Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information

Photoswitchable carbosilane-based polycatenars forming nematic, tilted smectic, hexatic, and cubic liquid crystalline phases

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Contents

S1. Characterization methods

Polarized 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 or in uncoated 6 µm ITO-cells purchased by EHC Japan.

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) in sealed 30 µL aluminum pans with heating and cooling rates of 10 K/min under an N_2 stream; peak temperatures are given in Table 1

X-ray scattering

X-ray investigations were carried out with an Incoatec (Geesthacht, Germany) IµS microfocus source with a monochromator for CuKα radiation ($\lambda = 0.154$ nm), calibration with the powder pattern of $Pb(NO_3)_2$. A droplet of the sample was placed on a glass plate on a Linkam hot stage HFS-X350-GI (rate: 1 Kmin-1 – 0.01 Kmin-1). Exposure time was 5 min; the sample-detector distance was 9.00 cm for WAXS and 26.80 cm for SAXS. The diffraction patterns were recorded with a Vantec 500 area detector (Bruker AXS, Karlsruhe) and transformed to 1D plots using GADDS software.

Synchrotron-based X-ray scattering

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 based on 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, 3D electron density maps can be reconstructed based on the general formula.

$$E(xyz) = \sum_{hkl} F(hkl)\, e^{[i2\pi(hx+ky+lz)]} \qquad (1)$$

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

$$I(xy) = K \cdot F(hkl) = F \cdot (hkl) = K \cdot |F(hkl)|^2 \qquad (2)$$

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

$$E(xyz) = \sum_{hkl} \sqrt{I(hkl)}\, e^{[i2\pi(hx+ky+lz)+\Phi_{hkl}]} \qquad (3)$$

As the observed diffraction intensity, $I(hkl)$ is only related to the amplitude of the structure factor $|F(hkl)|$, the information about the phase of $F(hkl)$, Φ_{hkl}, cannot be determined directly from experiment. However, the problem is much simplified when the structure of the ordered phase is centrosymmetric; hence, the structure factor $F(hkl)$ is always real, and Φ_{hkl} 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.

S2. Additional data

S2.1. DSC traces

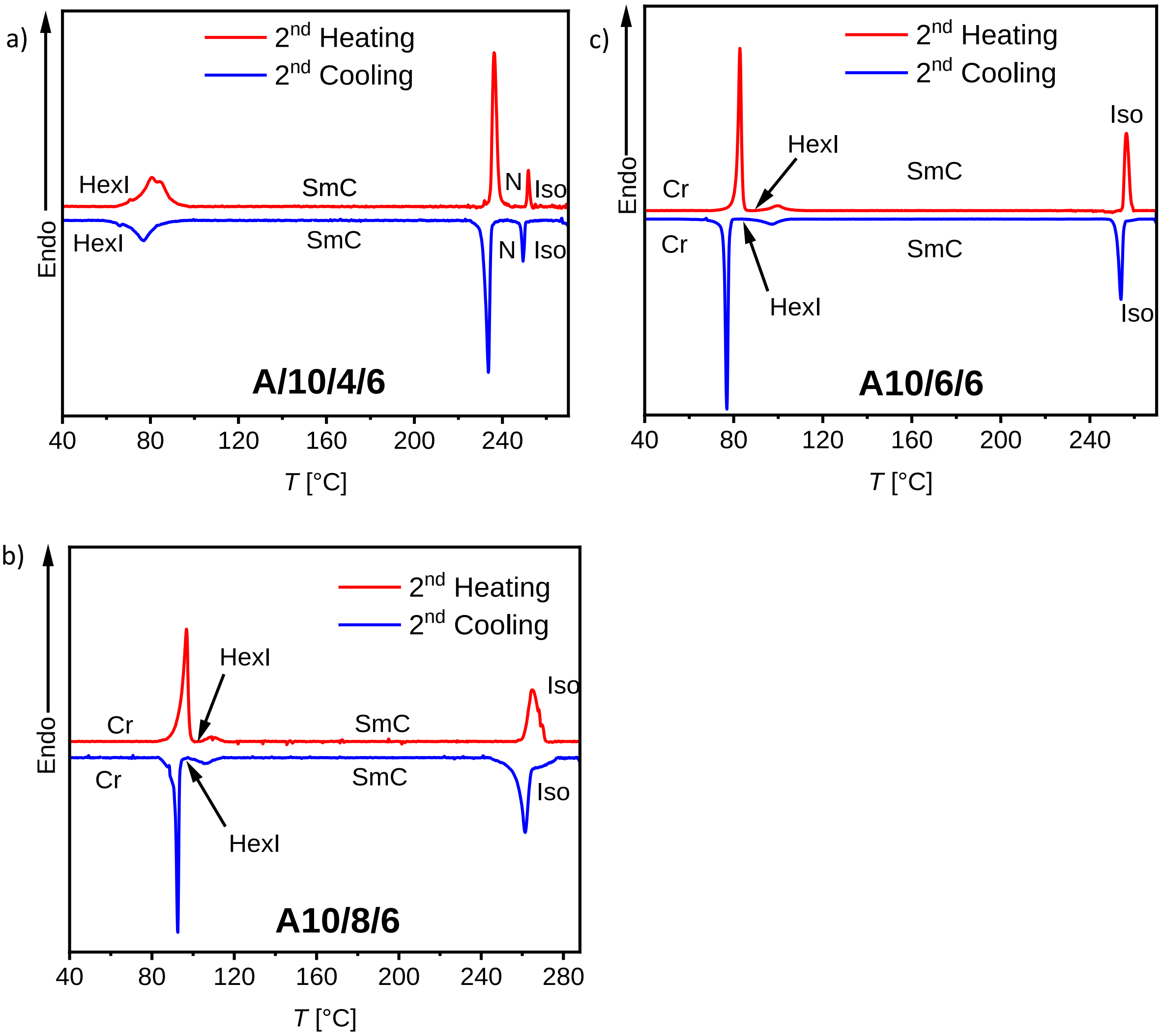

Figure S1. DSC heating and cooling traces of compounds **A10/*n*/*m***, recorded at 10 K min^{-1}.

S2.2 POM textures

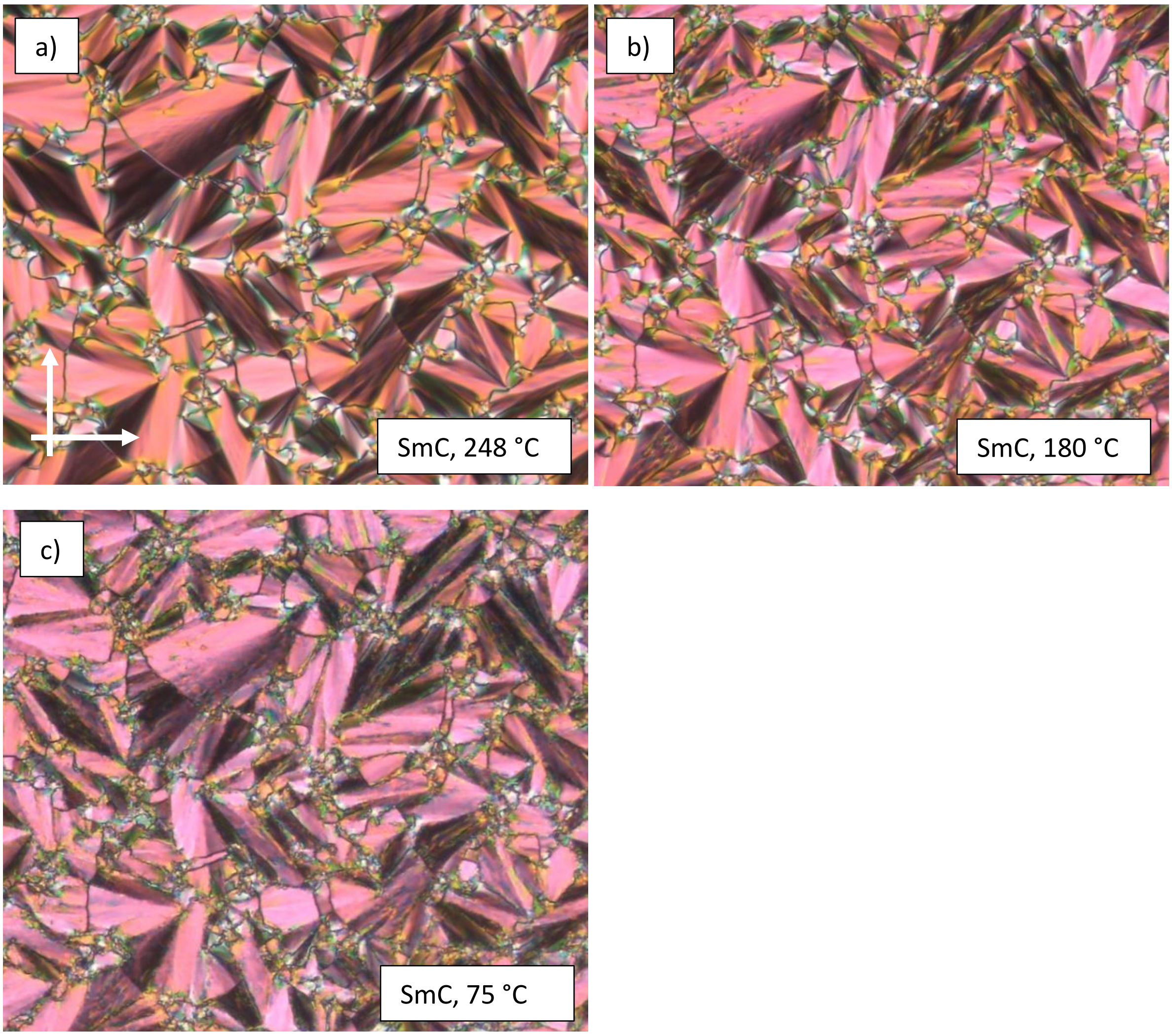

Figure S2. Textures of compounds **A6/6/8**, as observed upon cooling between crossed polarizers at the indicated temperatures (non-coated 6 µm ITO cell).

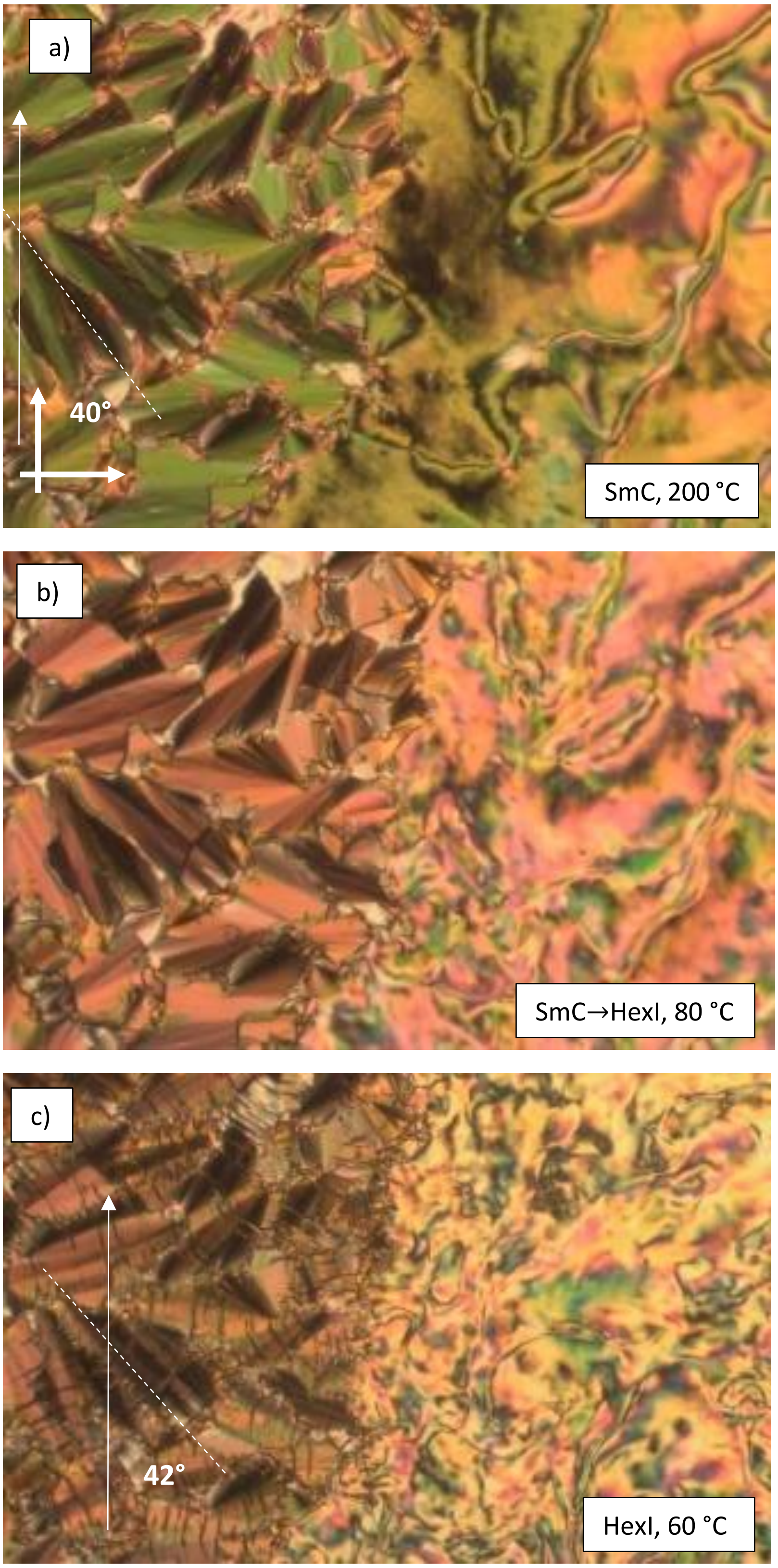

Figure S3. Textures of compounds **A10/4/6**, as observed between crossed polarizers between non-treated glass plates at the indicated temperatures upon cooling.

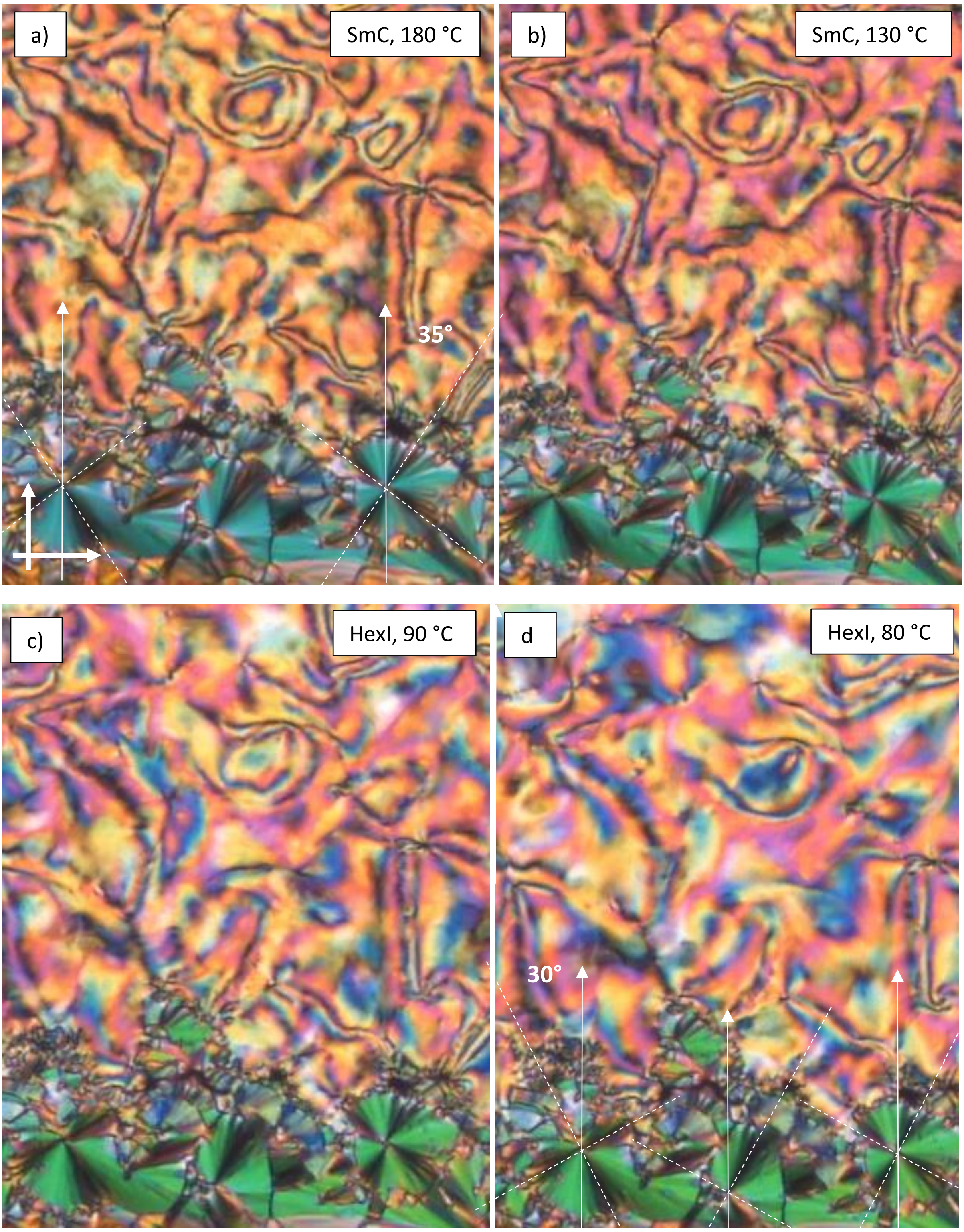

Figure S4. Textures of compounds **A10/6/6**, as observed between crossed polarizers, between non-treated glass plates at the indicated temperatures upon cooling.

