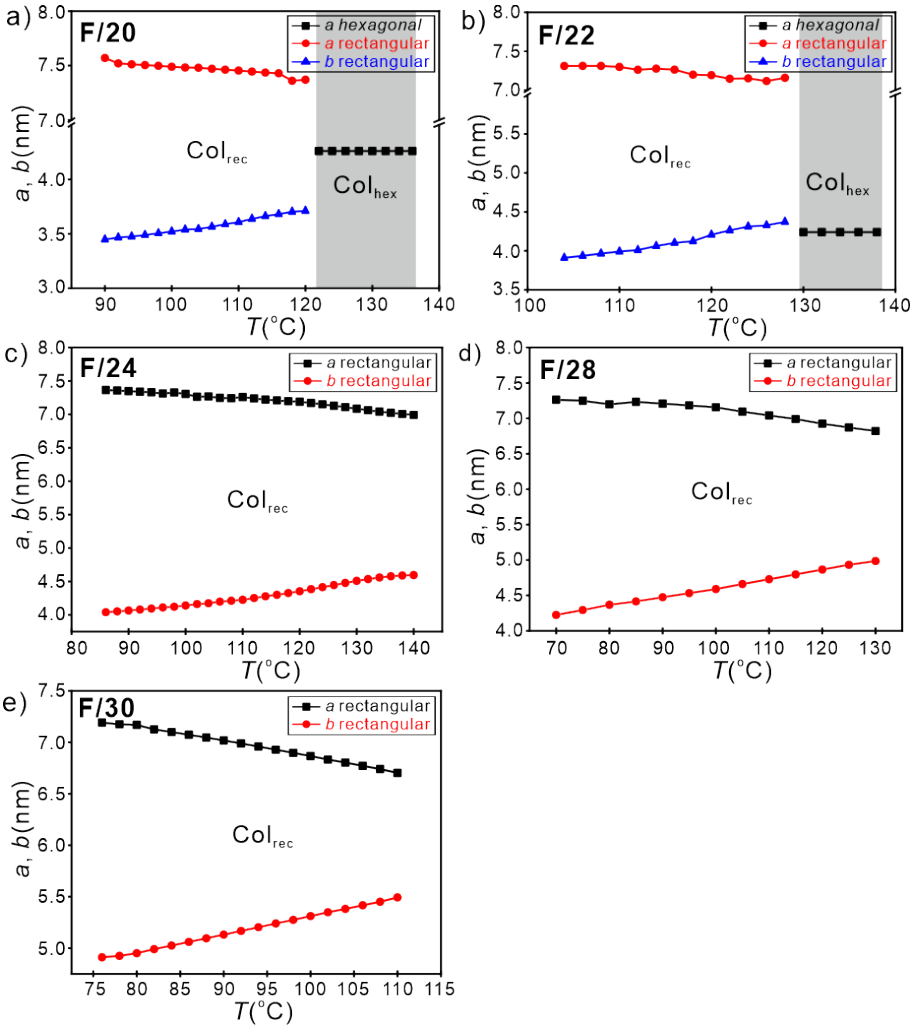


Figure S11. Temperature dependence of lattice parameters *a* and *b* for hexagonal and rectangular phases for compound (a) **F/20**; (b) **F/22**; (c) **F/24**; (d) **F/28**; and (e) **F/30**.

Table S2. Experimental and calculated *d*-spacing for the observed SAXS reflections of the Col_{hex}/*p6mm* phase of compound **H/22** at T = 132 ºC. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$ – *spacing* (nm)	$d_{cal.}$ – *spacing* (nm)	*Intensity*	*Phase*
(10)	3.67	3.67	100	0
(20)	1.83	1.84	29.8	0
(21)	1.38	1.39	0.20	π
a_{hex} = 4.26 nm				

Table S3. Experimental and calculated *d*-spacing for the observed SAXS reflections of the Col_{rec}/*c2mm* phase of compound **H/24** at T = 120 ºC. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$ – *spacing* (nm)	$d_{cal.}$ – *spacing* (nm)	*Intensity*	*Phase*
(11)	3.86	3.86	100	0
(20)	3.49	3.49	0.48	0
(02)	2.31	2.31	5.41	π
(31)	2.08	2.08	2.08	0
(22)	1.93	1.93	15.26	0
(40)	1.74	1.74	7.62	0
a_{rec} = 6.98 nm, b_{rec} = 4.63 nm				

Table S4. Experimental and calculated *d*-spacing for the observed SAXS reflections of the Col_{rec}/*c*2*mm* phase of compound **H/26** at T = 110 ºC. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$ – *spacing* (nm)	$d_{cal.}$ – *spacing* (nm)	*Intensity*	*Phase*
(11)	4.03	4.03	100	0
(20)	3.39	3.39	1.22	0
(02)	2.50	2.51	5.5	π
(31)	2.06	2.06	1.7	0
(22)	2.01	2.01	17.8	0
(40)	1.70	1.70	5.02	0
(42)	1.40	1.40	0.24	π
a_{rec} = 6.78 nm, b_{rec} = 5.01 nm				

Table S5. Experimental and calculated *d*-spacing for the observed SAXS reflections of the Col_{squ}/*p*4*mm* phase of compound **H/28** at T = 120 ºC. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$ – *spacing* (nm)	$d_{cal.}$ – *spacing* (nm)	*Intensity*	*Phase*
(10)	4.24	4.24	100	π
(11)	2.99	2.99	4.40	π
(20)	2.12	2.12	26.1	0
(21)	1.89	1.89	0.08	0
(22)	1.49	1.49	0.23	0
(30)	1.41	1.41	0.23	π
(31)	1.34	1.34	0.17	π
a_{squ} = 4.24 nm				

Table S6. Experimental and calculated *d*-spacing for the observed SAXS reflections of the $Col_{squ}/p4mm$ phase of compound **H/30** at $T = 112$ ºC. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$ – *spacing* (nm)	$d_{cal.}$ – *spacing* (nm)	*Intensity*	*Phase*
(10)	4.30	4.30	100	π
(11)	3.03	3.03	3.0	π
(20)	2.14	2.14	28.8	0
(21)	1.91	1.91	0.08	0
(22)	1.51	1.51	0.51	0
(30)	1.42	1.42	0.41	π
(31)	1.35	1.35	0.37	π
$a_{squ} = 4.29$ nm				

Table S7. Experimental and calculated *d*-spacing for the observed SAXS reflections of the $Col_{squ}/p4mm$ phase of compound **H/32** at $T = 120$ ºC. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$ – *spacing* (nm)	$d_{cal.}$ – *spacing* (nm)	*Intensity*	*Phase*
(10)	4.27	4.27	100	π
(11)	3.02	3.02	4.1	π
(20)	2.13	2.14	32.2	0
(21)	1.91	1.91	0.1	0
(22)	1.51	1.51	0.6	0
(30)	1.42	1.42	0.5	π
(31)	1.35	1.35	0.4	π
$a_{squ} = 4.27$ nm				

Table S8. Experimental and calculated *d*-spacing for the observed SAXS reflections of the Col_{hex}/*p6mm* phase of compound **F/20** at T = 130 °C. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$ – *spacing* (nm)	$d_{cal.}$ – *spacing* (nm)	*Intensity*	*Phase*
(10)	3.69	3.69	100	0
(11)	2.13	2.13	0.31	π
(20)	1.84	1.84	4.96	0
(21)	1.39	1.39	1.25	π
a_{hex} = 4.27 nm				

Table S9. Experimental and calculated *d*-spacing for the observed SAXS reflections of the Col_{rec}/*c2mm* phase of compound **F/20** at T = 110 °C. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$ – *spacing* (nm)	$d_{cal.}$ – *spacing* (nm)	*Intensity*	*Phase*
(20)	3.72	3.72	13.0	0
(11)	3.25	3.24	100	0
(31)	2.04	2.04	3.2	0
(40)	1.86	1.86	0.25	0
(02)	1.81	1.80	0.94	π
(22)	1.62	1.62	0.32	0
(51)	1.37	1.37	4.2	/
(60)	1.24	1.24	45.6	/
a_{rec} = 7.45 nm, b_{rec} = 3.61 nm				

Table S10. Experimental and calculated *d*-spacing for the observed SAXS reflections of the Col_{hex}/*p6mm* phase of compound **F/22** at T = 130 ºC. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$ – *spacing* (nm)	$d_{cal.}$ – *spacing* (nm)	*Intensity*	*Phase*
(10)	3.66	3.66	100	0
(20)	1.83	1.83	4.12	0
(21)	1.38	1.38	0.86	π
a_{hex} = 4.23 nm				

Table S11. Experimental and calculated *d*-spacing for the observed SAXS reflections of the Col_{rec}/*c2mm* phase of compound **F/22** at T = 110 ºC. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$ – *spacing* (nm)	$d_{cal.}$ – *spacing* (nm)	*Intensity*	*Phase*
(20)	3.67	3.67	12.0	0
(11)	3.52	3.52	100	0
(31)	2.08	2.08	2.28	0
(02)	2.01	2.01	1.19	π
(40)	1.83	1.83	0.45	0
(22)	1.75	1.75	1.28	0
(51)	1.37	1.37	3.56	/
(60)	1.22	1.22	14.7	/
a_{rec} = 7.34 nm, b_{rec} = 4.02 nm				

Table S12. Experimental and calculated *d*-spacing for the observed SAXS reflections of the $Col_{rec}/c2mm$ phase of compound **F/24** at T = 130 ºC. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$ – *spacing* (nm)	$d_{cal.}$ – *spacing* (nm)	*Intensity*	*Phase*
(11)	3.80	3.80	100	0
(20)	3.54	3.54	10.7	0
(02)	2.25	2.25	2.33	π
(31)	2.09	2.09	0.78	0
(22)	1.90	1.90	5.65	0
(40)	1.77	1.77	0.44	0
(13)	1.47	1.47	0.38	/
(42)	1.39	1.39	0.61	/
(51)	1.35	1.35	1.89	/
a_{rec} = 7.08 nm, b_{rec} = 4.51 nm				

Table S13. Experimental and calculated *d*-spacing for the observed SAXS reflections of the $Col_{rec}/c2mm$ phase of compound **F/28** at T = 110 ºC. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$ – *spacing* (nm)	$d_{cal.}$ – *spacing* (nm)	*Intensity*	*Phase*
(11)	3.92	3.92	100	0
(20)	3.52	3.52	4.56	0
(02)	2.36	2.36	2.93	π
(31)	2.10	2.10	0.56	0
(22)	1.96	1.96	10.5	0
(13)	1.54	1.54	0.80	0
(42)	1.41	1.41	0.62	/
(51)	1.34	1.34	1.82	/
a_{rec} = 7.04 nm, b_{rec} = 4.73 nm				

Table S14. Experimental and calculated *d*-spacing for the observed SAXS reflections of the $Col_{rec}/c2mm$ phase of compound **F/30** at T = 76 °C. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$ – *spacing* (nm)	$d_{cal.}$ – *spacing* (nm)	*Intensity*	*Phase*
(11)	4.07	4.07	100	0
(20)	3.61	3.61	6.87	0
(02)	2.47	2.47	2.21	π
(31)	2.16	2.16	0.88	0
(22)	2.03	2.03	8.29	0
(13)	1.60	1.60	0.55	0
(42)	1.45	1.45	0.39	/
(51)	1.38	1.38	1.41	/
a_{rec} = 7.22 nm, b_{rec} = 4.94 nm				

Table S15. Experimental and calculated *d*-spacing for the observed SAXS reflections of the $Col_{squ}/p4mm$ phase of compound **F/32** at T = 120 °C. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$ – *spacing* (nm)	$d_{cal.}$ – *spacing* (nm)	*Intensity*	*Phase*
(10)	4.24	4.24	100	π
(11)	2.99	2.99	0.03	π
(20)	2.11	2.12	17.5	0
(21)	1.89	1.89	0.11	0
(30)	1.41	1.41	0.35	π
(31)	1.33	1.33	0.53	π
a_{squ} = 4.24 nm				

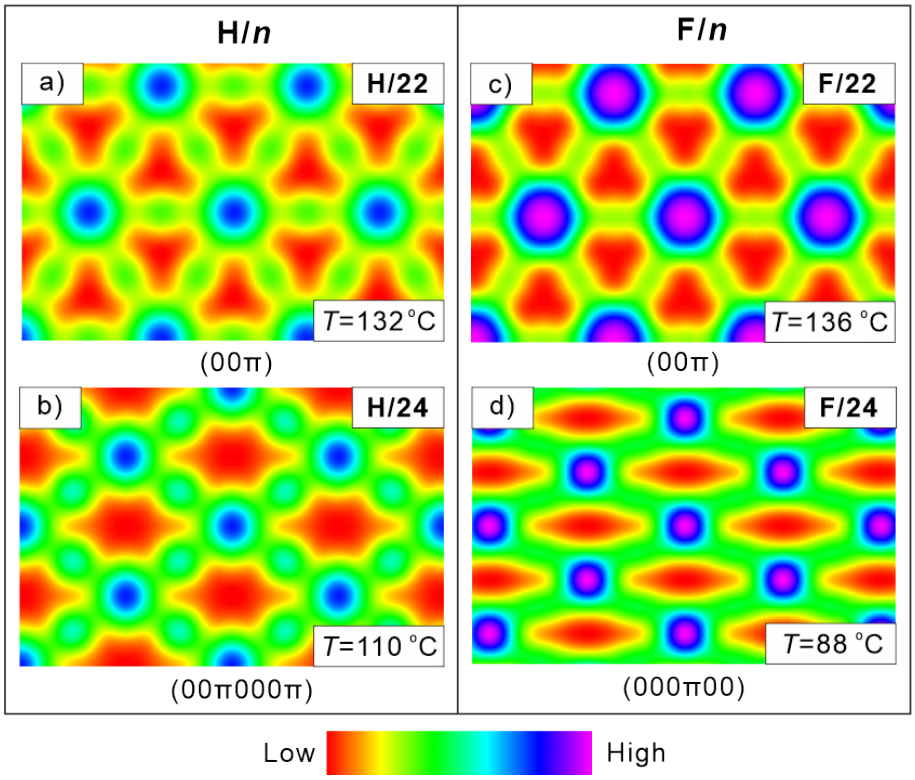


Figure S12. Reconstructed ED maps of the non-fluorinated compounds **H/*n***. (a) Col_{hex} phase of **H/22**; (b) Col_{rec} phase of **H/24** and fluorinated compounds **F/*n***. (c) Col_{hex} phase of **F/22**; (d) Col_{rec} phase of **F/24**.

