Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

Liquid crystalline self-assembly of 2,5-diphenyl-1,3,4-oxadiazole based bent-core molecules and the influence of carbosilane end-groups

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S1. Additional data

S1.1 Additional data of compound 1Si$_3$12

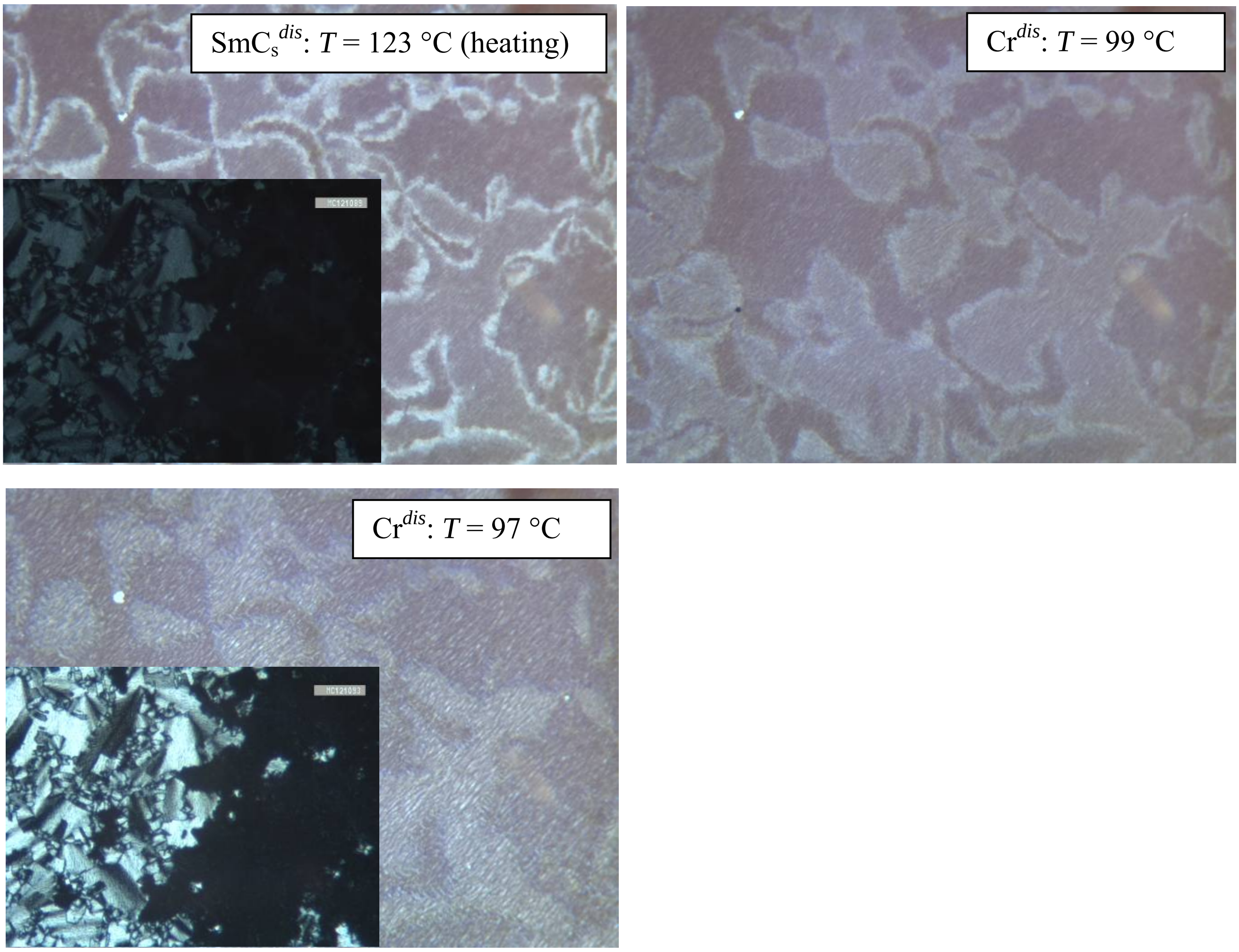


Figure S1. Textures of the homeotropically aligned SmC$_s^{dis}$ phase and the crystalline phase (Cr^{dis}) as observed between crossed polarizers on cooling (overexposed). The insets show the textures in the planar and homeotropic areas with normal exposure time.

Table S1. SAXS data and lattice parameter of compound **1Si$_3$12**.

Mesophase (T/°C)	Miller indices (hkl)	q / nm^{-1}	d_{obs}/nm	d_{calc}/nm	$d_{obs} - d_{calc}$	Unit cell parameter
SmC$_s$P$_R$ (185)	01	1.562	4.02	4.02	0.00	d = 4.02 nm
	02	3.128	2.01	2.01	0.00	
Sm$\tilde{C}_s$P$_{AR}$ (140)	01	1.416	4.44	4.44	0.00	a = 4.08 nm
	10	1.564	4.02	4.02	0.00	b = 4.50 nm
	-11	1.914	3.28	3.27	0.01	γ = 80.1 °
	11	2.277	2.76	2.75	0.01	
	20	3.125	2.01	2.01	0.00	
SmC$_s$P$_A^{dis}$ (110)	01	1.490	4.22	4.22	0.00	d = 4.22 nm
	02	2.282	2.11	2.11	0.00	

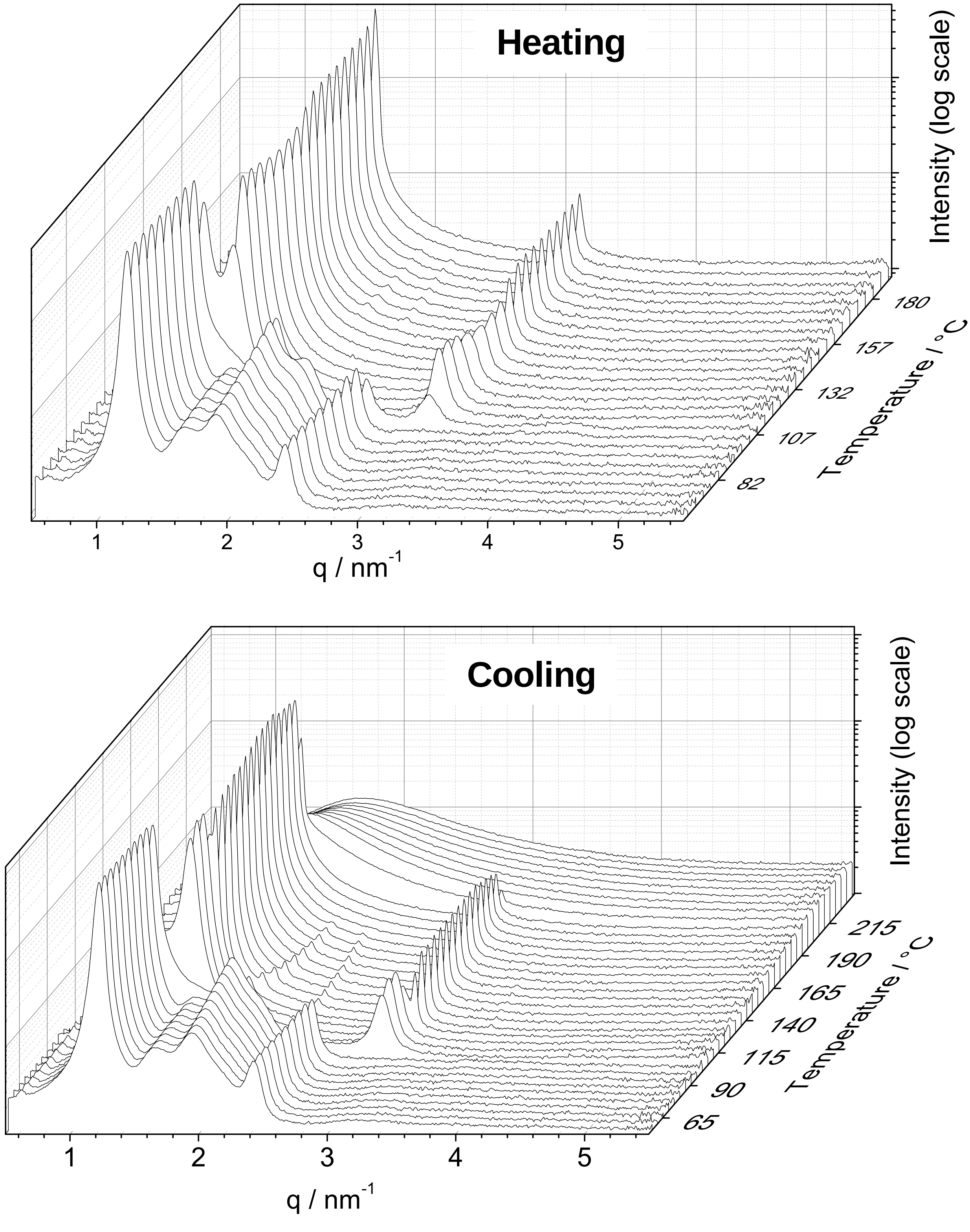


Figure S2. Waterfall plot of the diffraction pattern obtained for **1Si$_3$12** upon heating and cooling.

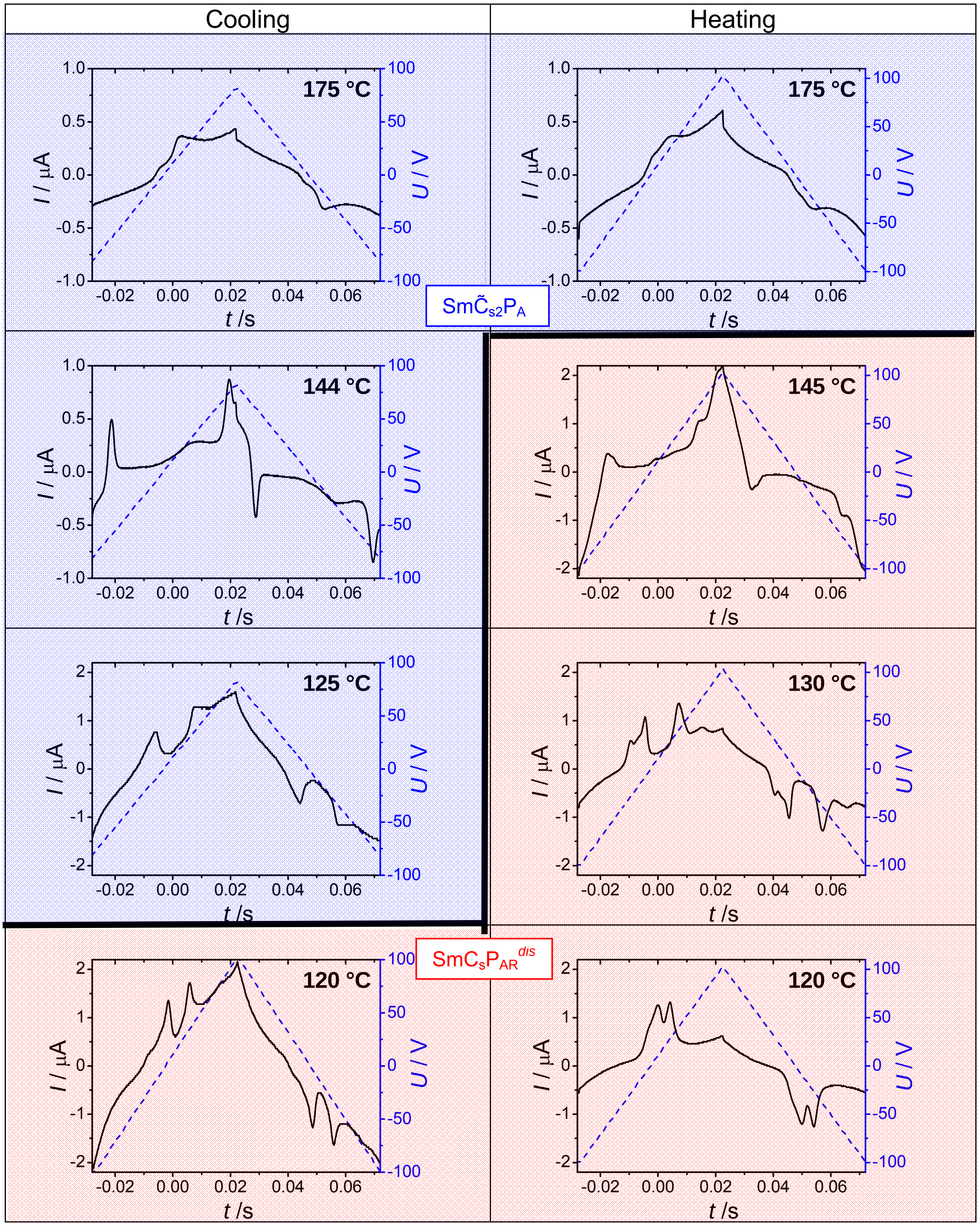


Figure S3. Polarization current response under influence of an applied triangular wave voltage (200 V_{pp}, 10 Hz, 6µm polyimide coated ITO cell and 5kΩ) of compound **1Si$_3$12** on cooling (left column) and on heating (right column) at approximately the same temperatures.

S1.2 Additional data of compound 1Si36

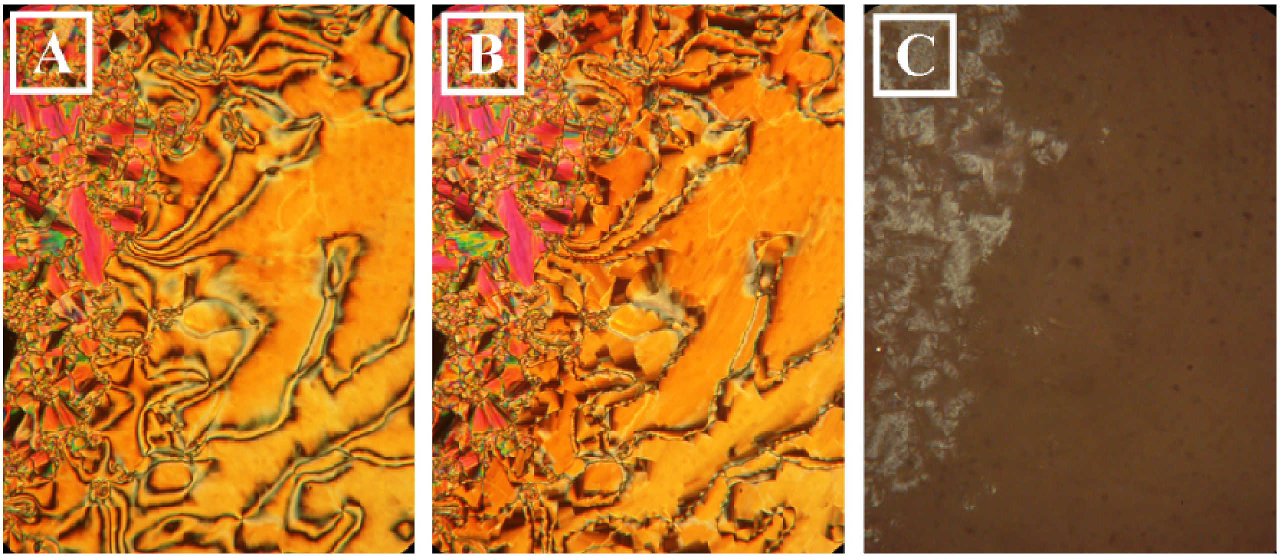


Figure S4. Optical textures observed by POM under crossed polarizers for **1Si36** on cooling: a) Schlieren texture of the SmC$_s$P$_R$ phase at 178 °C; b) Mosaic texture of the Sm$\tilde{C}_s$P$_R$ phase at 167 °C and c) low birefringence texture of the SmC$_s^{dis(L)}$ phase at 150 °C.

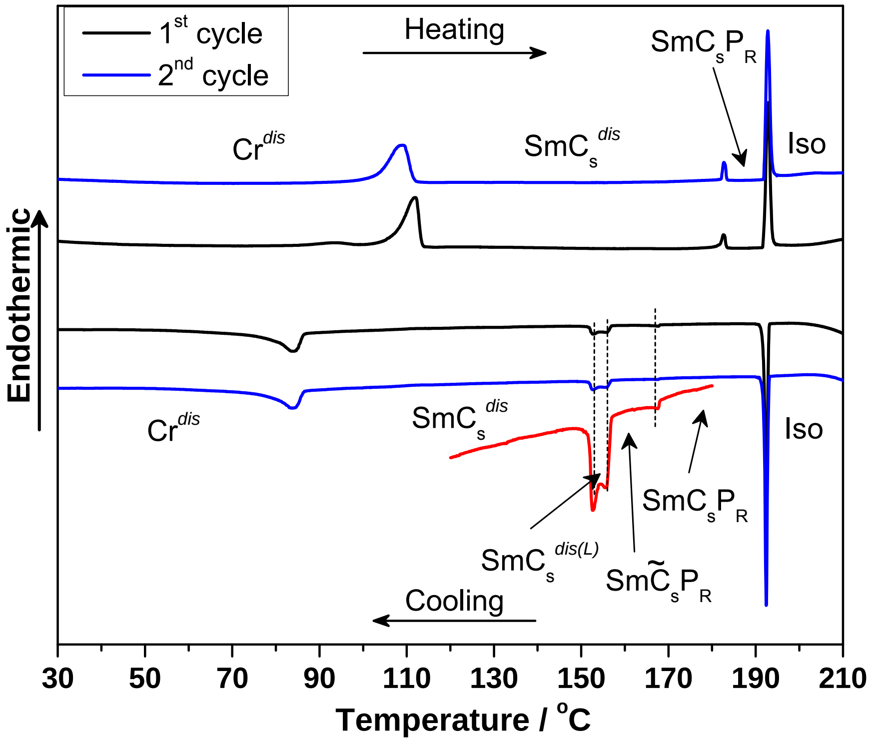


Figure S5. DSC traces for compound **1Si36** showing the first (black) and second (blue) cycles (10 K min^{-1}). In red, a 10x magnification of part of the second scan (cooling) for better visualization of the low enthalpy transitions.

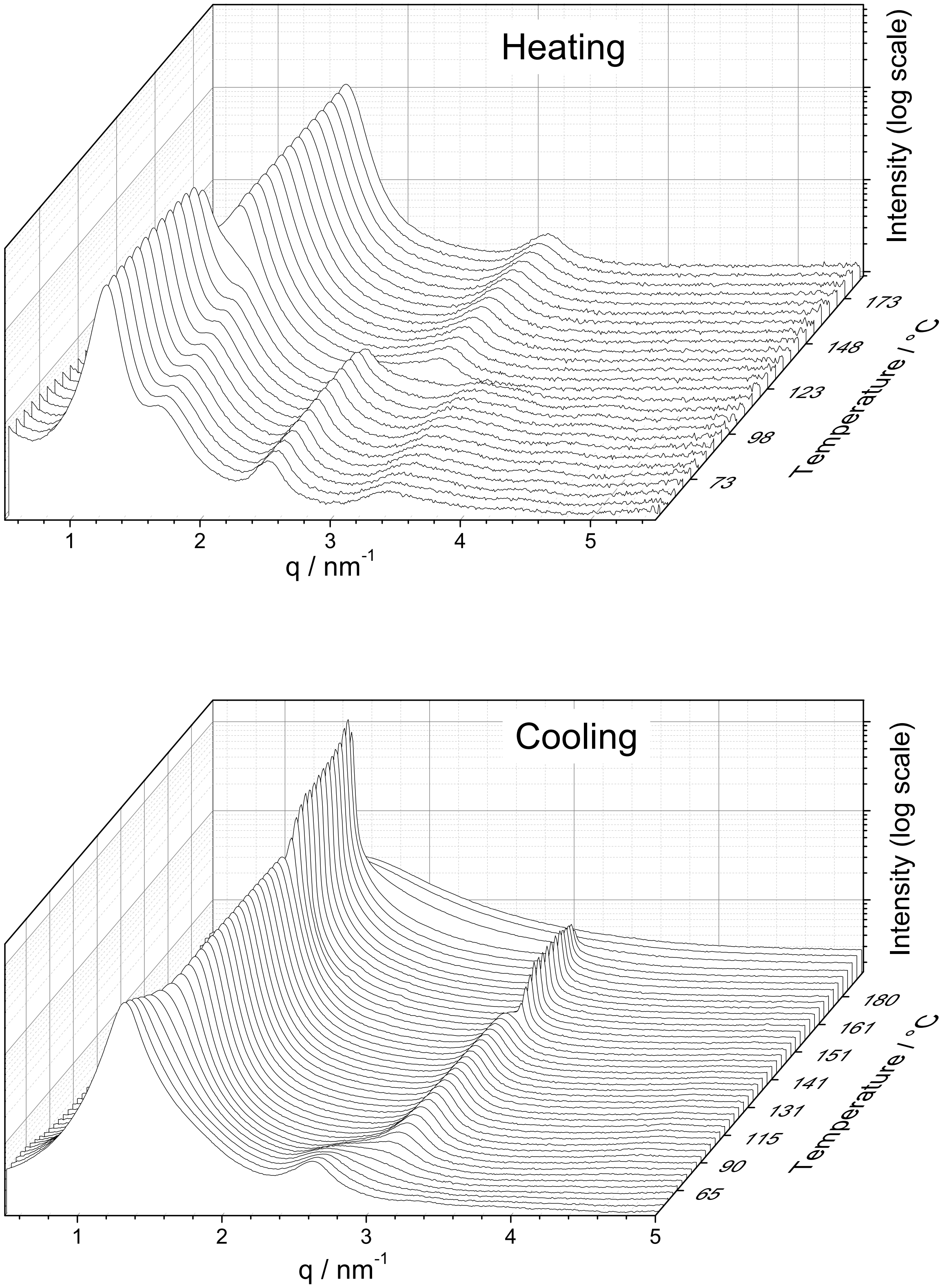


Figure S6. Waterfall plot of the diffraction pattern obtained for **1Si$_3$6** upon heating and cooling.