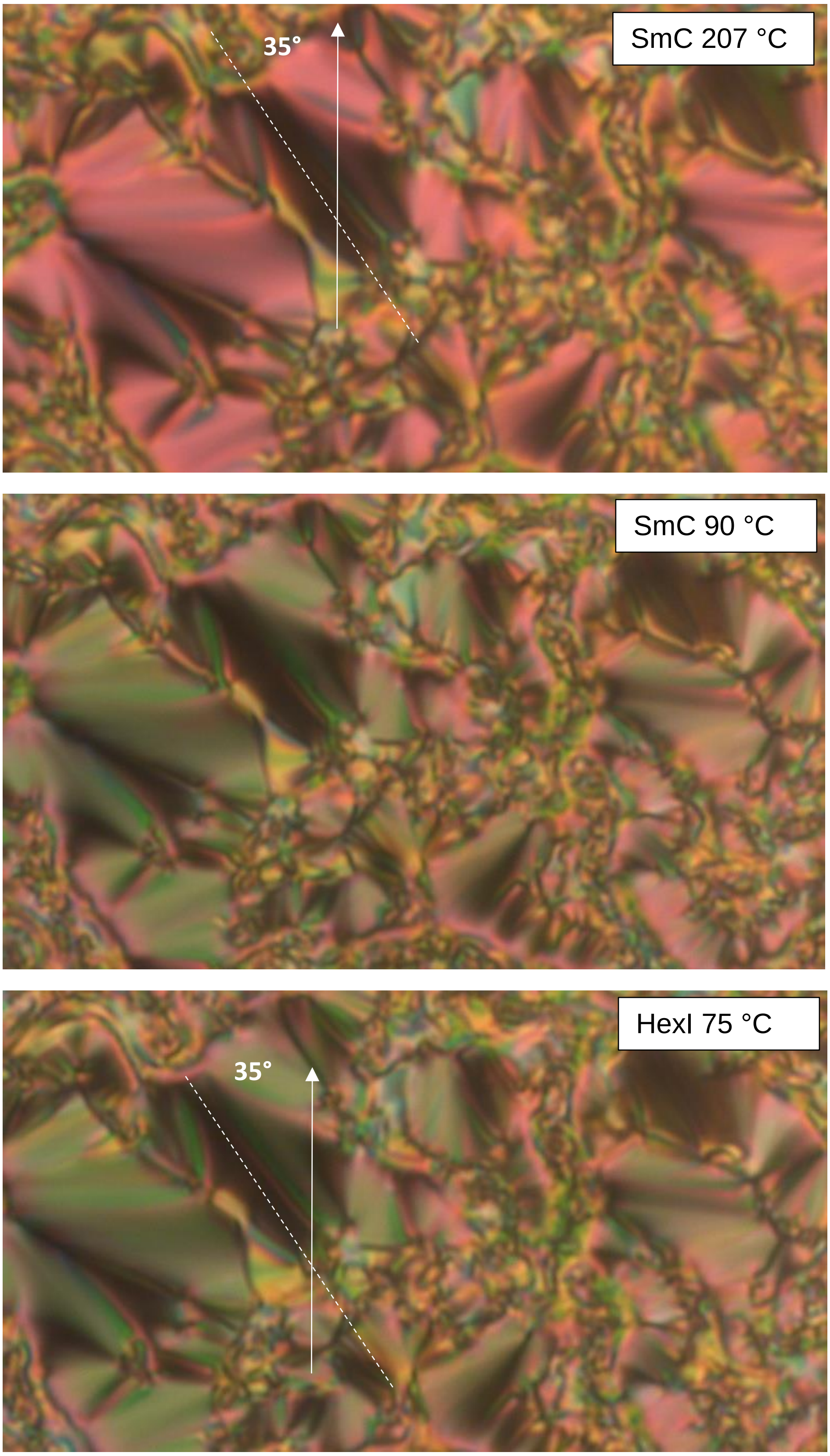

Figure S5. Textures of compounds **A10/6/8**, as observed between crossed polarizers, between non-treated glass plates at the indicated temperatures upon cooling.

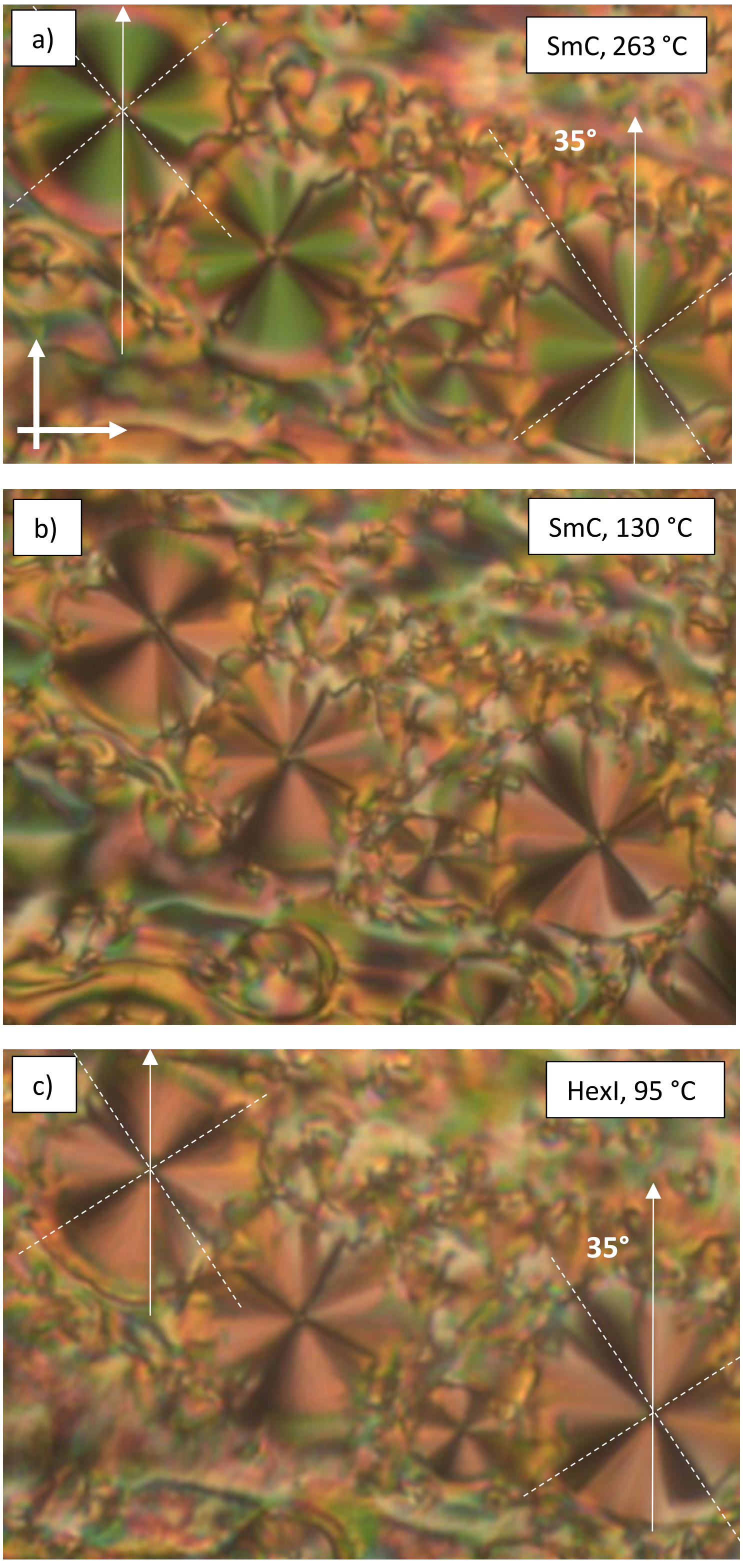

Figure S6. Textures of compounds **A10/8/6**, as observed between crossed polarizers, between non-treated glass plates at the indicated temperatures upon cooling.

S2.3. XRD data

S2.3.1 Additional SAXS pattern

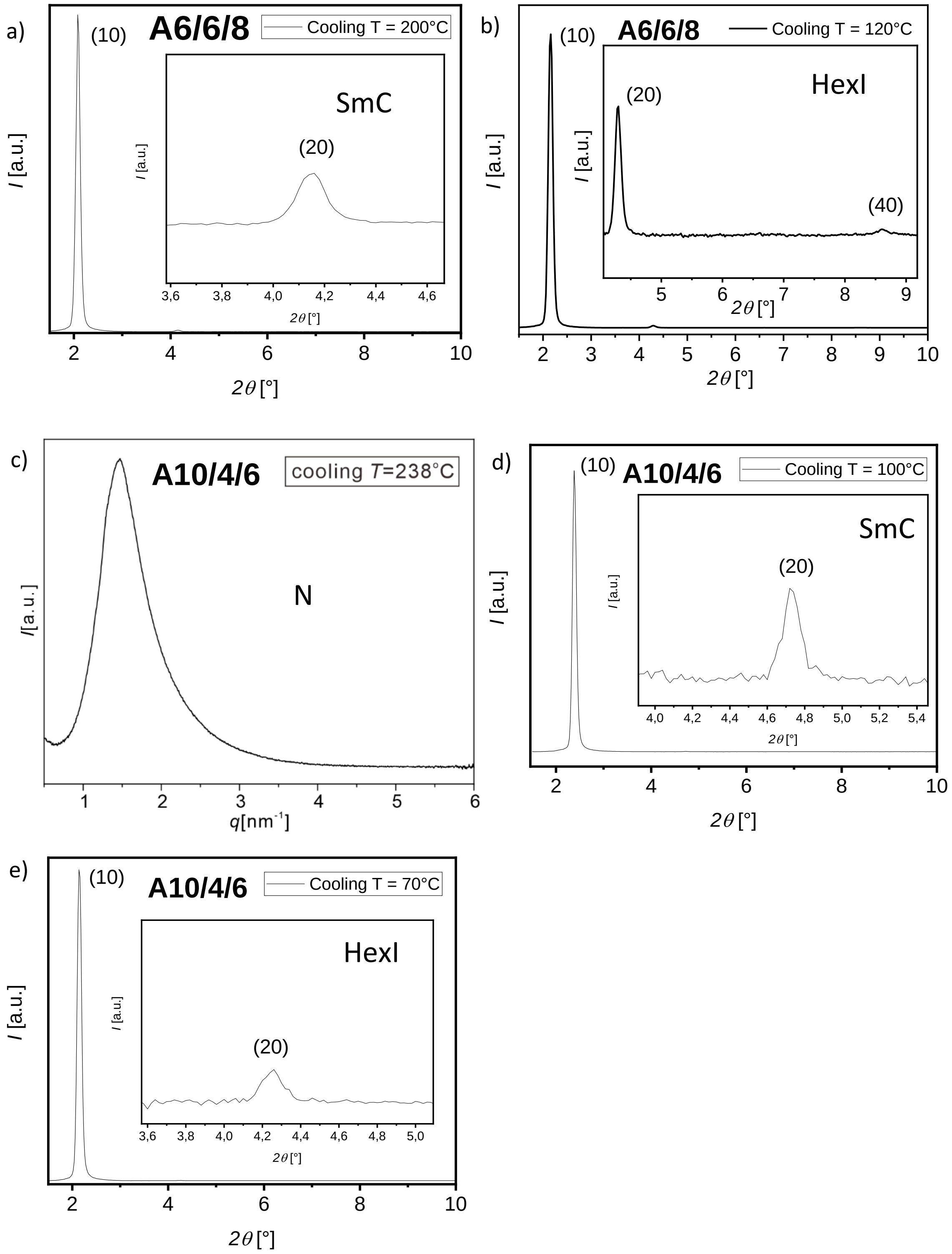

Figure S7. SAXS diffractograms of compounds **A6/6/8** and **A10/4/6** at the indicated temperatures.

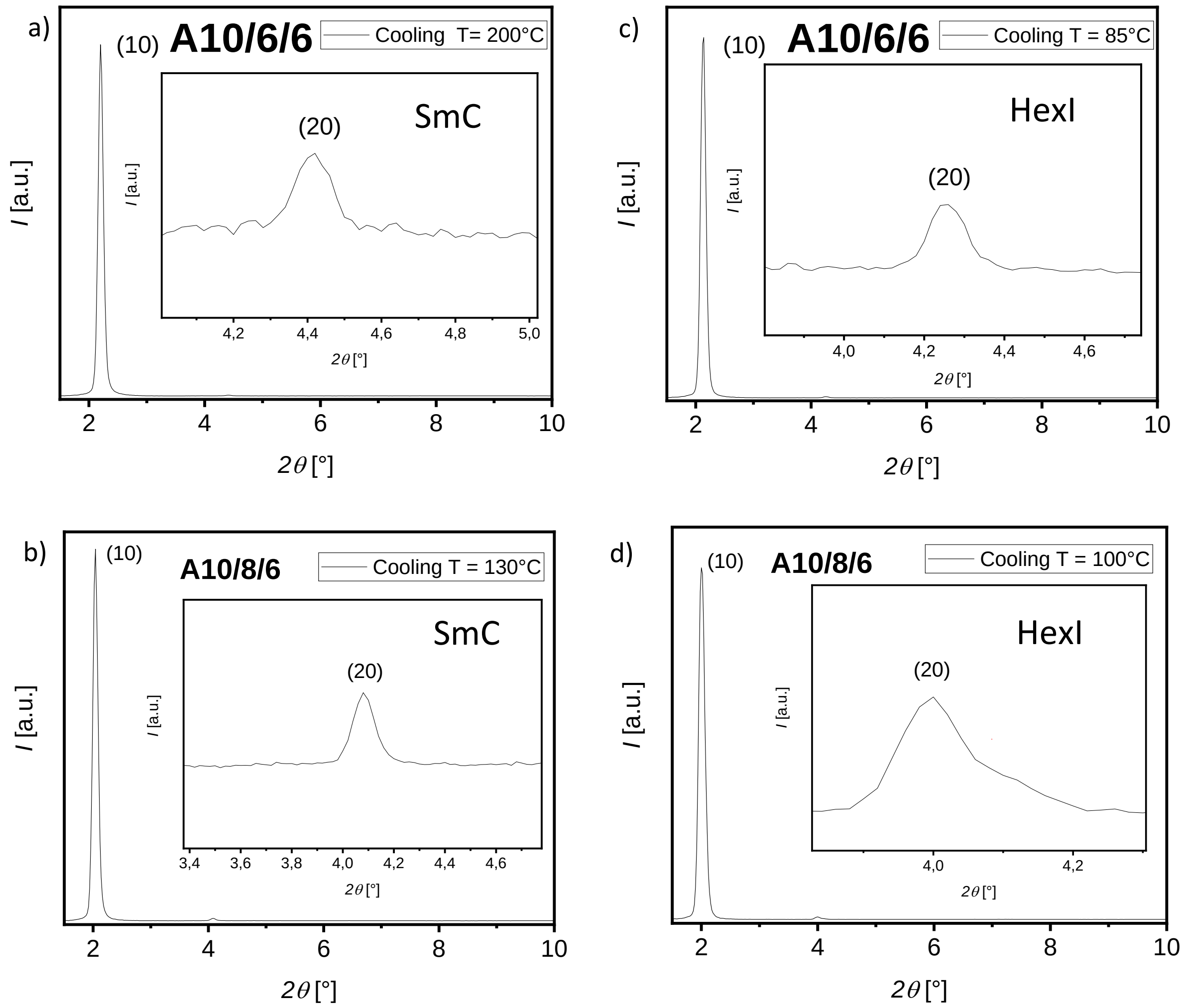

Figure S8. SAXS diffractograms of compounds **A10/6/6** and **A10/8/6** at the indicated temperatures.