3. Structural Data and Models

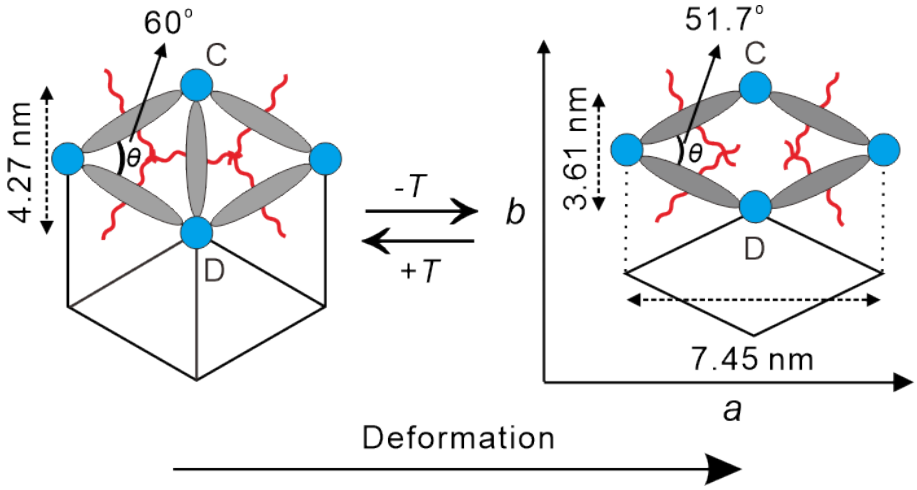


Figure S13. Model shows the possible deformation of the hexagonal lattice to the $Col_{rec}/c2mm$ mesophase at a lower temperature (T = 110 °C) of compound **F/20**; or Model shows the reduction in the area of rhombus during the phase transition from Col_{hex} to Col_{rec} phase.

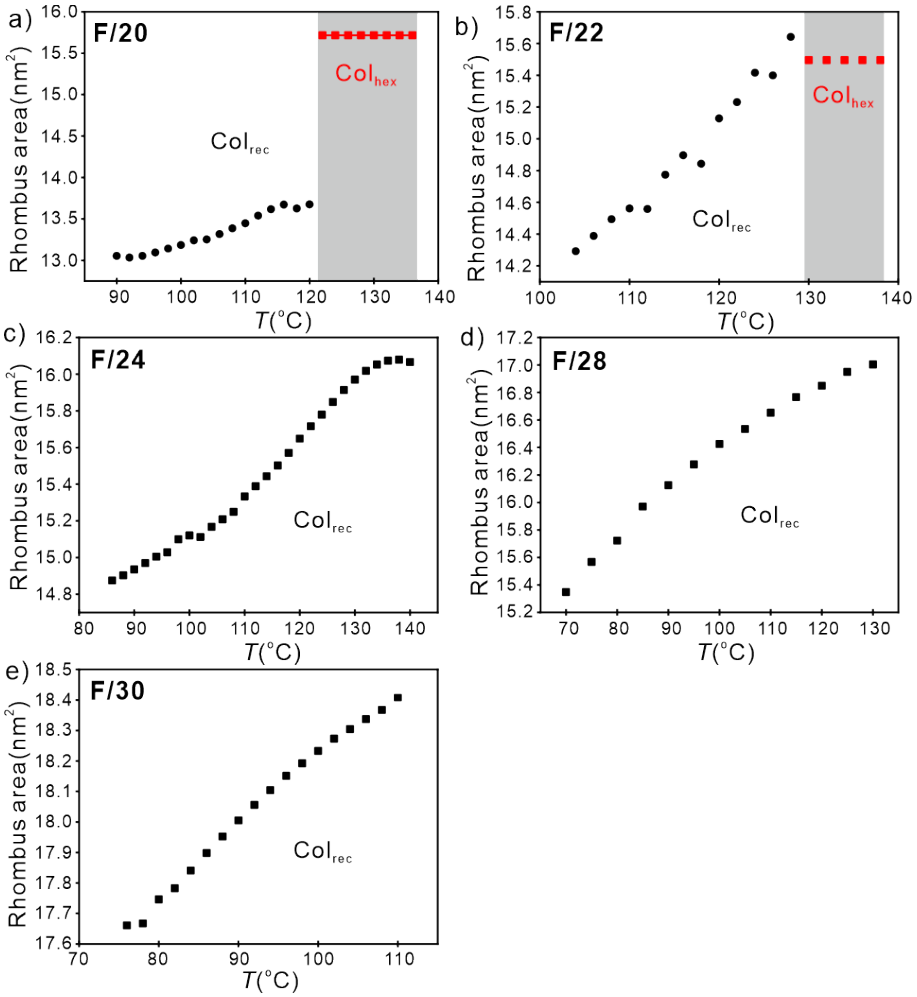
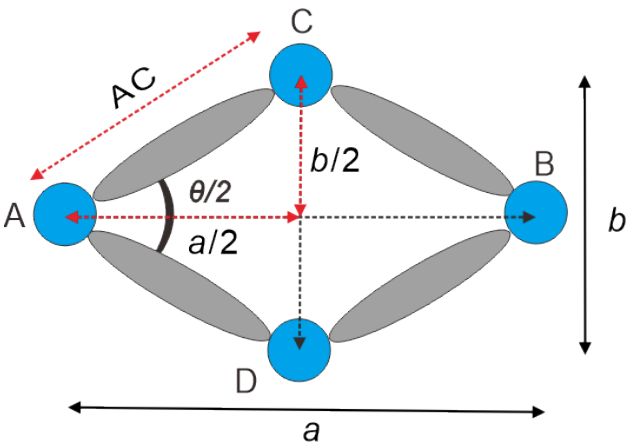


Figure S14. Temperature-dependent rhombus area of hexagonal (formed by the convergence of two adjacent triangles) and rhombus in rectangular phases of compounds (continuous cooling) (a) **F/20**; (b) **F/22;** (c) **F/24**; (d) **F/28**; and (e) **F/30**.



$\frac{(A)^{1/2}}{C}$ = 0.23-0.24

Area of the rhombus = $\frac{(a \times b)}{2}$

Circumference of rhombus = 4×AC

Inner angle = 48.98°-78.99°

$\tan(\theta/2) = \frac{b/2}{a/2}$

$\theta = 2 \times \tan^{-1}(b/a)$

Figure S15. Calculation of the $\frac{\sqrt{A}}{C}$ and inner angle (θ) of Col_{rec} phase (or for rhombus lattice).

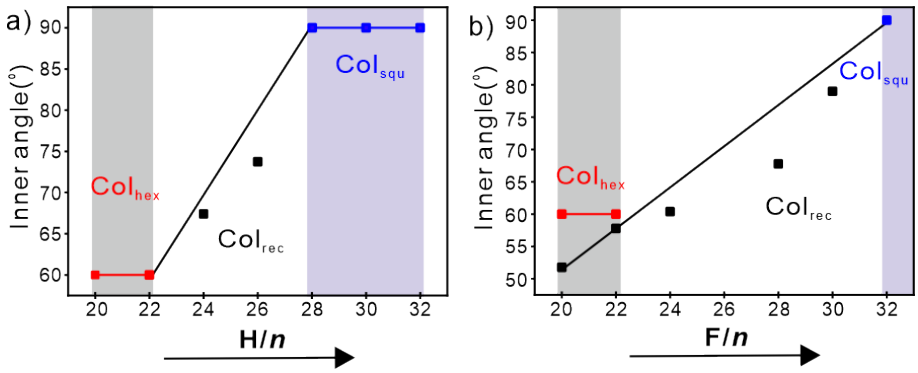


Figure S16. Plot of chain length dependence of inner angle of rhombus cell of series (a) **H/*n*** (**H/20** at T = 135 °C; **H/22** at T = 132 °C; **H/24** at T = 120 °C; **H/26** at T = 120 °C; **H/28** at T = 120 °C, **H/30** at T = 120 °C; and **H/32** at T = 120 °C) and (b) **F/*n*** (**F/20** at T = 130 °C and 110 °C; **F/22** at T = 130 °C and 110 °C; **F/24** at T = 110 °C; **F/28** at T = 110 °C; **F/30** at T = 110 °C; and **F/32** at T = 120 °C).

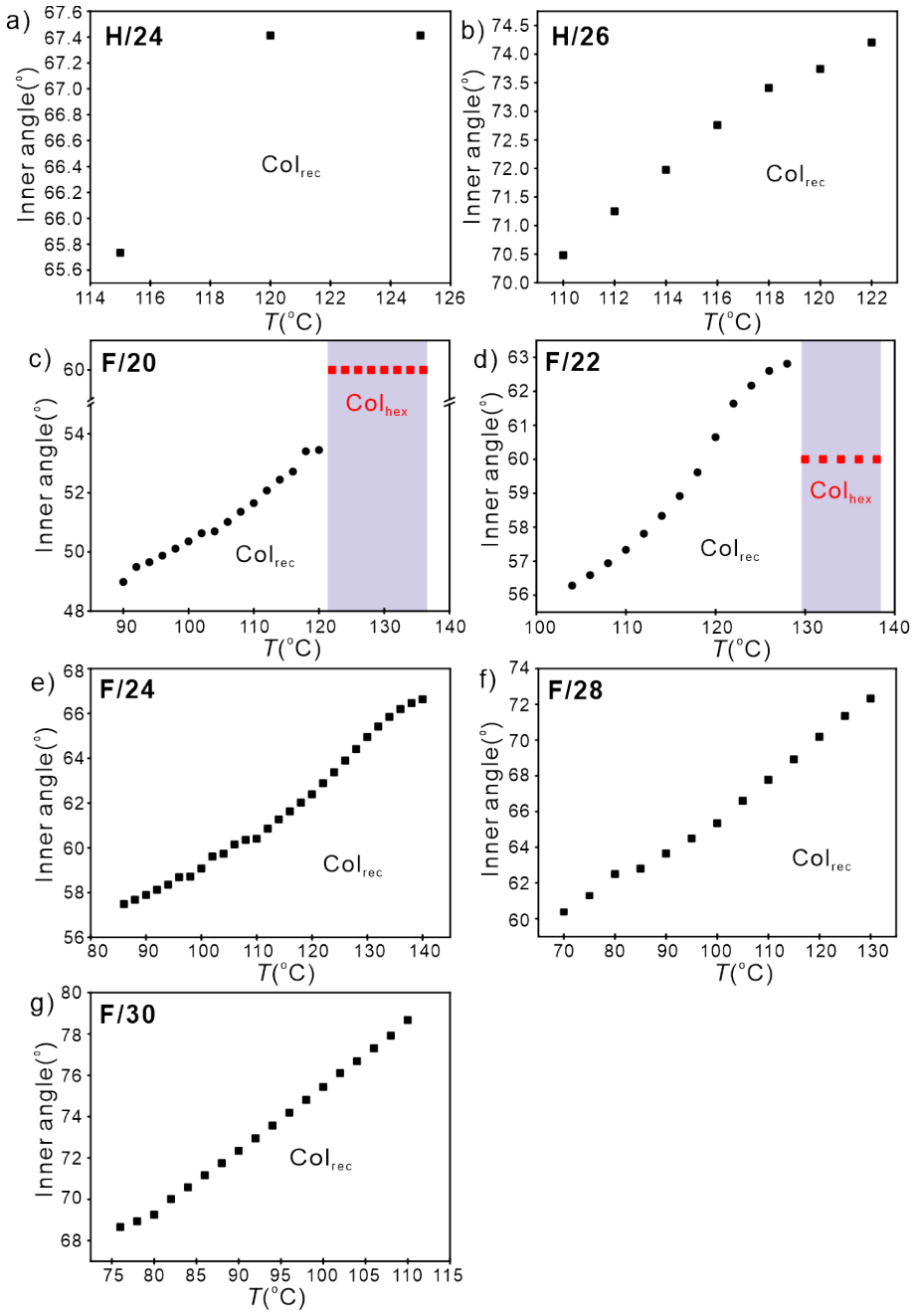


Figure S17. Temperature-dependent inner angle of hexagonal and rectangular phases of compounds (continuous cooling) (a) **H/24**; (b) **H/26**; (c) **F/20**; (d) **F/22**; (e) **F/24**; (f) **F/28**; and (g) **F/30.**

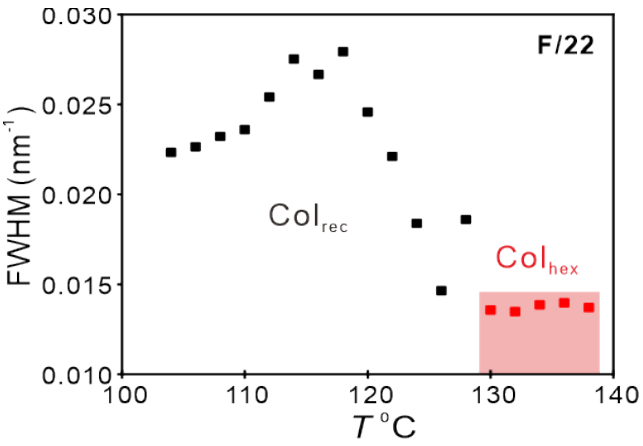


Figure S18. Temperature-dependent FWHM for the hexagonal and rectangular phases of compound **F/22** on cooling.