Table S2. SAXS data and lattice parameter of compound **1Si$_3$6.**

Mesophase (T/°C)	Miller indices (hkl)	d_{obs}/nm	d_{calc}/nm	$d_{obs} - d_{calc}$	Lattice parameters
SmC$_s$P$_R$ (185)	01	4.06	4.06	0.00	4.06
	02	2.03	2.03	0.00	
Sm$\tilde{C}_s$P$_R$ (157)	01	3.98	3.98	0.00	$a = 4.03$ nm
	-11	3.34	3.34	0.00	$b = 4.87$ nm
	11	2.85	2.85	0.00	$\gamma = 80.9$ °
	02	2.00	2.00	0.00	
SmC$_s$P$_A^{dis}$ (120)	01	4.08	4.08	0.00	4.08°
	02	2.04	2.04	0.00	
	03	1.36	1.36	0.00	

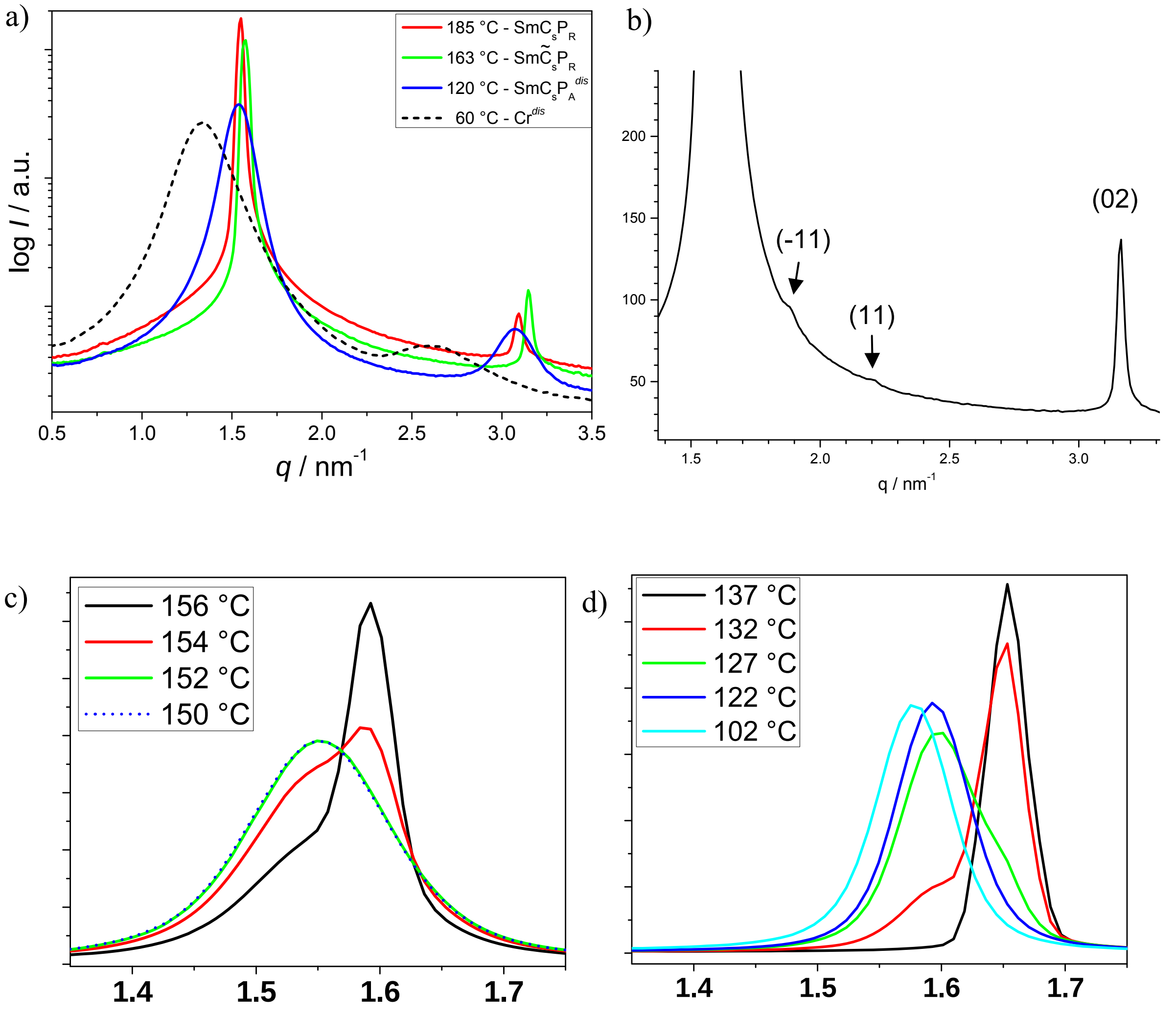


Figure S7. a) SAXS pattern of compound **1Si$_3$6** at different temperatures, recorded on cooling with synchrotron radiation source; b) shows the enlarged diffraction pattern at T = 157 °C; the (kh) reflections are very weak in this case and can only be observed shortly before the transition to the next SmC$_s$P$_{AR}^{dis(L)}$ phase, though the typical texture (Fig. S4b) is observed in the whole temperature range of the Sm$\tilde{C}_s$P$_R$ phase; c,d) development of the profile of the main SAXS at the Sm$\tilde{C}_s$-SmC$_s^{dis}$ transition c) on cooling and d) on heating.

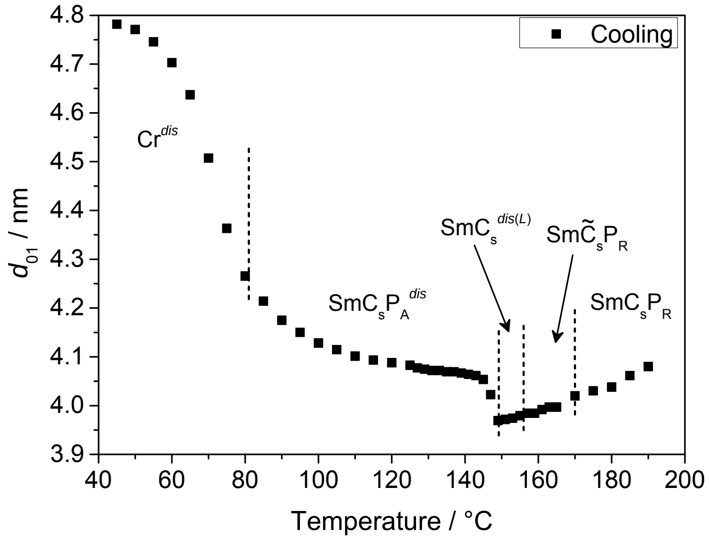


Figure S8. Dependence of the layer reflection in the mesophases of compound **1Si$_3$6** on temperature, on cooling from the isotropic liquid.

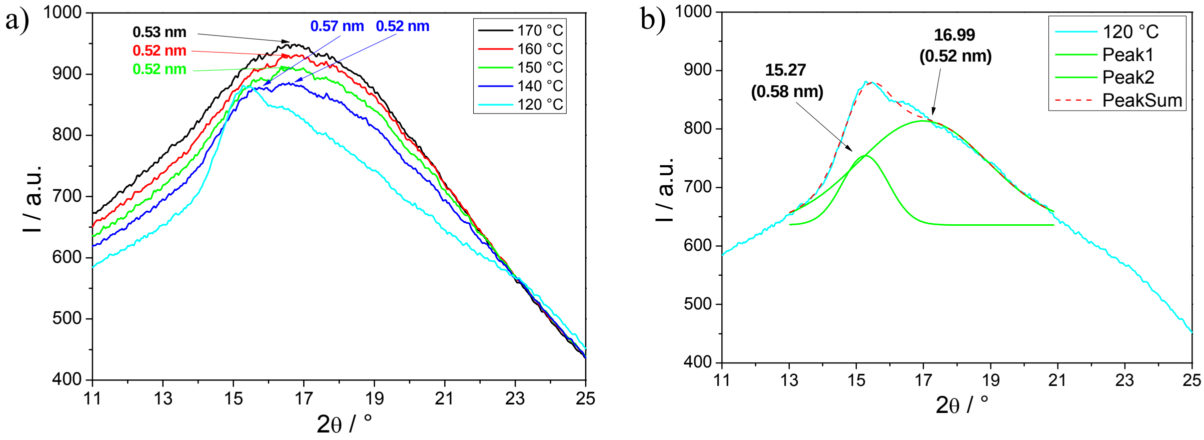


Figure S9. a) WAXS scattering of the mesophases of **1Si$_3$6** recorded on cooling; b) deconvolution of the broad wide angle peak at 120 °C, suggesting the carbosilane phase segregation.

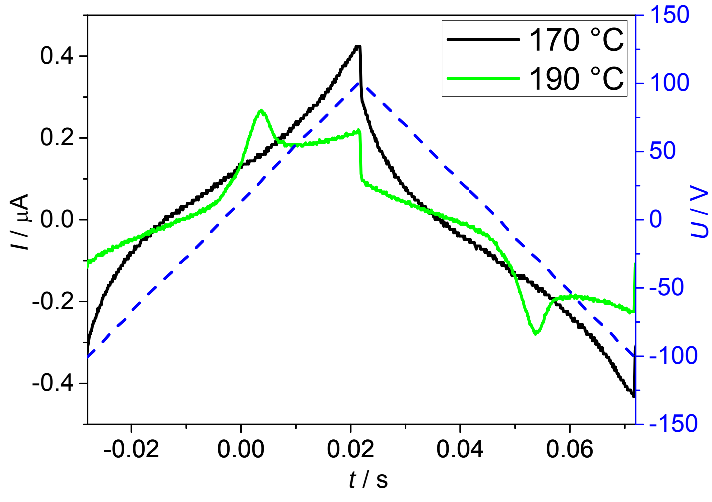


Figure S10: Polarization current curves of **1Si$_3$6** in the SmC$_s$P$_A^{dis}$ (170 °C) and the SmC$_s$P$_R$ phase (190 °C) as observed on heating. Polarization current response when under influence of an applied triangular wave voltage (200 V$_{pp}$, 10 Hz, 6µm polyimide coated ITO cell and 5kΩ). The blue dashed curve indicates the applied triangular wave voltage.

S1.3 Additional data of compound 1Si$_3$Ph12

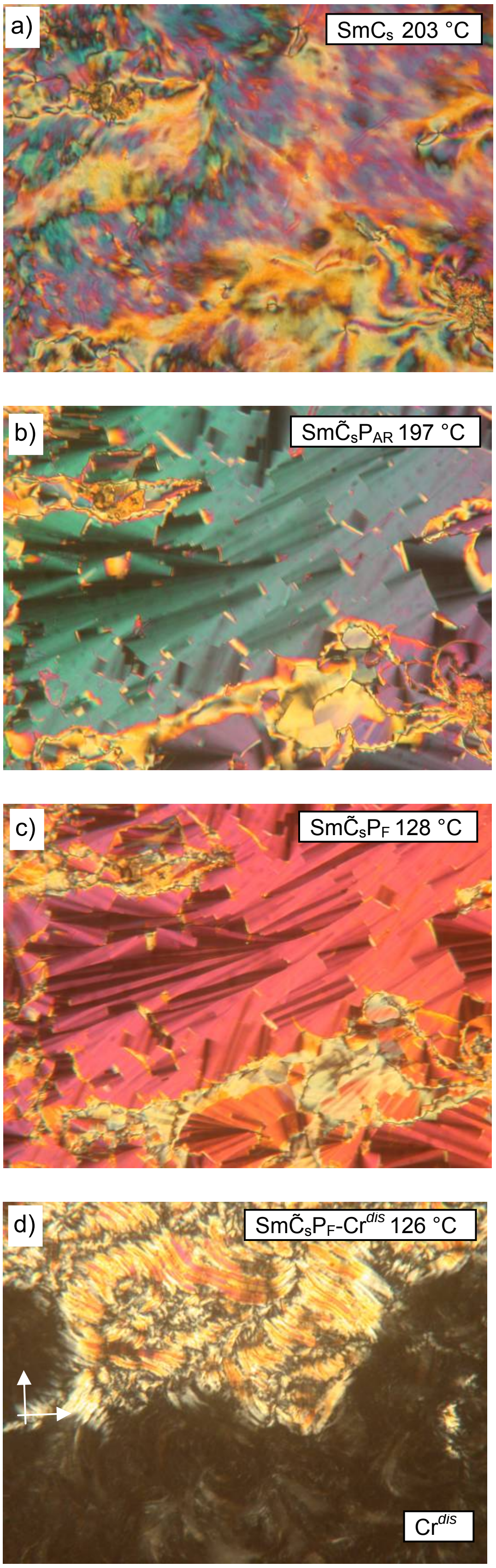


Figure S11. Optical textures of compound as observed for compound **1Si$_3$Ph12** at the given temperatures in the distinct LC phases by POM under crossed polarizers on cooling.

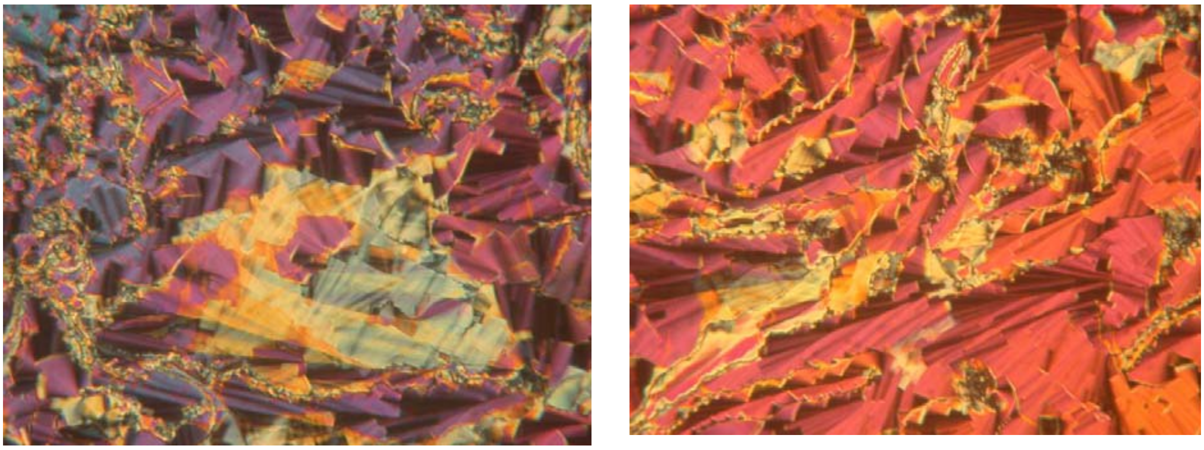


Figure S12. Optical textures observed by POM under crossed polarizers for **1Si$_3$Ph12** in the Sm$\tilde{C}_s$P$_{AR}$ at 132 °C.

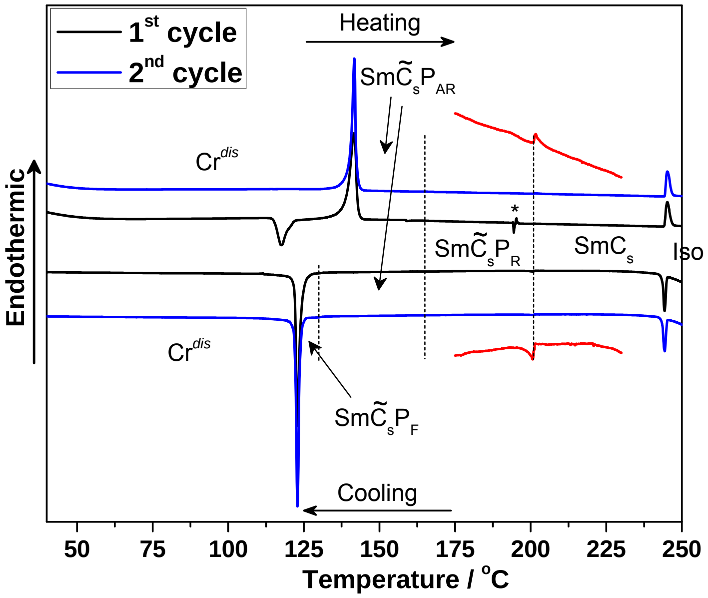


Figure S13. DSC traces for compound **1Si$_3$Ph12** showing the first (black) and second (blue) cycles (10 K min^{-1}). In red, a 20x magnification of part of the second scan (heating and cooling) for better visualization of the low enthalpy transitions. * = artificial signal from the equipment.

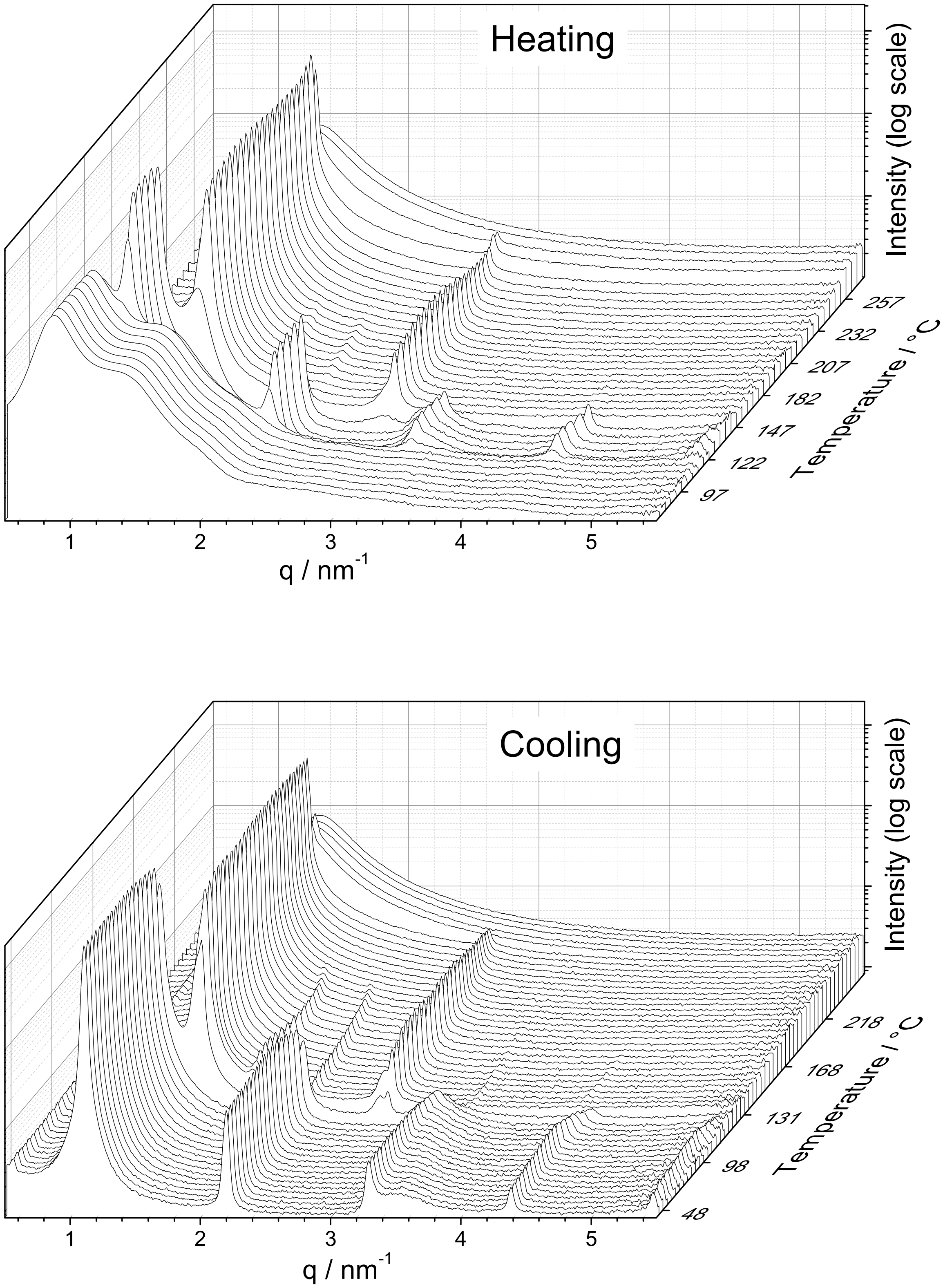


Figure S14. Waterfall plot of the diffraction pattern obtained for **1Si$_3$Ph12** upon heating and cooling.

Table S3. SAXS data and lattice parameter of compound **1Si$_3$Ph12**.

Mesophase (T/°C)	Miller indices (hkl)	d_{obs}/nm	d_{calc}/nm	$d_{obs} - d_{calc}$	Cell parameter
SmC$_s$ (218)	01	4.44	4.44	0.00	d = 4.44 nm
	02	2.22	2.22	0.00	
Sm$\tilde{\mathrm{C}}_s$P$_{AR}$ **(Col$_{ob}$)** (178)	10	4.35	4.35	0.00	a = 4.41 nm
	-11	3.37	3.37	0.00	b = 4.41 nm
	11	2.84	2.84	0.00	γ = 80.2 °
	20	2.17	2.17	0.00	

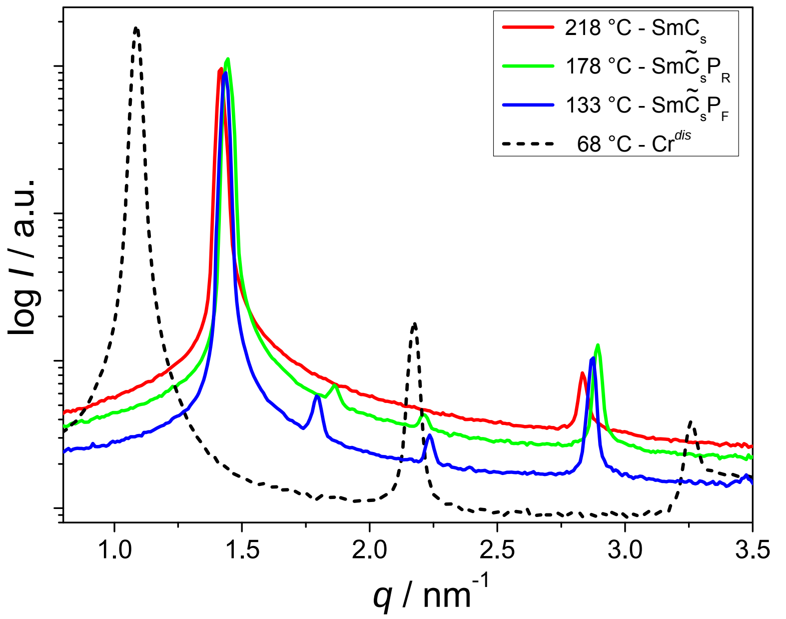


Figure S15. SAXS pattern of compound **1Si$_3$Ph12** at different temperatures, recorded on cooling with synchrotron radiation source.

