Supplementary Material (ESI) for *Soft Matter*

Supporting Information

Nematic phases of bent-core mesogens

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Content

1. Additional crystallographic data

1.1 Compound 1/2

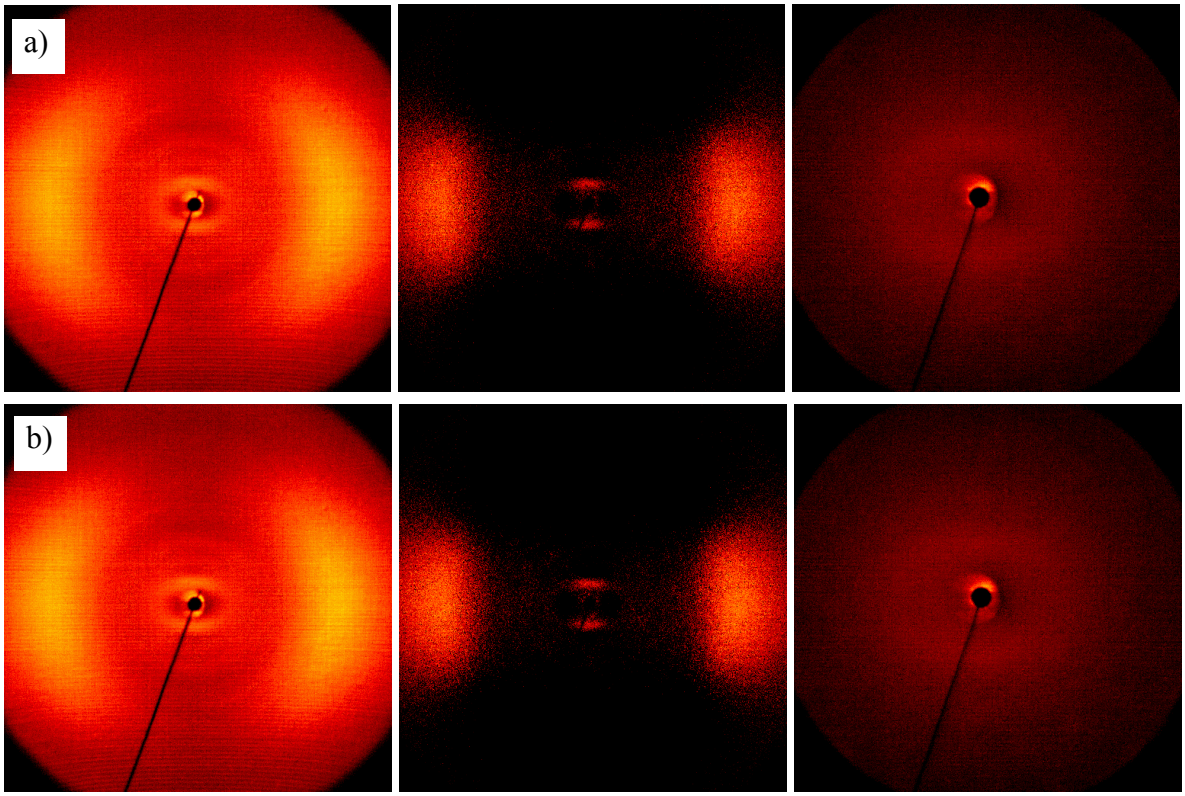


Figure S1: X-ray diffraction patterns of an oriented sample of compound **1/2** under a magnetic field; a) N phase at 115 °C and b) N phase at at 105 °C; the left row shows the original wide angle patterns, the middle row shows the same patterns after subtraction of the scattering in the isotropic liquid state (at T = 140 °C); the right row shows the small angle patterns.