Table S16. Structural data of the $Col_{hex}/p6mm$, $Col_{squ}/p4mm$ and $Col_{rec}/c2mm$ LC-phases of compounds **H/*n*** and **F/*n***.[a]

Comp.	Phase transition (T/°C)	Lattice parameters (nm)	$V_{mol, crys}$ (nm^3)	V_{cell} (nm^3)	$V_{mol, LC}$ (nm^3)	n_{cell}	n_{wall}	Inner angle (θ/°)
H/20	135 °C ($Col_{hex}/p6mm$)	a_{hex} = 4.24	1.86	7.01	2.11	3.4	1.1	60
H/22	132 °C ($Col_{hex}/p6mm$)	a_{hex} = 4.26	1.96	7.07	2.22	3.2	1.1	60
H/24	120 °C ($Col_{rec}/c2mm$)	a_{rec} = 6.98, b_{rec} = 4.63	2.06	14.5	2.34	6.3	1.6	67.1
H/26	110 °C ($Col_{rec}/c2mm$)	a_{rec} = 6.78, b_{rec} = 5.01	2.16	15.29	2.45	6.3	1.5	70.5
H/28	120 °C ($Col_{squ}/p4mm$)	a_{squ} = 4.24	2.26	8.08	2.56	3.2	1.6	90
H/30	112 °C ($Col_{squ}/p4mm$)	a_{squ} = 4.29	2.36	8.28	2.57	3.1	1.5	90
H/32	120 °C ($Col_{squ}/p4mm$)	a_{squ} = 4.27	2.46	8.20	2.80	2.9	1.5	90
F/20	130 °C ($Col_{hex}/p6mm$) 110 °C ($Col_{rec}/c2mm$)	a_{hex} = 4.27 a_{rec} = 7.45, b_{rec} = 3.61	1.91	7.10 12.10	2.17	3.3 5.7	1.1 1.4	60 51.7
F/22	130 °C ($Col_{hex}/p6mm$) 110 °C ($Col_{rec}/c2mm$)	a_{hex} = 4.23 a_{rec} = 7.34, b_{rec} = 4.02	2.01	6.97 13.28	2.28	3.1 5.9	1.0 1.5	60 57.8
F/24	130 °C ($Col_{rec}/c2mm$) 110 °C ($Col_{rec}/c2mm$)	a_{rec} = 7.08, b_{rec} = 4.51 a_{rec} = 7.26, b_{rec} = 4.22	2.11	14.4 13.8	2.40	6.1 5.8	1.5 1.4	64.9 60.4
F/28	130 °C ($Col_{rec}/c2mm$) 110 °C ($Col_{rec}/c2mm$)	a_{rec} = 6.82, b_{rec} = 4.98 a_{rec} = 7.04, b_{rec} = 4.73	2.31	15.28 14.98	2.62	5.9 5.8	1.5 1.4	72.3 67.7
F/30	76 °C ($Col_{rec}/c2mm$)	a_{rec} = 7.22, b_{rec} = 4.94	2.41	16.05	2.73	5.9	1.5	68.8
F/32	120 °C ($Col_{squ}/p4mm$)	a_{squ} = 4.24	2.51	8.08	2.85	2.87	1.4	90

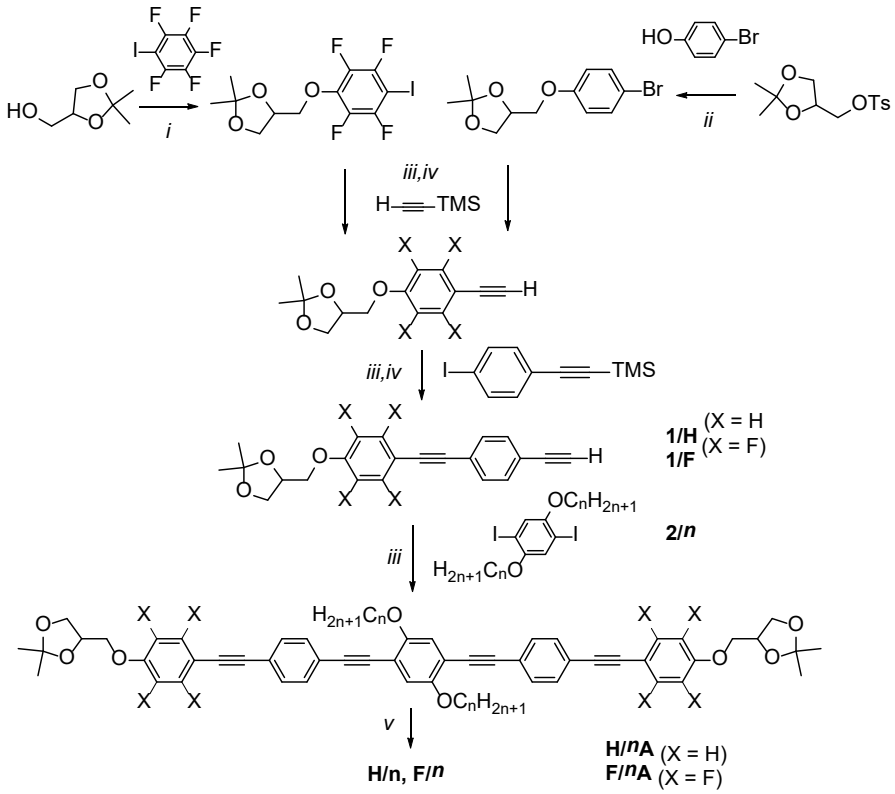
[a] V_{cell} = volume of the unit cell defined by $3^{½}a_{hex}^2/2 \times h$ for hexagonal, $a_{rec} \cdot b_{rec} \cdot h$ for rectangular and $a_{squ}^2 \times h$ for square with h = 0.45 nm corresponding to the maximum of the diffuse wide angle scattering; $V_{mol,cr}$ = volume for a single molecule as calculated using the crystal volume increments;[S2] $V_{mol,LC}$ = volume for a single molecule in the LC-state (average packing coefficient in the crystal) is assumed to be k = 0.7,[S3] independent on the LC phase type; although a slightly denser packing in the Col_{rec} phase is likely, this difference is assumed to be small; $V_{mol,liq}$ = volume for a single molecule in the isotropic liquid with an average packing coefficient k = 0.55, calculated according to $V_{mol,liq}$ =

0.7/0.55 × $V_{cell,cr}$, $V_{cell,LC}$ = in the LC phase estimated as the average of $V_{mol,cr}$ and $V_{mol,liq}$), $n_{cell,LC}$ = number of molecules in the unit cell in LC state, calculated according to n_{wall} = number of molecules in the lateral cross section of the cylinder walls. The number of about 1.1-1.6 means that on average 1.1-1.6 molecules are laterally arranged in each hypothetical segment with h = 0.45 nm, i.e. there is a lateral staggering of the molecules in the cylinder walls or the packing of the aromatic cores is a bit closer than the assumed distance of 0.45 nm. θ = Inner angle of rhombic lattice.

4. Synthesis and analytical data

4.1 General

The general synthesis pathway and the assignment of the compound numbers are given in Scheme S1. The compounds were synthesized from *rac*-1,2-*O*-isopropylideneglycerol and therefore all compounds **H/*n*** and **F/*n*** represent racemic mixtures of diastereomers. 3-[4-(4-Ethynylphenylethynyl)-2,3,5,6-tetrafluorophenyl]-1,2-*O*-isopropylidenepropane-1,2-diol (**1/F**) was synthesized according to the procedures described in the given reference.[S4] The long chain 1-bromoalkanes were synthesized according to the procedures given in references.[S5] The 2,5-diiodo-1,4-dialkoxybenzenes **2/*n*** were synthesized according to the procedures given in references.[S6,S7] The synthesis of the non-fluorinated compound **1/H** has been described in reference.[S6]



Scheme S1. Synthesis of compounds **H/*n*** and **F/*n***; reagents and conditions: i) K_2CO_3, DMF, 60 °C, 24 h, 85%, ii) K_2CO_3, DMF, TBAI, 120 °C, 3 d, 40 °C, 70%, iii) $[Pd(PPh_3)_4]$, CuI, NEt_3, reflux, 6 h, 60 – 95%, iv) K_2CO_3, CH_2Cl_2/MeOH, (2:1), 20 °C, 2 h, 60 – 95%; i) PPTS, MeOH/THF (1:1), 50 °C, 12 h, 40 – 60%.

The purity of all compounds 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 CaH_2 and stored over molecular sieve.

^{1}H-, ^{13}C-NMR spectra (Varian Unity 500 and Varian Unity 400 spectrometers) were recorded in $CDCl_3$ 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 LiCl.

4.2 Synthesis of 1,4-dialkoxy-2,5-diiodobenzenes (2/*n*)

P1: Etherification[S7]: A mixture of 2,6-diiodohydroquinon (1 equ.), *n*-bromoalkane (2.5 equ.), K_2CO_3 (5 equ.) and Bu_4NI (tip of a spatula) in anhydrous DMF (25 mL/~5 mmol dihalobenzene) 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_2O (3x50 mL). The combined organic layers were washed with saturated aqu. LiCl, water and brine. After drying over anhydrous Na_2SO_4, filtration and evaporation of the solvent, the crude product was purified by column chromatography.

1,4-Dieicosyloxy-2,5-diiodobenzene (2/20): Synthesized according to **P1** from 2,6-diiodohydroquinon (1.0 g, 2.80 mmol), 1-bromoeicosane (2.2 g, 6.10 mmol), K_2CO_3 (3.9 g, 28.0 mmol), Bu_4NI (10 mg, 0.03 mmol) in DMF (50 mL); purification by column chromatography (eluent: *n*-hexane), colourless solid, $C_{46}H_{84}I_2O_2$, M = 922.97 g/mol, yield: 800 mg (31%), mp. 82 °C, **^{1}H-NMR** ($CDCl_3$, 400 MHz): δ / ppm = 7.17 (s, 2H, Aryl-*H*), 3.92 (t, $^3J_{H,H}$ = 6.4 Hz, 4H, OC*H*$_2$), 1.58 – 1.18 (m, 72H, C*H*$_2$), 0.88 (t, $^3J_{H,H}$ = 6.8 Hz, 6H, C*H*$_3$).

1,4-Didocosyloxy-2,5-diiodobenzene (2/22): Synthesized according to **P1** from 2,6-diiodohydroquinon (2.0 g, 5.52 mmol), 1-bromodocosane (12.6 g, 31.22 mmol), K_2CO_3 (7.6 g, 55.20 mmol), Bu_4NI (10 mg, 0.03 mmol) in DMF (50 mL); purification by column chromatography (eluent: *n*-hexane), colourless solid, $C_{50}H_{92}I_2O_2$, M = 979.09 g/mol, yield: 2.2 mg (41%), mp. 53 °C, **^{1}H-NMR** ($CDCl_3$, 500 MHz): δ / ppm = 7.17 (s, 2H, Aryl-*H*), 3.92 (t, $^3J_{H,H}$ = 6.4 Hz, 4H, OC*H*$_2$), 1.82 – 1.76 (m, 4H, C*H*$_2$), 1.52 – 1.27 (m, 76H, C*H*$_2$), 0.88 (t, $^3J_{H,H}$ = 6.8 Hz, 6H, C*H*$_3$).

1,4-Ditetracosyloxy-2,5-diiodobenzene (2/24): Synthesized according to **P1** from 2,6-diiodohydroquinon (0.14 g, 0.38 mmol), 1-bromotetracosane[S5] (0.35 g, 0.84 mmol), K_2CO_3 (0.5 g, 3.80 mmol), Bu_4NI (10 mg, 0.03 mmol) in DMF (50 mL); purification by column chromatography (eluent: *n*-hexane), colourless solid, $C_{54}H_{100}I_2O_2$, M = 1035.18 g/mol, yield: 240 mg (61%), mp. 89 °C, **^{1}H-NMR** ($CDCl_3$, 400 MHz): δ / ppm = 7.17 (s, 2H, Aryl-*H*), 3.92 (t, $^3J_{H,H}$ = 6.4 Hz, 4H, OC*H*$_2$), 1.42 – 1.15 (m, 88H, C*H*$_2$), 0.88 (t, $^3J_{H,H}$ = 6.8 Hz, 6H, C*H*$_3$).

1,4-Dihexacosyloxy-2,5-diiodobenzene (2/26): Synthesized according to **P1** from 2,6-diiodohydroquinon (0.2 g, 0.56 mmol), 1-bromohexacosane[S5] (0.50 g, 1.12 mmol), K_2CO_3 (0.8 g, 5.60 mmol), Bu_4NI (10 mg, 0.03 mmol) in DMF (50 mL); purification by column chromatography (eluent: *n*-hexane), colourless solid, $C_{58}H_{108}I_2O_2$, M = 1091.29 g/mol, yield: 0.14 g (23%), mp. 55 °C, **^{1}H-NMR** ($CDCl_3$, 400 MHz): δ / ppm = 7.17 (s, 2H, Aryl-*H*), 3.92 (t, $^3J_{H,H}$ = 6.4 Hz, 4H, OC*H*$_2$), 1.57 – 1.19 (m, 96H, C*H*$_2$), 0.88 (t, $^3J_{H,H}$ = 6.8 Hz, 6H, C*H*$_3$).

1,4-Dioctacosyloxy-2,5-diiodobenzene (2/28): Synthesized according to **P1** from 2,6-diiodohydroquinon (1.0 g, 2.77 mmol), 1-bromooctacosane[S5] (2.9 g, 6.09 mmol), K_2CO_3 (3.8 g, 27.70 mmol), Bu_4NI (10 mg, 0.03 mmol) in DMF (50 mL); purification by column chromatography (eluent: *n*-hexane), colourless solid, $C_{62}H_{116}I_2O_2$, M = 1147.42 g/mol,

yield: 0.16 g (5%), mp. 61 °C, **^{1}H-NMR** ($CDCl_3$, 400 MHz): δ / ppm = 7.17 (s, 2H, Aryl-*H*), 3.91 (t, $^3J_{H,H}$ = 6.5 Hz, 4H, OC*H*$_2$), 1.57 – 1.19 (m, 104H, C*H*$_2$), 0.88 (t, $^3J_{H,H}$ = 6.8 Hz, 6H, C*H*$_3$).

1,4-Ditriacontyloxy-2,5-diiodobenzene (2/30): Synthesized according to **P1** from 2,6-diiodohydroquinon (1.0 g, 2.76 mmol), 1-bromotriacontane[S5] (2.8 g, 5.52 mmol), K_2CO_3 (7.6 g, 55.20 mmol), Bu_4NI (10 mg, 0.03 mmol) in DMF (50 mL); purification by column chromatography (eluent: *n*-hexane), colourless solid, $C_{66}H_{124}I_2O_2$, M = 1203.50 g/mol, yield: 0.35 g (11%), mp. 77 °C, **^{1}H-NMR** ($CDCl_3$, 500 MHz): δ / ppm = 7.17 (s, 2H, Aryl-*H*), 3.92 (t, $^3J_{H,H}$ = 6.4 Hz, 4H, OC*H*$_2$), 1.83 – 1.76 (m, 4H, C*H*$_2$), 1.54 – 1.44 (m, 4H, C*H*$_2$), 1.39 – 1.21 (m, 104H, C*H*$_2$), 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, C*H*$_3$).