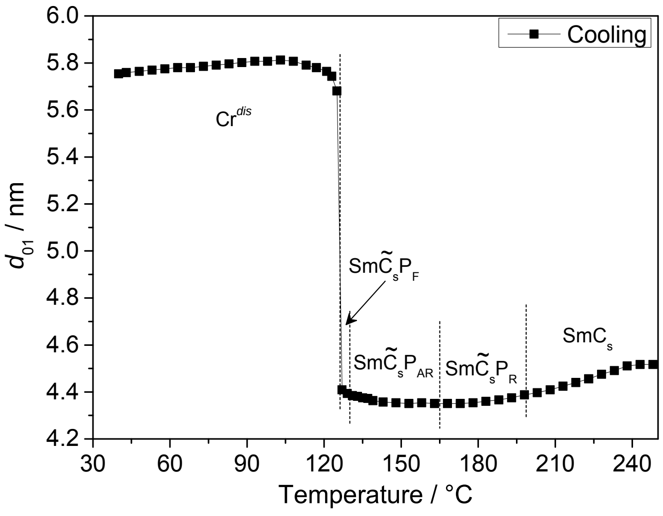


Figure S16. Dependence of the layer reflection in the mesophases of compound **1Si$_3$Ph12** on temperature, as on cooling from the isotropic liquid.

S1.4 Additional data of compound 1Si$_2$12

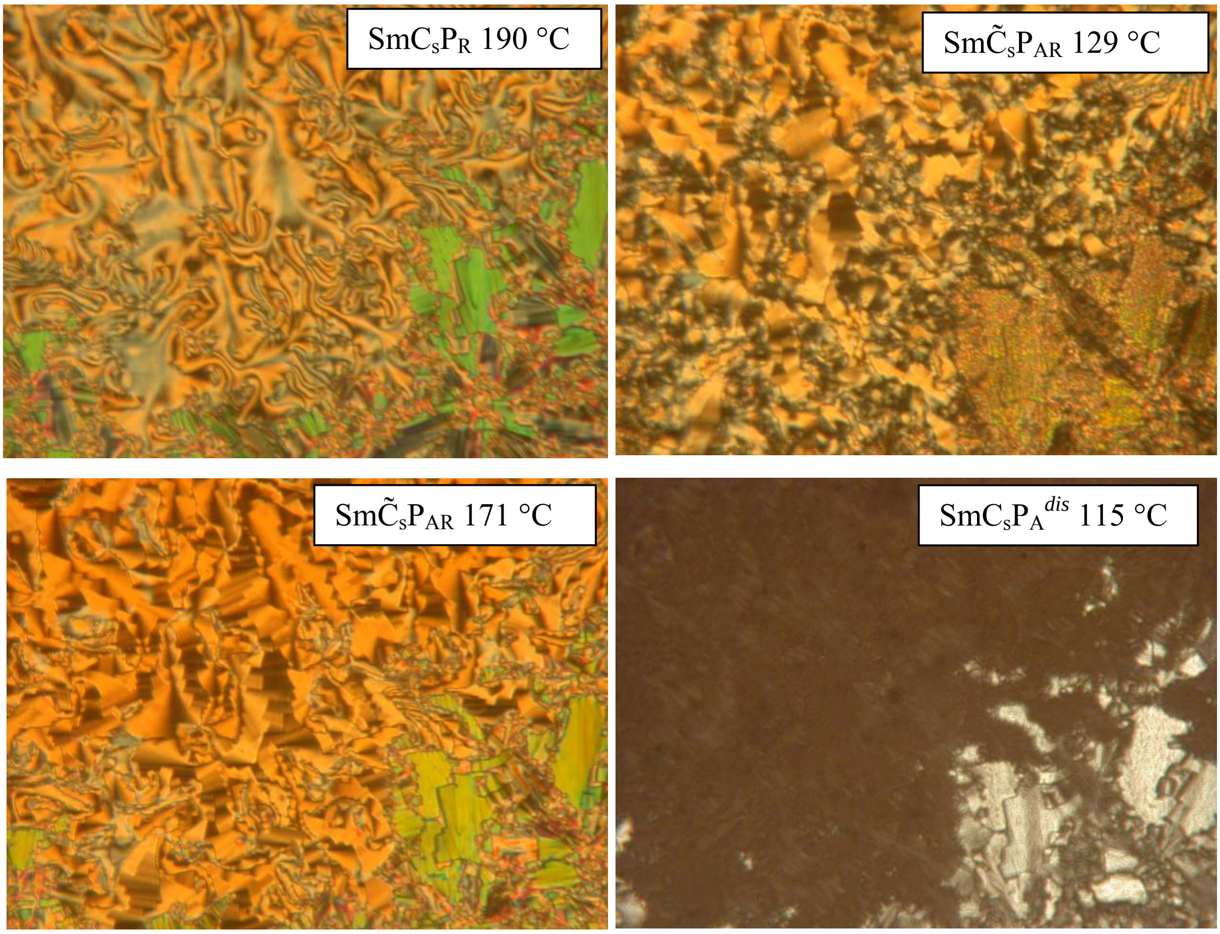


Figure S17. Optical textures observed by POM under crossed polarizers for **1Si$_2$12** on cooling.

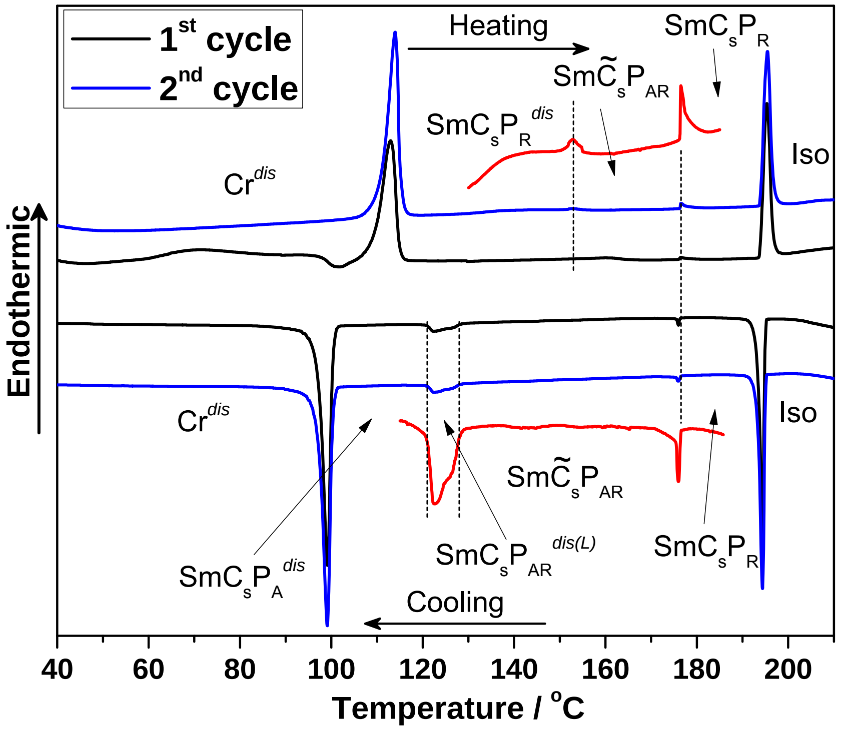


Figure S18. DSC traces for compound **1Si$_2$12** showing the first (black) and second (blue) cycles (10 K min^{-1}). In red, a 10x magnification of part of the second scan (heating and cooling) for better visualization of the low enthalpy transitions.

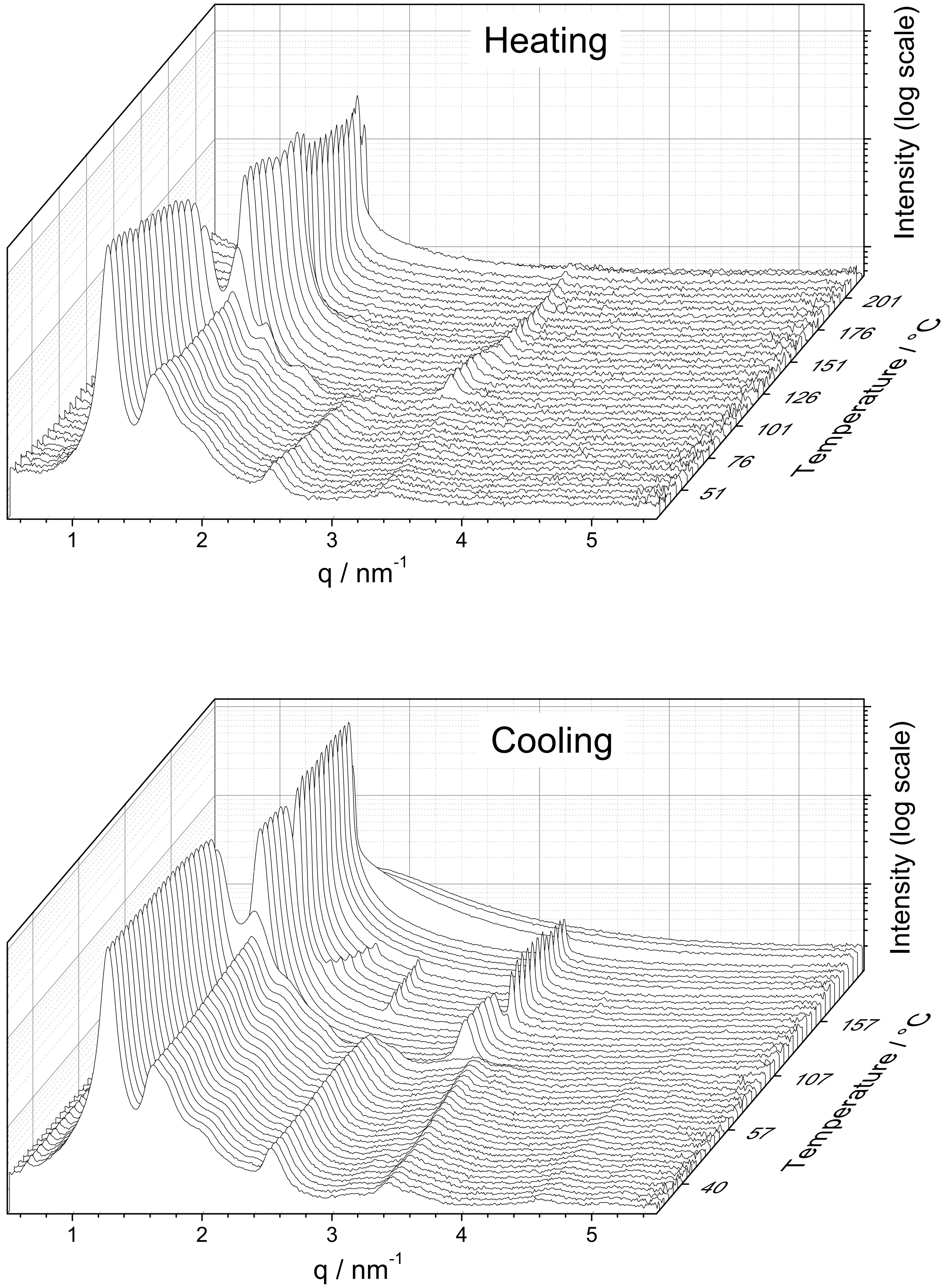


Figure S19: Waterfall plot of the diffraction pattern obtained for **$1Si_212$** upon heating and cooling.

Table S4. SAXS data and lattice parameter of compound **1Si$_2$12**.

Mesophase (*T*/°C)	Miller indices (*hkl*)	d_{obs}/nm	d_{calc}/nm	$d_{obs} - d_{calc}$	Cell parameter
SmC$_s$P$_R$ (190)	01	3.79	3.78	0.01	*d* = 3.78 nm
	02	1.89	1.89	0.00	
Sm$\tilde{\mathrm{C}}_s$P$_{AR}$ (141)	01	4.41	4.41	0.00	*a* = 3.85 nm
	10	3.79	3.79	0.00	*b* = 4.48 nm
	-11	3.17	3.17	0.00	γ = 79.6 °
	11	2.65	2.65	0.00	
	20	1.89	1.89	0.00	
	21	1.64	1.64	0.00	
	30	1.26	1.26	0.00	
SmC$_s$P$_A$^{dis} (110)	01	3.96	3.96	0.00	*d* = 3.96 nm
	02	1.98	1.98	0.00	
	03	1.32	1.32	0.00	

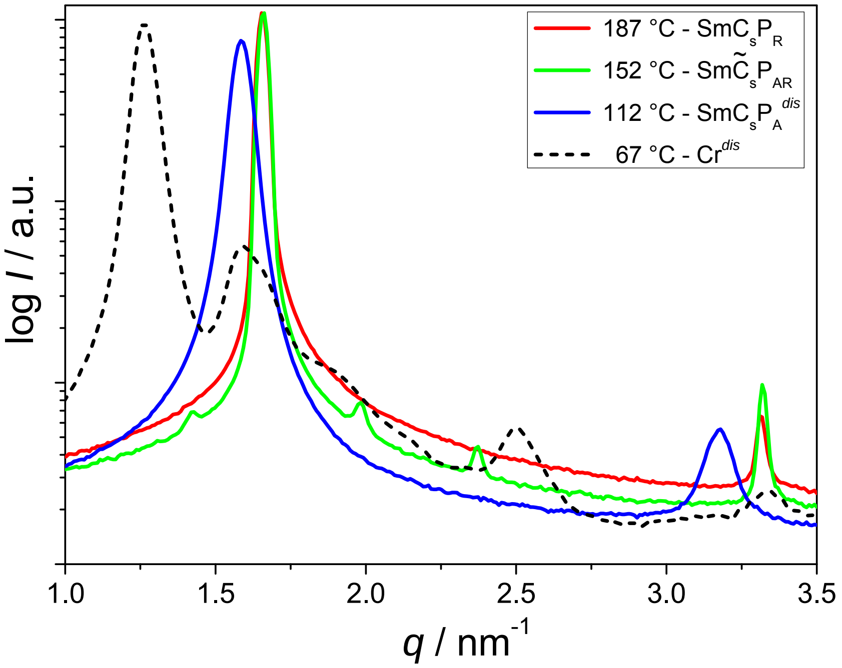


Figure S20. SAXS pattern of compound **1Si$_2$12** at different temperatures, recorded on cooling with synchrotron radiation source.

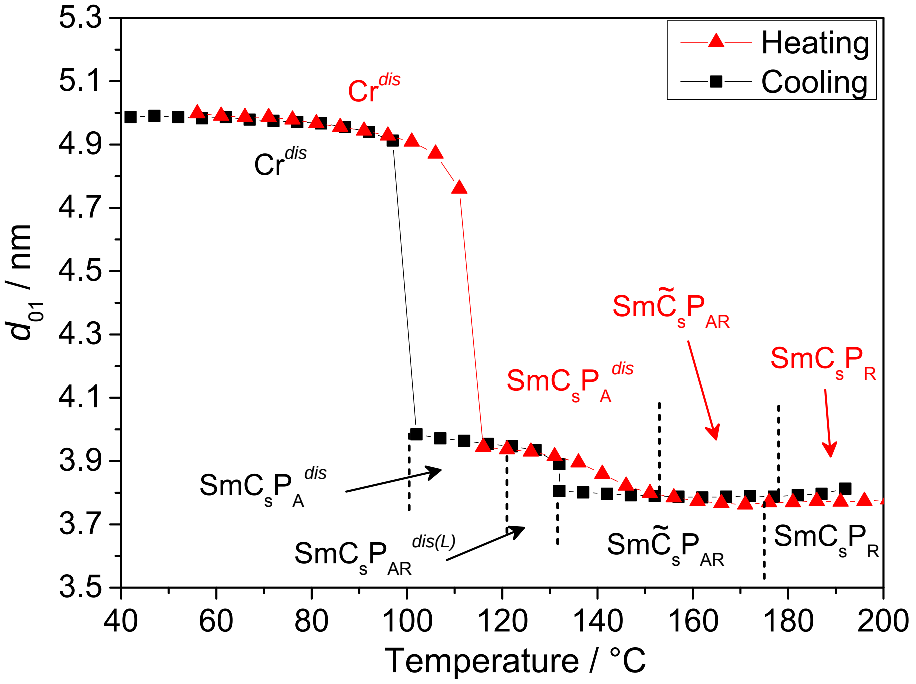


Figure S21. Dependence of the layer reflection in the mesophases of compound **1Si$_2$12** on temperature, on cooling from the isotropic liquid.

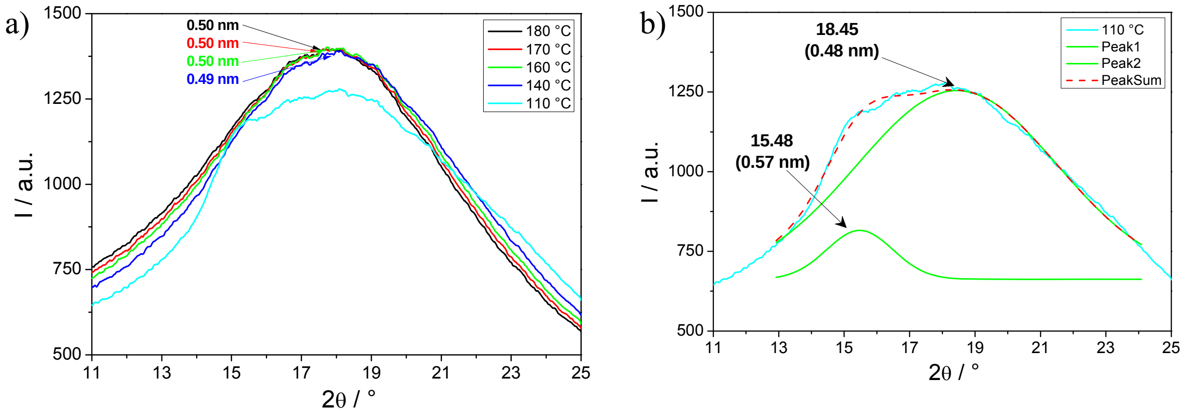


Figure S22. a) WAXS scattering of the mesophases of **1Si$_2$12** recorded on cooling; b) beconvolution of the broad wide angle peak at 110 °C, suggesting the carbosilane phase segregation.

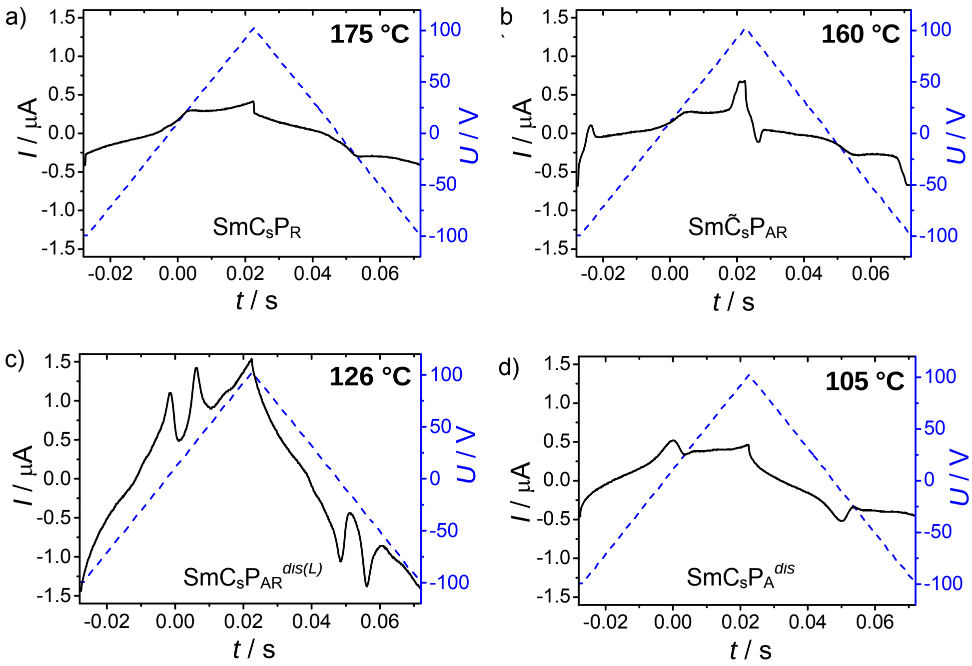


Figure S23: Current response curves of **1Si$_2$12** in the SmC$_s$P$_A$^{dis} phase at the given temperatures on cooling under an applied triangular wave voltage (200 V$_{pp}$, 10 Hz, 6μm polyimide coated ITO cell). The blue slashed curve indicates the applied triangular wave voltage.

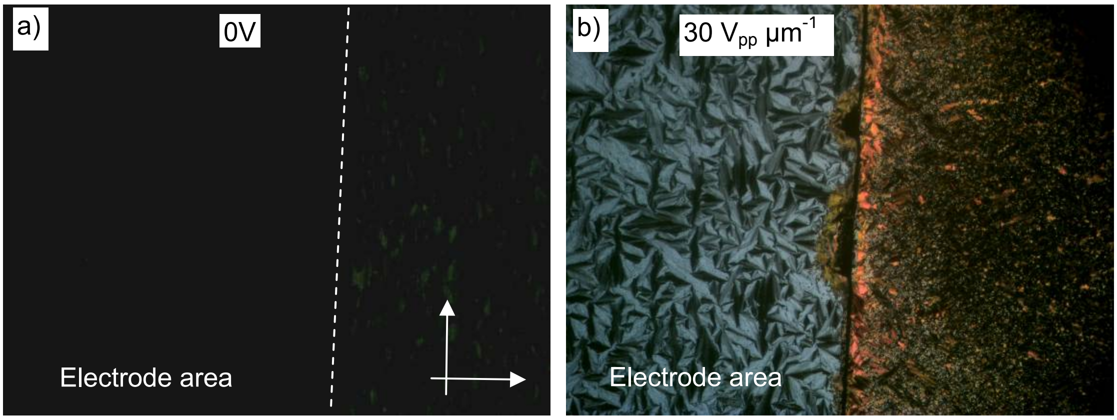


Figure S24. Textures of compound **1Si$_2$12** as observed in the temperature range of the SmC$_s$P$_A$^{dis} phase at T = 125°C in a PI coated 6 μm ITO cell between two electrodes (left) and besides the electrodes (right), a) before application of an electric field and after removal of the field and b) under an applied triangular wave field (10 s^{-1}, 30 V$_{pp}$ μm^{-1}). In the area of the electrodes transition to a field-induced low birefringent SmC$_a$P$_F$ phase is observed (extinction crosses coincide with the directions of polarizer and analyzer); outside the electrodes the dark texture is retained, but close to the electrode area the weaker electric field induces a synclinic SmC$_s$P$_A$ phase. After removing the applied field in b) the dark appearance as in a) is recovered.