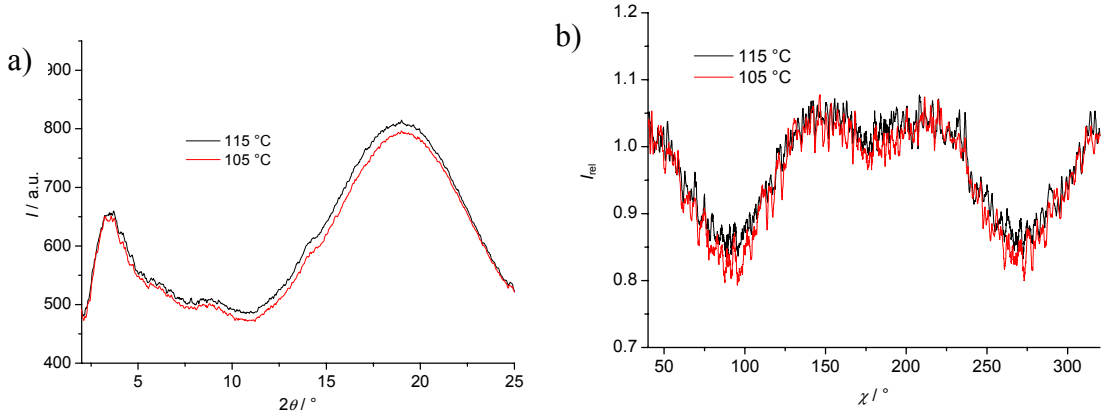
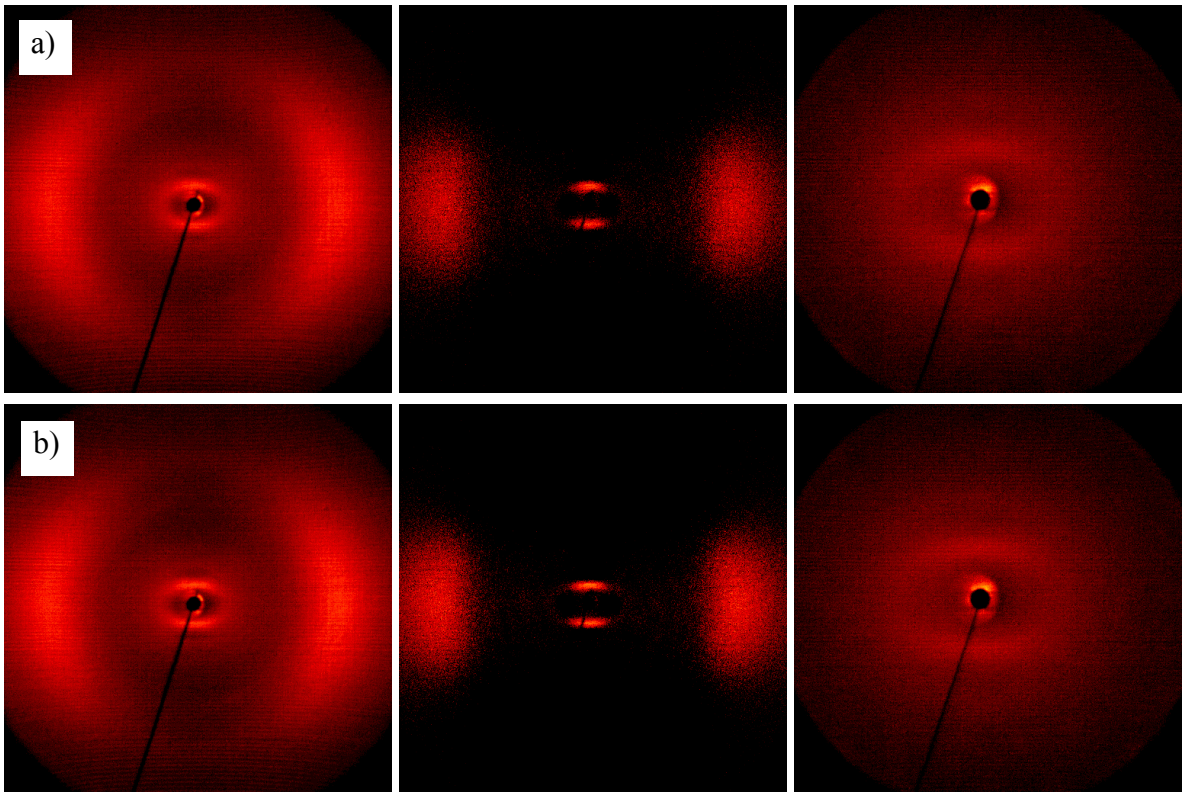