1,4-Didotriacontyloxy-2,5-diiodobenzene (2/32): Synthesized according to **P1** from 2,6-diiodohydroquinon (0.1 g, 0.26 mmol), 1-bromodotriacontane[S5] (0.3 g, 0.53 mmol), K_2CO_3 (0.4 g, 2.64 mmol), Bu_4NI (10 mg, 0.03 mmol) in DMF (50 mL); purification by column chromatography (eluent: *n*-hexane), colourless solid, $C_{70}H_{132}I_2O_2$, M = 1259.54 g/mol, yield: 0.1 g (30%), mp. 71 °C, **^{1}H-NMR** ($CDCl_3$, 400 MHz): δ / ppm = 7.17 (s, 2H, Aryl-*H*), 3.92 (t, $^3J_{H,H}$ = 6.4 Hz, 4H, OC*H*$_2$), 1.42 – 1.15 (m, 120H, C*H*$_2$), 0.88 (t, $^3J_{H,H}$ = 6.8 Hz, 6H, C*H*$_3$).

4.3 Synthesis of the acetonides H/*n*A and F/*n*A

P2. Sonogashira cross coupling[S6]**:** A mixture of 1,4-dialkoxy-2,5-diiodobenzene **2/*n*** (1 equ.) and the appropriate acetylene **1/H** or **1/F** (2.1 equ.) was dissolved in purified Et_3N (50 mL/~5 mmol **2/*n***). After degassing with argon for 30 min [$Pd(PPh_3)_4$] (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-Dieicosyloxy-2,5-bis{4-[4-(2,3-isopropylidene-2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (H/20A): Synthesized according to **P2** from **2/20** (200 mg, 0.22 mmol), **1/H** (144 mg, 0.43 mmol), [$Pd(PPh_3)_4$] (7.5 mg, 0.006 mmol), CuI (0.8 mg, 0.004 mmol) in NEt_3 (50 mL); purification by column chromatography (eluent: $CHCl_3$). Yellow solid, $C_{90}H_{122}O_8$, M = 1331.93 g/mol, yield: 150 mg (52%), mp. 148 °C, **^{1}H-NMR** ($CDCl_3$, 400 MHz): δ / ppm = 7.53 – 7.43 (m, 12H, Aryl-*H*), 7.01 (s, 2H, Aryl-*H*), 6.93 – 6.87 (m, 4H, Ar-*H*), 4.52 – 4.46 (m, 2H, -OC*H*$_2$-), 4.18 (dd, $^3J_{H,H}$ = 8.5 Hz, $^3J_{H,H}$ = 6.4 Hz, 2H, -OC*H*$_2$-), 3.95 – 3.89 (m, 10H, -OC*H*$_2$-), 1.88 – 1.82 (m, 4H, -C*H*$_2$-), 1.47 (s, 6H, -C*H*$_3$), 1.41 (s, 6H, -C*H*$_3$), 1.38 – 1.18 (m, 74H, -C*H*$_2$-), 0.88 (t, $^3J_{H,H}$ = 6.8 Hz, 6H, -C*H*$_3$).

1,4-Didocosyloxy-2,5-bis{4-[4-(2,3-isopropylidene-2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (H22/A): Synthesized according to **P2** from **2/22** (196 mg, 0.20 mmol), **1/H** (139 mg, 0.42 mmol), [$Pd(PPh_3)_4$] (6.9 mg, 0.006 mmol), CuI (0.8 mg, 0.004 mmol) in NEt_3 (50 mL); purification by column chromatography (eluent: $CHCl_3$). Yellow solid, $C_{94}H_{130}O_8$, M = 1386.98 g/mol, yield: 240 mg (87%), mp. 146 °C, **^{1}H-NMR** ($CDCl_3$, 400 MHz): δ / ppm = 7.51 – 7.43 (m, 12H, Ar–*H*), 7.01 (s, 2H, Ar–*H*), 6.93 – 6.87 (m, 4H, Ar–*H*), 4.53 – 4.44 (m, 2H, –OC*H*–), 4.18 (dd, $^3J_{H,H}$ = 8.4 Hz, $^3J_{H,H}$ = 6.4 Hz, 2H, –OC*H*$_2$–), 4.12 – 4.01 (m, 4H, –OC*H*$_2$–), 4.01 – 3.87 (m, 6H, –OC*H*$_2$–), 1.91 – 1.80 (m, 4H, –C*H*$_2$–), 1.65 – 1.16 (m, 88H, –C*H*$_2$–, –C*H*$_3$), 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, –C*H*$_3$).

1,4-Ditetracosyloxy-2,5-bis{4-[4-(2,3-isopropylidene-2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (H/24A): Synthesized according to **P2** from **2/24** (143 mg, 0.14 mmol), **1/H** (97 mg, 0.29 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, $C_{98}H_{138}O_8$, M = 1443.04 g/mol, yield: 180 mg (89%), mp. 122 °C, **^{1}H-NMR** ($CDCl_3$, 400 MHz): δ / ppm = 7.51 – 7.44 (m, 12H, Ar–*H*), 7.01 (s, 2H, Ar–*H*), 6.93 – 6.86 (m, 4H, Ar–*H*), 4.53 – 4.45 (m, 2H, –OC*H*–), 4.18 (dd, $^3J_{H,H}$ = 7.2 Hz, $^3J_{H,H}$ = 5.2 Hz, 2H, –OCH_2–), 4.08 (dd, $^3J_{H,H}$ = 9.5 Hz, $^3J_{H,H}$ = 5.4 Hz, 2H, –OCH_2–), 4.03 (t, $^3J_{H,H}$ = 6.5 Hz, 4H, –OCH_2–), 3.97 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 5.9 Hz, 2H, –OCH_2–), 3.91 (dd, $^3J_{H,H}$ = 9.5 Hz, $^3J_{H,H}$ = 5.9 Hz, 2H, –OCH_2–), 1.90 – 1.82 (m, 4H, –CH_2–), 1.61 – 1.07 (m, 96H, –CH_2–, –CH_3), 0.88 (t, $^3J_{H,H}$ = 7.0 Hz, 6H, –CH_3).

1,4-Dihexacosyloxy-2,5-bis{4-[4-(2,3-isopropylidene-2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (H/26A): Synthesized according to **P2** from **2/26** (140 mg, 0.13 mmol), **1/H** (97 mg, 0.29 mmol), [Pd(PPh_3)$_4$] (4.6 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, $C_{102}H_{146}O_8$, M = 1500.25 g/mol, yield: 160 mg (82%), mp. 119 °C, **^{1}H-NMR** ($CDCl_3$, 400 MHz): δ / ppm = 7.51 – 7.44 (m, 12H, Ar–*H*), 7.01 (s, 2H, Ar–*H*), 6.93 – 6.86 (m, 4H, Ar–*H*), 4.53 – 4.45 (m, 2H, –OC*H*–), 4.18 (dd, $^3J_{H,H}$ = 7.2 Hz, $^3J_{H,H}$ = 5.2 Hz, 2H, –OCH_2–), 4.08 (dd, $^3J_{H,H}$ = 9.5 Hz, $^3J_{H,H}$ = 5.4 Hz, 2H, –OCH_2–), 4.03 (t, $^3J_{H,H}$ = 6.5 Hz, 4H, –OCH_2–), 3.97 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 5.9 Hz, 2H, –OCH_2–), 3.91 (dd, $^3J_{H,H}$ = 9.5 Hz, $^3J_{H,H}$ = 5.9 Hz, 2H, –OCH_2–), 1.90 – 1.82 (m, 4H, –CH_2–), 1.61 – 1.07 (m, 104H, –CH_2–, –CH_3), 0.88 (t, $^3J_{H,H}$ = 7.0 Hz, 6H, –CH_3).

1,4-Dioctacosyloxy-2,5-bis{4-[4-(2,3-isopropylidene-2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (H/28A): Synthesized according to **P2** from **2/28** (160 mg, 0.14 mmol), **1/H** (102 mg, 0.31 mmol), [Pd(PPh_3)$_4$] (5.1 mg, 0.005 mmol), CuI (0.6 mg, 0.003 mmol) in NEt_3 (50 mL); purification by column chromatography (eluent: $CHCl_3$). Yellow solid, $C_{106}H_{154}O_8$, M = 1528.34 g/mol, yield: 200 mg (94%), mp. 112 °C, **^{1}H-NMR** ($CDCl_3$, 400 MHz): δ / ppm = 7.51 – 7.44 (m, 12H, Ar–*H*), 7.01 (s, 2H, Ar–*H*), 6.93 – 6.86 (m, 4H, Ar–*H*), 4.53 – 4.45 (m, 2H, –OC*H*–), 4.18 (dd, $^3J_{H,H}$ = 7.2 Hz, $^3J_{H,H}$ = 5.2 Hz, 2H, –OCH_2–), 4.08 (dd, $^3J_{H,H}$ = 9.5 Hz, $^3J_{H,H}$ = 5.4 Hz, 2H, –OCH_2–), 4.03 (t, $^3J_{H,H}$ = 6.6 Hz, 4H, –OCH_2–), 3.97 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 5.9 Hz, 2H, –OCH_2–), 3.91 (dd, $^3J_{H,H}$ = 9.5 Hz, $^3J_{H,H}$ = 5.9 Hz, 2H, –OCH_2–), 1.90 – 1.82 (m, 4H, –CH_2–), 1.61 – 1.07 (m, 112H, –CH_2–, –CH_3), 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, –CH_3).

1,4-Ditriacontyloxy-2,5-bis{4-[4-(2,3-isopropylidene-2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (H/30A): Synthesized according to **P2** from **2/30** (300 mg, 0.25 mmol), **1/H** (200 mg, 0.60 mmol), [Pd(PPh_3)$_4$] (8.7 mg, 0.011 mmol), CuI (1.5 mg, 0.008 mmol) in NEt_3 (50 mL); purification by column chromatography (eluent: $CHCl_3$). Yellow solid, $C_{110}H_{162}O_8$, M = 1614.78 g/mol, yield: 210 mg (52%), mp. 112 °C, **^{1}H-NMR** ($CDCl_3$, 500 MHz): δ / ppm = 7.51 – 7.44 (m, 12H, Ar–*H*), 7.01 (s, 2H, Ar–*H*), 6.93 – 6.86 (m, 4H, Ar–*H*), 4.53 – 4.45 (m, 2H, –OC*H*–), 4.18 (dd, $^3J_{H,H}$ = 7.2 Hz, $^3J_{H,H}$ = 5.2 Hz, 2H, –OCH_2–), 4.08 (dd, $^3J_{H,H}$ = 8.5 Hz, $^3J_{H,H}$ = 6.4 Hz, 2H, –OCH_2–), 4.03 (t, $^3J_{H,H}$ = 6.4 Hz, 4H, –OCH_2–), 3.97 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 5.9 Hz, 2H, –OCH_2–), 3.91 (dd, $^3J_{H,H}$ = 9.5 Hz, $^3J_{H,H}$ = 5.9 Hz, 2H, –OCH_2–), 1.90 – 1.82 (m, 4H, –CH_2–), 1.61 – 1.07 (m, 120H, –CH_2–, –CH_3), 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, –CH_3).

1,4-Didotriacontyloxy-2,5-bis{4-[4-(2,3-isopropylidene-2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (H/32A): Synthesized according to **P2** from **2/32** (100 mg, 0.08 mmol), **1/H** (58 mg, 0.17 mmol), [$Pd(PPh_3)_4$] (2.8 mg, 0.002 mmol), CuI (0.3 mg, 0.002 mmol) in NEt_3 (50 mL); purification by column chromatography (eluent: $CHCl_3$). Yellow solid, $C_{114}H_{170}O_8$, M = 1668.48 g/mol, yield: 80 mg (60%), mp. 113 °C, **^{1}H-NMR** ($CDCl_3$, 400 MHz): δ / ppm = 7.51 – 7.44 (m, 12H, Ar–*H*), 7.01 (s, 2H, Ar–*H*), 6.93 – 6.86 (m, 4H, Ar–*H*), 4.53 – 4.45 (m, 2H, –OC*H*–), 4.18 (dd, $^3J_{H,H}$ = 7.2 Hz, $^3J_{H,H}$ = 5.2 Hz, 2H, –OCH_2–), 4.08 (dd, $^3J_{H,H}$ = 9.5 Hz, $^3J_{H,H}$ = 5.4 Hz, 2H, –OCH_2–), 4.03 (t, $^3J_{H,H}$ = 6.4 Hz, 4H, –OCH_2–), 3.97 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 5.9 Hz, 2H, –OCH_2–), 3.91 (dd, $^3J_{H,H}$ = 9.5 Hz, $^3J_{H,H}$ = 5.9 Hz, 2H, –OCH_2–), 1.90 – 1.82 (m, 4H, –CH_2–), 1.61 – 1.07 (m, 128H, –CH_2–, –CH_3), 0.88 (t, $^3J_{H,H}$ = 6.8 Hz, 6H, –CH_3).

1,4-Dieicosyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(2,3-isopropylidene-2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (F/20A): Synthesized according to **P2** from **2/20** (156 mg, 0.17 mmol), **1/F** (144 mg, 0.36 mmol), [$Pd(PPh_3)_4$] (5.9 mg, 0.005 mmol), CuI (0.7 mg, 0.003 mmol) in NEt_3 (50 mL); purification by column chromatography (eluent: $CHCl_3$). Yellow solid, $C_{90}H_{114}F_8O_8$, M = 1474.84 g/mol, yield: 240 mg (96%), mp. 103 °C, **^{1}H-NMR** ($CDCl_3$, 400 MHz): δ / ppm = 7.58 – 7.51 (m, 8H, Ar–*H*), 7.02 (s, 2H, Ar–*H*), 4.50 – 4.42 (m, 2H, –OC*H*–), 4.33 (dd, $^3J_{H,H}$ = 10.1 Hz, $^3J_{H,H}$ = 5.1 Hz, 2H, –OCH_2–), 4.24 (dd, $^3J_{H,H}$ = 10.1 Hz, $^3J_{H,H}$ = 5.5 Hz, 2H, –OCH_2–), 4.16 (dd, $^3J_{H,H}$ = 8.5 Hz, $^3J_{H,H}$ = 6.5 Hz, 2H, –OCH_2–), 4.04 (t, $^3J_{H,H}$ = 6.3 Hz, 4H, –OCH_2–), 3.96 (dd, $^3J_{H,H}$ = 8.6 Hz, $^3J_{H,H}$ = 5.6 Hz, 2H, –OCH_2–), 1.92 – 1.79 (m, 4H, –CH_2–), 1.61 – 1.07 (m, 80H, –CH_2–, –CH_3), 0.87 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, –CH_3). **^{19}F-NMR** ($CDCl_3$, 470 MHz) δ /ppm = -137.47 – -137.57 (m, Ar–*F*), -156.86 – -156.97 (m, Ar–*F*).