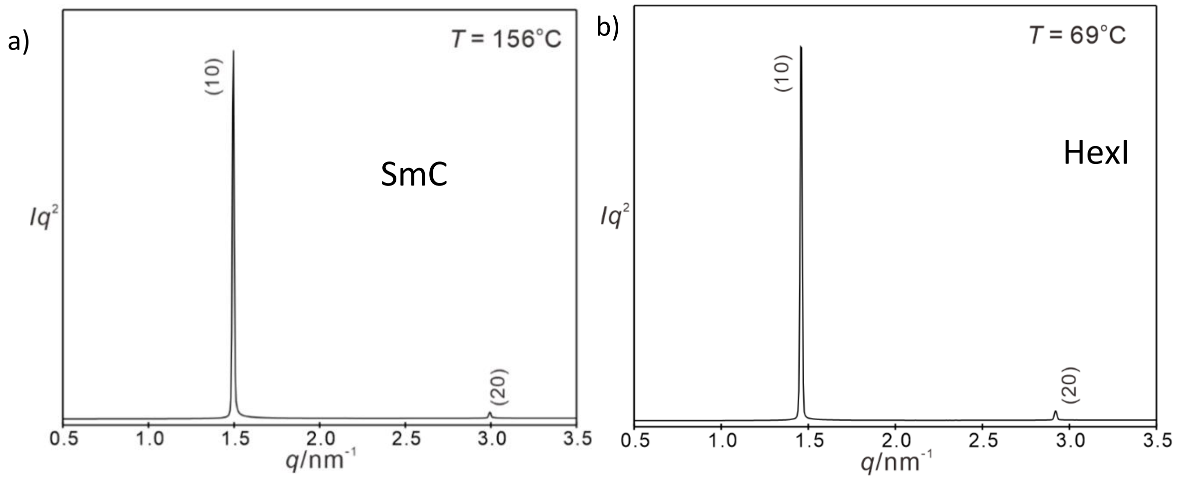

Figure S9. SAXS diffractograms of compounds **A10/6/8** in the different mesophases at the indicated temperatures.

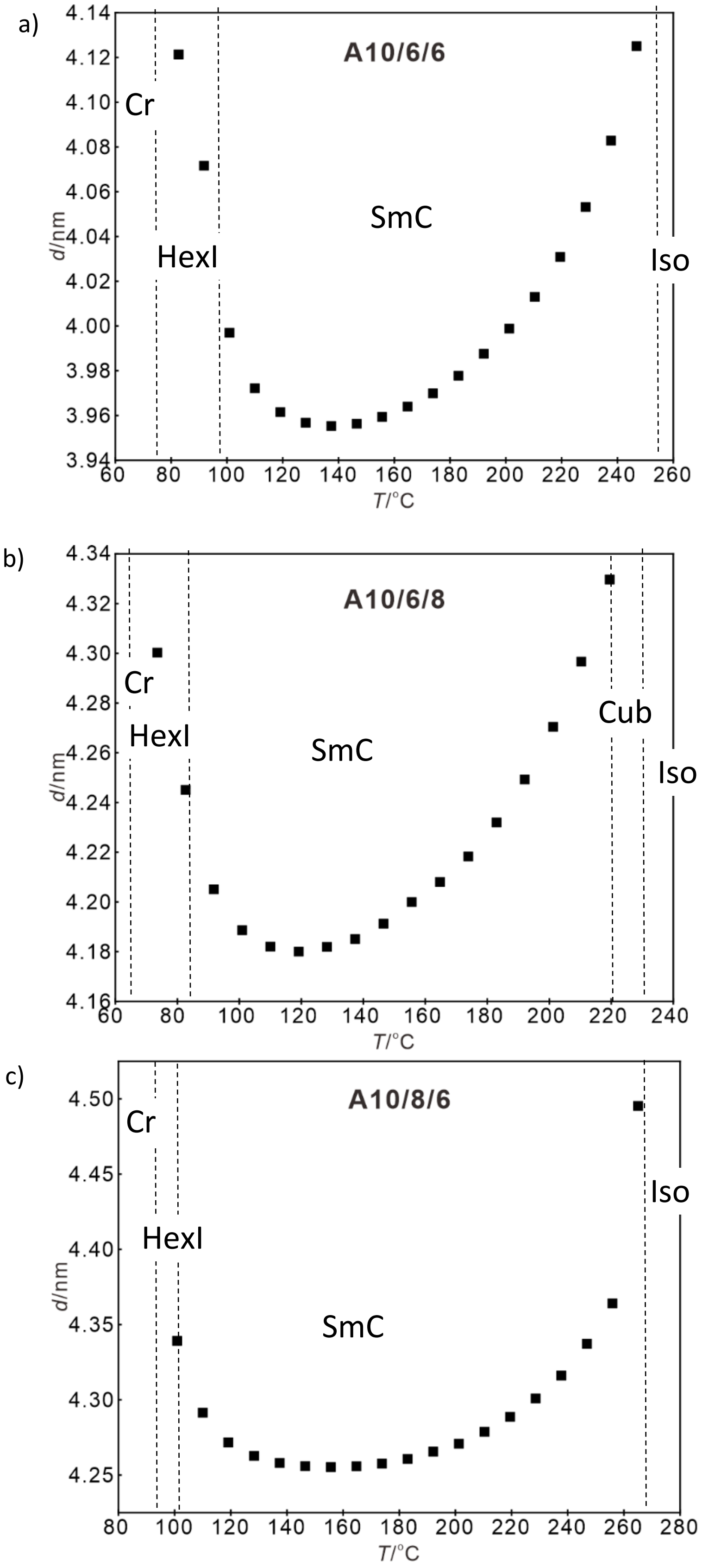

Figure S10. Temperature dependent of *d*-values of compounds SAXS diffractograms of compounds **A*x/n/m*** as recorded on cooling.

S2.3.2 Additional WAXS pattern

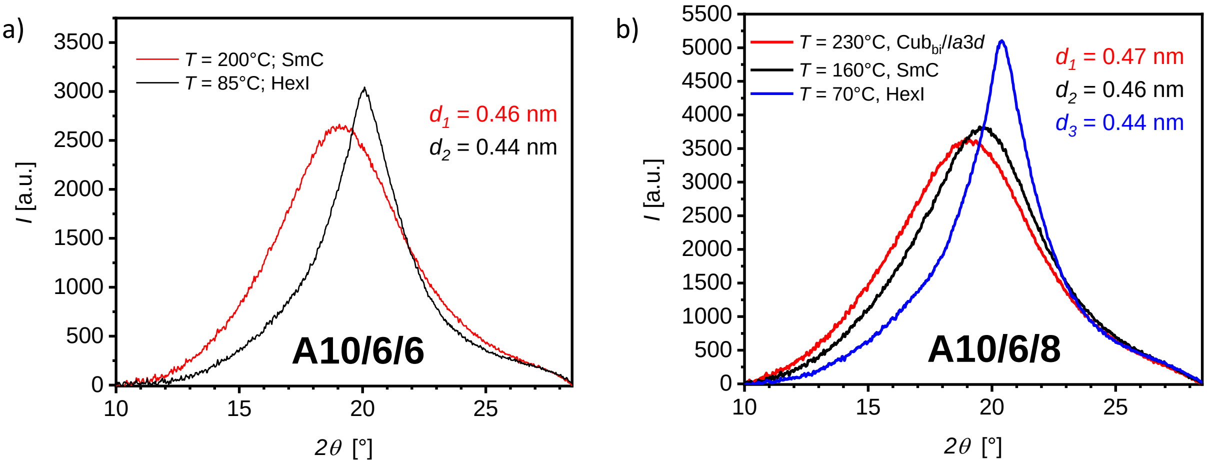

Figure S11. WAXS diffractograms of compounds **A10/*n*/*m*** at the indicated temperatures.

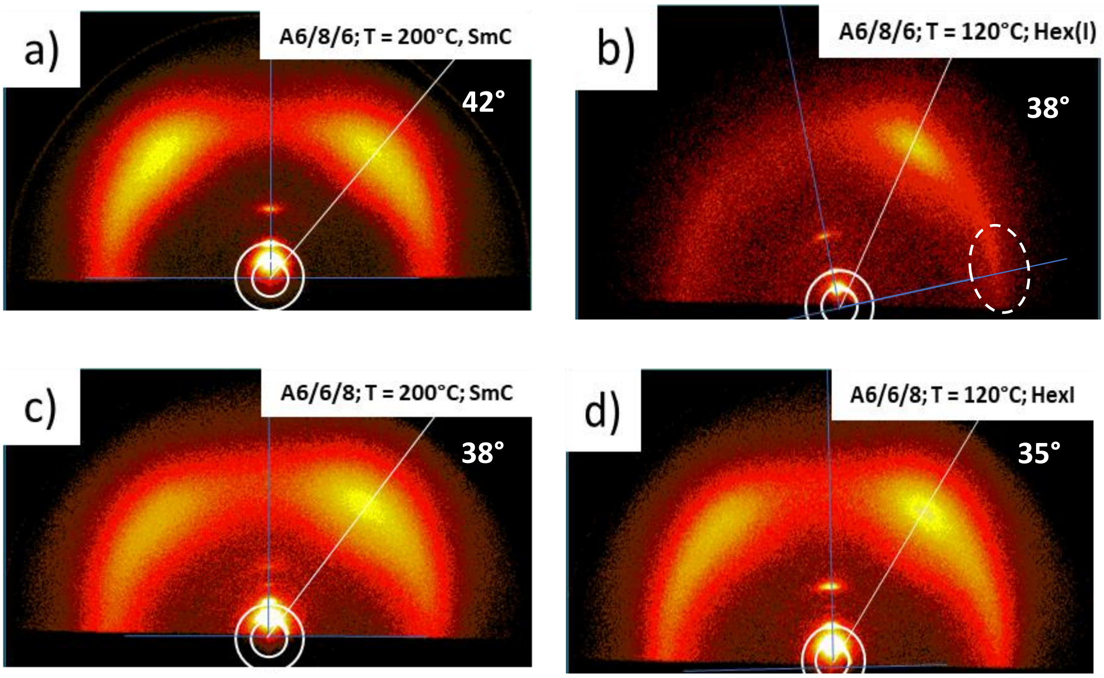

Figure S12. 2D wide-angle scattering of compounds **A6/*n*/*m*** at the indicated temperatures. Alignment is obtained with a droplet on a flat glass surface after slow cooling. Blue lines indicate the meridional and horizontal orientation, while white lines point to the maximum of the broad WAXS signal.

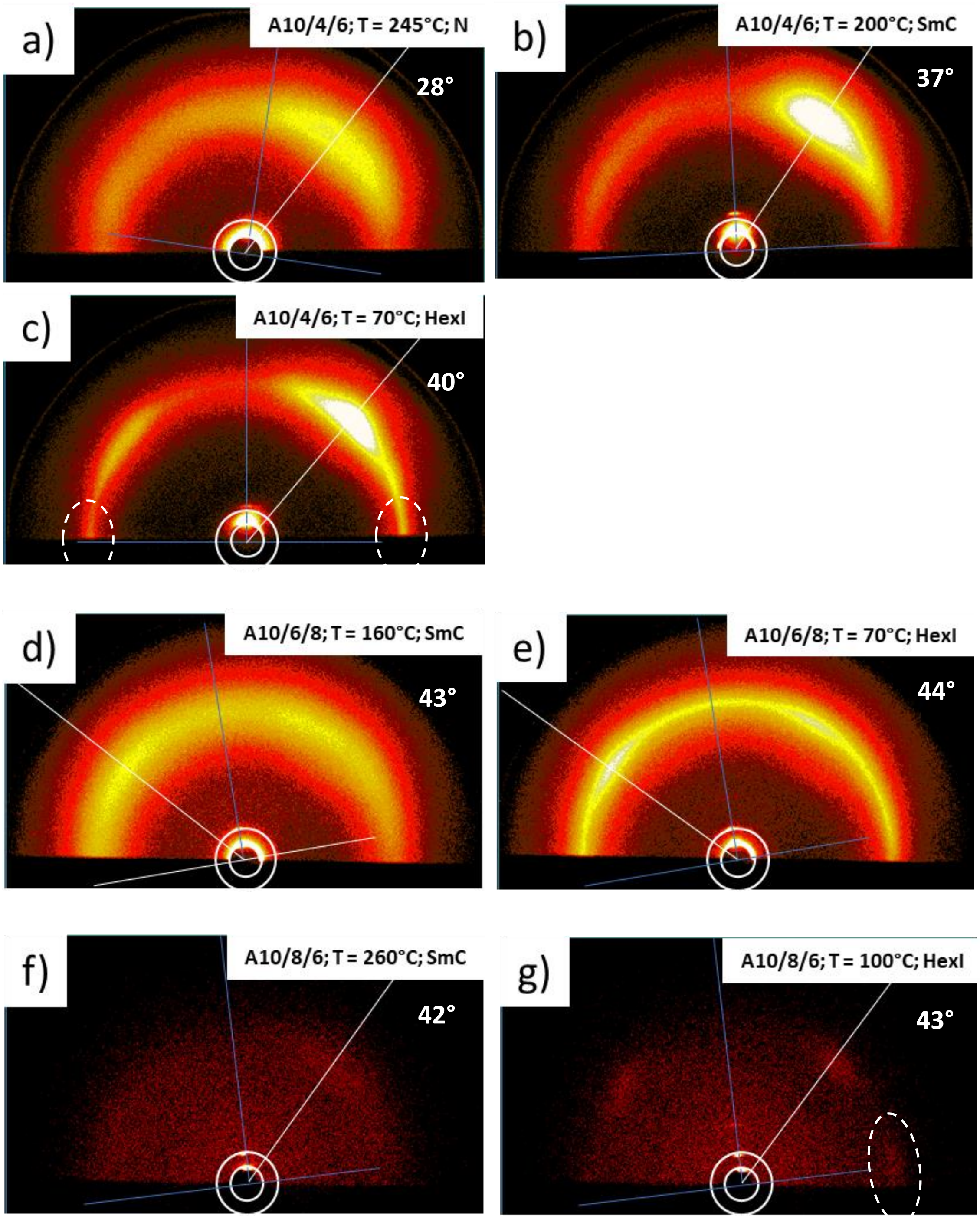

Figure S13. 2D wide-angle scattering of compounds **A10/*n*/*m*** at the indicated temperatures. Alignment is obtained with a droplet on a flat glass surface after slow cooling. Blue lines indicate the meridional and horizontal orientation, while white lines point to the maximum of the broad WAXS signal.