Figure S2: a) θ–scans and b) χ–scans over the diffuse small angle scattering of the N phase of compound **1/2** (for 2θ = 2-5°) at 105 and 115 °C, $I_{rel} = I(T) / I(140\ °C, Iso)$.

Table S1. Crystallographic data of compound **1/2**.

	Small angle scattering			Wide angle scattering	
T / °C	θ / °	d/nm	$\Delta\chi/2$ / °	θ / °	d/nm
115	1.781	2.48	38.0	9.469	0.47
105	1.760	2.51	39.9	9.531	0.47

1.2 Compound 1/4



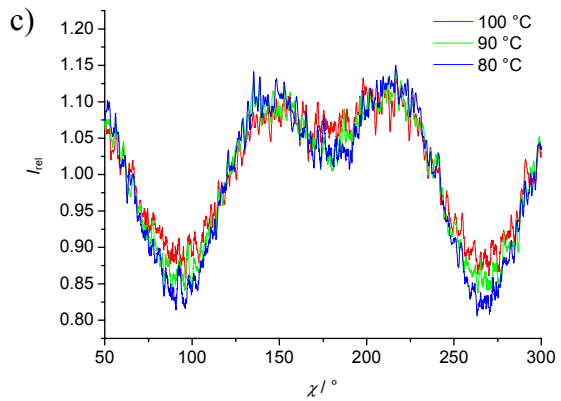
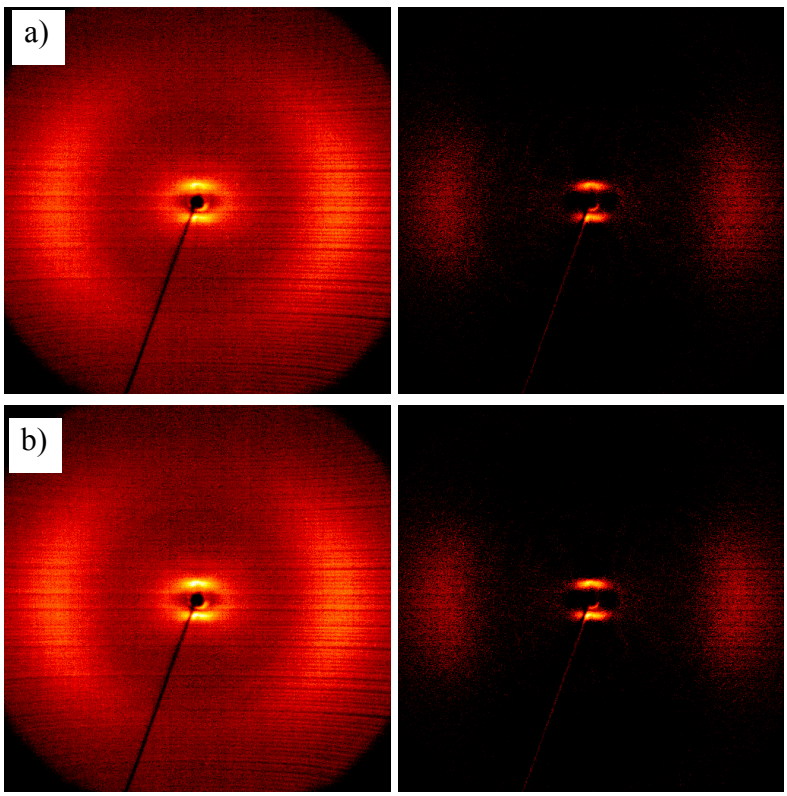


Figure S3: X-ray diffraction patterns of an oriented sample of the N phase of compound **1/4** under a magnetic field; a) at 100 °C and b) at 80 °C; the left row shows the original wide angle pattern, the middle row shows the same patterns after subtraction of the scattering in the isotropic liquid state (at T = 125 °C); the right row shows the small angle patterns; c)χ–scans over the diffuse small angle scattering (for 2θ = 2-5°) at 80, 90 and 100 °C, $I_{rel} = I(T) / I(125\ °C, Iso)$.