1,4-Didocosyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(2,3-isopropylidene-2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (F/22A): Synthesized according to **P2** from **2/22** (160 mg, 0.16 mmol), **1/F** (136 mg, 0.34 mmol), [$Pd(PPh_3)_4$] (5.5 mg, 0.005 mmol), CuI (0.6 mg, 0.003 mmol) in NEt_3 (50 mL); purification by column chromatography (eluent: $CHCl_3$). Yellow solid, $C_{94}H_{122}F_8O_8$, M = 1530.90 g/mol, yield: 240 mg (98%), mp. 108 °C, **^{1}H-NMR** ($CDCl_3$, 400 MHz): δ / ppm = 7.58 – 7.50 (m, 8H, Ar–*H*), 7.02 (s, 2H, Ar–*H*), 4.50 – 4.42 (m, 2H, –OC*H*–), 4.33 (dd, $^3J_{H,H}$ = 9.8 Hz, $^3J_{H,H}$ = 4.8 Hz, 2H, –OCH_2–), 4.24 (dd, $^3J_{H,H}$ = 9.8 Hz, $^3J_{H,H}$ = 5.5 Hz, 2H, –OCH_2–), 4.16 (dd, $^3J_{H,H}$ = 8.6 Hz, $^3J_{H,H}$ = 6.4 Hz, 2H, –OCH_2–), 4.04 (t, $^3J_{H,H}$ = 6.3 Hz, 4H, –OCH_2–), 3.96 (dd, $^3J_{H,H}$ = 8.6 Hz, $^3J_{H,H}$ = 5.6 Hz, 2H, –OCH_2–), 1.91 – 1.81 (m, 4H, –CH_2–), 1.61 – 1.16 (m, 88H, –CH_2–, –CH_3), 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, –CH_3). **^{19}F-NMR** ($CDCl_3$, 376 MHz) δ /ppm =-137.46 – -137.58 (m, Ar–*F*), -156.85 – -156.97 (m, Ar–*F*).

1,4-Ditetracosyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(2,3-isopropylidene-2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (F/24A): Synthesized according to **P2** from **2/24** (240 mg, 0.32 mmol), **1/F** (206 mg, 0.51 mmol), [$Pd(PPh_3)_4$] (8.0 mg, 0.007 mmol), CuI (0.9 mg, 0.005 mmol) in NEt_3 (50 mL); purification by column chromatography (eluent: $CHCl_3$). Yellow solid, $C_{98}H_{130}F_8O_8$, M = 1588.06 g/mol, yield: 300 mg (81%), mp. 99 °C, **^{1}H-NMR** ($CDCl_3$, 400 MHz): δ / ppm = 7.58 – 7.50 (m, 8H, Ar–*H*), 7.02 (s, 2H, Ar–*H*), 4.50 – 4.42 (m, 2H, –OC*H*–), 4.33 (dd, $^3J_{H,H}$ = 9.8 Hz, $^3J_{H,H}$ = 4.8 Hz, 2H, –OCH_2–), 4.24 (dd, $^3J_{H,H}$ = 9.8 Hz, $^3J_{H,H}$ = 5.5 Hz, 2H, –OCH_2–), 4.16 (dd, $^3J_{H,H}$ = 8.6 Hz, $^3J_{H,H}$ = 6.4 Hz, 2H, –OCH_2–), 4.04 (t, $^3J_{H,H}$ = 6.3 Hz, 4H, –OCH_2–), 3.96 (dd, $^3J_{H,H}$ = 8.6 Hz, $^3J_{H,H}$ = 5.6 Hz, 2H, –OCH_2–), 1.91 – 1.81 (m, 4H, –CH_2–), 1.61 – 1.16

(m, 96H, –CH_2–, –CH_3), 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, –CH_3). **^{19}F-NMR** ($CDCl_3$, 376 MHz) δ /ppm =-137.48 – -137.56 (m, Ar–*F*), -156.82 – -156.98 (m, Ar–*F*).

1,4-Dioctacosyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(2,3-isopropylidene-2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (F/28A): Synthesized according to **P2** from **2/28** (200 mg, 0.174 mmol), **1/F** (155.3 mg, 0.384 mmol), [$Pd(PPh_3)_4$] (12 mg, 0.01 mmol), CuI (2 mg, 0.01 mmol) in NEt_3 (50 mL); purification by column chromatography (eluent: $CHCl_3$). Yellow solid, $C_{16}H_{146}F_8O_8$, M = 1700.31 g/mol, yield: 90 mg (30.4%), mp. 78 °C, **^{1}H-NMR** ($CDCl_3$, 400 MHz): δ / ppm = 7.55 – 7.51 (m, 8H, Ar–*H*), 7.02 (s, 2H, Ar–*H*), 4.50 – 4.42 (m, 2H, –OC*H*–), 4.33 (dd, $^3J_{H,H}$ = 10.2 Hz, $^3J_{H,H}$ = 5.1 Hz, 2H, –OCH_2–), 4.24 (dd, $^3J_{H,H}$ = 10.0 Hz, $^3J_{H,H}$ = 5.6 Hz, 2H, –OCH_2–), 4.16 (dd, $^3J_{H,H}$ = 8.6 Hz, $^3J_{H,H}$ = 6.3 Hz, 2H, –OCH_2–), 4.04 (t, $^3J_{H,H}$ = 6.4 Hz, 4H, –OCH_2–), 3.96 (dd, $^3J_{H,H}$ = 8.8 Hz, $^3J_{H,H}$ = 5.3 Hz, 2H, –OCH_2–), 1.90 – 1.81 (m, 4H, –CH_2–), 1.45 – 1.16 (m, 112H, –CH_2–, –CH_3), 0.87 (t, $^3J_{H,H}$ = 6.8 Hz, 6H, –CH_3). **^{19}F-NMR** ($CDCl_3$, 376 MHz) δ /ppm =-137.44 – -137.60 (m, Ar–*F*), -156.82 – -157.00 (m, Ar–*F*).

1,4-Ditriacontyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(2,3-isopropylidene-2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (F/30A): Synthesized according to **P2** from **2/30** (300 mg, 0.25 mmol), **1/F** (240 mg, 0.60 mmol), [$Pd(PPh_3)_4$] (8.7 mg, 0.008 mmol), CuI (1.0 mg, 0.005 mmol) in NEt_3 (50 mL); purification by column chromatography (eluent: $CHCl_3$). Yellow solid, $C_{110}H_{154}F_8O_8$, M = 1755.14 g/mol, yield: 200 mg (46%), mp. 92 °C, **^{1}H-NMR** ($CDCl_3$, 400 MHz): δ / ppm = 7.58 – 7.50 (m, 8H, Ar–*H*), 7.02 (s, 2H, Ar–*H*), 4.50 – 4.42 (m, 2H, –OC*H*–), 4.33 (dd, $^3J_{H,H}$ = 9.8 Hz, $^3J_{H,H}$ = 4.8 Hz, 2H, –OCH_2–), 4.24 (dd, $^3J_{H,H}$ = 9.8 Hz, $^3J_{H,H}$ = 5.5 Hz, 2H, –OCH_2–), 4.16 (dd, $^3J_{H,H}$ = 8.6 Hz, $^3J_{H,H}$ = 6.4 Hz, 2H, –OCH_2–), 4.04 (t, $^3J_{H,H}$ = 6.3 Hz, 4H, –OCH_2–), 3.96 (dd, $^3J_{H,H}$ = 8.6 Hz, $^3J_{H,H}$ = 5.6 Hz, 2H, –OCH_2–), 1.91 – 1.81 (m, 4H, –CH_2–), 1.61 – 1.16 (m, 120H, –CH_2–, –CH_3), 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, –CH_3). **^{19}F-NMR** ($CDCl_3$, 376 MHz) δ /ppm =-137.32 – -137.46 (m, Ar–*F*), -156.78 – -156.93 (m, Ar–*F*).

1,4-Didotriacontyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(2,3-isopropylidene-2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (F/32A): Synthesized according to **P2** from **2/32** (315 mg, 0.25 mmol), **1/F** (240 mg, 0.60 mmol), [$Pd(PPh_3)_4$] (8.7 mg, 0.008 mmol), CuI (1.0 mg, 0.005 mmol) in NEt_3 (50 mL); purification by column chromatography (eluent: $CHCl_3$). Yellow solid, $C_{114}H_{162}F_8O_8$, M = 1812.49 g/mol, yield: 208 mg (46%), mp. 93 °C, **^{1}H-NMR** ($CDCl_3$, 400 MHz): δ / ppm = 7.57 – 7.50 (m, 8H, Ar–*H*), 7.02 (s, 2H, Ar–*H*), 4.49 – 4.42 (m, 2H, –OC*H*–), 4.33 (dd, $^3J_{H,H}$ = 10.2 Hz, $^3J_{H,H}$ = 5.2 Hz, 2H, –OCH_2–), 4.24 (dd, $^3J_{H,H}$ = 10.1 Hz, $^3J_{H,H}$ = 5.7 Hz, 2H, –OCH_2–), 4.16 (dd, $^3J_{H,H}$ = 8.6 Hz, $^3J_{H,H}$ = 6.4 Hz, 2H, –OCH_2–), 4.04 (t, $^3J_{H,H}$ = 6.4 Hz, 4H, –OCH_2–), 3.96 (dd, $^3J_{H,H}$ = 8.6 Hz, $^3J_{H,H}$ = 5.6 Hz, 2H, –OCH_2–), 1.90 – 1.81 (m, 4H, –CH_2–), 1.43 (s, 6H, -CH_3), 1.39 (s, 6H, -CH_3), 1.59 – 1.16 (m, 128H, –CH_2–, –CH_3), 0.88 (t, $^3J_{H,H}$ = 6.8 Hz, 6H, –CH_3). **^{19}F-NMR** ($CDCl_3$, 376 MHz) δ /ppm =-137.43 – -137.60 (m, Ar–*F*), -156.84 – -156.96 (m, Ar–*F*).

4.4 Synthesis and analytical data of compounds H/*n* and F/*n*

P3. Deprotection of acetonides with PPTS[S6]: A mixture of the appropriate isopropylidene acetal **H/nA** or **F/nA** (1 equ.) and PPTS (tip of a spatula) was dissolved in THF/MeOH (1:1, 60 mL/~7 mmol) and stirred at 50 °C for 12 h. After finishing the reaction, the solvent was removed and the residue dissolved in DCM. The organic layer

was washed with $NaHCO_3$ solution (3 x 50 mL), water and brine (50 mL each). After drying over Na_2SO_4 the solvent was removed and the residue purified by column chromatography.

1,4-Dieicosyloxy-2,5-bis{4-[4-(2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenyl-ethynyl}benzene (H/20): Synthesized according to the **P3** from **H/20A** (160 mg, 0.11 mmol), PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL: 30 mL); purification by column chromatography (eluent: $CHCl_3$/MeOH = 9:1). Yellow solid, $C_{84}H_{114}O_8$, M = 1251.80 g/mol, yield: 50 mg (36%), **^{1}H-NMR** (500 MHz, Pyridine-d_5) δ / ppm = 7.78 – 7.73 (m, 4H, Ar–*H*), 7.70 – 7.65 (m, 4H, Ar–*H*), 7.65 – 7.59 (m, 4H, Ar–*H*), 7.47 (s, 2H, Ar–*H*), 7.10 – 7.08 (m, 4H, Ar–*H*), 4.59 – 4.51 (m, 2H, –OC*H*–), 4.49 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 4.3 Hz, 2H, –OCH_2–), 4.41 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 6.3 Hz, 2H, –OCH_2–), 4.26 – 4.16 (m, 4H, –OCH_2–), 4.12 (t, $^3J_{H,H}$ = 6.3 Hz, 4H, –OCH_2–), 1.9 – 1.8 (m, 4H, –CH_2–), 1.7 – 1.6 (m, 4H, –CH_2–), 1.5 – 1.3 (m, 64H, –CH_2–), 0.86 (t, $^3J_{H,H}$ = 6.6 Hz, 6H, –CH_3) ppm. **^{13}C-NMR** (101 MHz, Pyridine-d_5) δ 160.05, 154.11 (C_{Ar}-O), 133.37, 131.83, 131.75 (C_{Ar}–H), 123.96 (Ar_{quart}), 117.29, 115.18 (C_{Ar}–H), 114.95, 114.35 (Ar_{quart}), 95.22, 92.45, 88.92, 88.31 (–C≡C–), 71.11, 70.84, 69.56, 64.02 (-OCH-, –O*C*H_2–), 31.89, 29.78, 29.76, 29.69, 29.45, 29.38, 26.22, 22.70 (–*C*H_2–), 14.05 (–*C*H_3) ppm. Anal. calcd. for $C_{84}H_{114}O_8$ [%]: C 80.60, H 9.18; found: C 80.76, H 9.18.