S2.3.3 Numerical SAXS data

Table S1. Experimental and calculated *d*-spacing of the observed SAXS reflection of the *Ia*3*d* phase in **A10/6/8** at 219 °C.[a]

(hk)	$d_{obs.}$ [nm]	$d_{calc.}$ [nm]	Δ	Intensity	Phase
211	5.29	5.29	0.00	100.0	π
220	4.58	4.58	0.00	45.0	π
321	3.46	3.46	0.00	0.1	-
400	3.23	3.24	0.01	1.7	-
420	2.89	2.90	0.01	0.9	-
332	2.76	2.76	0.00	0.2	-
422	2.64	2.65	0.01	0.04	-
431	2.54	2.54	0.00	0.3	-
440	2.29	2.29	0.00	0.2	-
611	2.10	2.10	0.00	0.2	-
a = 12.96 nm					
$V_{cell} = a^3 = 2177\ nm^3$					
$V_{mol} = 1.676 nm^3$					
$n_{cellL,}$ = 1159					
L_{net} = 110 nm					
n_{raft}= 4.74					
$\Phi = 6.92°$					

[a] V_{mol} = molecular volume as calculated with the crystal volume increments of Immirzi;[S1] n_{cell} number of molecules in a unit cell, calculated according to 0.893 $V_{\mathrm{cell}}/V_{\mathrm{mol}}$, where the factor 0.893 is a correction for the different packing density in the crystalline and the LC state; L_{net} = total length of the networks per unit cell (L_{net} = 8.485 a_{cub}; n_{raft} = number of molecules organized in each 0.45 nm tick raft of the networks, calculated according to $n_{\mathrm{raft}} = n_{\mathrm{cell}}/(L_{\mathrm{net}}/0.45)$; Φ = twist angle between adjacent rafts of molecules in the networks; Φ = 70.5°/[0.354 a_{cub}/0.45nm].[S2]

S2.4 Additional CPK models

Partial bilayer $L_d > L_{mol}$	Monolayer = $L_1 = L_{mol}$
	
A6/8/6	
	
A10/8/6	

Figure S14. Space-filling CPK models of compounds **A6/8/6** and **A10/8/6.**

S2.5 Tilt angles

Table S2. Tilt angles (optical and WAXS tilt from aligned samples) of the **A*x/n/m*** compounds in the different mesophases.[a]

Comp.	Phase	β_{opt} /°	β_{WAXS} /°	T/ °C
A6/6/8	SmC	28		85
	SmC	29		100
	SmC	30	35	120
	SmC	32	38	200
	SmC	30		235
A6/8/6	Hex(I)	42	38	117
	SmC	39	42	200
A10/4/6	HexI	43		50
	HexI	41	40	70
	SmC	38		90
	SmC	38		120
	SmC	39		150
	SmC	40	37	200
	SmC	40		230
	N		28	245
A10/6/6	HexI	30	41	85
	SmC	35	39	200
A10/6/8	HexI	35	44	70
	SmC	35	43	160
A10/8/6	HexI	35	43	100
	SmC	35	42	250

[a] ß$_{\mathrm{opt}}$ = optical tilt as determined by POM (orientation of extinction crosses or angle of maximum extinction in uniform planar alignment); ß$_{\mathrm{WAXS}}$ = X-ray tilt (orientation of the maximum of the diffuse wide-angle scattering with respect to the direction of the layer reflections, determined with surface-aligned samples with the layers (almost) parallel to the substrate surface.

S2.6 Photoisomerization

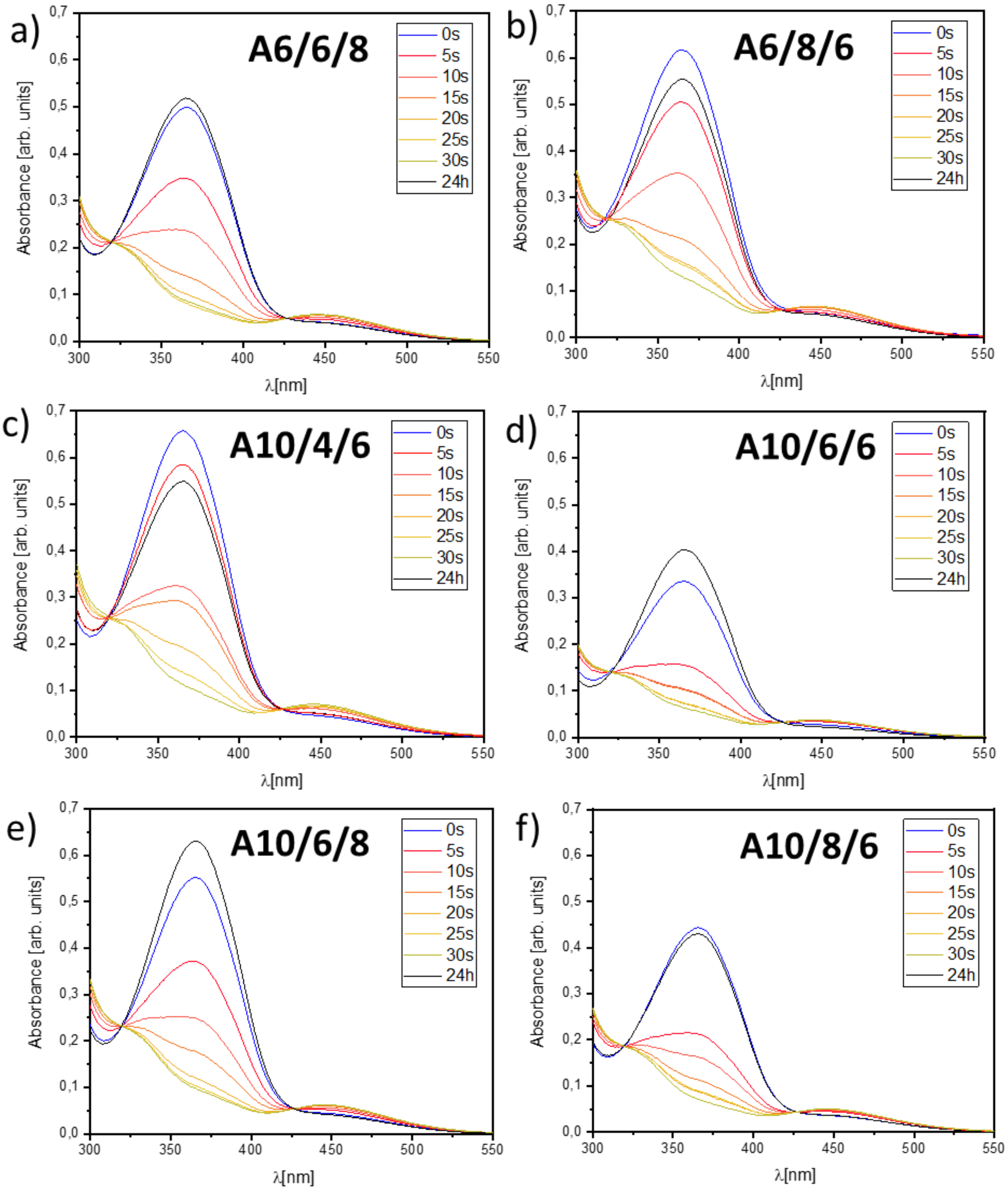

Figure S15. UV–Vis absorption spectra of all investigated azobenzene-based polycatenar compounds **A*x/n/m*** under 365 nm irradiation, showing characteristic changes associated with *trans–cis* photoisomerization. The spectra confirm fast and reversible switching behavior across the series.

S2.7 Structural formula

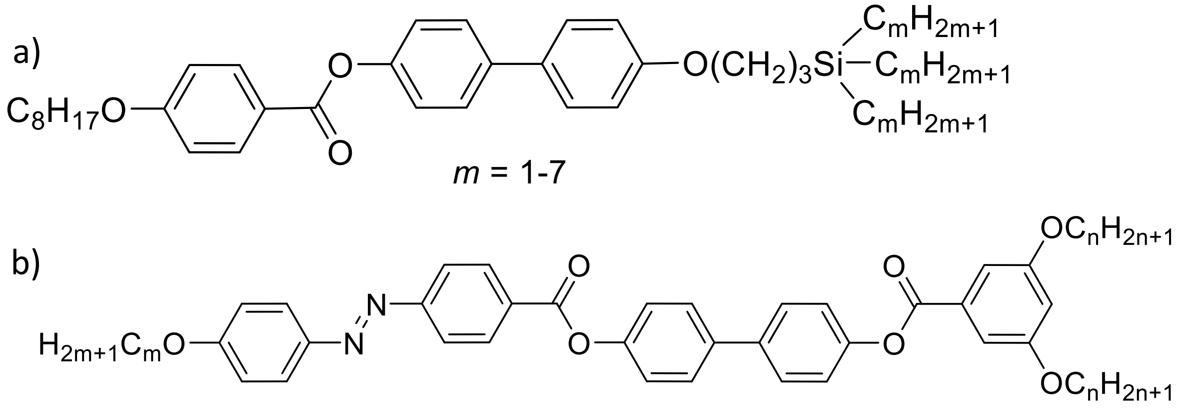

Figure S16. Formula of a) the previously reported polycatenar with highly branched R_3Si end-group [S3] and b) structure of Y-shaped tricatenars with 3,5-disubstiturion pattern forming hexatic LC phases.[S4]

S3. Synthesis

S3.1. General

The synthesis as well as the compound numbers are shown in Scheme 2 of the main text. 1-bromohexane, 1-bromooctane, trichlorosilane, 4,4′-dihydroxybiphenyl, ethyl 4-hydroxybenzoate, ethyl 4-aminobenzoate were obtained from Sigma-Aldrich; 4-bromo-1-butene, 6- bromo 1-hexene, and 8-bromo-1-octene were received from ABCR. All compounds were used as received. The synthesis of 4-(4-decyloxyphenyldiazenyl)benzoic acid and 4-(4-hexyloxyphenyldiazenyl)benzoic acid was performed according to our previously reported procedures.[S5]

Solvents used were ethanol, dichloromethane, triethylamine, N, N`-dimethylformamide, and pyridine, which were purchased by Sigma-Aldrich as HPLC standards and used as received.

Column chromatography was performed with silica gel 60 (0.063-0.2, Merck), and flash chromatography with silica gel 60 (0.040-0.063, Merck).

The purity of all compounds was checked by thin-layer chromatography (TLC, silica gel 60 F254, Merck). ^{1}H-, ^{13}C-, ^{29}Si-NMR spectra (Varian Unity 500 and Varian Unity 400 spectrometers) were recorded in $CDCl_3$ or pyridine-d_5 solutions. Tetramethylsilane was used as a reference for ^{1}H-NMR, ^{13}C-NMR, and ^{29}Si-NMR chemical shifts. All measurements were performed at 27 °C.

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 in negative Mode.

S3.2 Intermediates

S3.2.1 Tri-*n*-alkylsilanes 4/*m*[S6]

The appropriate *n*-alkylmagnesium bromide solution was prepared from magnesium turnings (3.5 equ.) and the corresponding *n*-alkyl bromide (4 equ.) in dry THF. The magnesium turnings were activated with a small amount of CH_2Br_2, and the *n*-alkyl bromide was added dropwise with stirring under an inert atmosphere. Upon initiation, the reaction mixture heated up spontaneously to reflux, accompanied by boiling of the solvent and a change in the colour of the solution. After completion of the reaction, as evidenced by cooling from reflux, the reaction mixture was stirred for an additional 30 min to ensure full consumption of magnesium.

The appropriate *n*-alkylmagnesium bromide solution (3.5 equ) in THF was cooled with stirring to 0 °C. LiCl (0.9 equ.) was added, followed by trichlorosilane (1 equ.) by adding with a syringe. The reaction is heated up to room temperature and stirred for 24h. Afterward, the reaction is quenched with water (1 mL / 1 mL THF), and the aqueous layers were extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with water and brine. After drying over anhydrous Na_2SO_4, filtration, and evaporation of the solvent (850 mbar, 60°C), the crude product was purified by column chromatography.

Tri-*n*-hextylsilane 4/6: Synthesized from *n*-hexylmangnesium bromide solution, LiCl (1.0 g, 23.2 mmol), trichlorosilane (3.5 g, 2.6 mL, 25.8 mmol) purification by column chromatography (eluent: *n*-hexane); colorless liquid, $C_{18}H_{40}Si$ M = 284.60 g/mol, yield: 5.96 g (81 %), ^{1}H-NMR ($CDCl_3$, 400 MHz): δ / ppm = 3.73 – 3.63 (m, 1H, -*SiH*), 1.43 – 1.22 (m, 24H, -C*H₂*), 0.89 (t, $^3J_{H,H}$ = 7.0 Hz, 9H, -C*H₃*), 0.63 – 0.54 (m, 6H, -SiC*H₂*). ^{29}Si-NMR ($CDCl_3$, 79 MHz): δ / ppm = -6.49 (*Si*).

Tri-*n*-octylsilane 4/8: Synthesized from *n*-octylmagnesium bromide solution, LiCl (0.9 g, 22.0 mmol), trichlorosilane (3.3 g, 2.5 mL, 24.4 mmol) purification by column chromatography (eluent: *n*-hexane); colorless liquid, $C_{24}H_{52}Si$ M =368.77 g/mol, yield 7.50 g (84 %), ^{1}H-NMR ($CDCl_3$, 500 MHz): δ / ppm = 3.72 – 3.63 (m, 1H, -Si*H*), 1.42 – 1.22 (m, 36H, -C*H₂*), 0.90 (t, $^3J_{H,H}$ = 6.9 Hz, 9H, -C*H₃*), 0.92 – 0.87 (m, 6H, -SiC*H₂*). ^{29}Si-NMR ($CDCl_3$, 79 MHz): δ / ppm = -6.47 (*Si*).

S3.2.2 ω-Bromoalkyltri-*n*-alkylsilanes 5/*n*/*m*[S7]

The appropriate trialkylsilane (1 equ.), ω-bromoalk-1-ene (1.5 equ), and Karstedt-cat. ~ 2% Pt in xylene (3 mol%) were added to anhydrous CH_2Cl_2 (20 mL/mmol) and stirred at RT for 3 days. Afterwards, the solvent was evaporated, and the crude product was purified by column chromatography.

4-Bromobutyltri-*n*-hexylsilane 5/6/8: Synthesized from tri-*n*-hexylsilane (2.5 g, 8.8 mmol), 4-bromobut-1-ene (1.8 g, 1.3 mL, 13.2 mmol), Karstedt-cat. (0.11 mL) in anhydrous CH_2Cl_2 (20 mL); purification by column chromatography (eluent: *n*-hexane); colorless liquid, $C_{22}H_{47}SiBr$ M = 419.61 g/mol, yield: 3.27 g (88 %), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.39 (t, $^3J_{H,H}$ = 6.9 Hz, 2H, BrC*H₂*-), 1.90 – 1.81 (m, 2H, $BrCH_2$C*H₂*-), 1.50 – 1.40 (m, 2H, $BrCH_2CH_2$C*H₂*-), 1.40 – 1.21 (m, 24H, -C*H₂*-), 0.90 (t, $^3J_{H,H}$ = 6.6 Hz, 9H, -C*H₃*), 0.58 – 0.45 (m, 8H, -SiC*H₂*-). ^{29}Si-NMR ($CDCl_3$, 79 MHz): δ / ppm = 2.91 (Si).

6-Bromohexyltri-*n*-hexylsilane 5/6/6: Synthesized from tri-*n*-hexylsilane (3.0 g, 10.5 mmol), 6-bromohex-1-ene (2.6 g, 2.3 mL, 15.8 mmol), Karstedt-cat. (0.28 mL) in anhydrous CH_2Cl_2 (20 mL); purification by column chromatography (eluent: *n*-hexane); colorless liquid,

$C_{24}H_{51}SiBr$ M = 447.66 g/mol, yield: 2.30 g (47 %), ^{1}H-NMR (CDCl$_3$, 400 MHz): δ / ppm = 3.40 (t, $^3J_{H,H}$ = 6.9 Hz, 2H, BrCH_2-), 1.90 – 1.80 (m, 2H, BrCH$_2$CH_2-), 1.47 – 1.38 (m, 2H, BrCH$_2$CH$_2$CH_2-), 1.38 – 1.20 (m, 28H, -CH_2-), 0.88 (t, $^3J_{H,H}$ = 6.3 Hz, 9H, -CH_3), 0.53 – 0.43 (m, 8H, -SiCH_2-). ^{29}Si-NMR (CDCl$_3$, 79 MHz): δ / ppm = 2.90 (*Si*).