Table S2. Crystallographic data of compound **1/4**.

	Small angle scattering			Wide angle scattering	
T / °C	θ / °	d/nm	$\Delta\chi/2$ / °	θ / °	d/nm
100	1.609	2.746	37.7	9.596	0.462
90	1.583	2.791	39.4	9.661	0.459
80	1.573	2.809	39.8	9.725	0.456

1.3 Compound 1/6



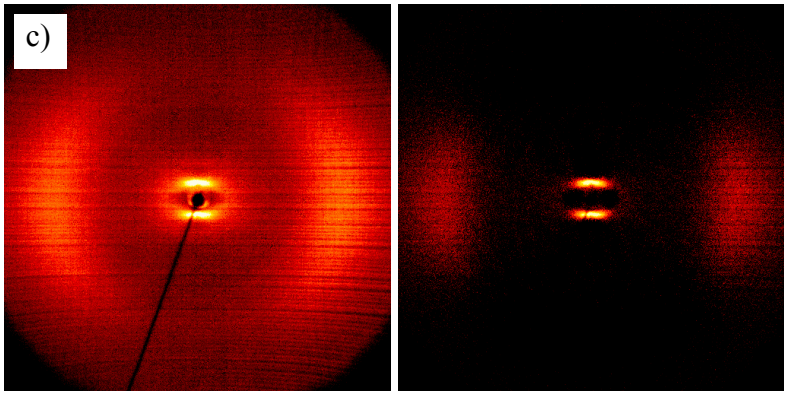


Figure S4: X-ray diffraction patterns of an oriented sample of compound the N_{cybC} phase of **1/6** under a magnetic field; a) at 90 °C; b) 80 °C and c) at 60 °C; the left row shows the original wide angle patterns, the right row the same patterns after subtraction of the scattering in the isotropic liquid state (at T = 110 °C).

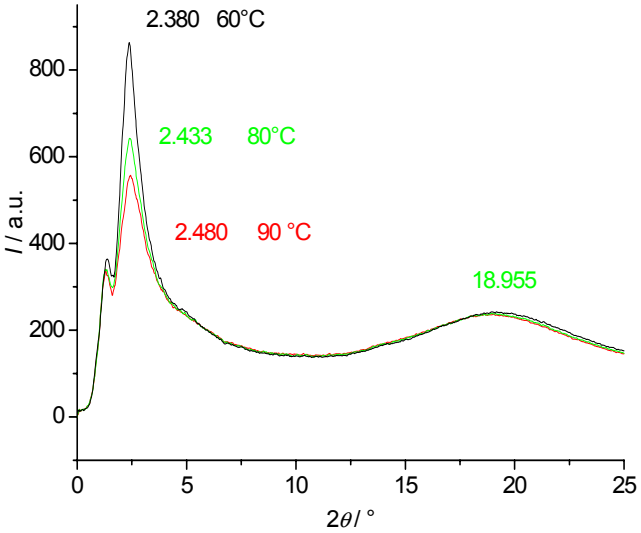


Figure S5. θ-scans of the N_{cybC} phase of compound **1/6** at different temperatures.

Table S3. Crystallographic data of compound **1/6**.