1,4-Didocosyloxy-2,5-bis{4-[4-(2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenyl-ethynyl}benzene (H/22): Synthesized according to **P3** from **H/22A** (220 mg, 0.16 mmol), PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL: 30 mL); purification by column chromatography (eluent: $CHCl_3$/MeOH = 9:1). Yellow solid, $C_{88}H_{122}O_8$, M = 1306.91 g/mol, yield: 95 mg (45%), **^{1}H-NMR** (400 MHz, Pyridine-d_5) δ / ppm = 7.78 – 7.72 (m, 4H, Ar–H), 7.69 – 7.65 (m, 4H, Ar–H), 7.64 – 7.59 (m, 4H, Ar–H), 7.48 (s, 2H, Ar–H), 7.20 – 7.07 (m, 4H, Ar–H), 4.60 – 4.51 (m, 2H, –OCH–), 4.49 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 4.3 Hz, 2H, –OCH_2–), 4.40 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 6.3 Hz, 2H, –OCH_2–), 4.25 – 4.15 (m, 4H, –OCH_2–), 4.12 (t, $^3J_{H,H}$ = 6.3 Hz, 4H, –OCH_2–), 1.93 – 1.82 (m, 4H, –CH_2–), 1.66 – 1.54 (m, 4H, –CH_2–), 1.46 – 1.17 (m, 72H, –CH_2–), 0.85 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, –CH_3). **^{13}C-NMR** (101 MHz, Pyridine-d_5) δ 158.88, 152.87 (C_{Ar}-O),132.19, 130.64, 130.57 (C_{Ar}–H), 122.77 (Ar_{quart}), 116.13, 115.98 (C_{Ar}–H), 113.81, 113.16, (Ar_{quart}), 94.13, 91.31, 87.70, 87.15 (–C≡C–), 69.91, 69.66, 68.36, 62.83 (–OCH-, OCH_2–), 30.70, 28.59, 28.49, 28.26, 28.18, 25.03, 21.51 (–CH_2–), 12.85 (–CH_3). **HRMS** (m/z): [M]+Li^+ calcd. for $C_{88}H_{122}O_8Li$, 1313.929; found: 1313.933. Anal. calcd. for $C_{88}H_{122}O_8 \cdot H_2O$ [%]: C 79.71, H 9.43; found: C 79.53, H 9.32.

1,4-Ditetracosyloxy-2,5-bis{4-[4-(2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenyl-ethynyl}benzene (H/24): Synthesized according to **P3** from **H/24A** (180 mg, 0.12 mmol), PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL: 30 mL); purification by column chromatography (eluent: $CHCl_3$/MeOH = 9:1). Yellow solid, $C_{92}H_{130}O_8$, M = 1362.98 g/mol, yield: 123 mg (75%), **^{1}H-NMR** (400 MHz, Pyridine-d_5) δ / ppm = 7.76 – 7.74 (m, 4H, Ar–*H*), 7.70 – 7.65 (m, 4H, Ar–*H*), 7.64 – 7.60 (m, 4H, Ar–*H*), 7.46 (s, 2H, Ar–*H*), 7.12 – 7.06 (m, 4H, Ar–*H*), 4.58 – 4.51 (m, 2H, –OC*H*–), 4.49 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 4.3 Hz, 2H, –OCH_2–), 4.40 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 6.3 Hz, 2H, –OCH_2–), 4.24 – 4.15 (m, 4H, –OCH_2–), 4.12 (t, $^3J_{H,H}$ = 6.3 Hz, 4H, –OCH_2–), 1.94 – 1.83 (m, 4H, –CH_2–), 1.66 – 1.55 (m, 4H, –CH_2–), 1.50 – 1.14 (m, 80H, –CH_2–), 0.85 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, –CH_3). **^{13}C-NMR** (101 MHz, Pyridine-d_5) δ 160.05, 154.11(C_{Ar}-O), 133.37, 131.82, 131.75 (C_{Ar}–H), 123.96 (Ar_{quart}), 117.28, 115.17 (C_{Ar}–H), 114.96, 114.35 (C_{quart}), 95.21, 92.45, 88.92, 88.31 (–C≡C–), 71.11, 70.86, 69.55, 64.03 (-OCH-, –O*C*H_2–), 31.89 29.80, 29.79, 29.69,

29.46, 29.44, 29.38, 26.22, 22.70 (–*C*H$_2$–), 14.05 (–*C*H$_3$). **HRMS** (m/z): [M]+Li$^+$ calcd. for $C_{92}H_{130}O_8Li$, 1369.992; found: 1369.992. Anal. calcd. for $C_{92}H_{130}O_8 \cdot H_2O$ [%]: C 79.95, H 9.63; found: C 79.91, H 9.68.

1,4-Dihexacosyloxy-2,5-bis{4-[4-(2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenyl-ethynyl}benzene (H/26): Synthesized according to **P3** from **H/26A** (160 mg, 0.11 mmol), PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL: 30 mL); purification by column chromatography (eluent: $CHCl_3$/MeOH = 9:1). Yellow solid, $C_{96}H_{138}O_8$, M = 1420.12 g/mol, yield: 120 mg (79%), **^{1}H-NMR** (500 MHz, Pyridine-d$_5$) δ / ppm = 7.78 – 7.72 (m, 4H, Ar–*H*), 7.69 – 7.65 (m, 4H, Ar–*H*), 7.64 – 7.59 (m, 4H, Ar–*H*), 7.46 (s, 2H, Ar–*H*), 7.10 – 7.06 (m, 4H, Ar–*H*), 4.59 – 4.51 (m, 2H, –OC*H*–), 4.49 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 4.3 Hz, 2H, –OC*H*$_2$–), 4.40 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 6.3 Hz, 2H, –OC*H*$_2$–), 4.27 – 4.16 (m, 4H, –OC*H*$_2$–), 4.12 (t, $^3J_{H,H}$ = 6.3 Hz, 4H, –OC*H*$_2$–), 1.94 – 1.83 (m, 4H, –C*H*$_2$–), 1.67 – 1.55 (m, 4H, –C*H*$_2$–), 1.50 – 1.20 (m, 88H, –C*H*$_2$–), 0.86 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, –C*H*$_3$). **^{13}C-NMR** (101 MHz, Pyridine-d$_5$) δ 160.05, 154.11 (C_{Ar}-O), 133.37, 131.82, 131.75, (*C*$_{Ar}$–H), 123.96 (Ar$_{quart}$), 117.28, 115.17 (*C*$_{Ar}$–H), 114.96, 114.35 (Ar$_{quart}$), 95.21, 92.45, 88.92, 88.31 (–C≡C–); 71.11, 70.86, 69.55, 64.03 (-OCH-, –O*C*H$_2$–), 31.89, 29.79, 29.69, 29.46, 29.38, 26.22, 22.70 (–*C*H$_2$–); 14.05 (–*C*H$_3$). Anal. calcd. for $C_{96}H_{138}O_8 \cdot H_2O$ [%]: C 81.19, H 9.79; Found: C 81.36, H 9.75.

1,4-Dioctacosyloxy-2,5-bis{4-[4-(2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenyl-ethynyl}benzene (H/28): Synthesized according to **P3** from **H/28A** (200 mg, 0.13 mmol), PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL: 30 mL); purification by column chromatography (eluent: $CHCl_3$/MeOH = 9:1). Yellow solid, $C_{100}H_{146}O_8$, M = 1476.26 g/mol, yield: 122 mg (64%), **^{1}H-NMR** (400 MHz, Pyridine-d$_5$) δ / ppm = 7.81 – 7.75 (m, 4H, Ar–*H*), 7.74 – 7.68 (m, 4H, Ar–*H*), 7.68 – 7.62 (m, 4H, Ar–*H*), 7.44 (s, 2H, Ar–*H*), 7.14 – 7.09 (m, 4H, Ar–*H*), 4.62 – 4.54 (m, 2H, –OC*H*–), 4.52 (dd, $^3J_{H,H}$ = 9.5 Hz, $^3J_{H,H}$ = 4.5 Hz, 2H, –OC*H*$_2$–), 4.46 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 6.4 Hz, 2H, –OC*H*$_2$–), 4.27 – 4.19 (m, 4H, –OC*H*$_2$–), 4.09 (t, $^3J_{H,H}$ = 6.4 Hz, 4H, –OC*H*$_2$–), 1.96 – 1.85 (m, 4H, –C*H*$_2$–), 1.70 – 1.58 (m, 4H, –C*H*$_2$–), 1.51 – 1.14 (m, 96H, –C*H*$_2$–), 0.83 (t, $^3J_{H,H}$ = 6.8 Hz, 6H, –C*H*$_3$). **^{13}C NMR** (101 MHz, Pyridine-d$_5$) δ 160.07, 154.14 (C_{Ar}-O, 133.38, 131.83, 131.76 (*C*$_{Ar}$–H), 123.97 (Ar$_{quart}$), 117.30, 115.18 (*C*$_{Ar}$–H), 114.98, 114.36 (Ar$_{quart}$), 95.22, 92.46, 88.92, 88.32 (–C≡C–); 71.11, 70.86, 69.55, 64.03 (-O*C*H$_2$–,–O*C*H$_2$–), 31.90 29.81, 29.77, 29.69, 29.46, 29.38, 26.22, 22.85 (–*C*H$_2$–), 14.05 (–*C*H$_3$). **HRMS** (m/z): [M]+Cl$^-$ calcd. for $C_{100}H_{146}O_8Cl$, 1511.0735; found: 1511.0699.

1,4-Ditriacontyloxy-2,5-bis{4-[4-(2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenyl-ethynyl}benzene (H/30): Synthesized according to **P3** from **H/30A** (210 mg, 0.12 mmol), PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL: 30 mL); purification by column chromatography (eluent: $CHCl_3$/MeOH = 9:1). Yellow solid, $C_{104}H_{154}O_8$, M = 1532.69 g/mol, yield: 30 mg (16%), **^{1}H-NMR** (500 MHz, Pyridine-d$_5$) δ / ppm = 7.78 – 7.72 (m, 4H, Ar–*H*), 7.71 – 7.65 (m, 4H, Ar–*H*), 7.65 – 7.60 (m, 4H, Ar–*H*), 7.46 (s, 2H, Ar–*H*), 7.12 – 7.08 (m, 4H, Ar–*H*), 4.60 – 4.51 (m, 2H, –OC*H*–), 4.52 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 4.3 Hz, 2H, –OC*H*$_2$–), 4.43 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 6.3 Hz, 2H, –OC*H*$_2$–), 4.25 – 4.17 (m, 4H, –OC*H*$_2$–), 4.12 (t, $^3J_{H,H}$ = 6.3 Hz, 4H, –OC*H*$_2$–), 1.96 – 1.85 (m, 4H, –C*H*$_2$–), 1.70 – 1.58 (m, 4H, –C*H*$_2$–), 1.51 – 1.14 (m, 104H, –C*H*$_2$–), 0.86 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, –C*H*$_3$). **^{13}C-NMR** (126 MHz, Pyridine-d$_5$) δ 160.05, 154.11(C_{Ar}-O), 133.36, 131.81, 131.74 (*C*$_{Ar}$–H), 123.95 (Ar$_{quart}$), 117.27, 115.16 (*C*$_{Ar}$–H), 114.96, 114.34 (Ar$_{quart}$), 95.19, 92.43, 88.90, 88.30 (–C≡C–); 71.09, 70.84, 69.53, 64.02 (-OCH–, O*C*H$_2$–), 31.88, 29.79, 29.77, 29.75,

29.73,29.67, 29.44, 29.36, 26.20, 22.69 (–*C*H$_2$–), 14.02 (–*C*H$_3$). **HRMS** (m/z): [M]+Cl$^-$ calcd. for $C_{104}H_{154}O_8Cl$, 1567.1366; found: 1567.1361.

1,4-Didotriacontyloxy-2,5-bis{4-[4-(2,3-dihydroxypropyl-1-oxy)phenylethynyl]-phenylethynyl}benzene (H/32): Synthesized according to **P3** from **H/32A** (80 mg, 0.05 mmol), PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL: 30 mL); purification by column chromatography (eluent: $CHCl_3$/MeOH = 9:1). Yellow solid, $C_{108}H_{162}O_8$, M = 1588.36 g/mol, yield: 10 mg (13%), **^{1}H-NMR** (500 MHz, Pyridine-d$_5$) δ / ppm = 7.73 (m, 4H, Ar–*H*), 7.65 (m, 4H, Ar–*H*), 7.61 (m, 4H, Ar–*H*), 7.54 (s, 2H, Ar–*H*), 7.07 (m, 4H, Ar–*H*), 4.55 – 4.50 (m, 2H, –OC*H*–), 4.48 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 4.3 Hz, 2H, –OC*H*$_2$–), 4.39 (dd, $^3J_{H,H}$ = 9.6 Hz, $^3J_{H,H}$ = 6.3 Hz, 2H, –OC*H*$_2$–), 4.23 – 4.15 (m, 4H, –OC*H*$_2$–), 4.11 (t, $^3J_{H,H}$ = 6.3 Hz, 4H, –OC*H*$_2$–), 1.87 (m, 4H, –C*H*$_2$–), 1.59 (m, 4H, –C*H*$_2$–), 1.50– 1.05 (m, 112H, –C*H*$_2$–), 0.84 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, –C*H*$_3$). **^{13}C-NMR** (126 MHz, Pyridine-d$_5$) δ 160.05, 154.11 (C$_{Ar}$-O), 13.36, 131.81, 131.74 (*C*$_{Ar}$–H), 123.95 (Ar$_{quart}$), 117.27, 115.16 (*C*$_{Ar}$–H), 114.96, 114.34 (Ar$_{quart}$), 95.20, 92.44, 88.90, 88.30 (–C≡C–), 71.09, 70.84, 69.53, 64.01 (-OCH-, –O*C*H$_2$–), 31.88, 29.79, 29.77,29.75, 29.67, 29.44, 29.42, 29.36, 26.20, 22.69 (–*C*H$_2$–), 14.02 (–*C*H$_3$). Anal. calcd. for $C_{108}H_{162}O_8 \cdot H_2O$ [%]: C 81.66, H 10.28; found: C 81.89, H 10.21.