6-Bromohexyltri-*n*-octylsilane 5/6/8: Synthesized from tri-*n*-octylsilane (3.0 g, 8.1 mmol), 6-bromohex-1-ene (2.0 g, 1.7 mL, 12.2 mmol), Karstedt-cat. (0.11 mL) in anhydrous CH$_2$Cl$_2$ (20 mL); purification by column chromatography (eluent: *n*-hexane); colorless liquid, $C_{30}H_{63}SiBr$ M = 531.82 g/mol, yield: 2.87 g (66 %), ^{1}H-NMR (CDCl$_3$, 400 MHz): δ / ppm = 3.40 (t, $^3J_{H,H}$ = 6.9 Hz, 2H, BrCH_2-), 1.97 – 1.75 (m, 2H, BrCH$_2$CH_2-), 1.48 – 1.38 (m, 2H, BrCH$_2$CH$_2$CH_2-), 1.38 – 1.19 (m, 40H, -CH_2-), 0.88 (t, $^3J_{H,H}$ = 7.0 Hz, 9H, -CH_3), 0.52 – 0.44 (m, 8H, -SiCH_2-). ^{29}Si-NMR (CDCl$_3$, 79 MHz): δ / ppm = 2.92 (*Si*).

8-Bromooctyltri-*n*-hexylsilane 5/8/6: Synthesized from tri-*n*-hexylsilane (2.5 g, 8.7 mmol), 8-bromooct-1-ene (2.5 g, 2.2 mL, 13.1 mmol), Karstedt-cat. (0.12 mL) in anhydrous CH$_2$Cl$_2$ (20 mL); purification by column chromatography (eluent: *n*-hexane); colorless liquid, $C_{26}H_{55}SiBr$ M = 475.72 g/mol, yield: 2.28 g (55 %), ^{1}H-NMR (CDCl$_3$, 400 MHz): δ / ppm = 3.40 (t, $^3J_{H,H}$ = 6.9 Hz, 2H, BrCH_2-), 1.91 – 1.80 (m, 2H, BrCH$_2$CH_2-), 1.48 – 1.38 (m, 2H, BrCH$_2$CH$_2$CH_2-), 1.38 – 1.20 (m, 32H, -CH_2-), 0.87 (t, $^3J_{H,H}$ = 7.1 Hz, 9H, -CH_3), 0.56 – 0.43 (m, 8H, -SiCH_2-). ^{29}Si-NMR (CDCl$_3$, 79 MHz): δ / ppm = 2.89 (*Si*).

S3.2.3 Ethyl 4-[ω-(tri-*n*-alkylsilyl)alkyloxy]benzoates 6/*n*/*m*[S8]

Under an inert atmosphere, ethyl 4-hydroxybenzoate (1 equ.) and **5/*n*/*m*** (1.1 equ.) were dissolved in DMF (5 mL / 2 mmol benzoate). K$_2$CO$_3$ (5 equ.) was suspended in the reaction mixture and stirred for 12h at 80°C. After cooling to room temperature, the reaction was quenched with water. The aqueous solution was extracted with ethyl acetate (3 x 50 mL). The combined organic layers were washed with water and dried over MgSO$_4$. The solvent was evaporated (850 mbar, 60°C), and the crude product was purified by column chromatography (eluent: 1. *n*-hexane; 2. ethyl acetate: *n*-hexane (3:7)).

Ethyl 4-[4-(tri-*n*-hexylsilyl)butyloxy]benzoate 6/4/6: Synthesized from **5/4/6** (2.8 g, 6.6 mmol), ethyl 4-hydroxybezoate (1.0 g, 6.0 mmol), K$_2$CO$_3$ (4.2 g, 30.0 mmol) in DMF (15 mL); purification by column chromatography (eluent: 1. *n*-hexane; 2. ethyl acetate: *n*-hexane (3:7)); white solid $C_{31}H_{56}O_3Si$, M = 504.87 g/mol; yield: 3.03 g (91 %); ^{1}H NMR (CDCl$_3$, 402 MHz): δ / ppm = 7.96 (d, $^3J_{H,H}$ = 8.4 Hz, 2H, Ar-*H*), 6.88 (d, $^3J_{H,H}$ = 8.6 Hz, 2H, Ar-*H*), 4.32 (q, $^3J_{H,H}$ = 7.2 Hz, 2H, -OCH_2-), 3.98 (t, $^3J_{H,H}$ = 6.6 Hz, 2H, -OCH_2-), 1.83 – 1.73 (m, 2H, -OCH$_2$CH_2-), 1.49 – 1.40 (m, 2H, -OCH$_2$CH$_2$CH_2-), 1.36 (t, $^3J_{H,H}$ = 7.2 Hz, 3H, -CH_3), 1.34 – 1.18 (m, 24H, -CH_2-), 0.87 (t, $^3J_{H,H}$ = 6.6 Hz, 9H, -CH_3), 0.53 – 0.40 (m, 8H, -SiCH_2-). ^{29}Si NMR (CDCl$_3$, 80 MHz): δ / ppm = 2.89 (*Si*).

Ethyl 4-[4-(tri-*n*-hexylsilyl)hexyloxy]benzoate 6/6/6: Synthesized from **5/6/6** (0.9 g, 2.2 mmol), ethyl 4-hydroxybezoate (0.3 g, 2.0 mmol), K$_2$CO$_3$ (1.4 g, 10.0 mmol) in DMF (5 mL); purification by column chromatography (eluent: 1. *n*-hexane; 2. ethyl acetate: *n*-hexane (3:7)); white solid $C_{33}H_{60}O_3Si$, M = 532.93 g/mol; yield: 0.82 g (77 %); ^{1}H-NMR (CDCl$_3$, 402 MHz): δ / ppm = 7.96 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, Ar-*H*), 6.88 (d, $^3J_{H,H}$ = 8.6 Hz, 2H, Ar-*H*), 4.32 (q, $^3J_{H,H}$ = 7.1 Hz, 2H, -OCH_2-), 3.98 (t, $^3J_{H,H}$ = 6.5 Hz, 2H, -OCH_2-), 1.83 – 1.72 (m, 2H, -OCH$_2$CH_2-), 1.51 – 1.41 (m, 2H, -OCH$_2$CH$_2$CH_2-), 1.36 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, -CH_3), 1.33 – 1.18 (m, 28H, -CH_2-), 0.87 (t, $^3J_{H,H}$ = 6.6 Hz, 9H, -CH_3), 0.55 – 0.43 (m, 8H, -SiCH_2-). ^{29}Si NMR (CDCl$_3$, 80 MHz): δ / ppm = 2.90 (*Si*).

Ethyl 4-[4-tri-*n*-hexylsilyl)octyloxy]benzoate 6/8/6: Synthesized from **5/8/6** (1.5 g, 3.3 mmol), ethyl 4-hydroxybezoate (0.5 g, 3.0 mmol), K_2CO_3 (2.1 g, 15.0 mmol) in DMF (7 mL); purification by column chromatography (eluent: 1. *n*-hexane; 2. ethyl acetate: *n*-hexane (3:7)); white solid $C_{35}H_{64}O_3Si$, M = 560.98 g/mol; yield: 1.40 g (83 %); ^{1}H-NMR ($CDCl_3$, 402 MHz): δ / ppm = 7.96 (d, $^3J_{H,H}$ = 9.2 Hz, 2H, Ar-*H*), 6.87 (d, $^3J_{H,H}$ = 9.0 Hz, 2H, Ar-*H*), 4.33 (q, $^3J_{H,H}$ = 7.1 Hz, 2H, -OCH_2-), 4.00 (t, $^3J_{H,H}$ = 6.4 Hz, 2H, -OCH_2-), 1.85 – 1.74 (m, 2H, -OCH$_2$CH_2-), 1.51 – 1.39 (m, 2H, -OCH$_2$CH$_2$CH_2-), 1.36 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, -CH_3), 1.33 – 1.16 (m, 32H, -CH_2-), 0.84 (t, $^3J_{H,H}$ = 6.1 Hz, 9H, -CH_3), 0.59 – 0.44 (m, 8H, -SiCH_2-). ^{29}Si-NMR ($CDCl_3$, 80 MHz): δ / ppm = 3.02 (*Si*).

Ethyl 4-[4-tri-*n*-octylsilyl)hexyloxy]benzoate 6/6/8: Synthesized from **5/6/8** (2.8 g, 5.2 mmol), ethyl 4-hydroxybezoate (0.8 g, 4.7 mmol), K_2CO_3 (3.2 g, 23.5 mmol) in DMF (10 mL); purification by column chromatography (eluent: 1. *n*-hexane; 2. ethyl acetate: *n*-hexane (3:7)); white solid $C_{39}H_{72}O_3Si$, M = 617.09 g/mol; yield: 1.96 g (66 %); ^{1}H-NMR ($CDCl_3$, 400 MHz): δ / ppm = 7.98 (d, $^3J_{H,H}$ = 9.1 Hz, 2H, Ar-*H*), 6.89 (d, $^3J_{H,H}$ = 9.1 Hz, 2H, Ar-*H*), 4.34 (q, $^3J_{H,H}$ = 7.1 Hz, 2H, -OCH_2-), 4.00 (t, $^3J_{H,H}$ = 6.5 Hz, 2H, -OCH_2-), 1.85 – 1.72 (m, 2H, -OCH$_2$CH_2-), 1.52 – 1.42 (m, 2H, -OCH$_2$CH$_2$CH_2-), 1.37 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, -CH_3), 1.34 – 1.19 (m, 40H, -CH_2-), 0.87 (t, $^3J_{H,H}$ = 6.3 Hz, 9H, -CH_3), 0.53 – 0.42 (m, 8H, -SiCH_2-). ^{29}Si-NMR ($CDCl_3$, 79 MHz): δ / ppm = 2.92 (*Si*).

S3.2.4 4-[ω-(*n*-Trialkyl silyl)alkyloxy]benzoic acid 7/*n*/*m*[S9]

The appropriate ethyl 4-[ω-(tri-*n*-alkylsilyl)alkyloxy]benzoate (1 equ.) was dissolved in ethanol (15 mL / mmol benzoate), and NaOH (50 equ.) dissolved in water (5 mL / 25 equ. NaOH) was added to the solution. After a quick precipitation, the reaction mixture became colorless, and the reaction progress was determined by TLC. After the reaction was finished, the mixture was added to a mixture of crushed ice (100 g) and 20 mL conc. HCl. The formed precipitate was filtered and washed with EtOH (3 x 50 mL).

4-[4-(Tri-*n*-hexylsilyl)butyloxy]benzoic acid 7/4/6: Synthesized from **6/4/6** (3.03 g, 6.0 mmol), NaOH (12 g, 300 mol) in EtOH (90 mL); colorless solid, $C_{29}H_{52}O_3Si$, M = 476.82 g/mol; yield: 5.52 g (92 %); ^{1}H-NMR ($CDCl_3$, 402 MHz): δ / ppm = 8.03 (d, $^3J_{H,H}$ = 9.0 Hz, 2H, Ar-*H*), 6.92 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, Ar-*H*), 4.02 (t, $^3J_{H,H}$ = 6.4 Hz, 2H, -OCH_2-), 1.86 – 1.75 (m, 2H, -OCH$_2$CH_2-), 1.51 – 1.39 (m, 2H, -OCH$_2$CH$_2$CH_2-), 1.34 – 1.16 (m, 24H, -CH_2-), 0.87 (t, $^3J_{H,H}$ = 7.1 Hz, 9H), 0.58 – 0.44 (m, 8H, -SiCH_2-). ^{29}Si-NMR ($CDCl_3$, 80 MHz): δ / ppm = 3.02 (*Si*).

4-[6-(Tri-*n*-hexylsilyl)hexyloxy]benzoic acid 7/6/6: Synthesized from **6/6/6** (0.82 g, 1.5 mmol), NaOH (3.0 g, 75 mol) in EtOH (23 mL); colorless solid, $C_{31}H_{56}O_3Si$, M = 504.87 g/mol; yield: 0.65 g (86 %); ^{1}H-NMR ($CDCl_3$, 402 MHz): δ / ppm = 8.03 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, Ar-*H*), 6.91 (d, $^3J_{H,H}$ = 9.1 Hz, 2H, Ar-*H*), 4.00 (t, $^3J_{H,H}$ = 6.5 Hz, 2H, -OCH_2-), 1.84 – 1.72 (m, 2H, -OCH$_2$CH_2-), 1.50 – 1.40 (m, 2H, -OCH$_2$CH$_2$CH_2-), 1.40 – 1.17 (m, 28H, -CH_2-), 0.86 (t, $^3J_{H,H}$ = 6.4 Hz, 9H, -CH_3), 0.54 – 0.42 (m, 8H, -SiCH_2-). ^{29}Si-NMR ($CDCl_3$, 80 MHz): δ / ppm = 2.90 (*Si*).

4-[8-(Tri-*n*-hexylsilyl)octyloxy]benzoic acid 7/8/6: Synthesized from **6/8/6** (1.4 g, 2.5 mmol), NaOH (5.0 g, 125 mol) in EtOH (38 mL); colorless solid, $C_{33}H_{60}O_3Si$, M = 532.93 g/mol; yield: 1.25 g (94 %); ^{1}H-NMR ($CDCl_3$, 502 MHz): δ / ppm = 8.05 (d, $^3J_{H,H}$ = 8.9 Hz, 2H, Ar-*H*), 6.95 (d, $^3J_{H,H}$ = 9.4 Hz, 2H, Ar-*H*), 4.03 (t, $^3J_{H,H}$ = 6.6 Hz, 2H, -OCH_2-), 1.87 – 1.77 (m, 2H, -OCH$_2$CH_2-), 1.52 – 1.43 (m, 2H, -OCH$_2$CH$_2$CH_2-), 1.41 – 1.21 (m, 32H, -CH_2-), 0.89 (t, $^3J_{H,H}$

= 7.0 Hz, 9H, -CH_3), 0.54 – 0.45 (m, 8H, -SiCH_2-). ^{29}Si NMR (CDCl$_3$, 100 MHz): δ / ppm = 2.91 (*Si*).

4-[6-(Tri-*n*-octylsilyl)hexyloxy]benzoic acid 7/6/8: Synthesized from **6/6/8** (2.0 g, 3.2 mmol), NaOH (6.4 g, 160 mol) in EtOH (45 mL); colorless solid, $C_{37}H_{68}O_3Si$, M = 589.03 g/mol; yield: 0.47 g (25 %); ^{1}H-NMR (CDCl$_3$, 400 MHz): δ / ppm = 8.05 (d, $^{3}J_{H,H}$ = 7.5 Hz, 2H, Ar-*H*), 6.93 (d, $^{3}J_{H,H}$ = 8.8 Hz, 2H, Ar-*H*), 4.02 (t, $^{3}J_{H,H}$ = 6.6 Hz, 2H, -OCH_2-), 1.86 – 1.76 (m, 2H, -OCH$_2$CH_2-), 1.53 – 1.42 (m, 2H, -OCH$_2$CH$_2$CH_2-), 1.42 – 1.35 (m, 2H, -OCH$_2$CH$_2$CH$_2$CH_2-), 1.35 – 1.22 (m, 38H, -CH_2-), 0.88 (t, $^{3}J_{H,H}$ = 6.7 Hz, 9H, -CH_3), 0.52 – 0.42 (m, 8H, -SiCH_2-). ^{29}Si-NMR (CDCl$_3$, 79 MHz): δ / ppm = 2.91 (*Si*).