S1.5 Additional data of compound C12O-OXD-OC12

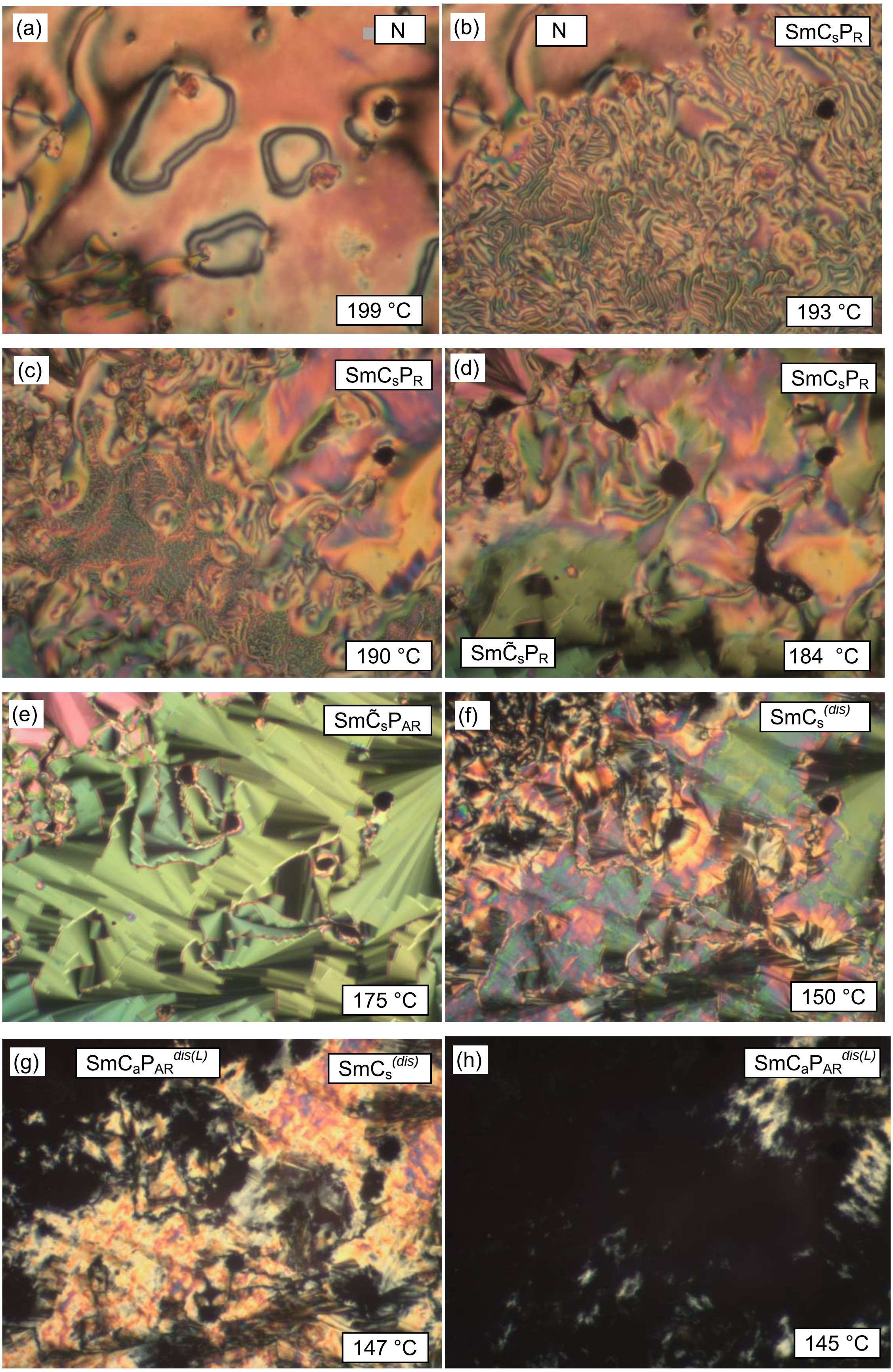


Figure S25. Textures of compound **1-12** as observed on cooling between crossed polarizers (horizontal and vertical) at the indicated temperatures.

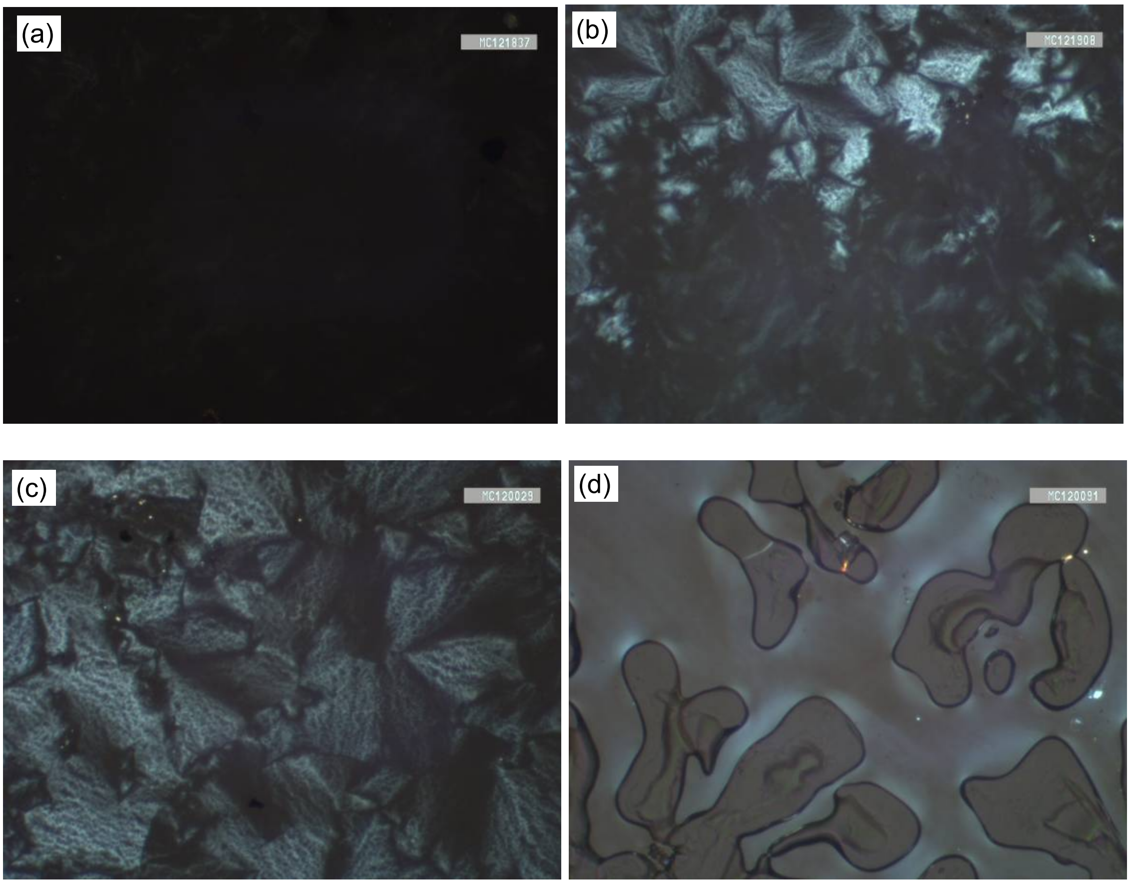


Figure S26. Textures of compound **1-12** as observed on cooling between crossed polarizers (horizontal and vertical) to the SmC$_a$P$_A^{dis}$ (DC) phase at 138 °C; a) under normal exposure as used for Fig. S25, b,c) with enhanced exposure time showing the surface layers by surface anchoring the synclinic organization in the b) planar (top) and homeotropically (bottom) aligned surface layers and d) shows the texture after shearing.

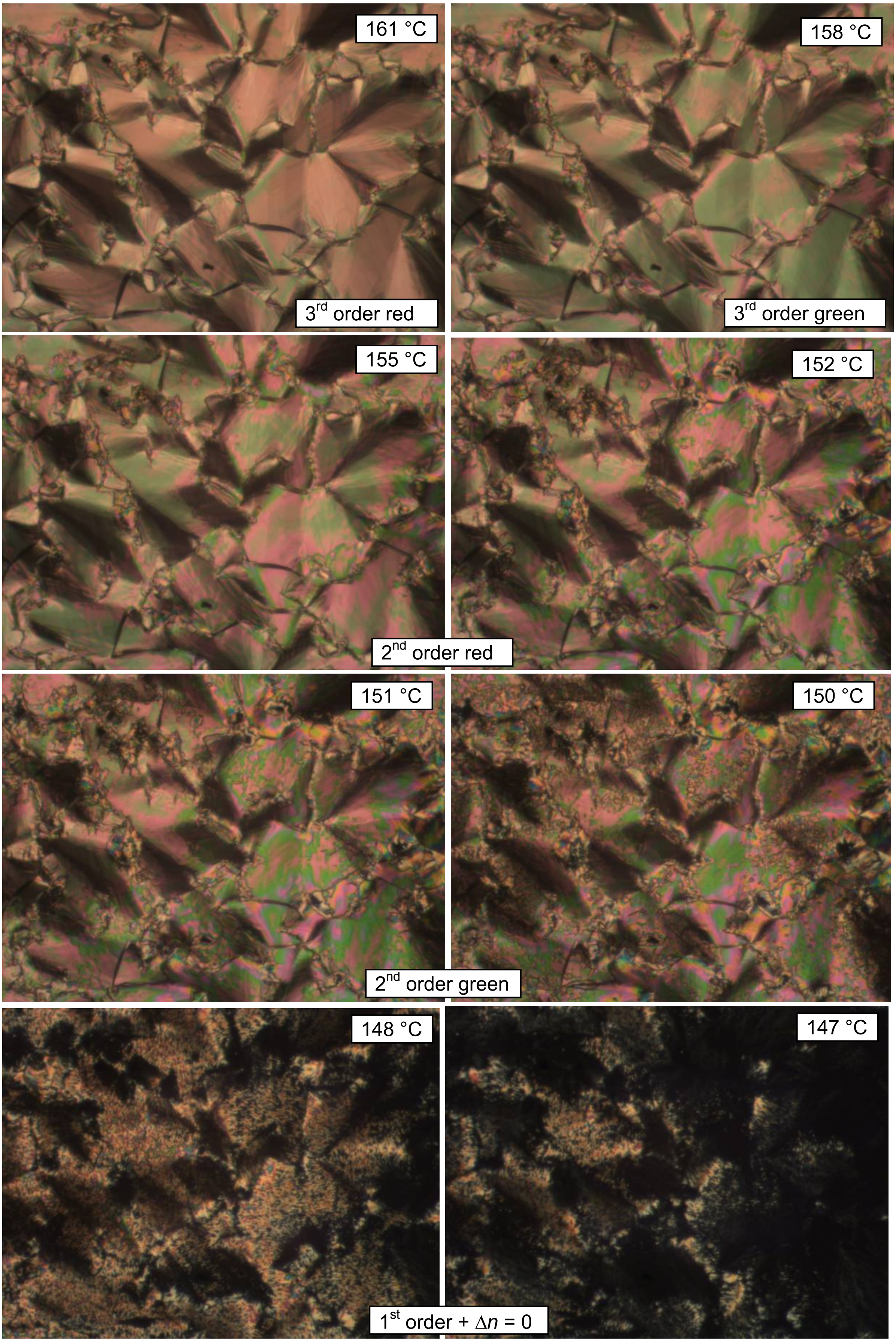
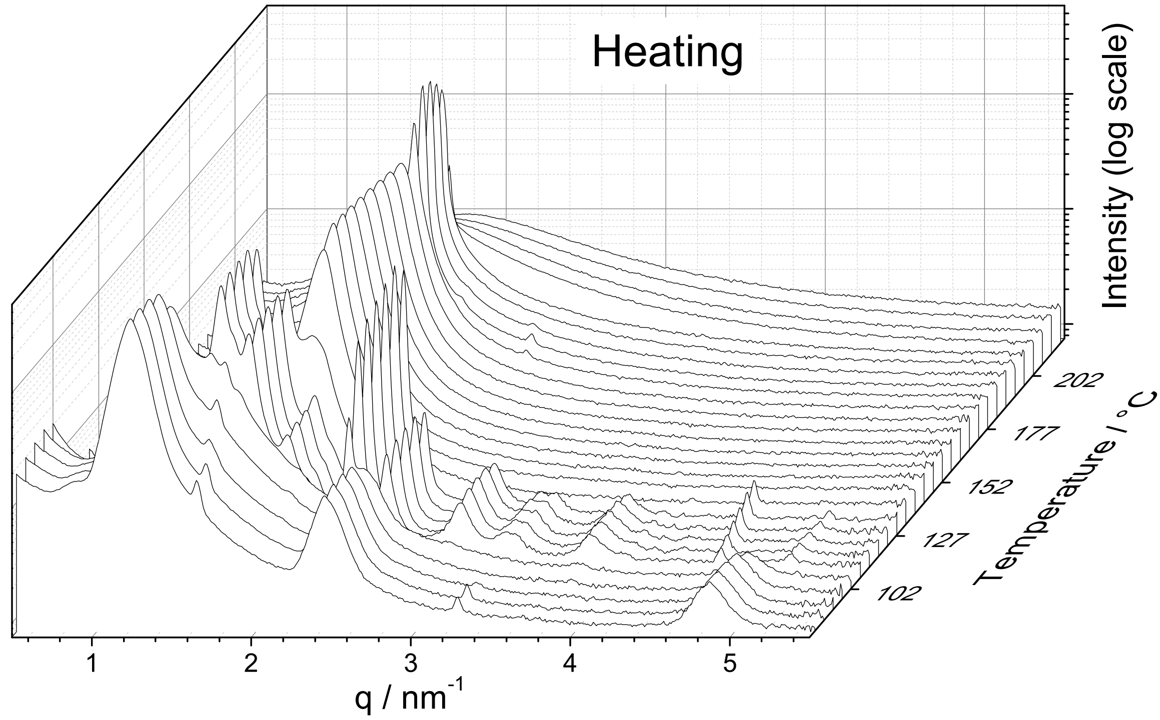


Figure S27. Textures of compound **1-12** as observed on cooling between crossed polarizers (horizontal and vertical) at the indicated temperatures in the Sm$\tilde{C}_s^{(dis)}$ range and showing the decreasing birefringence upon approaching the transition to the SmC$_a$P$_{AR}^{dis(L)}$ phase.



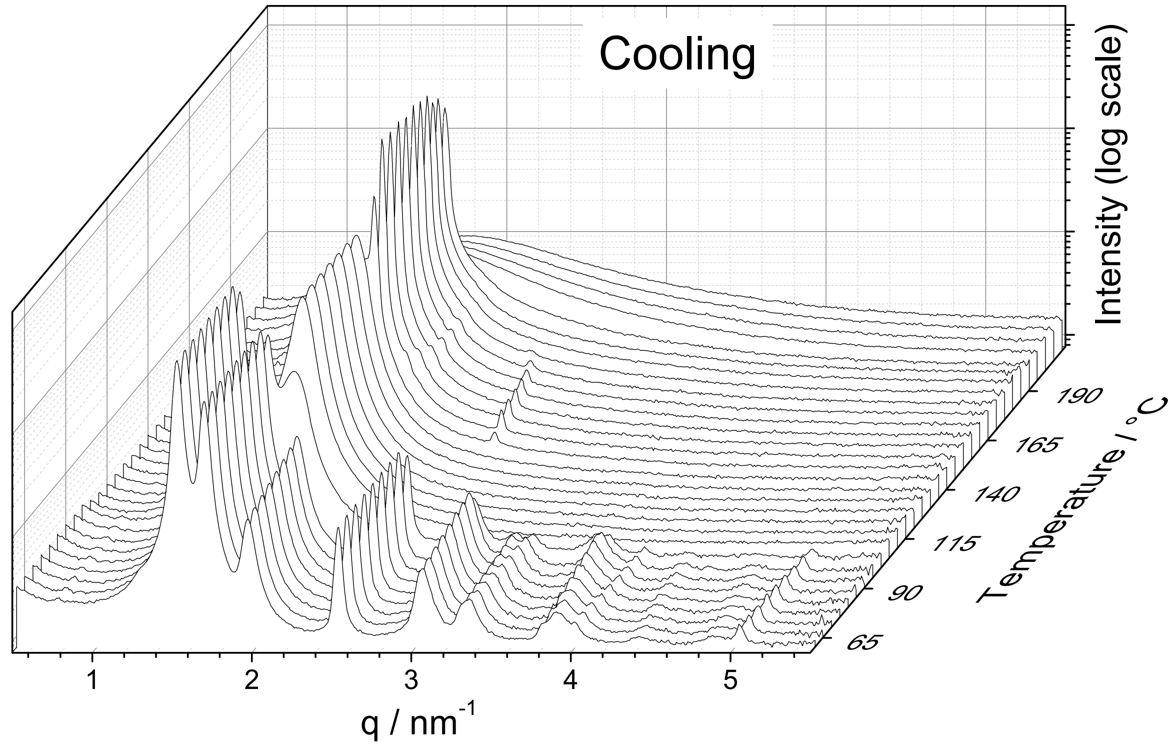


Figure S28. Waterfall plot of the diffraction pattern obtained for **1-12** upon heating and cooling.

Table S5. SAXS data and lattice parameter of compound **1-12.**

Mesophase (T/°C)	Miller indices (hkl)	d_{obs}/nm	d_{calc}/nm	$d_{obs} - d_{calc}$	Cell parameter
SmC_sP_R (185)	01	3.39			d = 3.39 nm
$Sm\tilde{C}_sP_{AR}$ (170)	01	4.38	4.38	0.00	a = 3.37 nm
	10	3.31	3.31	0.00	b = 4.46 nm
	-11	2.94	2.93	0.01	γ = 78.8 nm
	11	2.43	2.42	0.01	
$SmC_aP_A^{dis}$ (120)	01	3.41			d = 3.41 nm

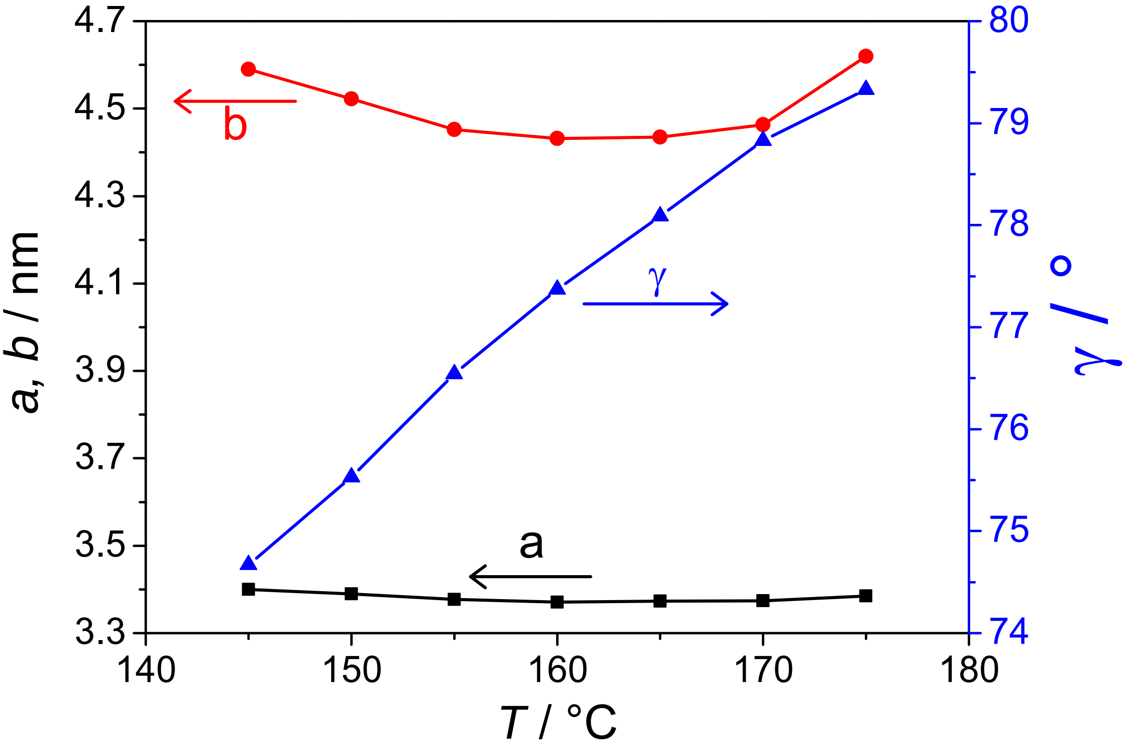


Figure S29. Cell parameter dependence on temperature for the $Sm\tilde{C}_s$ phases of compound **1-12**.