1,4-Dieicosyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (F/20): Synthesized according to **P3** from **F/20A** (240 mg, 0.16 mmol), PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL: 30 mL); purification by column chromatography (eluent: $CHCl_3$/MeOH = 9:1). Yellow solid, $C_{84}H_{106}F_8O_8$, M = 1394.78 g/mol, yield: 186 mg (83%), **^{1}H-NMR** (500 MHz, Pyridine-d$_5$) δ / ppm = 7.79 – 7.73 (m, 4H, Ar–*H*), 7.71 – 7.66 (m, 4H, Ar–*H*), 7.48 (s, 2H, Ar–*H*), 4.90 – 4.85 (m, 2H, –OC*H*$_2$–), 4.80 – 4.75 (m, 2H, –OC*H*$_2$–), 4.57 – 4.50 (m, 2H, –OC*H*–), 4.21 – 4.18 (m, 2H, –OC*H*$_2$–), 4.13 (t, $^3J_{H,H}$ = 6.3 Hz, 4H, –OC*H*$_2$–), 1.93 – 1.85 (m, 4H, –C*H*$_2$–), 1.65 – 1.57 (m, 4H, –C*H*$_2$–), 1.49 – 1.16 (m, 64H, –C*H*$_2$–), 0.86 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, –C*H*$_3$). **^{19}F-NMR** (470 MHz, Pyridine-d$_5$) δ / ppm = -140.18 – -140.35 (m, Ar–*F*), -158.37 – -158.56 (m, Ar–*F*). **^{13}C-NMR** (126 MHz, Pyridine-d$_5$) δ / ppm = 152.63 (C$_{Ar}$-O), 147.5, 141.5 (2 x m, *C*-F), 139.5 (m, *C*$_{ArF}$-O), 130.60, 130.34 (*C*$_{Ar}$–H), 123.26, 120.29, 115.74, 112.76, 99.20 (*C*$_{Ar}$, –C≡C–), 95.70 (m, quart-*C*$_{ArF}$), 93.40, 88.08 (–C≡C–), 76.03 (Ar$_F$-O-*C*H$_2$-), 74.85 (–C≡C–), 70.18, 68.01, 61.98 (–OCH-, -O*C*H$_2$–), 30.34, 28.25, 28.24, 28.21, 28.20, 28.14, 27.92, 27.88, 27.83, 24.68, 21.15 (–*C*H$_2$–), 12.49 (–*C*H$_3$). **HRMS** (m/z): [M]+Li$^+$ calcd. for $C_{84}H_{106}F_8O_8Li$, 1401.792, found: 1401.797. Anal. calcd. for $C_{84}H_{106}F_8O_8 \cdot H_2O$ [%]: C 71.36, H 7.70; found: C 71.43, H 7.45.

1,4-Didocosyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (F/22): Synthesized according to **P3** from **F/22A** (240 mg, 0.16 mmol), PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL: 30 mL); purification by column chromatography (eluent: $CHCl_3$/MeOH = 9:1). Yellow solid, $C_{88}H_{114}F_8O_8$, M = 1450.84 g/mol, yield: 168 mg (72%), **^{1}H-NMR** (400 MHz, Pyridine-d$_5$) δ / ppm = 7.81 – 7.74 (m, 4H, Ar–*H*), 7.71 – 7.65 (m, 4H, Ar–*H*), 7.48 (s, 2H, Ar–*H*), 4.92 – 4.84 (m, 2H, –OC*H*$_2$–), 4.81 – 4.74 (m, 2H, –OC*H*$_2$–), 4.58 – 4.50 (m, 2H, –OC*H*–), 4.23 – 4.17 (m, 2H, –OC*H*$_2$–), 4.13 (t, $^3J_{H,H}$ = 6.3 Hz, 4H, –OC*H*$_2$–), 1.97 – 1.85 (m, 4H, –C*H*$_2$–), 1.68 – 1.55 (m, 4H, –C*H*$_2$–), 1.59 – 1.17 (m, 72H, –C*H*$_2$–), 0.86 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, –C*H*$_3$). **^{19}F-NMR** (376 MHz, Pyridine-d$_5$) δ / ppm = -139.82 – -139.97 (m, Ar–*F*), -158.01 – -158.18 (m, Ar–*F*). **^{13}C-NMR** (126 MHz, Pyridine-d$_5$) δ / ppm = 154.20 (C$_{Ar}$-O), 147.5, 141.2 (2 x m, C-F), 139.5 (m, *C*$_{ArF}$-O), 132.16, 131.91 (*C*$_{Ar}$–H), 124.82, 121.85, 117.30, 114.32, 99.99 (C$_{Ar}$, –C≡C–), 97.26 (m, quart-C$_{ArF}$), 94.96, 89.65 (–C≡C–),77.58 (d, Ar$_F$-

O-*C*H$_2$-), 76.40 (–C≡C–), 71.75, 69.57, 63.54 (-OCH-, –O*C*H$_2$–), 31.90, 29.81, 29.71, 29.48, 29.44, 29.40, 26.25, 22.72 (–*C*H$_2$–), 14.05 (–*C*H$_3$). **HRMS** (m/z): [M]+Li$^+$ calcd. for $C_{88}H_{114}F_8O_8Li$, 1457.854, found: 1457.855. Anal. calcd. for $C_{88}H_{114}F_8O_8 \cdot H_2O$ [%]: C 71.91, H 7.95; found: C 71.58, H 7.70.

1,4-Ditetracosyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (F/24): Synthesized according to **P3** from **F/24A** (300 mg, 0.16 mmol), PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL: 30 mL); purification by column chromatography (eluent: $CHCl_3$/MeOH = 9:1). Yellow solid, $C_{92}H_{122}F_8O_8$, M = 1507.94 g/mol, yield: 70 mg (25%), **^{1}H-NMR** (500 MHz, Pyridine-d$_5$) δ / ppm = 7.78 – 7.74 (m, 4H, Ar–*H*), 7.70 – 7.66 (m, 4H, Ar–*H*), 7.56 (s, 2H, Ar–*H*), 4.90 – 4.84 (m, 2H, –OC*H*$_2$–), 4.80 – 4.74 (m, 2H, –OC*H*$_2$–), 4.57 – 4.50 (m, 2H, –OC*H*–), 4.21 – 4.18 (m, 4H, –OC*H*$_2$–), 4.13 (t, $^3J_{H,H}$ = 6.4 Hz, 4H, –OC*H*$_2$–), 1.93 – 1.84 (m, 4H, –C*H*$_2$–), 1.66 – 1.57 (m, 4H, –C*H*$_2$–), 1.49 – 1.20 (m, 80H, –C*H*$_2$–), 0.86 (t, $^3J_{H,H}$ = 6.5 Hz, 6H, –C*H*$_3$). **^{19}F-NMR** (470 MHz, Pyridine-d$_5$) δ / ppm = -139.82 – -139.97 (m, Ar–*F*), -158.01 – -158.18 (m, Ar–*F*). **^{13}C-NMR** (101 MHz, Pyridine-d$_5$) δ / ppm = 154.18 (C$_{Ar}$-O), 132.15, 131.89 (*C*$_{Ar}$–H), 147.4, 141.1 (2 x m, C-F), 139.5 (m, *C*$_{ArF}$-O), 124.81, 121.83, 117.28, 114.31, 99.95 (C$_{Ar}$, –C≡C–), 97.24 (m, quart-C$_{ArF}$), 94.92, 89.61 (–C≡C–), 77.56 (Ar$_F$-O-*C*H$_2$-), 76.38 (–C≡C–), 71.71, 69.53, 63.51 (–-OCH-, O*C*H$_2$–), 31.88, 29.78, 29.75, 29.73, 29.67, 29.45, 29.41, 29.36, 26.21, 22.69 (–*C*H$_2$–), 14.02 (–*C*H$_3$). Anal. calcd. for $C_{92}H_{122}F_8O_8 \cdot H_2O$ [%]: C 73.28, H 8.15; found: C 72.95, H 8.09.

1,4-Dioctaacosyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (F/28): Synthesized according to **P3** from **F/28A** (140 mg, 0.08 mmol), PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL: 30 mL); purification by column chromatography (eluent: $CHCl_3$/MeOH = 9:1). Yellow solid, $C_{100}H_{138}F_8O_8$, M = 1620.18 g/mol, yield: 24.4 mg (19%), **^{1}H-NMR** (500 MHz, Pyridine-d$_5$) δ / ppm = 7.82 – 7.78 (m, 4H, Ar–*H*), 7.76 – 7.68 (m, 4H, Ar–*H*), 7.52 (s, 2H, Ar–*H*), 4.93 – 4.86 (m, 2H, –OC*H*$_2$–), 4.83 – 4.78 (m, 2H, –OC*H*$_2$–), 4.60 – 4.54 (m, 2H, –OC*H*–), 4.24 – 4.21 (m, 4H, –OC*H*$_2$–), 4.16 (t, $^3J_{H,H}$ = 6.4 Hz, 4H, –OC*H*$_2$–), 1.97 – 1.88 (m, 4H, –C*H*$_2$–), 1.69 – 1.61 (m, 4H, –C*H*$_2$–), 1.49 – 1.21 (m, 96H, –C*H*$_2$–), 0.89 (t, $^3J_{H,H}$ = 6.8 Hz, 6H, –C*H*$_3$). **^{19}F-NMR** (376 MHz, Pyridine-d$_5$) δ / ppm = -140.08 – -140.40 (m, Ar–*F*), -158.24 – -158.70 (m, Ar–*F*). **^{13}C-NMR** (126 MHz, Pyridine-d$_5$) δ / ppm = 152.69 (C$_{Ar}$-O), 143.8, 139.5 (2x m C-F), 136.8 (m, C$_{ArF}$-O), 130.65, 130.39 (*C*$_{Ar}$–H), 123.29, 120.33, 115.79, 112.81, 98.48 (*C*$_{Ar}$, -C≡C–), 95.90 (m, quart-C$_{ArF}$), 93.45, 88.13 (–C≡C–), 76.88 (Ar$_F$-O-CH$_2$), 74.90 (–C≡C–), 70.23, 68.06, 62.03 (-OCH-, –O*C*H$_2$–), 30.39, 28.29, 28.27, 28.19, 27.96, 27.92, 27.88, 24.73, 21.20 (–*C*H$_2$–), 12.54(–*C*H$_3$). **HRMS** (m/z): [M]+Cl$^-$ calcd. for $C_{100}H_{138}F_8O_8Cl$,1654.999; found: 1654.971.

1,4-Ditriacontyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (F/30): Synthesized according to **P3** from **F/30A** (200 mg, 0.11 mmol), PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL: 30 mL); purification by column chromatography (eluent: $CHCl_3$/MeOH = 9:1). Yellow solid, $C_{104}H_{146}F_8O_8$, M = 1675.61 g/mol, yield: 40 mg (22%), **^{1}H-NMR** (400 MHz, Pyridine-d$_5$) δ / ppm = 7.83 – 7.77 (m, 4H, Ar–*H*), 7.74 – 7.69 (m, 4H, Ar–*H*), 7.51 (s, 2H, Ar–*H*), 4.94 – 4.86 (m, 2H, –OC*H*$_2$–), 4.85 – 4.76 (m, 2H, –OC*H*$_2$–), 4.61 – 4.53 (m, 2H, –OC*H*–), 4.26 – 4.20 (m, 4H, –OC*H*$_2$–), 4.16 (t, $^3J_{H,H}$ = 6.4 Hz, 4H, –OC*H*$_2$–), 1.99 – 1.86 (m, 4H, –C*H*$_2$–), 1.71 – 1.59 (m, 4H, –C*H*$_2$–), 1.52 – 1.18 (m, 104H, –C*H*$_2$–), 0.89 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, –C*H*$_3$). **^{19}F-NMR** (376 MHz, Pyridine-d$_5$) δ / ppm = -138.71 (m, Ar–*F*), -156.89 (m, Ar–*F*). **^{13}C-NMR** (101 MHz, Pyridine-d$_5$) δ / ppm = 154.17 (Ar-O), 147.4, 140.9 (2 x m, C-

F), 139.5 (m, C_{ArF}-O), 132.13, 131.87 (C_{Ar}–H), 124.79, 121.82, 117.27, 114.30, 99.91 (C_{Ar}, –C≡C–), 97.20 (m, quart-C_{ArF}), 94.93, 89.62 (–C≡C–), 77.59, 76.31, 71.71, 69.54, 63.51 (-OCH-, –OCH_2–), 31.88, 29.75, 29.68, 29.45, 29.41, 29.36, 26.21, 22.69 (–CH_2–), 14.02 (–CH_3). **HRMS** (m/z): $[M]+Cl^-$ calcd. for $C_{104}H_{146}F_8O_8Cl$, 1711.0613; found: 1711.0607.

1,4-Didotriacontyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(2,3-dihydroxypropyl-1-oxy)phenylethynyl]phenylethynyl}benzene (F/32): Synthesized according to **P3** from **F/32A** (240 mg, 0.16 mmol), PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL: 30 mL); purification by column chromatography (eluent: $CHCl_3$/MeOH = 9:1). Yellow solid, $C_{108}H_{154}F_8O_8$, M = 1732.40 g/mol, yield: 168 mg (72%), **^{1}H-NMR** (400 MHz, Pyridine-d_5) δ / ppm = 7.76 – 7.73 (m, 4H, Ar–*H*), 7.69 – 7.65 (m, 4H, Ar–*H*), 7.47 (s, 2H, Ar–*H*), 4.91 – 4.86 (m, 2H, –OC*H*$_2$–), 4.78 – 4.73 (m, 2H, –OC*H*$_2$–), 4.56 – 4.48 (m, 2H, –OC*H*–), 4.21 – 4.16 (m, 4H, –OC*H*$_2$–), 4.11 (t, $^3J_{H,H}$ = 6.4 Hz, 4H, –OC*H*$_2$–), 1.96 – 1.80 (m, 4H, –C*H*$_2$–), 1.67 – 1.53 (m, 4H, –C*H*$_2$–), 1.52 – 1.18 (m, 112H, –C*H*$_2$–), 0.84 (t, $^3J_{H,H}$ = 6.9 Hz, 6H, –C*H*$_3$). **^{19}F-NMR** (376 MHz, Pyridine-d_5) δ / ppm = -138.74 (m, Ar–*F*), -156.87 (m, Ar–*F*). **^{13}C-NMR** (126 MHz, Pyridine-d_5) δ / ppm = 154.15 (Ar-O), 147.2, 141,1 (2 x m, C-F), 139.5 (m, C_{ArF}-O), 132.11, 131.86 (C_{Ar}–H), 124.78, 121.79, 117.25, 114.28, 99.97 (C_{Ar}, –C≡C–) 97.08 (m, quart-C_{ArF}), 94.91, 89.61 (–C≡C–), 77.55, 76.37, 71.70, 69.52, 63.50 (-OCH-, –OCH_2–), 31.88, 29.78, 29.77, 29.68, 29.44, 29.41, 29.37, 26.21, 22.69 (–CH_2–), 14.02 (–CH_3). **HRMS** (m/z): $[M]+Cl^-$ calcd. for $C_{108}H_{154}F_8O_8Cl$, 1766.1162; found: 1766.1199.