S3.2.5 4'-Hydroxy[1,1'-biphenyl] derivatives 8/*n*/*m*[S10]

In an inert atmosphere, ω-[4-(tri-*n*-alkylsilyl)alkyloxy]benzoic acid (1 equ.) and DMF (cat.) were added to an excess of thionyl chloride (2 mL / mmol acid). The solution was stirred for 15 min at RT, followed by 2h of reflux. The reaction is cooled down to RT, and thionyl chloride is removed by vacuum distillation. Afterwards, 4,4’-dihydroxibiphenyl (5equ.) dissolved in a mixture of pyridine (2 mL / mmol biphenyl) and THF (15 drops) is added via syringe to the reaction mixture, and the solution is stirred at 60°C for 6h. The reaction is monitored by TLC, and after the reaction is completed, the reaction mixture is poured into a mixture of ice and conc. HCL. The precipitated solid is filtered of and the crude product is purified by column chromatography (eluent: DCM : ethyl acetate (95:5))

4'-Hydroxy-[1,1'-biphenyl]-4-yl 4-[4-(tri-*n*-hexylsilyl)butyloxy]benzoate 8/4/6*:* Synthesized from **7/4/6** (1.0 g, 2.1 mmol), DMF (3 drops) in thionyl chloride (4 mL), 4,4’-dihydroxibiphenyl (2.0 g, 10.4 mmol), pyridine (20 mL), THF; purification by column chromatography (eluent: DCM : ethyl acetate (95:5)); colorless solid, $C_{41}H_{60}O_4Si$, M = 645.01 g/mol; yield: 0.87 g (64 %); ^{1}H-NMR (CDCl$_3$, 402 MHz): δ / ppm = 8.14 (d, $^{3}J_{H,H}$ = 9.0 Hz, 2H, Ar-*H*), 7.58 – 7.51 (m, 2H, Ar-*H*), 7.49 – 7.41 (m, 2H, Ar-*H*), 7.23 (d, $^{3}J_{H,H}$ = 8.4 Hz, 2H, Ar-*H*), 7.00 – 6.92 (m, 2H, Ar-*H*), 6.92 – 6.84 (m, 2H, Ar-*H*), 4.91 (s, 1H, -OH), 4.05 (t, $^{3}J_{H,H}$ = 6.4 Hz, 2H, -OCH_2-), 1.51 – 1.42 (m, 2H, -OCH$_2$CH_2-), 1.37 – 1.18 (m, 26H, -CH_2-), 0.87 (t, $^{3}J_{H,H}$ = 6.7 Hz, 9H, -CH_3), 0.59 – 0.44 (m, 8H, -SiCH_2-). ^{29}Si-NMR (CDCl$_3$, 80 MHz): δ / ppm = 2.94.

4'-Hydroxy-[1,1'-biphenyl]-4-yl 4-[6-(tri-*n*-hexylsilyl)hexyloxy]benzoate 8/6/6*:* Synthesized from **7/4/6** (0.65 g, 1.3 mmol), DMF (3 drops) in thionyl chloride (2 mL), 4,4’-dihydroxibiphenyl (1.2 g, 6.3 mmol), pyridine (12 mL), THF; purification by column chromatography (eluent: DCM : ethyl acetate (95:5)); colorless solid, $C_{43}H_{64}O_4Si$, M = 673.07 g/mol; yield: 0.60 g (69 %); ^{1}H NMR (CDCl$_3$, 402 MHz): δ / ppm = 8.15 (d, $^{3}J_{H,H}$ = 8.9 Hz, 2H, Ar-*H*), 7.60 – 7.52 (m, 2H, Ar-*H*), 7.50 – 7.42 (m, 2H, Ar-*H*), 7.24 (d, $^{3}J_{H,H}$ = 8.5 Hz, 2H, Ar-*H*), 7.01 – 6.94 (m, 2H, Ar-*H*), 6.94 – 6.85 (m, 2H, Ar-*H*), 4.05 (t, $^{3}J_{H,H}$ = 6.6 Hz, 2H, -OCH_2-), 1.92 – 1.76 (m, 2H, -OCH$_2$CH_2-), 1.53 – 1.44 (m, 2H, -OCH$_2$CH$_2$CH_2-), 1.43 – 1.22 (m, 28H, -CH_2-), 0.89 (t, $^{3}J_{H,H}$ = 6.6 Hz, 9H, -CH_3), 0.55 – 0.45 (m, 8H, -SiCH_2-). ^{29}Si NMR (CDCl$_3$, 80 MHz): δ / ppm = 2.91 (*Si*).

4'-Hydroxy-[1,1'-biphenyl]-4-yl 4-[8-(tri-*n*-hexylsilyl)octyloxy]benzoate 8/8/6*:* Synthesized from **7/4/6** (1.25 g, 2.3 mmol), DMF (3 drops) in thionyl chloride (4 mL), 4,4’-dihydroxibiphenyl (2.2 g, 11.7 mmol), pyridine (22 mL), THF; purification by column chromatography (eluent: DCM : ethyl acetate (95:5)); colorless solid, $C_{45}H_{68}O_4Si$, M = 701.12

g/mol; yield: 0.97 g (60 %); ^{1}H-NMR (CDCl$_3$, 402 MHz): δ 8.14 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, Ar-*H*), 7.58 – 7.50 (m, 2H, Ar-*H*), 7.48 – 7.40 (m, 2H, Ar-*H*), 7.23 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, Ar-*H*), 6.99 – 6.92 (m, 2H, Ar-*H*), 6.92 – 6.84 (m, 2H, Ar-*H*), 4.95 (s, 1H, -OH), 4.03 (t, $^3J_{H,H}$ = 6.5 Hz, 2H, -OC*H*$_2$-), 1.90 – 1.75 (m, 2H, -OCH$_2$C*H*$_2$-), 1.51 – 1.42 (m, 2H, -OCH$_2$CH$_2$C*H*$_2$-), 1.40 – 1.19 (m, 32H, -C*H*$_2$-), 0.87 (t, $^3J_{H,H}$ = 6.5 Hz, 9H, -C*H*$_3$), 0.51 – 0.42 (m, 8H, -SiC*H*$_2$-). ^{29}Si-NMR (CDCl$_3$, 80 MHz): δ 2.89.

4'-Hydroxy-[1,1'-biphenyl]-4-yl 4-[6-(tri-*n*-octylsilyl)hexyloxy]benzoate 8/6/8*:* Synthesized from **7/4/6** (0.47 g, 0.8 mmol), DMF (3 drops) in thionyl chloride (10 mL), 4,4’-dihydroxibiphenyl (0.74 g, 4.0 mmol), pyridine (8 mL), THF; purification by column chromatography (eluent: DCM : ethyl acetate (95:5)); colorless solid, $C_{49}H_{76}O_4Si$, M = 757.23 g/mol; yield: 0.34 g (56 %); ^{1}H-NMR (CDCl$_3$, 400 MHz): δ / ppm = 8.16 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, Ar-*H*), 7.57 – 7.49 (m, 2H, Ar-*H*), 7.46 – 7.34 (m, 2H, Ar-*H*), 7.23 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, Ar-*H*), 6.98 (d, $^3J_{H,H}$ = 9.0 Hz, 2H, Ar-*H*), 6.89 – 6.76 (m, 2H, Ar-*H*), 4.05 (t, $^3J_{H,H}$ = 6.5 Hz, 2H, -OC*H*$_2$-), 1.87 – 1.78 (m, 2H, -OCH$_2$C*H*$_2$-), 1.53 – 1.44 (m, 2H, -OCH$_2$CH$_2$C*H*$_2$-), 1.44 – 1.37 (m, 2H, -OCH$_2$CH$_2$CH$_2$C*H*$_2$-), 1.37 – 1.21 (m, 38H, -C*H*$_2$-), 0.89 (t, $^3J_{H,H}$ = 7.0 Hz, 9H, -C*H*$_3$), 0.57 – 0.45 (m, 8H, -SiC*H*$_2$-). ^{29}Si-NMR (CDCl$_3$, 79 MHz): δ / ppm = 2.94 (*Si*).

S3.3 Compounds Ax/*n*/*m*[S10]

In an inert atmosphere, the appropriate 4-(4-alkyloxyphenyldiazenyl)benzoic acid (1 equ.) and DMF (1 drop) were added to an excess of thionyl chloride (2 mL / mmol acid). The solution was stirred for 15 min at RT, followed by 2h of reflux. The reaction is cooled down to RT, and thionyl chloride is removed by vacuum distillation. Afterwards, **8/*m*/*n*** (1 equ.), dissolved in a mixture of pyridine (1 drop), Et$_3$N (1 equ.), and DCM (20 mL / mmol acid) is added via syringe to the reaction mixture, and the solution is stirred at 60 °C for 6h. The reaction is monitored by TLC, and after the reaction is completed, the solvents are distilled under vacuum (850 mbar, 60°C). The crude product is purified by column chromatography (eluent: DCM)

4'-[4-(4-Decyloxyphenyldiazenyl)benzoyloxy]-[1,1'-biphenyl]-4-yl 4-[4-(tri-*n*-hexylsilyl)butyloxy]benzoate (A10/4/6)

Synthesized from 4-(4-decyloxyphenyldiazenyl)benzoic acid (130 mg, 0.34 mmol), DMF (1 drop), in thionyl chloride (2 mL), **8/4/6** (220 mg, 0.34 mmol), pyridine (1 drop), Et$_3$N (35 mg, 0.05 mL, 0.34 mmol) DCM (20 mL), purification by column chromatography (eluent: DCM); orange solid, $C_{64}H_{88}O_6N_2Si$, M = 1009.50 g/mol; yield: 290.9 mg (85 %); **^{1}H-NMR** (CDCl$_3$, 502 MHz): δ / ppm = 8.34 (d, $^3J_{H,H}$ = 8.1 Hz, 2H, Ar-*H*), 8.15 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, Ar-*H*), 8.00 – 7.93 (m, 4H, Ar-*H*), 7.66 – 7.60 (m, 4H, Ar-*H*), 7.34 – 7.25 (m, 4H, Ar-*H*), 7.04 – 6.94 (m, 4H, Ar-*H*), 4.08 – 4.01 (m, 4H, -OC*H*$_2$-), 1.87 – 1.77 (m, 4H, -OCH$_2$C*H*$_2$-), 1.52 – 1.42 (m, 4H, -OCH$_2$CH$_2$C*H*$_2$-), 1.40 – 1.18 (m, 36H, -C*H*$_2$-), 0.88 (t, $^3J_{H,H}$ = 6.7 Hz, 12H, -C*H*$_3$), 0.59 – 0.52 (m, 2H, -SiC*H*$_2$-), 0.52 – 0.47 (m, 6H, -SiC*H*$_2$-). **^{13}C-NMR** (CDCl$_3$, 126 MHz): δ / ppm = 164.93 (C_{Ar}-O), 164.72, 163.61 (*C*=O), 162.48 (C_{Ar}-O), 155.81 (C_{Ar}-N), 150.61 (2x C_{Ar}-OC=O), 150.37 (C_{Ar}-N), 146.84, (2x C_{Ar}-O) 138.34, 137.94 ($C_{Ar,\,quart}$), 132.27, 131.20 (C_{Ar}-H), 130.35 (C_{Ar}-COO), 128.20, 128.13, 125.29, 122.50, 122.12, 121.97 (C_{Ar}-H), 121.44 (C_{Ar}-COO), 114.82, 114.30 (C_{Ar}-H), 68.44, 67.81 (-O*C*H$_2$-), 33.54 (3x -*C*H$_2$-), 32.95, 31.85, 31.52 (3x -*C*H$_2$-), 29.52, 29.51, 29.33, 29.27, 29.13, 25.96, 23.84 (3x -*C*H$_2$-), 22.63, 22.59 (3x -*C*H$_2$-), 20.35 (-*C*H$_2$-), 14.10 (3x -*C*H$_3$), 14.06 (-*C*H$_3$), 12.41 (3x Si-*C*H$_2$-), 12.18 (Si*C*H$_2$-). **^{29}Si-NMR**

($CDCl_3$, 100 MHz): δ / ppm = 3.00 (*Si*). **HRMS** (m/z): [M]+Cl- calcd. For $C_{64}H_{88}O_6N_2SiCl$, 1043.6095; found: 1043.6075.

4'-[4-(4-Decyloxyphenyldiazenyl)benzoyloxy]-[1,1'-biphenyl]-4-yl 4-[6-(tri-*n*-hexylsilyl)hexyloxy]benzoate (A10/6/6)

Synthesized from 4-(4-decyloxyphenyldiazenyl)benzoic acid (49 mg, 0.15 mmol), DMF (1 drop), in thionyl chloride (2 mL), **8/6/6** (100 mg, 0.15 mmol), pyridine (1 drop), Et_3N (15 mg, 0.02 mL, 0.15 mmol) DCM (20 mL), purification by column chromatography (eluent: DCM); orange solid, $C_{66}H_{92}O_6N_2Si$, M = 1037.56 g/mol; yield: 52 mg (34 %); ^{1}H-NMR ($CDCl_3$, 502 MHz): δ / ppm = 8.36 (d, $^3J_{H,H}$ = 6.8 Hz, 2H, Ar-*H*), 8.17 (d, $^3J_{H,H}$ = 8.3 Hz, 2H, Ar-*H*), 8.04 – 7.92 (m, 4H, Ar-*H*), 7.69 – 7.61 (m, 4H, Ar-*H*), 7.36 – 7.26 (m, 4H, Ar-*H*), 7.07 – 6.96 (m, 4H, Ar-*H*), 4.10 – 4.03 (m, 4H, -OCH_2-), 1.88 – 1.78 (m, 4H, -OCH_2CH_2-), 1.53 – 1.45 (m, 4H, -$OCH_2CH_2CH_2$-), 1.45 – 1.21 (m, 42H, -CH_2-)), 0.89 (t, $^3J_{H,H}$ = 6.8 Hz, 12H, -CH_3), 0.55 – 0.45 (m, 8H, -$SiCH_2$-). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ / ppm = 164.97 (C_{Ar}-O), 164.77, 163.61 (*C*=O), 162.53 (C_{Ar}-O), 155.85 (C_{Ar}-N), 150.64 (2x C_{Ar}-OC=O), 150.39 (C_{Ar}-N), 146.88 (2x C_{Ar}-O), 138.39, 137.99 ($C_{Ar, quart}$), 132.31, 131.25 (C_{Ar}-H), 130.39 (C_{Ar}-COO), 128.24, 128.17, 125.35, 122.57, 122.16, 122.01 (C_{Ar}-H), 121.48 (C_{Ar}-COO), 114.87, 114.32 (C_{Ar}-H), 68.49, 68.38 (-OCH_2-), 33.59 (3x -CH_2-), 33.57, 31.88, 31.56 (3x -CH_2-), 29.55, 29.54, 29.36, 29.30, 29.16, 29.06, 26.00, 25.63, 23.89 (3x -CH_2-), 23.87, 22.66, 22.63 (3x -CH_2-), 14.13 (3x -CH_3), 14.09 (-CH_3), 12.50 (4x SiCH_2-). ^{29}Si-NMR ($CDCl_3$, 100 MHz): δ / ppm = 2.93. **HRMS** (m/z): [M]+Cl- calcd. For $C_{66}H_{92}O_6N_2SiCl$, 1071.6408; found: 1071.6414.