S1.6 Additional models

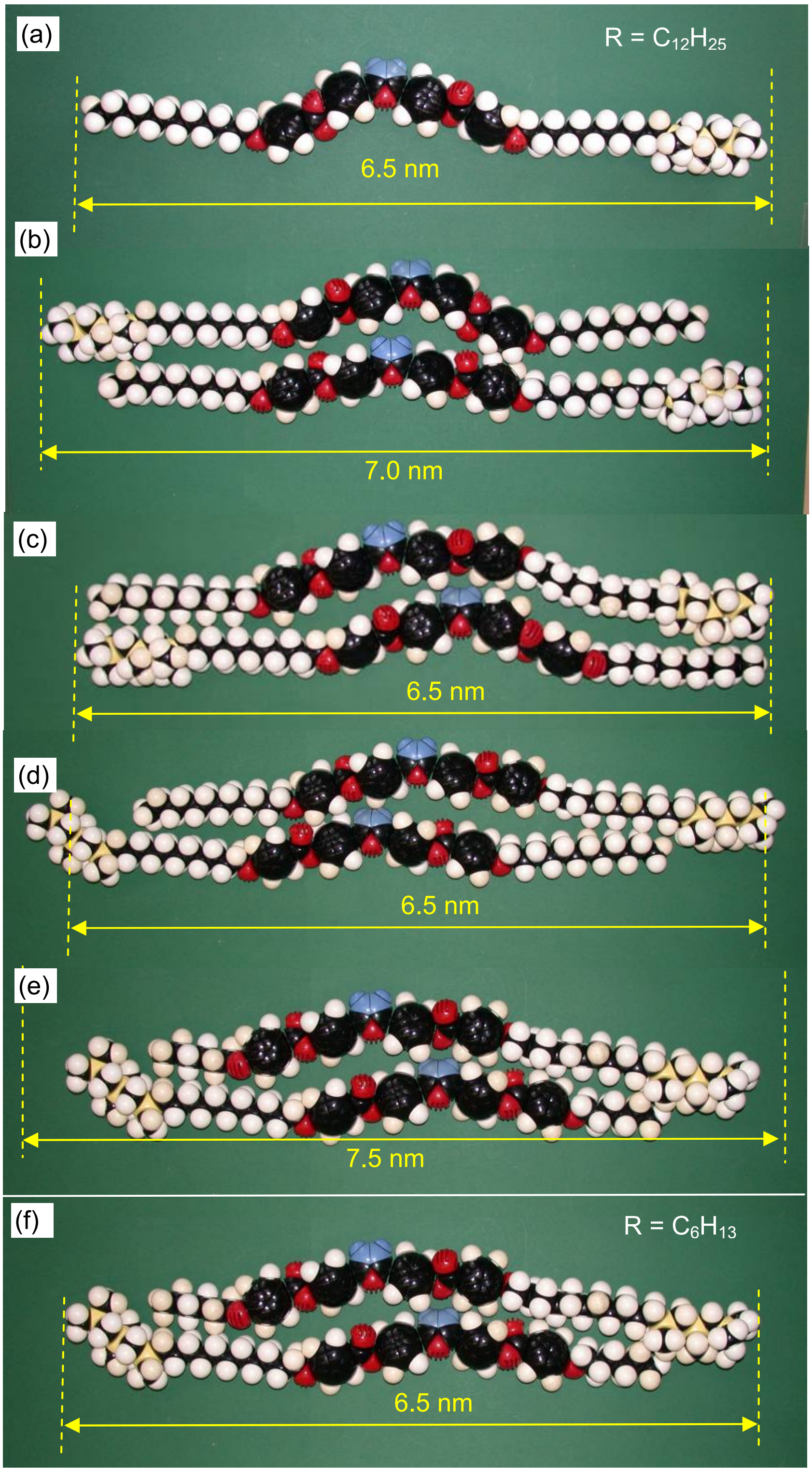
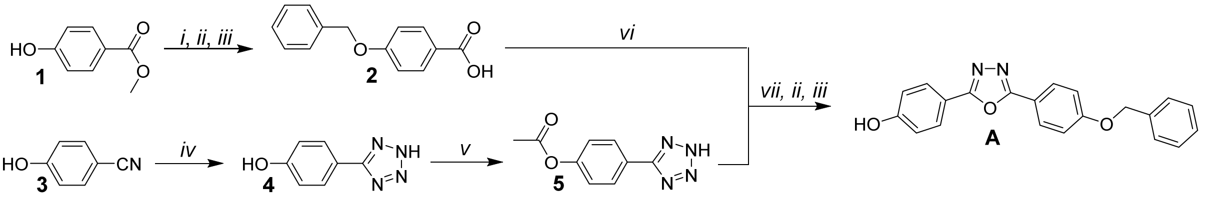


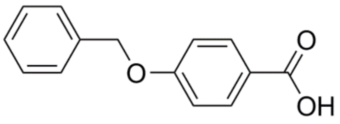
Figure S30. CPK models showing (a-e) compound **1Si₃12** and (f) compound **1Si₃6** with stretched conformations. a) Calculated molecular length (L_{mol}) of compound **1Si₃12** and (b-e) different arrangements in the deeply intercalated smectic phases with antiparallel arrangement of the molecules (tilt is not considered); (b) with complete segregation of aromatics and aliphatics; (c) complete intercalation without segregation; (d,e) different arrangements with segregation of carbosilanes and alkyl chains (f) shows a antiparallel packing of compound **1Si₃6** providing the same layer thickness as arrangements (c,d) for compound **1Si₃12**.

S2. Syntheses and analytical data



Scheme S1. *Reagents: i)* benzyl chloride, K_2CO_3, butanone; *ii)* KOH, MeOH, H_2O; *iii*) HCl; *iv*) NaN_3, NH_4Cl, DMF; *v*) NaOH, H_2O, acetic anhydride; *vi*) $SOCl_2$, DMF catalytic; *vii*) anhydrous pyridine.

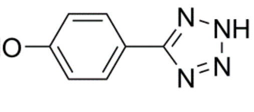
4-Benzyloxybenzoic acid (2)



i) Methyl 4-benzyloxybenzate (benzylation): To a round-bottomed flask equipped with a condenser 13.42 g (88.3 mmol) of methyl 4-hydroxybenzoate (**1**), 10.0 mL (86.9 mmol) benzyl chloride, 24.37 g (176.6 mmol) of K_2CO_3 and 200 mL butanone were added and the suspension refluxed for 20 h. After this period, the suspension was filtered, washed with hot butanone and the solvent removed under reduced pressure. The resulting off-white solid was used in the next step without purifications.

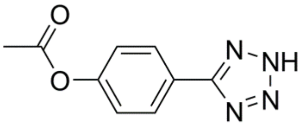
ii) 4-Benzyloxybenzoic acid (deprotection): To the round-bottomed flask containing the methyl 4-benzyloxybenzate prepared in the previous step, 14.83 g (264.9 mmol) of KOH, 100 mL of methanol and 200 mL of water were added. The solution was refluxed for 7 h, poured into 200 mL of water/ice and acidified to pH ≈ 1 with HCl (10 %). The precipitate was filtered, washed with water and recrystallized over ethanol/water, affording 16.9 g (88 %) of a colorless crystalline powder. **m.p.**: 187.6 – 189.4 ºC (lit. 185 - 187 °C)[S1]. **^{1}H NMR** (DMSO-d_6) δ ppm: 5.17 (s, 2H, OCH_2Bn), 7.09 (d, J = 8.8 Hz, 2H, Ar-H), 7.31-7.48 (m, 5H, Ar-H), 7.90 (d, J = 8.8 Hz, 2H, Ar-H), 12.65 (broad, 1H, Ar-COOH). **^{13}C NMR** (DMSO-d_6) δ ppm: 69.48, 114.62, 123.20, 127.83, 128.03, 128.51, 131.39, 136.54, 161.96, 167.02.

5-(4-Hydroxyphenyl)-tetrazole (4)



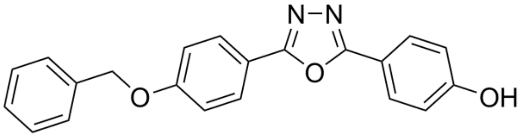
To a round-bottomed flask were added 4-cyanophenol (**3**) (15.00 g; 126.0 mmol), NaN_3 (24.60 g; 378.5 mmol), NH_4Cl (20.20 g; 378.5 mmol) and 100 mL DMF. The mixture was heated to 125 °C, strongly stirred for 28 hours, cooled to room temperature and poured into 300 mL water. The pH of the suspension was adjusted to ≈ 1 with HCl (20 %) and the crude product collected by filtration. The product was recrystallized over water, affording 18.58 g (91 %) of a crystalline solid. **m.p.:** 239.6 ºC (dec.) (lit. 241.8 °C (dec.))[S2]. **^{1}H NMR** (DMSO-d_6) δ ppm: 3.52 (broad, 1H, tet-H), 6.98 (d, J = 8.9 Hz, 2H, Ar-H), 7.89 (d, J = 8.9 Hz, 2H, Ar-H), 10.23 (broad, 1H, Ar-OH). **^{13}C NMR** (DMSO-d_6) δ ppm: 115.27, 116.82, 129.43, 155.44, 160.78.

5-(4-Acetoxyphenyl)-tetrazole (5)

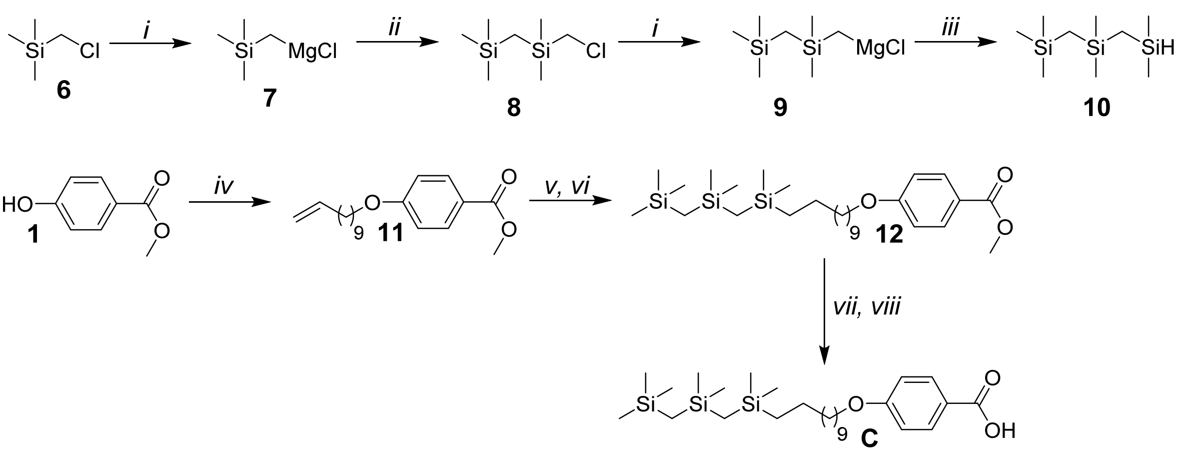


To a round-bottomed flask 19.00 g (117.0 mmol) of 5-(4-hydroxyphenyl)-tetrazole (**4**) and 80 mL of H_2O were added. To the strong stirred suspension, a sodium hydroxide aqueous solution (3M) was added until the solid was completely dissolved. The mixture was cooled to 5 °C with a ice bath and 12.0 mL (127 mmol) of acetic anhydride were then added. The suspension was stirred at 5 °C for 5 minutes, at room temperature for further 15 minutes and poured into 300 mL of ice/water. The pH was adjusted to ≈ 2 with HCl (20 %), the crude product collected by filtration and recrystallized over water, affording 20.31 g (85 %) of a crystalline solid. **m.p.:** 182.3 – 183.0 ºC (dec.) (lit. 182 °C)[S3]. **^{1}H NMR** (DMSO-d_6) δ ppm: 2.33 (s, 3H, -COOCH$_3$), 7.41 (d, *J* = 8.8 Hz, 2H, Ar-H), 8.10 (d, *J* = 8.8 Hz, 2H, Ar-H). **^{13}C NMR** (DMSO-d_6) δ ppm: 21.54, 122.45, 123.71, 129.06, 153.21, 169.67.

2-(4-Benzyloxyphenyl)-5-(4-hydroxyphenyl)-1,3,4-oxadiazole (A)

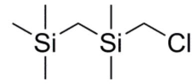


To a round-bottomed flask equipped with a condenser and a $CaCl_2$ drying tube 5.00 g (21.9 mmol) of 4-benzyloxybenzoic acid (**2**), 15 mL of $SOCl_2$ and 1 drop of DMF were added. The mixture was refluxed for 15 hours and the remaining $SOCl_2$ was removed by vacuum distillation. To the freshly prepared acid chloride 4.47 g (21.9 mmol) of 5-(4-acetoxyphenyl)-tetrazole (**5**) and 30 mL of anhydrous pyridine were added and the mixture stirred at 100 °C for further 30 h. The solution was then cooled to room temperature, poured into 500 mL of water/ice, filtered and washed with water. The crude solid was transferred to a 500 mL round-bottomed flask equipped with a condenser together with 3.68 g (65.7 mmol) of KOH, 200 mL of methanol and 50 mL of water. The mixture was heated to 70 °C and stirred for further 5 h. The solvent was partially removed under reduced pressure, the remaining fraction poured into 300 mL water, acidified to pH ≈ 1with HCl (10 %). The precipitate was filtered, washed with water and recrystallized over acetonitrile, affording 6.26 g (83 %) of an yellowish solid. **m.p.**: 212.3 – 214.0 ºC. **^{1}H NMR** (DMSO-d_6) δ ppm: 5.22 (s, 2H, OCH$_2$Bn), 6.99 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.24 (d, *J* = 9.2 Hz, 2H, Ar-H), 7.33-7.51 (m, 5H, Ar-H), 7.96 (d, *J* = 8.8 Hz, 2H, Ar-H), 8.04 (d, *J* = 9.2 Hz, 2H, Ar-H), 10.34 (s, 1H, Ar-OH). **^{13}C NMR** (DMSO-d_6) δ ppm: 69.52, 114.19, 115.62, 116.08, 116.14, 127.82, 128.01, 128.31, 128.48, 128.53, 136.47, 160.71, 160.97, 163.17, 163.74.



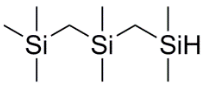
Scheme S2. *Reagents: i)* Mg, anhydrous THF; *ii)* chloro(chloromethyl)dimethylsilane, anhydrous THF; *iii)* chlorodimethylsilane, anhydrous THF; *iv)* 11-bromo-1-undecene, K_2CO_3, butanone, 18-crown-6; *v)* 2,2,4,4,6-pentamethyl-2,4,6-trisilaheptane (**10**), Karstedt catalyst, anhydrous toluene; *vi)* OsO_4 solution, $NaIO_4$, t-BuOH, H_2O; *vii)* KOH, THF, MeOH, H_2O; *viii*) HCl.

1-Chloro-2,2,4,4-tetramethyl-2,4-disilapentane (8)



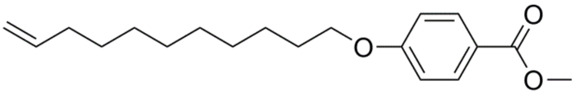
To a two-necked Schlenk flask equipped with a dropping funnel and condenser, 2.18 g (89.7 mmol) of Mg turnings and 60 mL of anhydrous THF were added under argon atmosphere. An iodine crystal followed by a small amount of 1,2-dibromoethane were added and the mixture stirred until the Grignard reaction was initiated. To this mixture 10.0 g (81.5 mmol) of chloromethyltrimethylsilane (**6**) dissolved in 20 mL of anhydrous THF was added dropwise (≈ 20 min). The mixture was then refluxed for 2 h, cooled to room temperature and 10.5 g (73.4 mmol) of neat chloro(chloromethyl)dimethylsilane were slowly added (≈ 40 min). The mixture was then refluxed for further 20 h. The reaction mixture was cooled to room temperature, 200 mL of water were carefully added followed by 100 mL of hexanes. The aqueous phase was separated and then extracted with hexanes (3x30 mL). The combined organic phases were dried with anhydrous Na_2SO_4 and the solvent removed under reduced pressure. The resultant oil was passed through a short pad of silica gel using hexanes as the eluent. The solvent was removed under reduced pressure, affording 13.9 g (97 %) of a colorless oil. The ^{1}H NMR spectrum showed a purity between 90 - 95 %, which is good enough to proceed to the next step without the need for further purifications. **^{1}H NMR** ($CDCl_3$) δ ppm: -0.14 (s, 2H, -Si$C\underline{H_2}$Si-), 0.05 (s, 9H, -Si$(CH_3)_3$), 0.14 (s, 6H, -Si$(CH_3)_2$-), 2.75 (s, 2H, -CH_2Cl). **^{13}C NMR** ($CDCl_3$) δ ppm: -2.02, 1.19, 1.26, 32.39.

2,2,4,4,6-Pentamethyl-2,4,6-trisilaheptane (10)



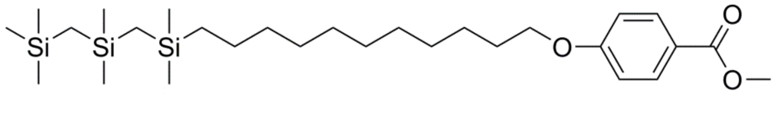
To a two-necked Schlenk flask equipped with a dropping funnel and condenser, 1.90 g (78.0 mmol) of Mg turnings and 60 mL of anhydrous THF were added under argon atmosphere. An iodine crystal followed by a small amount of 1,2-dibromoethane were added and the mixture stirred until the Grignard reaction was initiated. To this mixture 13.8 g (70.9 mmol) of 1-chloro-2,2,4,4-tetramethyl-2,4-disilapentane (**8**) dissolved in 20 mL of anhydrous THF was added dropwise (≈ 20 min). The mixture was then refluxed for 3 h, cooled to room temperature and 7.41 g (78.3 mmol) of neat chlorodimethylsilane were slowly added (≈ 30 min). The mixture was then refluxed for further 20 h. The reaction mixture was cooled to room temperature, 200 mL of water were carefully added followed by 100 mL of hexanes. The aqueous phase was separated and then extracted with hexanes (3x30 mL). The combined organic phases were dried with anhydrous Na_2SO_4 and the solvent removed under reduced pressure. The resultant oil was purified by vacuum distillation (b.p. ≈ 56 °C at 0.45 mbar), affording 11.2 g (72 %) of a colorless oil. **^{1}H NMR** ($CDCl_3$) δ ppm: -0.23 (s, 2H, $-SiC\underline{H}_2Si-$), -0.22 (d, J = 3.9 Hz, 2H, $-SiC\underline{H}_2Si-$), 0.02 (s, 9H, $-Si(CH_3)_3$), 0.06 (s, 6H, $-Si(CH_3)_2-$), 0.10 (d, J = 3.5 Hz, 2H, $-Si(C\underline{H}_3)_2H$), 3.97 (m, J = 3.9 Hz, 1H, SiH). **^{13}C NMR** ($CDCl_3$) δ ppm: -1.43, 1.43, 1.84, 2.89, 5.18. **^{29}Si NMR** ($CDCl_3$) δ ppm: -16.64, 0.10, 0.77.

Methyl 4-(10-undecenyloxy)benzoate (11)



A mixture of methyl 4-hydroxybenzoate (**1**) (5.10 g; 33.5 mmol), 11-bromo-1-undecene (7.0 mL; 31.9 mmol), K_2CO_3 (3.81 g; 67.1 mmol), 100 mL butanone and catalytic amount of 18-crown-6 were added to a round-bottomed flask and stirred under reflux for 20 h. After this period, the suspension was filtered, washed with THF and the solvent removed under reduced pressure. The crude product was purified by silica column chromatography using chloroform/hexanes (1:1) as the eluent, affording 9.40 g (97 %) of a colorless solid. **m.p.**: 40.6 – 41.5 °C (lit. 40.2 – 40.6 °C)[S4]. **^{1}H NMR** ($CDCl_3$) δ ppm: 1.28-1.40 (m, 10H, $-CH_2-$), 1.45 (m, 2H, $-CH_2-$), 1.79 (m, 2H, $-C\underline{H}_2CH_2O-$), 2.04 (m, 2H, $-C\underline{H}_2CH=CH_2$), 3.88 (s, 3H, $-OCH_3$), 4.00 (t, J = 6.6 Hz, 2H, $-OCH_2-$), 4.93 (ddt, J = 1.2 Hz, 2.3 Hz e 10.2 Hz, 1H, $-CH=C\underline{H}_{2(cis)}$), 4.99 (ddt, J = 1.6 Hz, 2.3 Hz e 17.0 Hz, 1H, $-CH=C\underline{H}_{2(trans)}$), 5.81 (ddt, J = 6.6 Hz, 10.2 Hz e 17.0 Hz, 1H, $-CH_2C\underline{H}=CH_2$), 6.90 (d, J = 9.0 Hz, 2H, Ar-H), 7.98 (d, J = 9.0 Hz, 2H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: 25.96, 28.90, 29.07, 29.08, 29.31, 29.38, 29.47, 33.77, 51.78, 68.17, 114.04, 114.11, 122.31, 131.53, 139.16, 162.94, 166.87.