4.5 Representative NMR spectra

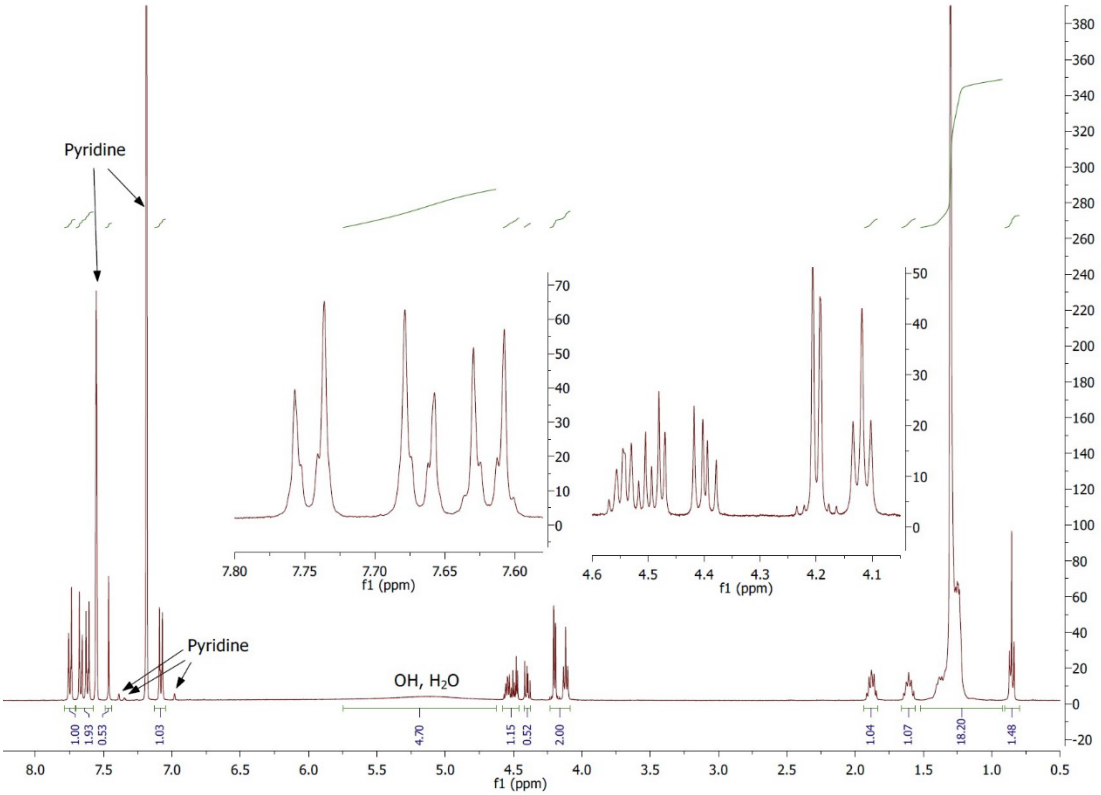


Figure 19. ^{1}H-NMR of compound **H/24** (500 MHz, pyridine-d_5).

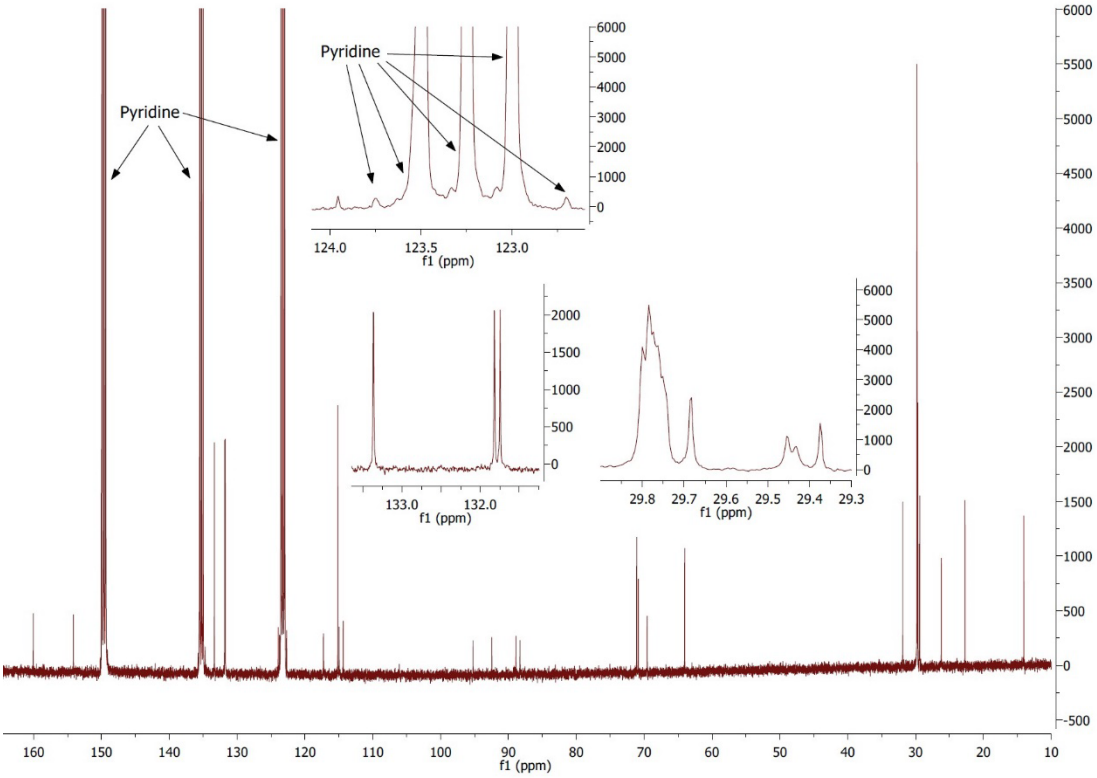


Figure 20. ^{13}C-NMR of compound **H/24** (126 MHz, pyridine-d$_5$).

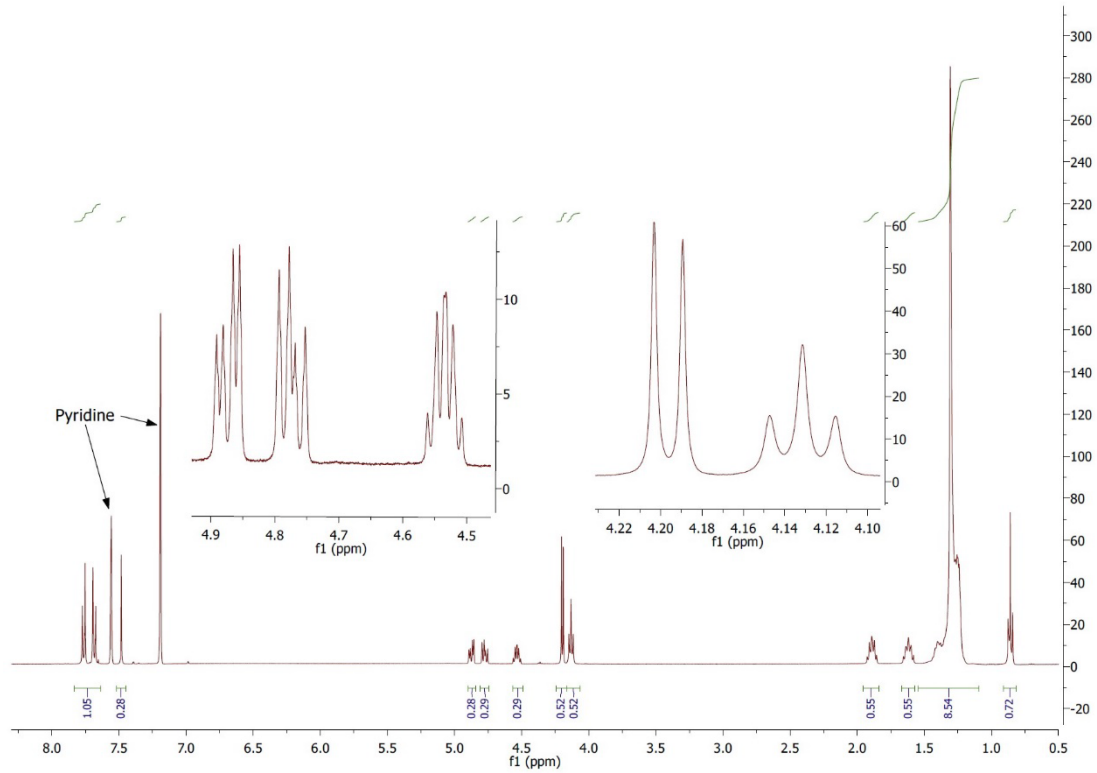


Figure 21. ^{1}H-NMR of compound **F/22** (500 MHz, pyridine-d$_5$).

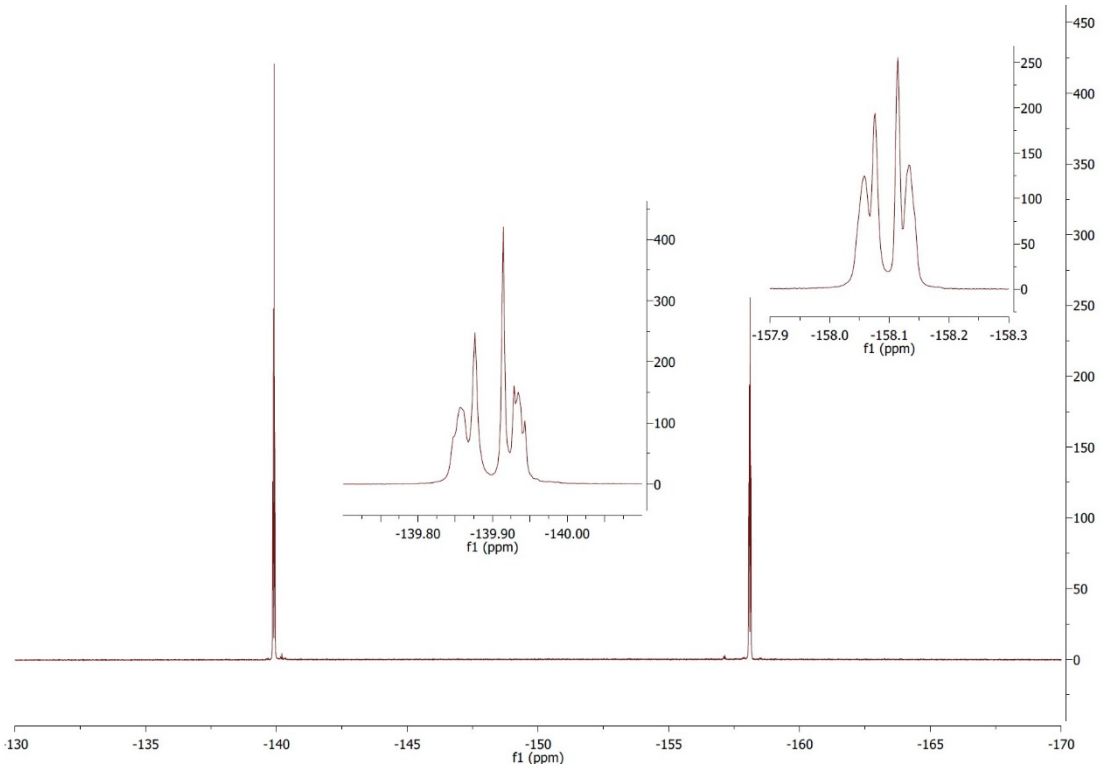


Figure 22. ^{19}F-NMR of compound **F/22** (376 MHz, pyridine-d_5).

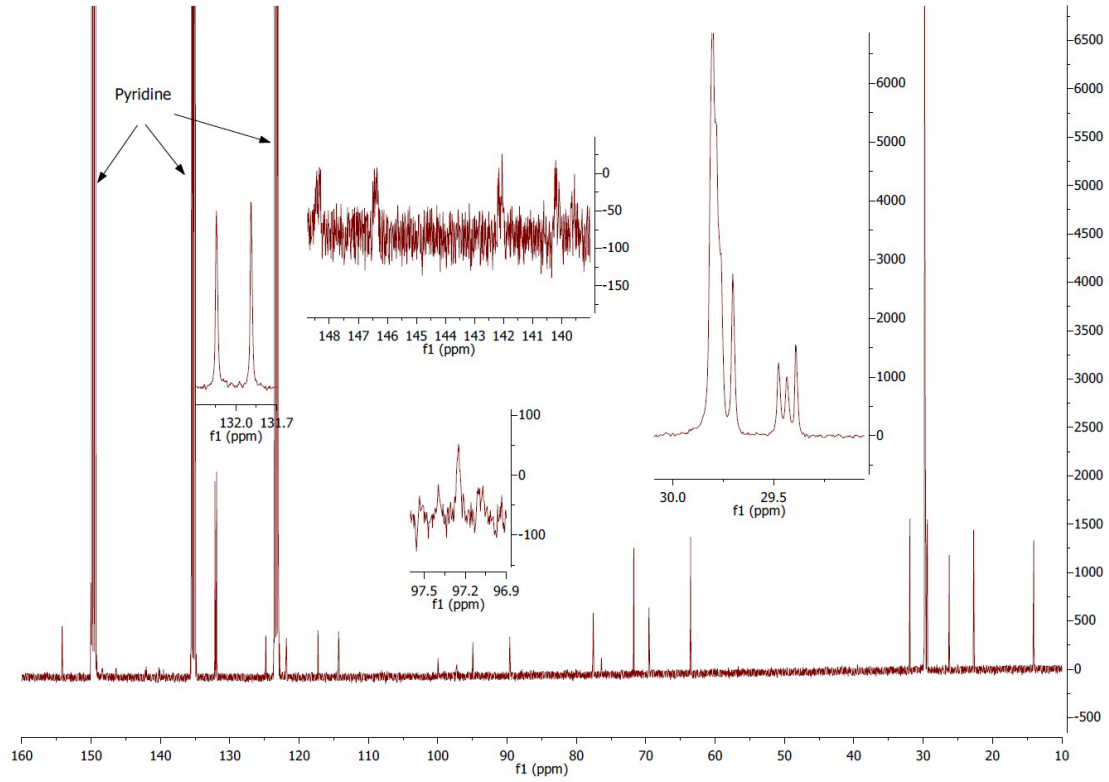


Figure 23. ^{13}C-NMR of compound **F/22** (126 MHz, pyridine-d_5).

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