4'-[4-(4-Decyloxyphenyldiazenyl)benzoyloxy]-[1,1'-biphenyl]-4-yl 4-[8-(tri-*n*-hexylsilyl)octyloxy]benzoate (A10/8/6)

Synthesized from 4-(4-decyloxyphenyldiazenyl)benzoic acid (55 g, 0.14 mmol), DMF (1 drop), in thionyl chloride (2 mL), **8/8/6** (100 g, 0.14 mmol), pyridine (1 drop), Et_3N (14 mg, 0.02 mL, 0.14 mmol) DCM (20 mL), purification by column chromatography (eluent: DCM); orange solid, $C_{68}H_{96}O_6N_2Si$, M = 1065.61 g/mol; yield: 26 mg (17 %); ^{1}H-NMR ($CDCl_3$, 502 MHz): δ / ppm = 8.36 (d, $^3J_{H,H}$ = 8.2 Hz, 2H, Ar-*H*), 8.17 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, Ar-*H*), 8.02 – 7.94 (m, 4H, Ar-*H*), 7.69 – 7.61 (m, 4H, Ar-*H*), 7.37 – 7.27 (m, 4H, Ar-*H*), 7.05 – 6.95 (m, 4H, Ar-*H*), 4.10 – 4.03 (m, 4H, -OCH_2-), 1.88 – 1.79 (m, 4H, -OCH_2CH_2-), 1.52 – 1.44 (m, 4H, -$OCH_2CH_2CH_2$-), 1.42 – 1.22 (m, 44H, -CH_2-), 0.89 (t, $^3J_{H,H}$ = 7.2 Hz, 12H, -CH_3), 0.53 – 0.45 (m, 8H, -$SiCH_2$-). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ / ppm = 164.97 (C_{Ar}-O), 164.76, 163.60 (*C*=O), 162.51 (C_{Ar}-O), 155.84 (C_{Ar}-N), 150.63 (2x C_{Ar}-OC=O), 150.40 (C_{Ar}-N), 146.87 (2x C_{Ar}-O), 138.38, 137.98 ($C_{Ar, quart}$), 132.31, 131.24 (C_{Ar}-H), 130.39 (C_{Ar}-COO), 128.24, 128.17, 125.33, 122.53, 122.16, 122.01 (C_{Ar}-H), 121.48 (C_{Ar}-COO), 114.85, 114.32 (C_{Ar}-H), 68.48, 68.36 (-OCH_2-), 33.82, 33.59 (3x -CH_2-), 31.89, 31.63, 31.56 (3x -CH_2-), 29.56, 29.54, 29.37, 29.32, 29.30, 29.19, 29.16, 29.11, 26.02, 26.00, 23.91, 23.89 (3x -CH_2-), 22.67, 22.62 (3x -CH_2-), 14.13 (3x -CH_3), 14.09 (-CH_3), 12.51 (4x SiCH_2-). ^{29}Si-NMR ($CDCl_3$, 100 MHz): δ / ppm = 2.92 (*Si*). **HRMS** (m/z): [M]+Cl- calcd. For $C_{68}H_{96}O_6N_2SiCl$, 1099.6721; found: 1099.6747.

4'-[4-(4-Decyloxy)phenyldiazenyl)benzoyloxy]-[1,1'-biphenyl]-4-yl 4-[6-(tri-*n*-octylsilyl)hexyloxy]benzoate (A10/6/8)

Synthesized from 4-(4-decyloxyphenyldiazenyl)benzoic acid (51 g, 0.13 mmol), DMF (1 drop), in thionyl chloride (2 mL), **8/6/8** (100 g, 0.13 mmol), pyridine (1 drop), Et_3N (13 mg, 0.02 mL, 0.13 mmol) DCM (20 mL), purification by column chromatography (eluent: DCM); orange solid, $C_{72}H_{104}O_6N_2Si$, M = 1121.72 g/mol; yield: 96.6 mg (65 %); ^{1}H-NMR ($CDCl_3$, 502 MHz): δ / ppm = 8.36 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, Ar-*H*), 8.17 (d, $^3J_{H,H}$ = 8.3 Hz, 2H, Ar-*H*), 8.05 – 7.95 (m, 4H, Ar-*H*), 7.69 – 7.61 (m, 4H, Ar-*H*), 7.37 – 7.27 (m, 4H, Ar-*H*), 7.06 – 6.96 (m, 4H, Ar-*H*), 4.10 – 4.03 (m, 4H, -OCH_2-), 1.88 – 1.78 (m, 4H, -OCH$_2$CH_2-), 1.54 – 1.46 (m, 4H, -OCH$_2$CH$_2$CH_2-), 1.43 – 1.22 (m, 52H, -CH_2-), 0.89 (t, $^3J_{H,H}$ = 7.1 Hz, 12H, -CH_3), 0.55 – 0.46 (m, 8H, -SiCH_2-). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ / ppm = 164.96 (C_{Ar}-O), 164.76, 163.60 (*C*=O), 162.52 (C_{Ar}-O), 155.84 (C_{Ar}-N), 150.64 (2x C_{Ar}-OC=O), 150.40 (C_{Ar}-N), 146.87 (2x C_{Ar}-O), 138.38, 137.98 ($C_{Ar,\,quart}$), 132.31, 131.24 (C_{Ar}-H), 130.39 (C_{Ar}-COO), 128.24, 128.17, 125.34, 122.56, 122.16, 122.01 (C_{Ar}-H), 121.49 (C_{Ar}-COO), 114.87, 114.32 (C_{Ar}-H), 68.49, 68.38 (-O*C*H$_2$-), 33.91 (3x -*C*H$_2$-), 33.58, 31.95 (3x -*C*H$_2$-), 31.89, 29.56, 29.54, 29.37, 29.30, 29.28 (6x -*C*H$_2$-), 29.16, 29.07, 26.00, 25.64, 23.92 (3x -*C*H$_2$-), 23.88, 22.68 (3x -*C*H$_2$-), 22.67 (-*C*H$_2$-), 14.11 (3x -*C*H$_3$), 14.09 (-*C*H$_3$), 12.50 (3x Si*C*H$_2$-), 12.48 (Si*C*H$_2$-). ^{29}Si-NMR ($CDCl_3$, 100 MHz): δ / ppm = 2.94 (*Si*). **HRMS** (m/z): [M]+Cl- calcd. For $C_{72}H_{104}O_6N_2SiCl$, 1155.7347; found: 1155.7350.

4'-[4-(4-Hexyloxyphenyldiazenyl)benzoyloxy]-[1,1'-biphenyl]-4-yl 4-[6-(tri-*n*-octylsilyl)hexyloxy]benzoate (A6/6/8)

Synthesized from 4-(4-hexyloxyphenyldiazenyl)benzoic acid (43 mg, 0.13 mmol), DMF (1 drop), in thionyl chloride (2 mL), **8/6/8** (100 mg, 0.13 mmol), pyridine (1 drop), Et_3N (13 mg, 0.02 mL, 0.13 mmol) DCM (20 mL), purification by column chromatography (eluent: DCM); orange solid, $C_{68}H_{96}O_6N_2Si$, M = 1064.71 g/mol; yield: 72.5 mg (52 %); ^{1}H-NMR ($CDCl_3$, 502 MHz): δ / ppm = 8.37 (d, $^3J_{H,H}$ = 8.6 Hz, 2H, Ar-*H*), 8.17 (d, $^3J_{H,H}$ = 9.0 Hz, 2H, Ar-*H*), 8.02 – 7.94 (m, 4H, Ar-*H*), 7.69 – 7.62 (m, 4H, Ar-*H*), 7.37 – 7.27 (m, 4H, Ar-*H*), 7.05 – 6.97 (m, 4H, Ar-*H*), 4.10 – 4.03 (m, 4H, -OCH_2-), 1.88 – 1.78 (m, 4H, -OCH$_2$CH_2-), 1.54 – 1.45 (m, 4H, -OCH$_2$CH$_2$CH_2-), 1.43 – 1.22 (m, 44H, -CH_2-), 0.93 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, -CH_3), 0.89 (t, $^3J_{H,H}$ = 6.9 Hz, 9H, -CH_3), 0.56 – 0.46 (m, 8H, -SiCH_2-). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ / ppm = 164.96 (C_{Ar}-O), 164.76, 163.60 (*C*=O), 162.51 (C_{Ar}-O), 155.85 (C_{Ar}-N), 150.64 (2x C_{Ar}-OC=O), 150.40 (C_{Ar}-N), 146.88 (2x C_{Ar}-O), 138.39, 137.98 ($C_{Ar,\,quart}$), 132.31, 131.24 (C_{Ar}-H), 130.39 (C_{Ar}-COO), 128.24, 128.17, 125.32, 122.53, 122.15, 122.01 (C_{Ar}-H), 121.49 (C_{Ar}-COO), 114.85, 114.32 (C_{Ar}-H), 68.48, 68.38 (-O*C*H$_2$-), 33.91 (3x -*C*H$_2$-), 33.58, 31.95 (3x -*C*H$_2$-), 31.55, 29.28 (6x -*C*H$_2$-), 29.13, 29.07, 25.67, 25.64, 23.92 (3x -*C*H$_2$-), 23.88, 22.68 (3x -*C*H$_2$-), 22.58 (-*C*H$_2$-), 14.10 (3x -*C*H$_3$), 14.01 (-*C*H$_3$), 12.50 (Si*C*H$_2$-), 12.48 (3x Si*C*H$_2$-). ^{29}Si-NMR ($CDCl_3$, 100 MHz): δ / ppm = 2.94 (*Si*). **HRMS** (m/z): [M]+Cl- calcd. For $C_{68}H_{96}O_6N_2SiCl$, 1099.6721; found: 1099.6725.

4'-[4-(4-Hexyloxyphenyldiazenyl)benzoyloxy]-[1,1'-biphenyl]-4-yl 4-[8-(tri-*n*-hexylsilyl)octyloxy] benzoate (A6/8/6)

Synthesized from 4-(4-hexyloxyphenyldiazenyl)benzoic acid (47 mg, 0.14 mmol), DMF (1 drop), in thionyl chloride (2 mL), **8/8/6** (100 mg, 0.14 mmol), pyridine (1 drop), Et_3N (14 mg, 0.02 mL, 0.14 mmol) DCM (20 mL), purification by column chromatography (eluent: DCM); orange solid, $C_{64}H_{88}O_6N_2Si$, M = 1009.50 g/mol; yield: 68.8 mg (49 %); ^{1}H-NMR ($CDCl_3$, 502 MHz): δ / ppm = 8.37 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, Ar-*H*), 8.17 (d, $^3J_{H,H}$ = 9.0 Hz, 2H, Ar-*H*), 8.02 – 7.94 (m, 4H, Ar-*H*), 7.69 – 7.61 (m, 4H, Ar-*H*), 7.37 – 7.27 (m, 4H, Ar-*H*), 7.07 – 6.95 (m, 4H, Ar-*H*), 4.10 – 4.03 (m, 4H, -OCH_2-), 1.88 – 1.79 (m, 4H, -OCH$_2$CH_2-), 1.54 – 1.44 (m, 4H, -OCH$_2$CH$_2$CH_2-), 1.42 – 1.22 (m, 36H, -CH_2-), 0.93 (t, $^3J_{H,H}$ = 6.7 Hz, 3H, -CH_3), 0.89 (t, $^3J_{H,H}$ = 7.0 Hz, 9H, -CH_3), 0.53 – 0.45 (m, 8H, -SiCH_2-). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ / ppm =

164.97 (C_{Ar}-O), 164.76, 163.60 (C=O), 162.50 (C_{Ar}-O), 155.86 (C_{Ar}-N), 150.64 (2x C_{Ar}-OC=O), 150.40 (C_{Ar}-N), 146.88 (2x C_{Ar}-O), 138.38, 137.98 ($C_{Ar, quart}$), 132.31, 131.24 (C_{Ar}-H), 130.39 (C_{Ar}-COO), 128.24, 128.17, 125.32, 122.53, 122.16, 122.01 (C_{Ar}-H), 121.49 (C_{Ar}-COO), 114.85, 114.32 (C_{Ar}-H), 68.47, 68.36 (-OCH$_2$-), 33.82, 33.59 (3x -CH$_2$-), 31.62, 31.56 (3x -CH$_2$-), 29.32, 29.19, 29.13, 29.11, 26.02, 25.67, 23.91, 23.89 (3x -CH$_2$-), 22.63 (3x -CH$_2$-), 22.58, 15.81 (-CH$_2$-), 14.13 (3x -CH$_3$), 14.01 (-CH$_3$), 12.51 (4x SiCH$_2$-). ^{29}Si-NMR (CDCl$_3$, 100 MHz): δ / ppm = 2.92 (*Si*). **HRMS** (m/z): [M]+Cl- calcd. For $C_{64}H_{88}O_6N_2SiCl$, 1043.6096; found: 1043.6104.

S3.4. Representative NMR Spectra

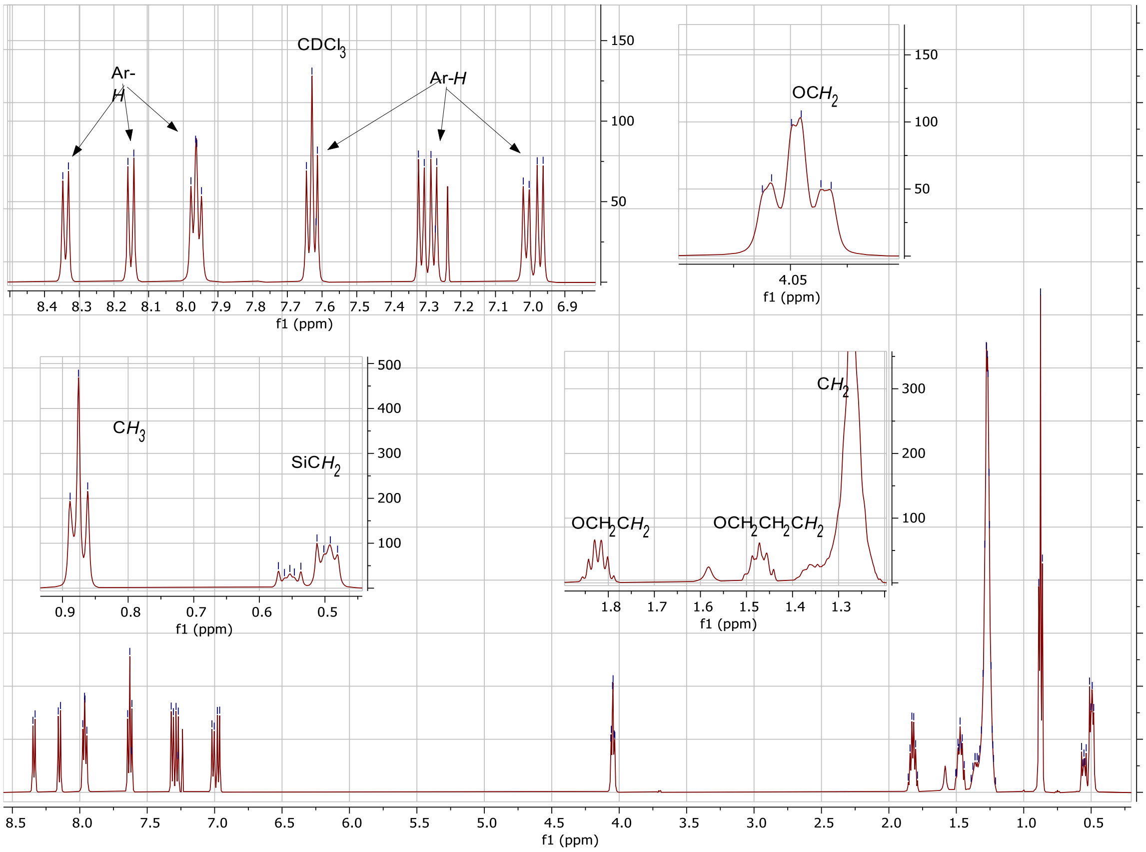

Figure S17. ^{1}H-NMR of compound **A10/4/6** (502 MHz, CDCl$_3$).