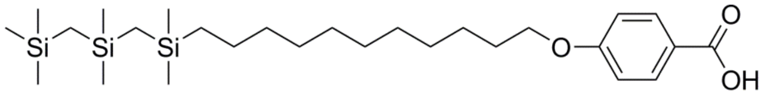
Methyl 4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy)benzoate (12)



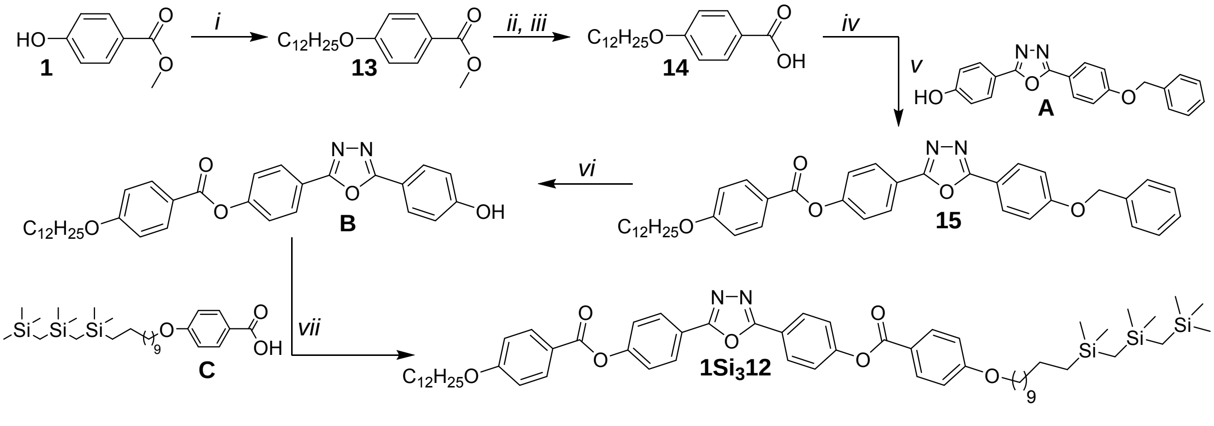
To a 250 mL Schlenk tube 5.00 g (16.4 mmol) of methyl 4-(10-undecenyloxy)benzoate (**11**), 5.00g (22.9 mmol) de 2,2,4,4,6-pentamethyl-2,4,6-trisilaheptane (**10**), 5 drops of Karstedt catalyst (≈ 2 % Pt solution in xylene) and 40 mL of anhydrous toluene were added under argon atmosphere. The system was protected from light with aluminum foil and stirred for 24 h at room temperature. The resultant solution was passed through a short pad of silica gel and eluted with chloroform. A dark oil was obtained after removal of the solvent. To the round-bottomed flask containing the dark oil, 70 mL of t-butanol, 30 mL of water, 5.0 mL of a 0.004M OsO_4 solution (in t-butanol) and 7.00 g (32.9 mmol) of $NaIO_4$ were added. The mixture was stirred at room temperature for 20 h. To the suspension 100 mL of $Na_2S_2O_4$

saturated aqueous solution were slowly added and stirred for further 30 min. The product was extracted using a 1:1 hexanes/ethyl acetate solution (1 x 100 mL e 2 x 50 mL), the combined organic phases dried with anhydrous Na_2SO_4 and the solvent removed under reduced pressure. The crude oil was purified by silica column chromatography using hexanes/ethyl acetate (20:1) as the eluent, affording 6.61 g (77 %) of a colorless oil. **^{1}H NMR** ($CDCl_3$) δ ppm: -0.28 (s, 2H, -SiC$\underline{H}_2$Si-), -0.26 (s, 2H, -SiC$\underline{H}_2$Si-), -0.01 (s, 6H, -Si(CH_3)$_2$-), 0.02 (s, 9H, -Si(CH_3)$_3$), 0.04 (s, 6H, -Si(C$\underline{H}_3$)$_2$-), 0.47 (broad, 2H, -CH_2C$\underline{H}_2$Si-), 1.24-1.38 (m, 14H, -CH_2-), 1.46 (m, 2H, -CH_2-), 1.80 (m, 2H, -C$\underline{H}_2$$CH_2$O-), 3.88 (s, 3H, -$OCH_3$), 4.00 (t, J = 6.6 Hz, 2H, -OCH_2-), 6.90 (d, J = 9.0 Hz, 2H, Ar-H), 7.98 (d, J = 9.0 Hz, 2H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: -0.43, 1.47, 2.47, 4.05, 5.81, 18.06, 23.98, 25.99, 29.13, 29.38, 29.55, 29.60, 29.62, 33,70, 51.81, 68.22, 114.07, 122.33, 131.55, 162.96, 166.90.

4-(12,12,14,14,16,16-Hexamethyl-12,14,16-trisilaheptadecyloxy)benzoic acid (C)

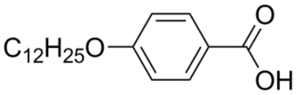


To a round-bottomed flask were added 6.00 g (11.5 mmol) of methyl 4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy)benzoate (**12**), 90 mL methanol and 60 mL of THF. The solution was heated to 40 °C and 1.93 g (34.5 mmol) of KOH dissolved in 15 mL of water was added at once. The solution was stirred at 40 °C for 20 h. The solvent was partially removed under reduced pressure, 200 mL of water was then added and the pH adjusted to ≈ 1 with HCl (10 %). The product was extracted using a 1:1 hexanes/ethyl acetate solution (3 x 70 mL), the combined organic phases dried with anhydrous Na_2SO_4 and the solvent removed under reduced pressure. Purification by silica column chromatography using hexanes/ethyl acetate (9:1) as the eluent, afforded 5.43 g (93 %) of a colorless solid. Iso – 91 °C – N – 84 °C – SmC – 43 °C – Cr (cooling). **^{1}H NMR** ($CDCl_3$) δ ppm: -0.28 (s, 2H, -SiC$\underline{H}_2$Si-), -0.26 (s, 2H, -SiC$\underline{H}_2$Si-), 0.00 (s, 6H, -Si(CH_3)$_2$-), 0.03 (s, 9H, -Si(CH_3)$_3$), 0.05 (s, 6H, -Si(C$\underline{H}_3$)$_2$-), 0.48 (broad, 2H, -CH_2C$\underline{H}_2$Si-), 1.26-1.39 (m, 14H, -CH_2-), 1.47 (m, 2H, -CH_2-), 1.81 (m, 2H, -C$\underline{H}_2$$CH_2$O-), 4.02 (t, J = 6.6 Hz, 2H, -OCH_2-), 6.93 (d, J = 9.0 Hz, 2H, Ar-H), 8.06 (d, J = 9.0 Hz, 2H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: -0.43, 1.47, 2.47, 4.05, 5.81, 18.06, 23.98, 25.98, 29.10, 29.37, 29.39, 29.55, 29.60, 29.62, 33,71, 68.29, 114.19, 121.38, 132.33, 163.69, 171.90. **^{29}Si NMR** ($CDCl_3$) δ ppm: 0.02, 0.57, 1.27.



Scheme S3. *Reagents: i)* 1-bromododecane, K_2CO_3, butanone; *ii)* KOH, MeOH, H_2O; *iii)* HCl; *iv)* $SOCl_2$, DMF; *v)* compound **A**, anhydrous CH_2Cl_2, anhydrous TEA, DMAP; *vi)* H_2, Pd/C (10%), THF; *vii)* compound **C**, DCC, DMAP, anhydrous CH_2Cl_2.

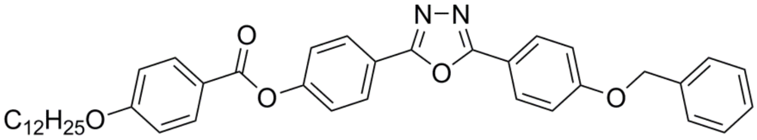
4-Dodecyloxybenzoic acid (14)



i) *Methyl 4-dodecyloxybenzoate (alkylation):* To a round-bottomed flask equipped with a condenser 3.32 g (21.8 mmol) of methyl 4-hydroxybenzoate (**1**), 5.0 mL (20.8 mmol) of 1-bromododecane, 5.75 g (41.6 mmol) of K_2CO_3 and 100 mL butanone were added and the suspension refluxed for 22 h. After this period, the suspension was filtered, washed with hot butanone and the solvent removed under reduced pressure. The resulting oil was used in the next step without purifications.

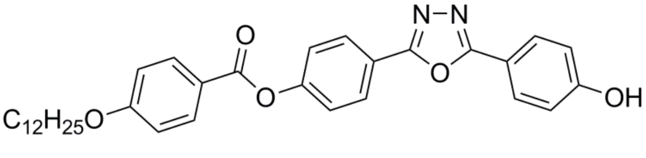
ii) *4-Dodecyloxybenzoic acid (deprotection):* To the round-bottomed flask containing the methyl 4-dodecyloxybenzate (**13**) prepared in the previous step, 3.67 g (65.5 mmol) of KOH, 100 mL of methanol and 50 mL of water were added. The solution was refluxed for 3 h, the solvent partially removed under reduced pressure, the remaining fraction poured into 500 mL water/ice and acidified to pH ≈ 1with HCl (10 %). The precipitate was filtered, washed with water and recrystallized over isopropanol/water, affording 6.18 g (97 %) of a colorless crystalline powder. Cr – 95 °C – SmA – 131 °C – N – 138 °C – Iso (lit. Cr – 95.1 °C – SmA – 128.9 °C – N – 137.2 °C – Iso)[S5]. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.89 (t, *J* = 6.8 Hz, 3H, $-CH_3$), 1.21-1.39 (m, 16H, $-CH_2-$), 1.46 (m, 2H, $-CH_2-$), 1.80 (m, 2H, $-C\underline{H_2}CH_2O-$), 4.02 (t, *J* = 6.6 Hz, 2H, $-OCH_2-$), 6.91 (d, *J* = 9.0 Hz, 2H, Ar-H), 8.01 (d, *J* = 9.0 Hz, 2H, Ar-H). **^{13}C NMR** ($CDCl_3$ + DMSO-d_6 drop) δ ppm: 14.31, 22.84, 26.13, 29.27, 29.49, 29.50, 29.70, 29.73, 29.78, 29.80, 32.06, 68.33, 114.12, 122.96, 131.99, 163.04, 168.91.

2-(4-Benzyloxyphenyl)-5-[4-(4-dodecyloxybenzoyloxy)phenyl]-1,3,4-oxadiazole (15)



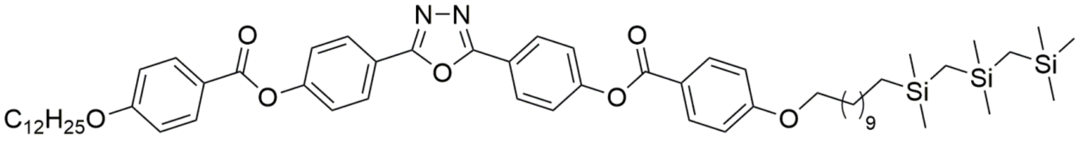
To a round-bottomed flask equipped with a condenser and a $CaCl_2$ drying tube 2.50 g (8.17 mmol) of 4-dodecyloxybenzoic acid (**14**), 5 mL of $SOCl_2$ and 1 drop of DMF were added. The mixture was refluxed for 16 hours and the remaining $SOCl_2$ was removed by vacuum distillation. To the freshly prepared acid chloride, 2.81 g (8.17 mmol) of 2-(4-benzyloxyphenyl)-5-(4-hydroxyphenyl)-1,3,4-oxadiazole (**A**), 80 mL of anhydrous CH_2Cl_2, 3.4 mL (24.5 mmol) of anhydrous TEA and catalytic amount of DMAP were added and the mixture refluxed for further 24 h. The solvent was removed under reduced pressure and recrystallized over isopropanol, affording 4.73 g (92 %) of an white solid. Iso – 165 °C – N – 113 °C – SmX – 105 °C – Cr (cooling) (lit. Iso – 159 °C – N – 126 °C – SmA – 117 °C – SmX – 112 °C – Cr)[S6]. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (t, *J* = 6.8 Hz, 3H, $-CH_3$), 1.20-1.41 (m, 16H, $-CH_2-$), 1.48 (m, 2H, $-CH_2-$), 1.82 (m, 2H, $-C\underline{H_2}CH_2O-$), 4.05 (t, *J* = 6.6 Hz, 2H, $-OCH_2-$), 5.15 (s, 2H, OCH_2Bn), 6.99 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.11 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.31-7.46 (m, 7H, Ar-H), 8.08 (d, *J* = 9.0 Hz, 2H, Ar-H), 8.15 (d, *J* = 9.0 Hz, 2H, Ar-H), 8.19 (d, *J* = 9.0 Hz, 2H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: 14.12, 22.68, 25.95, 29.04, 29.33, 29.54, 29.57, 29.61, 29.63, 31.89, 68.34, 70.12, 114.36, 115.34, 116.54, 120.88, 121.46, 122.64, 127.50, 128.16, 128.24, 128.71, 132.37, 136.12, 153.56, 161.46, 163.57, 163.75, 164.43, 164.49.

2-[4-(4-Dodecyloxybenzoyloxy)phenyl]-5-(4-hydroxyphenyl)-1,3,4-oxadiazole (B)

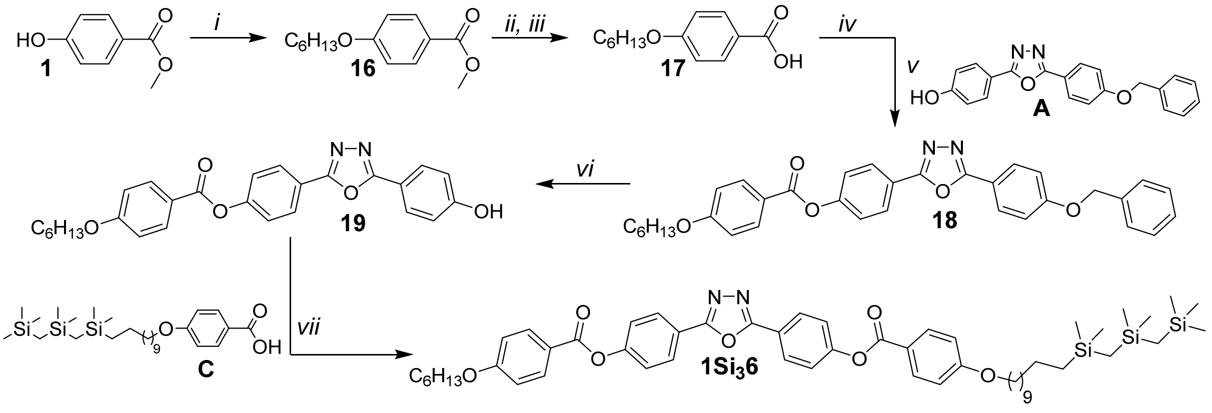


To a round-bottomed flask 4.30 g (6.80 mmol) of 2-(4-benzyloxyphenyl)-5-[4-(4-dodecyloxybenzoyloxy)phenyl]-1,3,4-oxadiazole (**15**), 0.43 g of Pd/C (10%) catalyst and 150 mL of THF were added. The system was purged inittialy with argon and then with hydrogen. The mixture was vigorously stirred at room temperature and hydrogen atmosphere for 24 h. The suspension was filtered through a celite pad, washed with THF and the solvent removed under reduced pressure. Purification by silica column chromatography using chloroform/ethyl acetate (8:2) as the eluent afforded 3.42 g (93 %) of a colorless solid. **m.p.**: 184.0 – 185.1 °C. **^{1}H NMR** ($CDCl_3$ + DMSO-d_6 drops) δ ppm: 0.89 (t, *J* = 6.8 Hz, 3H, $-CH_3$), 1.26-1.42 (m, 16H, $-CH_2-$), 1.49 (m, 2H, $-CH_2-$), 1.84 (m, 2H, $-C\underline{H}_2CH_2O-$), 4.07 (t, *J* = 6.6 Hz, 2H, $-OCH_2-$), 7.00 (m, 4H, Ar-H), 7.41 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.99 (d, *J* = 8.8 Hz, 2H, Ar-H), 8.15 (d, *J* = 9.0 Hz, 2H, Ar-H), 8.19 (d, *J* = 8.8 Hz, 2H, Ar-H), 9.61 (broad, 1H, Ar-OH). **^{13}C NMR** ($CDCl_3$ + DMSO-d_6 drops) δ ppm: 13.53, 22.06, 25.35, 28.46, 28.70, 28.72, 28.91, 28.94, 28.99, 29.01, 31.28, 67.79, 113.84, 114.22, 115.68, 120.31, 121.00, 122.06, 127.48, 128.17, 131.75, 152.95, 160.34, 162.72, 163.21, 163.81, 164.35.

2-[4-(4-Dodecyloxybenzoyloxy)phenyl]-5-{4-[4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy)benzoyloxy]phenyl}-1,3,4-oxadiazole ($1Si_312$)

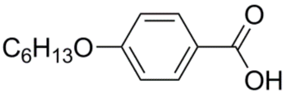


To a 125 mL Schlenk flask 0.40 g (0.74 mmol) of 2-[4-(4-dodecyloxybenzoyloxy)phenyl]-5-(4-hydroxyphenyl)-1,3,4-oxadiazole (**B**), 0.37 g (0.74 mmol) of 4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy)benzoic acid (**C**), 0.010 g (0.08 mmol) of DMAP and 20 mL of anhydrous CH_2Cl_2 were added under argon atmosphere. After 5 min, 0.17 g (0.81 mmol) of DCC dissolved in 10 mL of anhydrous CH_2Cl_2 was added at once. The mixture was stirred at room temperature and argon atmosphere for 16 h. The suspension was gravity filtered and the solvent removed under reduced pressure. Purification by silica flash column chromatography using chloroform as the eluent followed by maceration over boiling ethanol afforded 0.63 g (83 %) of a white solid. For transition temperatures, see Table 1. **^{1}H NMR** ($CDCl_3$) δ ppm: -0.28 (s, 2H, $-SiC\underline{H}_2Si-$), -0.26 (s, 2H, $-SiC\underline{H}_2Si-$), 0.00 (s, 6H, $-Si(CH_3)_2-$), 0.02 (s, 9H, $-Si(CH_3)_3$), 0.05 (s, 6H, $-Si(C\underline{H}_3)_2-$), 0.48 (broad, 2H, $-CH_2C\underline{H}_2Si-$), 0.89 (t, *J* = 7.0 Hz, 3H, $-CH_3$), 1.25-1.41 (m, 30H, $-CH_2-$), 1.49 (m, 4H, $-CH_2-$), 1.83 (m, 4H, $-C\underline{H}_2CH_2O-$), 4.06 (t, *J* = 6.6 Hz, 4H, $-OCH_2-$), 6.99 (d, *J* = 9.0 Hz, 4H, Ar-H), 7.42 (d, *J* = 8.8 Hz, 4H, Ar-H), 8.16 (d, *J* = 9.0 Hz, 4H, Ar-H), 8.22 (d, *J* = 8.8 Hz, 4H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: -0.43, 1.47, 2.47, 4.05, 5.81, 14.11, 18.06, 22.69, 23.98, 25.98, 25.99, 29.09, 29.34, 29.37, 29.39, 29.56, 29.58, 29.60, 29.63, 29.65, 31.91, 33,70, 68.40, 114.42, 120.97, 121.33, 122.72, 128.34, 132.41, 153.83, 163.82, 164.10, 164.41. **^{29}Si NMR** ($CDCl_3$) δ ppm: 0.02, 0.57, 1.28. **Elemental Analysis** – Calculated for $C_{60}H_{88}N_2O_7Si_3$: C 69.72 %; H 8.58 %; N 2.71 %. Found: C 69.74 %; H 8.33 %; N 2.82 %. **Q-TOF/MS** for $C_{60}H_{89}N_2O_7Si_3$ $[M+H]^+$: Calculated: 1033.5972; Found: 1033.5978.



Scheme S4. *Reagents: i)* 1-bromohexane, K_2CO_3, butanone; *ii)* KOH, MeOH, H_2O; *iii*) HCl; *iv*) $SOCl_2$, DMF; *v*) compound **A**, anhydrous CH_2Cl_2, anhydrous TEA, DMAP; *vi*) H_2, Pd/C (10%), THF; *vii*) compound **C**, DCC, DMAP, anhydrous CH_2Cl_2.

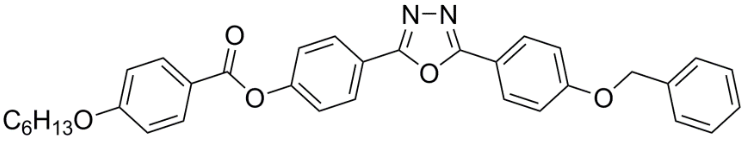
4-Hexyloxybenzoic acid (17)



i) *Methyl 4-hexyloxybenzoate (alkylation):* To a round-bottomed flask equipped with a condenser 11.30 g (74.4 mmol) of methyl 4-hydroxybenzoate (**1**), 10.0 mL (70.9 mmol) of 1-bromohexane, 20.53 g (148.8 mmol) of K_2CO_3 and 200 mL butanone were added and the suspension refluxed for 22 h. After this period, the suspension was filtered, washed with hot butanone and the solvent removed under reduced pressure. The resulting oil was used in the next step without purifications.

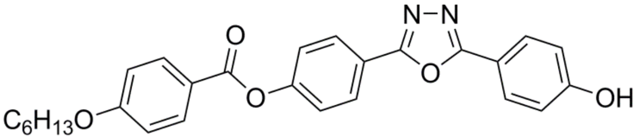
ii) *4-Hexyloxybenzoic acid (deprotection):* To the round-bottomed flask containing the methyl 4-hexyloxybenzate (**16**) prepared in the previous step, 12.50 g (223.2 mmol) of KOH, 200 mL of methanol and 100 mL of water were added. The solution was refluxed for 3 h, the solvent partially removed under reduced pressure, the remaining fraction poured into 500 mL water/ice and acidified to pH ≈ 1 with HCl (10 %). The precipitate was filtered, washed with water and recrystallized over ethanol/water, affording 14.60 g (93 %) of a colorless crystalline powder. Cr – 106 °C – N – 152 °C – Iso (lit. Cr – 106 °C – N – 153 °C – Iso)[S7]. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.91 (t, J = 6.9 Hz, 3H, $-CH_3$), 1.35 (m, 4H, $-CH_2-$), 1.47 (m, 2H, $-CH_2-$), 1.81 (m, 2H, $-\underline{CH_2}CH_2O-$), 4.02 (t, J = 6.5 Hz, 2H, $-OCH_2-$), 6.93 (d, J = 9.0 Hz, 2H, Ar-H), 8.06 (d, J = 9.0 Hz, 2H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: 14.01, 22.57, 25.64, 29.03, 31.52, 68.27, 114.16, 121.36, 132.31, 163.66, 172.03.

2-(4-Benzyloxyphenyl)-5-[4-(4-hexyloxybenzoyloxy)phenyl]-1,3,4-oxadiazole (18)



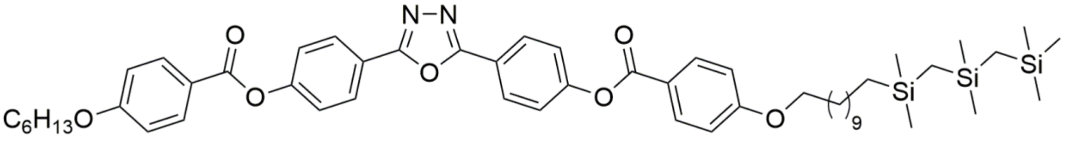
To a round-bottomed flask equipped with a condenser and a $CaCl_2$ drying tube 2.50 g (11.2 mmol) of 4-hexyloxybenzoic acid (**17**), 5 mL of $SOCl_2$ and 1 drop of DMF were added. The mixture was refluxed for 16 hours and the remaining $SOCl_2$ was removed by vacuum distillation. To the freshly prepared acid chloride 3.87 g (11.2 mmol) of 2-(4-benzyloxyphenyl)-5-(4-hydroxyphenyl)-1,3,4-oxadiazole (**A**), 80 mL of anhydrous CH_2Cl_2, 4.7 mL (33.6 mmol) of anhydrous TEA and catalytic amount of DMAP were added and the mixture refluxed for further 24 h. The solvent was removed under reduced pressure and recrystallized over acetonitrile, affording 5.84 g (95 %) of an white solid. Iso – 182 °C – N – 109 °C – Cr (cooling) (lit. Iso – 181 °C – N – 109 °C – Cr) [S6]. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.90 (t, *J* = 6.9 Hz, 3H, -CH_3), 1.34 (m, 4H, -CH_2-), 1.47 (m, 2H, -CH_2-), 1.81 (m, 2H, -$C\underline{H}_2CH_2O$-), 4.04 (t, *J* = 6.6 Hz, 2H, -OCH_2-), 5.14 (s, 2H, OCH_2Bn), 6.97 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.10 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.31-7.46 (m, 7H, Ar-H), 8.06 (d, *J* = 9.0 Hz, 2H, Ar-H), 8.14 (d, *J* = 9.0 Hz, 2H, Ar-H), 8.17 (d, *J* = 9.0 Hz, 2H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: 14.01, 22.57, 25.64, 29.03, 31.52, 68.37, 70.18, 114.39, 115.38, 116.61, 120.95, 121.51, 122.64, 127.49, 128.18, 128.24, 128.69, 128.73, 132.38, 136.16, 153.61, 161.50, 163.61, 163.78, 164.43, 164.51.

2-[4-(4-Hexyloxybenzoyloxy)phenyl]-5-(4-hydroxyphenyl)-1,3,4-oxadiazole (19)

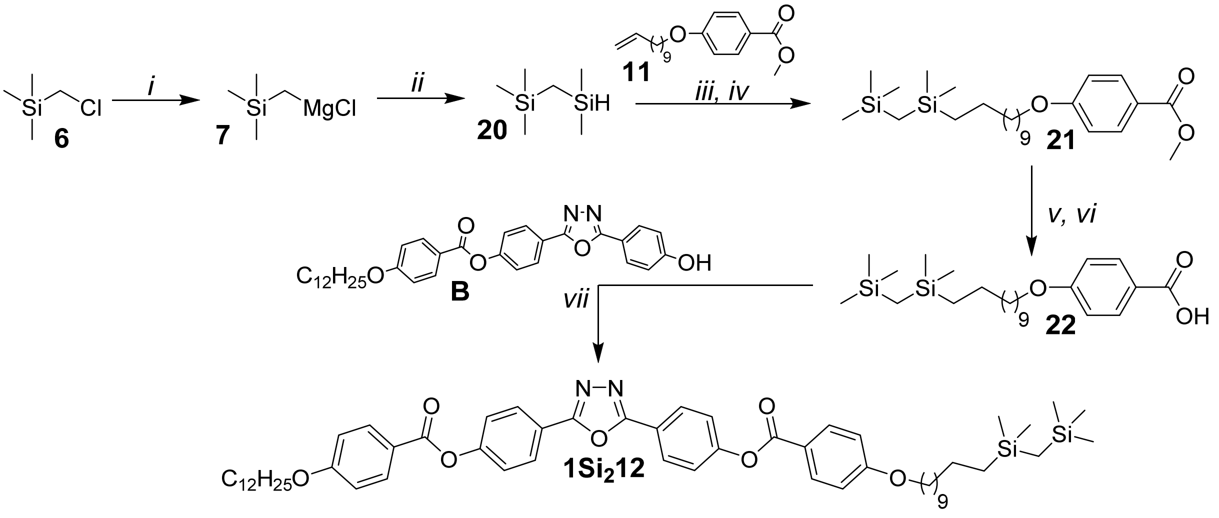


To a round-bottomed flask 2.50 g (4.56 mmol) of 2-(4-benzyloxyphenyl)-5-[4-(4-hexyloxybenzoyloxy)phenyl]-1,3,4-oxadiazole (**18**), 0.25 g of Pd/C (10%) catalyst and 100 mL of THF were added. The system was purged inittialy with argon and then with hydrogen. The mixture was vigorously stirred at room temperature and hydrogen atmosphere for 20 h. The suspension was filtered through a celite pad, washed with THF and the solvent removed under reduced pressure. Purification by silica column chromatography using chloroform/ethyl acetate (8:2) as the eluent afforded 1.91 g (92 %) of a colorless solid. **m.p.**: 186.7 – 188.1 °C. **^{1}H NMR** ($CDCl_3$ + DMSO-d_6 drops) δ ppm: 0.89 (t, *J* = 6.8 Hz, 3H, -CH_3), 1.33 (m, 4H, -CH_2-), 1.45 (m, 2H, -CH_2-), 1.79 (m, 2H, -$C\underline{H}_2CH_2O$-), 4.02 (t, *J* = 6.5 Hz, 2H, -OCH_2-), 6.95 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.96 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.36 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.95 (d, *J* = 8.2 Hz, 2H, Ar-H), 8.11 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.14 (d, *J* = 8.6 Hz, 2H, Ar-H). **^{13}C NMR** ($CDCl_3$ + DMSO-d_6 drops) δ ppm: 13.79, 22.32, 25.39, 28.79, 31.28, 68.16, 114.21, 114.58, 116.09, 120.68, 121.31, 122.43, 127.88, 128.57, 132.13, 153.34, 160.67, 163.12, 163.58, 164.23, 164.74.

2-[4-(4-Hexyloxybenzoyloxy)phenyl]-5-{4-[4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy)benzoyloxy]phenyl}-1,3,4-oxadiazole (1Si$_3$6)

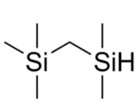


To a 125 mL Schlenk flask 0.30 g (0.65 mmol) of 2-[4-(4-hexyloxybenzoyloxy)phenyl]-5-(4-hydroxyphenyl)-1,3,4-oxadiazole (**19**), 0.33 g (0.65 mmol) of 4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy)benzoic acid (**C**), 0.008 g (0.07 mmol) of DMAP and 20 mL of anhydrous CH_2Cl_2 were added under argon atmosphere. After 5 min, 0.15 g (0.72 mmol) of DCC dissolved in 10 mL of anhydrous CH_2Cl_2 was added at once. The mixture was stirred at room temperature and argon atmosphere for 24 h. The suspension was gravity filtered and the solvent removed under reduced pressure. Purification by silica flash column chromatography using chloroform as the eluent followed by maceration over boiling ethanol afforded 0.43 g (69 %) of a white solid. For transition temperatures, see Table 1. **^{1}H NMR** ($CDCl_3$) δ ppm: -0.28 (s, 2H, -SiC$\underline{H}_2$Si-), -0.26 (s, 2H, -SiC$\underline{H}_2$Si-), 0.00 (s, 6H, -Si(CH_3)$_2$-), 0.02 (s, 9H, -Si(CH_3)$_3$), 0.05 (s, 6H, -Si(C$\underline{H}_3$)$_2$-), 0.48 (broad, 2H, -CH_2C$\underline{H}_2$Si-), 0.92 (t, J = 7.0 Hz, 3H, -CH_3), 1.26-1.39 (m, 18H, -CH_2-), 1.49 (m, 4H, -CH_2-), 1.83 (m, 4H, -C$\underline{H}_2$$CH_2$O-), 4.06 (m, 4H, -O$CH_2$-), 6.99 (d, J = 9.0 Hz, 4H, Ar-H), 7.42 (d, J = 8.8 Hz, 4H, Ar-H), 8.16 (d, J = 9.0 Hz, 4H, Ar-H), 8.22 (d, J = 8.8 Hz, 4H, Ar-H). **^{13}C NMR** ($CDCl_3$) δ ppm: -0.43, 1.46, 2.47, 4.05, 5.80, 14.01, 18.06, 22.58, 23.98, 25.65, 25.98, 29.05, 29.09, 29.38, 29.55, 29.59, 29.62, 31.53, 33,70, 68.38, 114.42, 120.97, 121.33, 122.71, 128.33, 132.39, 153.82, 163.82, 164.09, 164.40. **29Si NMR** ($CDCl_3$) δ ppm: 0.02, 0.57, 1.28. **Elemental Analysis** – Calculated for $C_{54}H_{76}N_2O_7Si_3$: C 68.31 %; H 8.07 %; N 2.95 %. Found: C 68.34 %; H 7.98 %; N 2.93 %. **Q-TOF/MS** for $C_{54}H_{77}N_2O_7Si_3$ $[M+H]^+$: Calculated: 949.5033; Found: 949.5026.



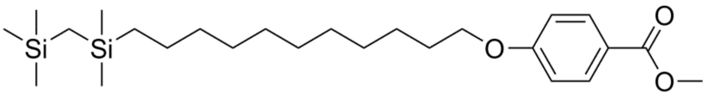
Scheme S5. *Reagents: i)* Mg, anhydrous THF; *ii)* chlorodimethylsilane, anhydrous THF; *iii)* 2,2,4-trimethyl-2,4-disilapentane (**20**), Karstedt catalyst, anhydrous toluene; i*v)* OsO_4 solution, $NaIO_4$, t-BuOH, H_2O; *v)* KOH, THF, MeOH, H_2O; *vi*) HCl; *vii*) compound **B**, DCC, DMAP, anhydrous CH_2Cl_2.

2,2,4-Trimethyl-2,4-disilapentane (20)



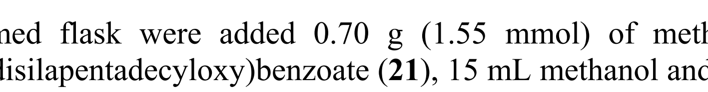
To a two-necked Schlenk flask equipped with a dropping funnel and condenser, 0.46 g (19.1 mmol) of Mg turnings and 15 mL of anhydrous THF were added under argon atmosphere. An iodine crystal followed by a small amount of 1,2-dibromoethane were added and the mixture stirred until the Grignard reaction was initiated. To this mixture 1.80 g (14.7 mmol) of chloromethyltrimethylsilane (**6**) dissolved in 5 mL of anhydrous THF was added dropwise (≈ 10 min). The mixture was then refluxed for 2 h, cooled to room temperature and 1.80 g (19.7 mmol) of neat chlorodimethylsilane were slowly added (≈ 10 min). The mixture was then refluxed for further 20 h. The reaction mixture was cooled to room temperature, 50 mL of water were carefully added followed by 50 mL of hexanes. The aqueous phase was separated and then extracted with hexanes (3x15 mL). The combined organic phases were dried with anhydrous Na_2SO_4 and the solvent carefully removed under reduced pressure, avoiding the product evaporation. The resultant oil was passed through a short pad of silica gel using hexanes as the eluent. The solvent was removed under reduced pressure, affording 1.31 g (61 %) of a colorless oil. ^{1}**H NMR** ($CDCl_3$) δ ppm: -0.24 (d, *J* = 3.9 Hz, 2H, -SiC$\underline{H}_2$Si-), 0.03 (s, 9H, -Si(CH_3)$_3$), 0.10 (d, *J* = 3.9 Hz, 2H, -Si(C$\underline{H}_3$)$_2$H), 3.97 (m, *J* = 3.9 Hz, 1H, SiH). ^{13}**C NMR** ($CDCl_3$) δ ppm: -1.52, 0.78, 1.46. ^{29}**Si NMR** ($CDCl_3$) δ ppm: -16.48, 0.57.

Methyl 4-(12,12,14,14-tetramethyl-12,14-disilapentadecyloxy)benzoate (21)



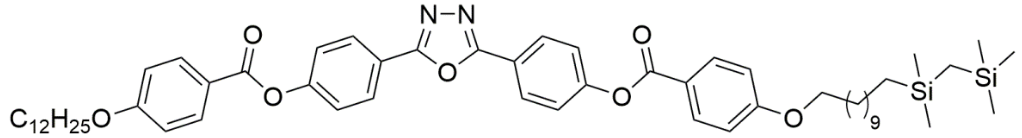
To a 50 mL Schlenk tube 1.04 g (3.42 mmol) of methyl 4-(10-undecenyloxy)benzoate (**11**), 0.70 g (4.78 mmol) de 2,2,4-trimethyl-2,4-disilapentane (**20**), 2 drops of Karstedt catalyst (≈ 2 % Pt solution in xylene) and 5 mL of anhydrous toluene were added under argon atmosphere. The system was protected from light with aluminum foil and stirred for 28 h at room temperature. The resultant solution was passed through a short pad of silica gel and eluted with chloroform. A dark oil was obtained after removal of the solvent. To the round-bottomed flask containing the dark oil, 15 mL of t-butanol, 8 mL of water, 2.0 mL of a 0.004M OsO_4 solution (in t-butanol) and 1.45 g (6.84 mmol) of $NaIO_4$ were added. The mixture was stirred at room temperature for 18 h. To the suspension 50 mL of $Na_2S_2O_4$ saturated aqueous solution were slowly added and stirred for further 30 min. The product was extracted using a 1:1 hexanes/ethyl acetate solution (3 x 50 mL), the combined organic phases dried with anhydrous Na_2SO_4 and the solvent removed under reduced pressure. The crude oil was purified by flash silica column chromatography using hexanes/ethyl acetate (20:1) as the eluent, affording 0.82 g (53 %) of a colorless oil. ^{1}**H NMR** ($CDCl_3$) δ ppm: -0.30 (s, 2H, -SiC$\underline{H}_2$Si-), -0.01 (s, 6H, -Si(CH_3)$_2$-), 0.02 (s, 9H, -Si(CH_3)$_3$), 0.47 (broad, 2H, -CH_2C$\underline{H}_2$Si-), 1.24-1.38 (m, 14H, -CH_2-), 1.46 (m, 2H, -CH_2-), 1.80 (m, 2H, -C$\underline{H}_2$$CH_2$O-), 3.88 (s, 3H, -$OCH_3$), 4.00 (t, *J* = 6.6 Hz, 2H, -OCH_2-), 6.90 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.98 (d, *J* = 9.0 Hz, 2H, Ar-H). ^{13}**C NMR** ($CDCl_3$) δ ppm: -0.57, 1.41, 2.61, 17.97, 23.97, 25.99, 29.13, 29.38, 29.55, 29.59, 29.61, 33,71, 51.80, 68.22, 114.06, 122.33, 131.55, 162.96, 166.90. ^{29}**Si NMR** ($CDCl_3$) δ ppm: 0.35, 1.47.

4-(12,12,14,14-Tetramethyl-12,14-disilapentadecyloxy)benzoic acid (22)

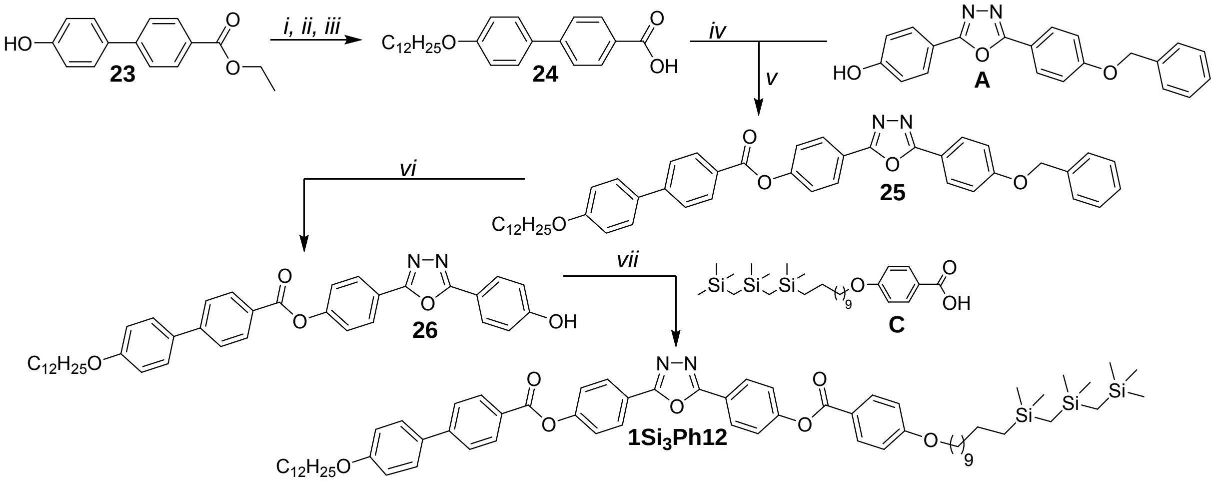


To a round-bottomed flask were added 0.70 g (1.55 mmol) of methyl 4-(12,12,14,14-tetramethyl-12,14-disilapentadecyloxy)benzoate (**21**), 15 mL methanol and 5 mL of THF. The solution was heated to 40 °C and 0.26 g (4.65 mmol) of KOH dissolved in 3 mL of water was added at once. The solution was stirred at 40 °C for 20 h. The solvent was partially removed under reduced pressure, 50 mL of water was then added and the pH adjusted to ≈ 1 with HCl (10 %). The product was extracted using a 1:1 hexanes/ethyl acetate solution (3 x 50 mL), the combined organic phases dried with anhydrous Na_2SO_4 and the solvent removed under reduced pressure. Purification by silica column chromatography using hexanes/ethyl acetate (9:1) as the eluent, afforded 0.55 g (82 %) of a colorless solid. Iso – 103 °C – SmC – 69 °C – Cr (cooling). ^{1}**H NMR** ($CDCl_3$) δ ppm: -0.30 (s, 2H, -SiC$\underline{H}_2$Si-), -0.01 (s, 6H, -Si(CH_3)$_2$-), 0.02 (s, 9H, -Si(CH_3)$_3$), 0.48 (broad, 2H, -CH_2C$\underline{H}_2$Si-), 1.26-1.39 (m, 14H, -CH_2-), 1.47 (m, 2H, -CH_2-), 1.81 (m, 2H, -C$\underline{H}_2$$CH_2$O-), 4.02 (t, *J* = 6.6 Hz, 2H, -OCH_2-), 6.93 (d, *J* = 9.0 Hz, 2H, Ar-H), 8.06 (d, *J* = 9.0 Hz, 2H, Ar-H). ^{13}**C NMR** ($CDCl_3$) δ ppm: -0.57, 1.40, 2.61, 17.97, 23.97, 25.98, 29.10, 29.37, 29.39, 29.55, 29.59, 29.62, 33,71, 68.30, 114.20, 121.35, 132.32, 163.69, 171.71. ^{29}**Si NMR** ($CDCl_3$) δ ppm: 0.35, 1.47.

2-[4-(4-Dodecyloxybenzoyloxy)phenyl]-5-{4-[4-(12,12,14,14-tetramethyl-12,14-disilapentadecyloxy)benzoyloxy]phenyl}-1,3,4-oxadiazole (1Si$_2$12)

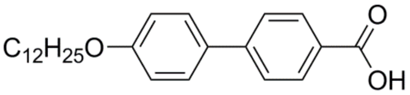


To a 125 mL Schlenk flask 0.40 g (0.74 mmol) of 2-[4-(4-dodecyloxybenzoyloxy)phenyl]-5-(4-hydroxyphenyl)-1,3,4-oxadiazole (**B**), 0.32 g (0.74 mmol) of 4-(12,12,14,14-tetramethyl-12,14-disilapentadecyloxy)benzoic acid (**22**), 0.011 g (0.09 mmol) of DMAP and 20 mL of anhydrous CH_2Cl_2 were added under argon atmosphere. After 5 min, 0.18 g (0.89 mmol) of DCC dissolved in 10 mL of anhydrous CH_2Cl_2 was added at once. The mixture was stirred at room temperature and argon atmosphere for 20 h. The suspension was gravity filtered and the solvent removed under reduced pressure. Purification was made in two steps. First by silica flash column chromatography using chloroform as the eluent. In the second step, the compound was solubilized in CH_2Cl_2, poured into methanol and filtered, yielding 0.51 g (73 %) of a pure white solid. For transition temperatures, see Table 1. ^{1}**H NMR** ($CDCl_3$) δ ppm: -0.30 (s, 2H, $-SiC\underline{H}_2Si-$), -0.01 (s, 6H, $-Si(CH_3)_2-$), 0.02 (s, 9H, $-Si(CH_3)_3$), 0.48 (broad, 2H, $-CH_2C\underline{H}_2Si-$), 0.89 (t, *J* = 6.9 Hz, 3H, $-CH_3$), 1.24-1.41 (m, 30H, $-CH_2-$), 1.48 (m, 4H, $-CH_2-$), 1.83 (m, 4H, $-C\underline{H}_2CH_2O-$), 4.06 (t, *J* = 6.7 Hz, 4H, $-OCH_2-$), 6.99 (d, *J* = 9.0 Hz, 4H, Ar-H), 7.42 (d, *J* = 8.8 Hz, 4H, Ar-H), 8.16 (d, *J* = 9.0 Hz, 4H, Ar-H), 8.22 (d, *J* = 8.8 Hz, 4H, Ar-H). ^{13}**C NMR** ($CDCl_3$) δ ppm: -0.56, 1.41, 2.61, 14.11, 17.98, 22.69, 23.97, 25.98, 25.99, 29.10, 29.34, 29.36, 29.37, 29.39, 29.55, 29.58, 29.60, 29.62, 29.63, 29.65, 31.92, 33,71, 68.40, 114.43, 120.97, 121.33, 122.72, 128.34, 132.40, 153.83, 163.82, 164.10, 164.41. ^{29}**Si NMR** ($CDCl_3$) δ ppm: 0.35, 1.47. **Elemental Analysis** – Calculated for $C_{57}H_{80}N_2O_7Si_2$: C 71.21 %; H 8.39 %; N 2.91 %. Found: C 71.22 %; H 8.19 %; N 2.96 %. **Q-TOF/MS** for $C_{57}H_{81}N_2O_7Si_2$ $[M+H]^+$: Calculated: 961.5577; Found: 961.5562.