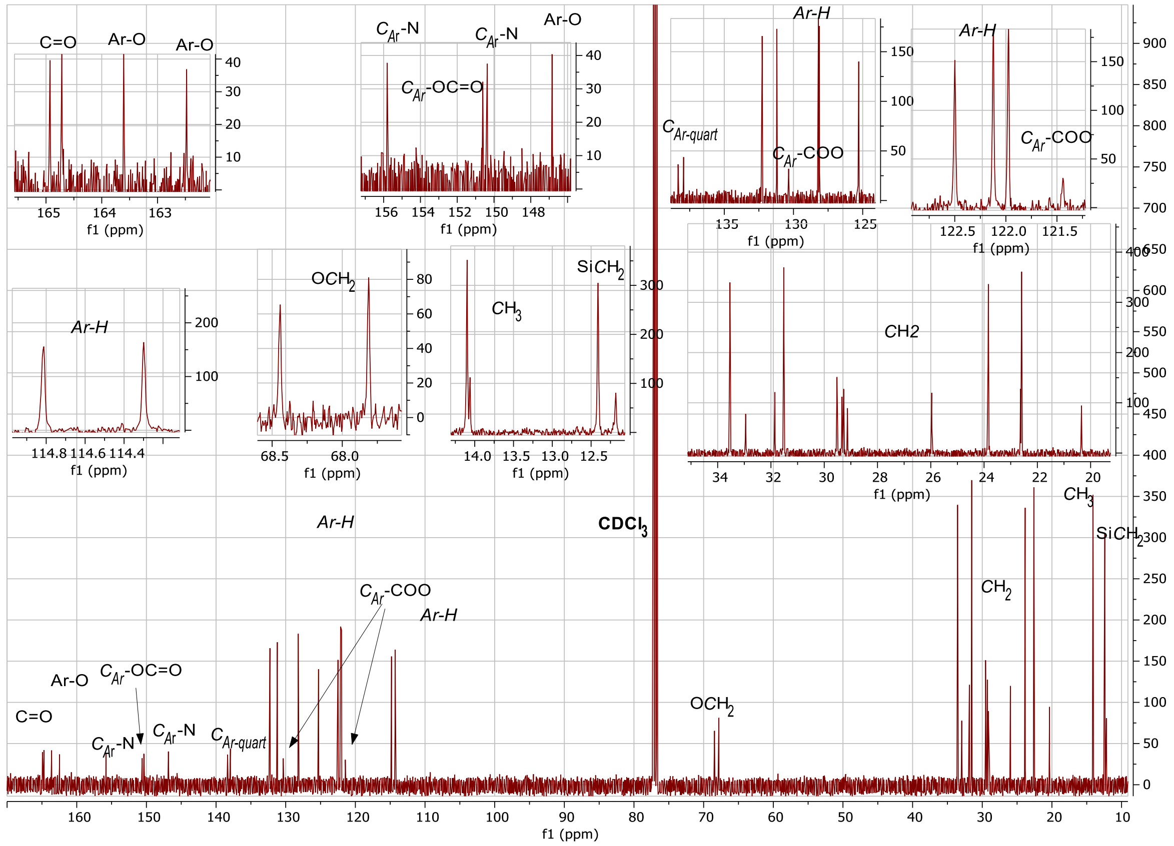

Figure S18. ^{13}C-NMR of compound **A10/4/6** (126 MHz, CDCl$_3$).

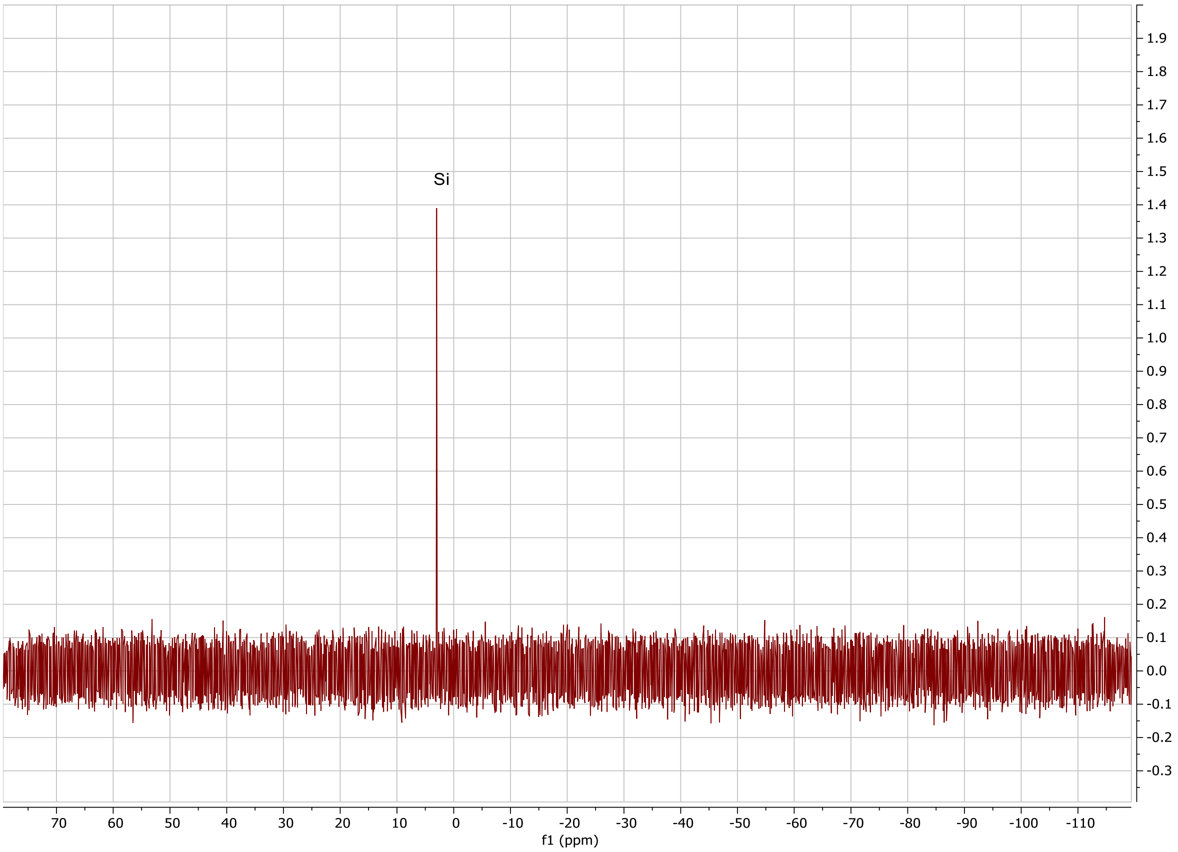

Figure S19. ^{29}Si-NMR of compound **A10/4/6** (100 MHz, CDCl$_3$).

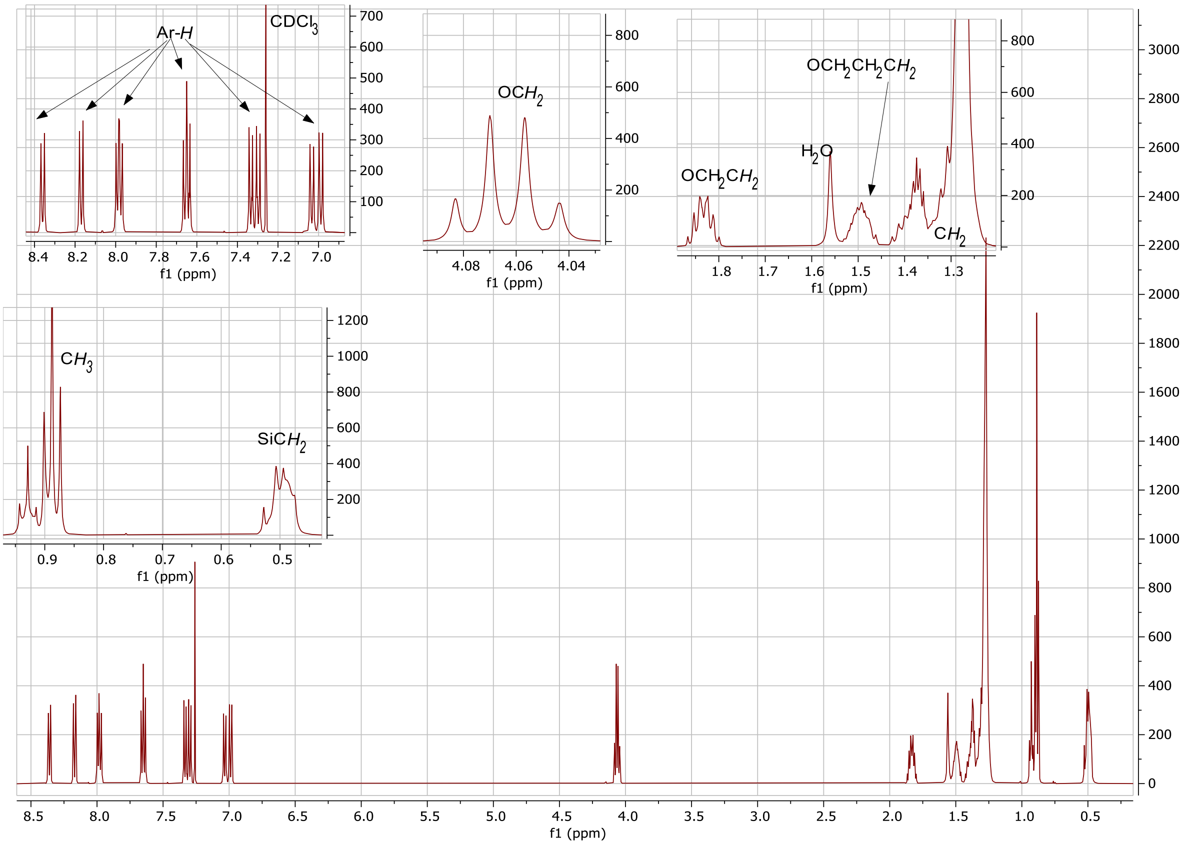

Figure S20. ^{1}H-NMR of compound **A6/6/8** (502 MHz, $CDCl_3$).

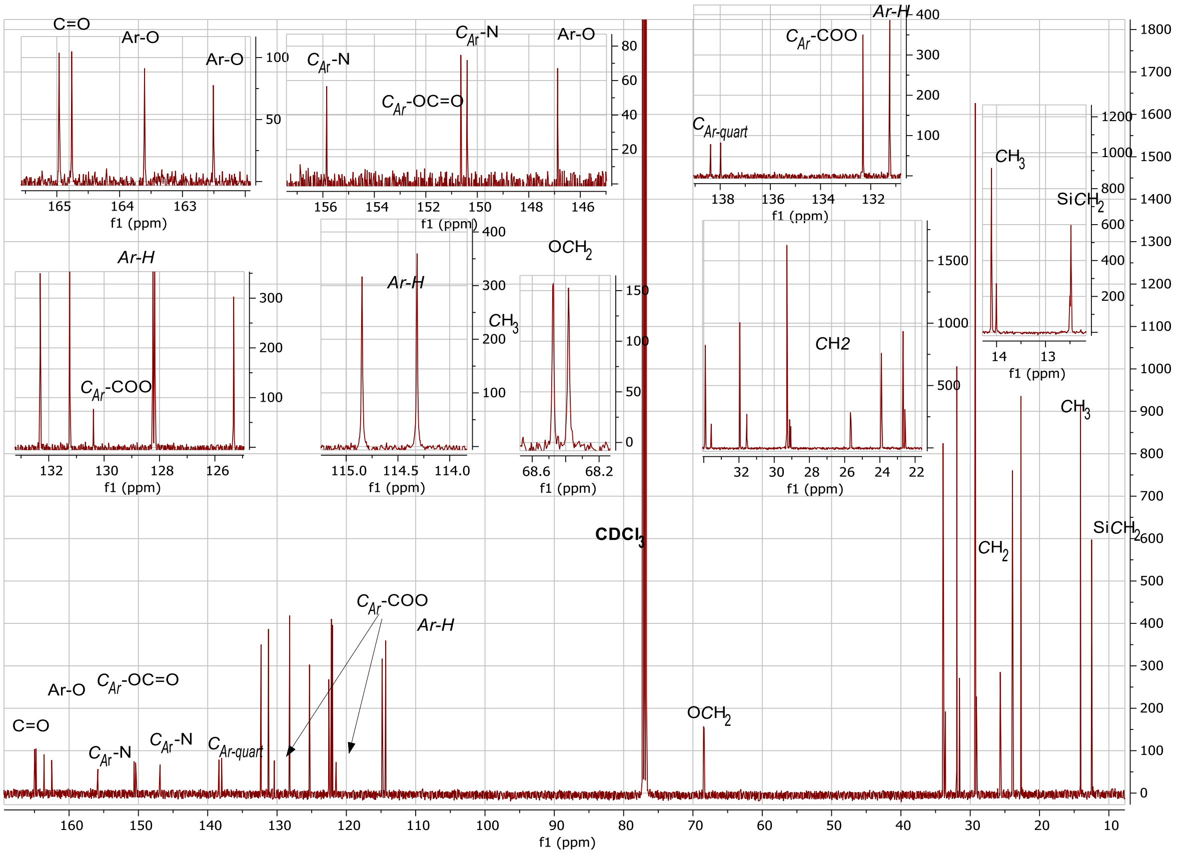

Figure S21. ^{13}C-NMR of compound **A6/6/8** (126 MHz, $CDCl_3$).

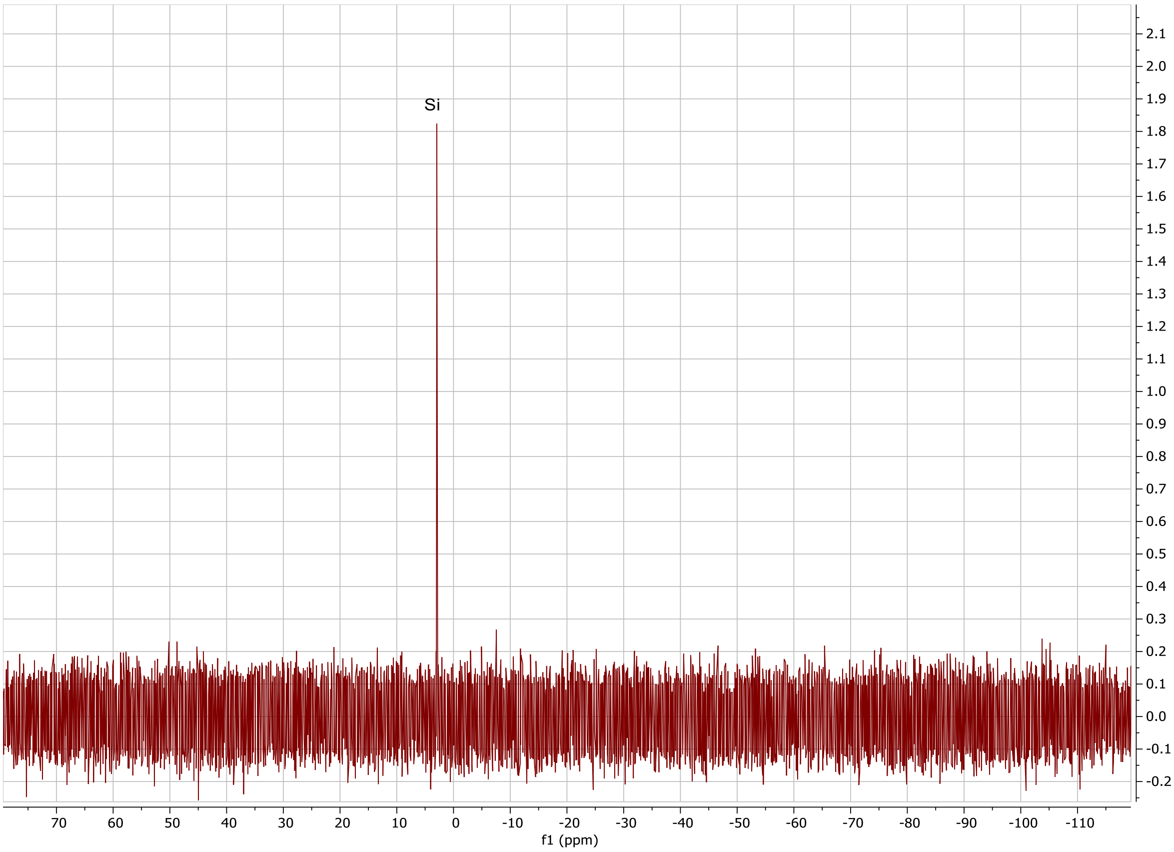

Figure S22. ^{29}Si-NMR of compound **A6/6/8** (100 MHz, $CDCl_3$).

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