Scheme S6. *Reagents: i)* 1-bromododecane, K_2CO_3, butanone; *ii)* KOH, MeOH, THF, H_2O; *iii*) HCl; *iv*) $SOCl_2$, DMF; *v*) compound **A**, anhydrous CH_2Cl_2, anhydrous TEA, DMAP; *vi*) H_2, Pd/C (10%), THF; *vii*) compound **C**, DCC, DMAP, anhydrous CH_2Cl_2.

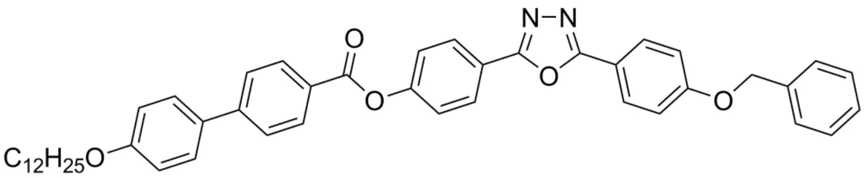
4’-Dodecyloxy-4-biphenylcarboxylic acid (24)



i) *Ethyl 4’-dodecyloxy-4-biphenylcarboxylate (alkylation):* To a round-bottomed flask equipped with a condenser 1.00 g (4.13 mmol) of ethyl 4'-hydroxy-4-biphenylcarboxylate (**23**), 1.1 mL (4.54 mmol) of 1-bromododecane, 1.14 g (8.26 mmol) of K_2CO_3 and 50 mL butanone were added and the suspension refluxed for 20 h. After this period, the suspension was filtered, washed with THF and the solvent removed under reduced pressure. The resulting solid was used in the next step without purifications.

ii) *4’-Dodecyloxy-4-biphenylcarboxylic acid (hydrolysis):* To the round-bottomed flask containing the ethyl 4’-dodecyloxy-4-biphenylcarboxylate prepared in the previous step, 0.69 g (12.4 mmol) of KOH, 30 mL of methanol, 30 mL of THF and 10 mL of water were added. The solution was stirred at room temperature for 18 h and refluxed for further 6 h. After this period, the solvent was partially removed under reduced pressure, the remaining fraction poured into 100 mL water and acidified to pH ≈ 3 with HCl (10 %). The precipitate was filtered, washed with water and recrystallized over isopropanol, affording 1.46 g (93 %) of a colorless powder. Cr – 166 °C – SmC – 251 °C – Iso (lit. Cr – 165 °C – SmC – 252 °C – Iso)[S8]. **^{1}H NMR** ($CDCl_3$ + DMSO-d_6 drops) δ ppm: 0.89 (t, *J* = 6.8 Hz, 3H, -CH_3), 1.26-1.40 (m, 16H, -CH_2-), 1.49 (m, 2H, -CH_2-), 1.82 (m, 2H, -$C\underline{H_2}CH_2O$-), 4.02 (t, *J* = 6.6 Hz, 2H, -OCH_2-), 7.00 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.58 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.63 (d, *J* = 8.2 Hz, 2H, Ar-H), 8.10 (d, *J* = 8.2 Hz, 2H, Ar-H). **^{13}C NMR** ($CDCl_3$ + DMSO-d_6 drops) δ ppm: 13.93, 22.48, 25.84, 29.06, 29.13, 29.18, 29.36, 29.38, 29.42, 29.45, 31.70, 67.95, 114.73, 126.11, 128.08, 128.77, 130.12, 132.08, 144.77, 159.15, 168,30.

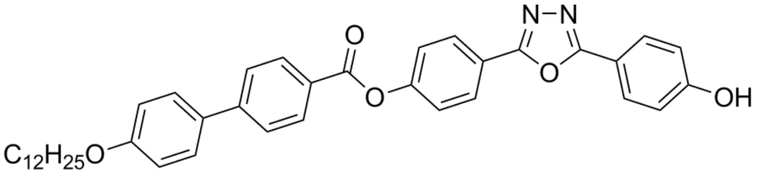
2-(4-Benzyloxyphenyl)-5-[4-(4’-dodecyloxy-4-biphenylcarboxyloxy)phenyl]-1,3,4-oxadiazole (25)



To a round-bottomed flask equipped with a condenser and a $CaCl_2$ drying tube 1.30 g (3.40 mmol) of 4’-dodecyloxy-4-biphenylcarboxylic acid (**24**), 10 mL of $SOCl_2$ and 2 drops of DMF were added. The mixture was refluxed for 8 hours and the remaining $SOCl_2$ was removed by vacuum distillation. To the freshly prepared acid chloride 1.17 g (3.40 mmol) of 2-(4-benzyloxyphenyl)-5-(4-hydroxyphenyl)-1,3,4-oxadiazole (**A**), 50 mL of anhydrous CH_2Cl_2, 1.4 mL (10 mmol) of anhydrous TEA and catalytic amount of DMAP were added and the mixture refluxed for further 24 h. The solvent was removed under reduced pressure, the crude product macerated over boiling ethanol and filtered while still hot, affording 1.95 g (81 %) of an white solid. Cr – 166 °C – SmC – 185 °C – SmA – 236 °C – N – 261 °C – Iso. **^{1}H NMR** ($CDCl_3$ + DMSO-d_6 drop) δ ppm: 0.91 (t, *J* = 6.8 Hz, 3H, -CH_3), 1.28-1.41 (m, 16H, -CH_2-), 1.50 (m, 2H, -CH_2-), 1.84 (m, 2H, -$C\underline{H_2}CH_2O$-), 4.05 (t, *J* = 6.6 Hz, 2H, -OCH_2-), 5.19 (s, 2H, OCH_2Bn), 7.04 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.15 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.37-7.50 (m, 7H, Ar-H), 7.63 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.74 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.11 (d, *J*

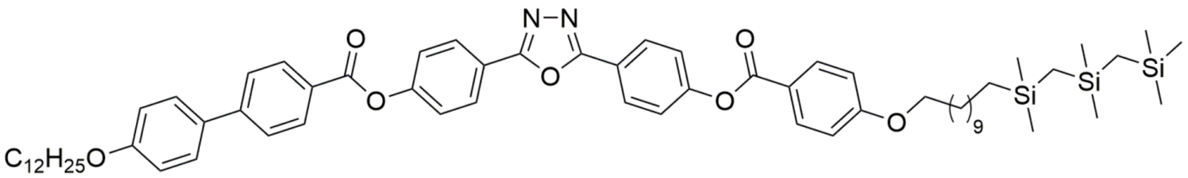
= 9.0 Hz, 2H, Ar-H), 8.23 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.27 (d, *J* = 8.6 Hz, 2H, Ar-H). ^{13}**C NMR** ($CDCl_3$ + DMSO-d_6 drop) δ ppm: 14.06, 22.62, 25.98, 29.19, 29.28, 29.33, 29.51, 29.54, 29.57, 29.60, 31.85, 68.14, 70.16, 114.98, 115.38, 116.56, 121.65, 122.58, 126.62, 126.89, 127.45, 128.19, 128.20, 128.33, 128.65, 128.70, 130.74, 131.74, 136.14, 146.28, 153.49, 159.63, 161.49, 164.60.

2-[4-(4'-Dodecyloxy-4-biphenylcarboxyloxy)phenyl]-5-(4-hydroxyphenyl)-1,3,4-oxadiazole (26)



To a round-bottomed flask 1.90 g (2.68 mmol) of 2-(4-benzyloxyphenyl)-5-[4-(4'-dodecyloxy-4-biphenylcarboxyloxy)phenyl]-1,3,4-oxadiazole (**25**), 0.20 g of Pd/C (10%) catalyst and 100 mL of THF were added. The system was purged inittialy with argon and then with hydrogen. The mixture was heated to 50 ºC and vigorously stirred under hydrogen atmosphere for 20 h. The suspension was filtered through a celite pad, washed with hot THF and the solvent removed under reduced pressure. Recrystallization over isopropanol, afforded 1.59 g (96 %) of a white powder. Cr – 191 °C – N – 229 °C – Iso. ^{1}**H NMR** ($CDCl_3$ + DMSO-d_6 (1:1 mixture)) δ ppm: 0.92 (t, *J* = 6.8 Hz, 3H, $-CH_3$), 1.28-1.46 (m, 16H, $-CH_2-$), 1.52 (m, 2H, $-CH_2-$), 1.84 (m, 2H, $-\underline{CH_2}CH_2O-$), 4.08 (t, *J* = 6.6 Hz, 2H, $-OCH_2-$), 7.03 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.08 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.56 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.73 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.85 (d, *J* = 8.4 Hz, 2H, Ar-H), 8.01 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.26 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.27 (d, *J* = 8.4 Hz, 2H, Ar-H). ^{13}**C NMR** ($CDCl_3$ + DMSO-d_6 (1:1 mixture)) δ ppm: 14.19, 22.47, 25.86, 29.05, 29.09, 29.17, 29.36, 29.40, 29.42, 31.68, 67.91, 114.38, 115.14, 116.31, 121.63, 123.00, 126.53, 126.81, 128.08, 128.37, 128.73, 130.76, 131.17, 145.80, 153.40, 159.59, 161.19, 163.02, 164.27, 164.63.

2-[4-(4'-Dodecyloxy-4-biphenylcarboxyloxy]-5-{4-[4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy)benzoyloxy]phenyl}-1,3,4-oxadiazole (1Si$_3$Ph12)



To a 125 mL Schlenk flask 0.40 g (0.64 mmol) of 2-[4-(4'-dodecyloxy-4-biphenylcarboxyloxy)phenyl]-5-(4-hydroxyphenyl)-1,3,4-oxadiazole (**26**), 0.33 g (0.64 mmol) of 4-(12,12,14,14,16,16-hexamethyl-12,14,16-trisilaheptadecyloxy)benzoic acid (**C**), 0.008 g (0.07 mmol) of DMAP and 30 mL of anhydrous CH_2Cl_2 were added under argon atmosphere. After 5 min, 0.15 g (0.71 mmol) of DCC dissolved in 10 mL of anhydrous CH_2Cl_2 was added at once. The mixture was stirred at room temperature and argon atmosphere for 18 h and refluxed for further 8 h. The suspension was gravity filtered and the solvent removed under reduced pressure. Purification by silica flash column chromatography using chloroform as the eluent followed by two maceration over boiling ethanol afforded 0.31 g (43 %) of a white solid. For transition temperatures, see Table 1. ^{1}**H NMR** ($CDCl_3$) δ ppm: -0.28 (s, 2H, -

SiC$\underline{H}_2$Si-), -0.26 (s, 2H, -SiC$\underline{H}_2$Si-), 0.00 (s, 6H, -Si(CH$_3$)$_2$-), 0.02 (s, 9H, -Si(CH$_3$)$_3$), 0.05 (s, 6H, -Si(C$\underline{H}_3$)$_2$-), 0.48 (broad, 2H, -CH$_2$C$\underline{H}_2$Si-), 0.89 (t, *J* = 7.0 Hz, 3H, -CH$_3$), 1.25-1.40 (m, 30H, -CH$_2$-), 1.49 (m, 4H, -CH$_2$-), 1.83 (m, 4H, -C$\underline{H}_2$CH$_2$O-), 4.02 (t, *J* = 6.6 Hz, 2H, -OCH$_2$-), 4.06 (t, *J* = 6.6 Hz, 2H, -OCH$_2$, 6.99 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.02 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.42 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.45 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.61 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.72 (d, *J* = 8.4 Hz, 2H, Ar-H), 8.16 (d, *J* = 8.8 Hz, 2H, Ar-H), 8.22 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.24 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.26 (d, *J* = 8.4 Hz, 2H, Ar-H). **^{13}C NMR** (CDCl$_3$) δ ppm: -0.43, 1.46, 2.47, 4.04, 5.80, 14.11, 18.06, 22.68, 23.98, 25.98, 26.04, 29.09, 29.34, 29.38, 29.55, 29.57, 29.60, 29.63, 29.66, 31.91, 33.69, 68.18, 68.39, 114.41, 115.02, 120.96, 121.30, 121.48, 122.66, 122.71, 126.65, 126.92, 128.33, 128.37, 130.80, 131.78, 132.39, 146.32, 153.71, 153.83, 159.67, 163.82, 164.03, 164.10, 164.37, 164.59. **^{29}Si NMR** (CDCl$_3$) δ ppm: 0.02, 0.57, 1.28. **Elemental Analysis** – Calculated for $C_{66}H_{92}N_2O_7Si_3$: C 71.43 %; H 8.36 %; N 2.52 %. Found: C 71.56 %; H 8.28 %; N 2.50 %. **Q-TOF/MS** for $C_{66}H_{93}N_2O_7Si_3$ $[M+H]^+$: Calculated: 1109.6285; Found: 1109.6282.

2,5-Bis[4-(4-dodecyloxybenzoyloxy)phenyl]-1,3,4-oxadiazole (1-12)

Compound was prepared according to a literature procedure. [S9]

S2.1 ^{1}H, ^{13}C and ^{29}Si NMR spectra of compound 1Si$_3$12

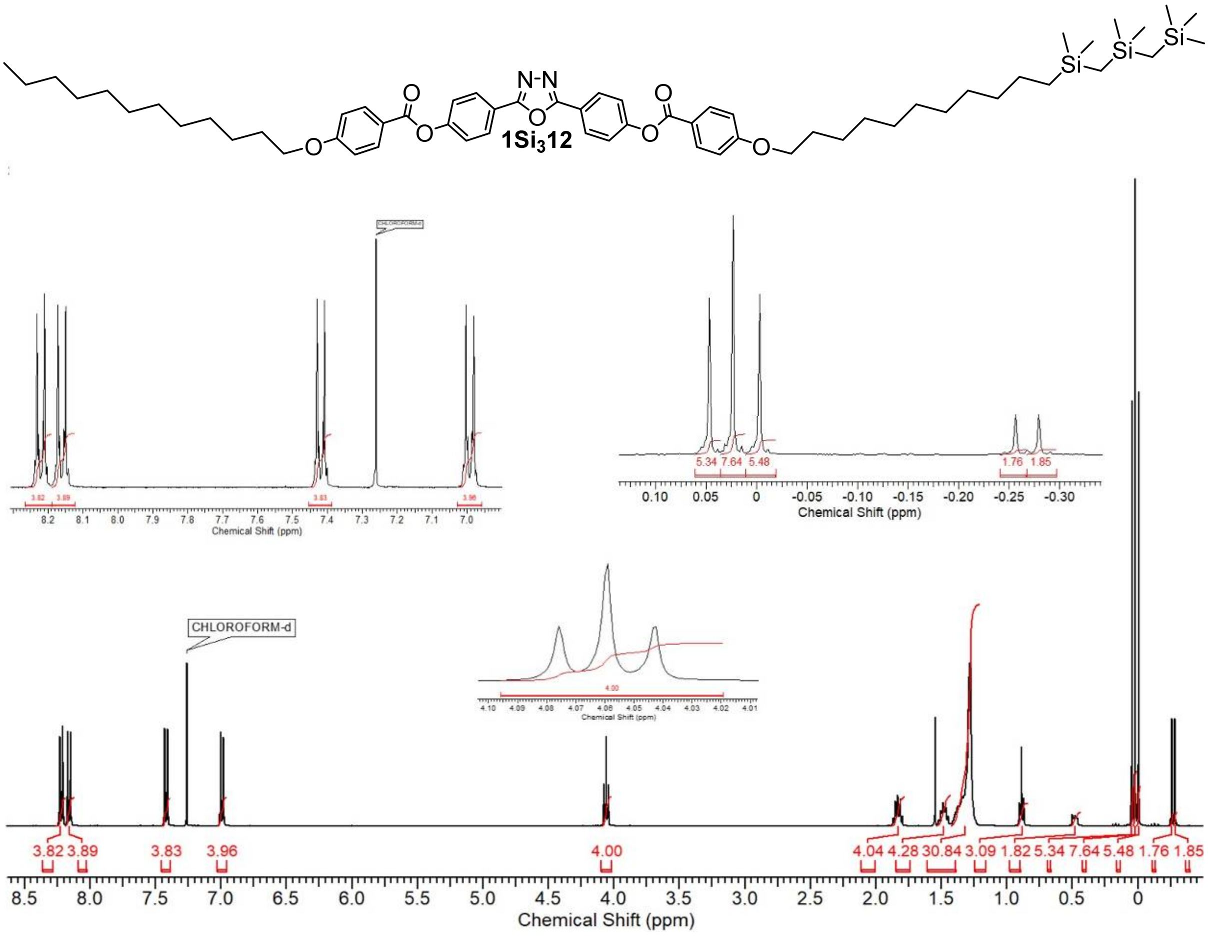


Figure S31. ^{1}H NMR spectra of compound **1Si$_3$12** in CDCl$_3$ (400 MHz).

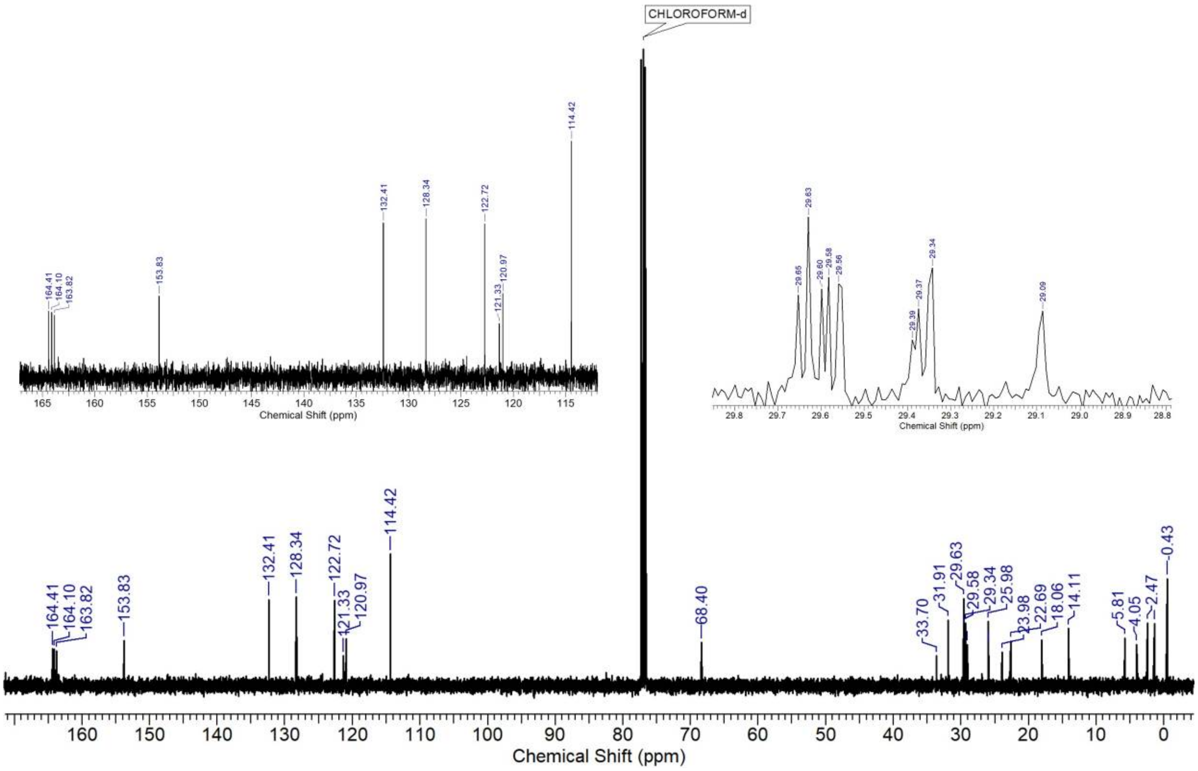


Figure S32. ^{13}C NMR spectra of compound **1Si$_3$12** in CDCl$_3$ (100.6 MHz).

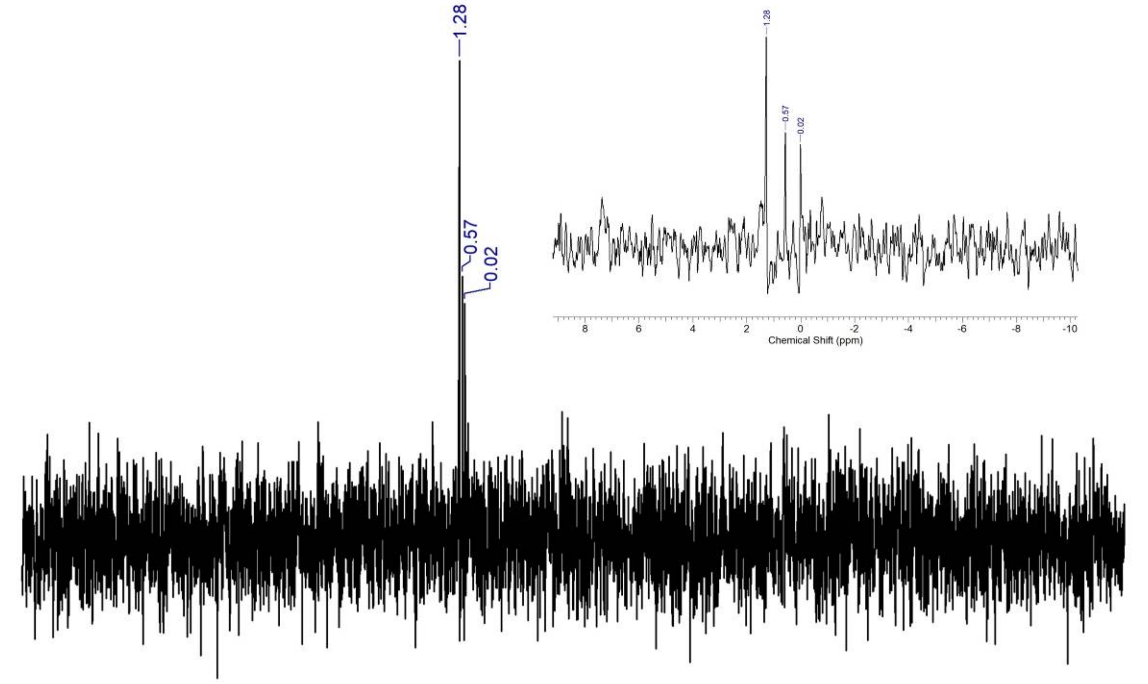


Figure S33. ^{29}Si NMR spectra of compound **1Si$_3$12** in CDCl$_3$ (79.5 MHz).

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