	Small angle scattering			Wide angle scattering	
T / °C	θ / °	d/nm	$\Delta\chi$/2 / °	θ / °	d/nm
90	1.240	3.562	34.1	9.414	0.471
80	1.217	3.631	32.9	9.479	0.468
60	1.190	3.712	30.0	9.594	0.463

1.4 Compound 1/7

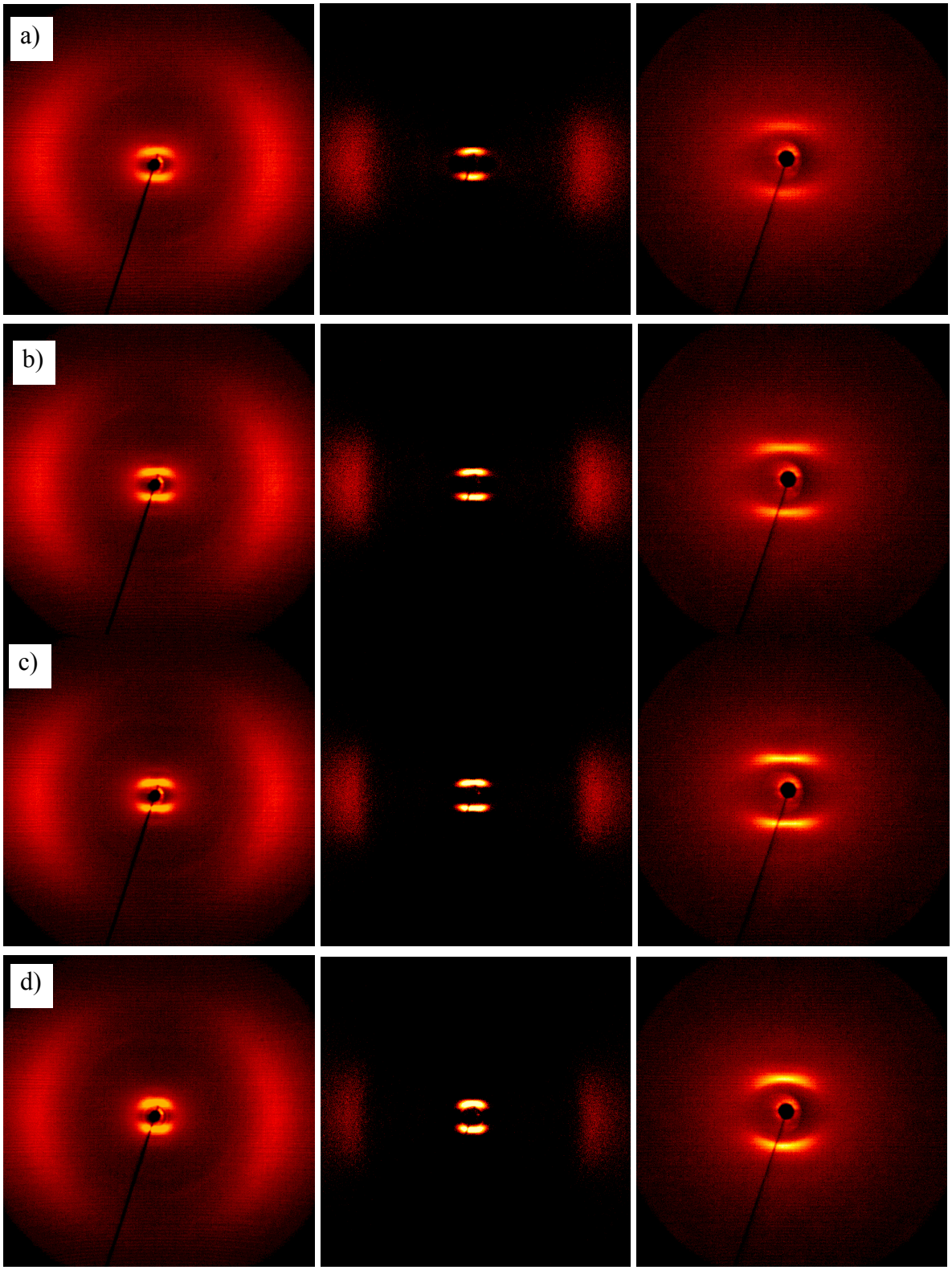
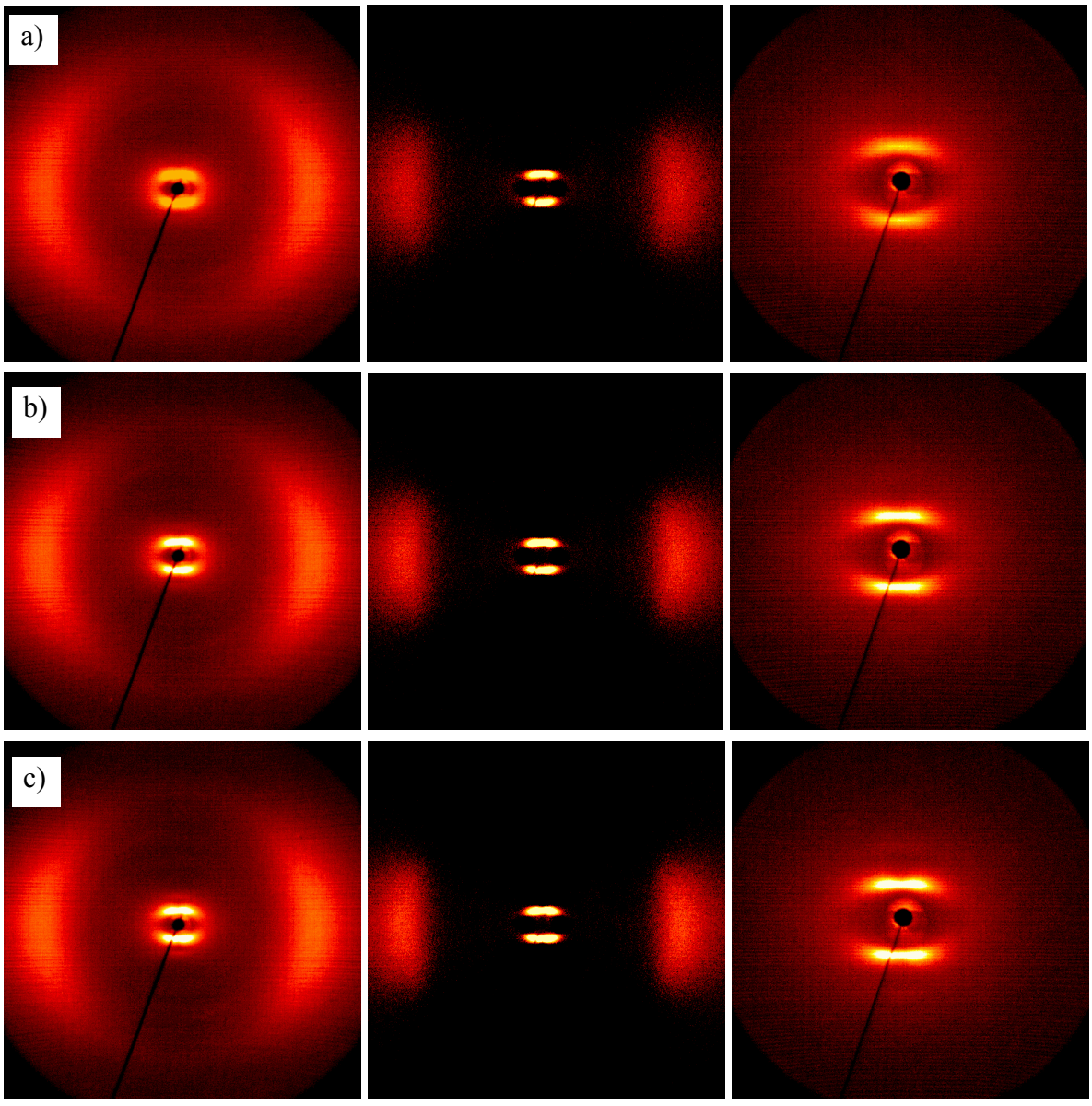


Figure S6: X-ray diffraction patterns of an oriented sample of compound **1/7** under a magnetic field; a-c) N_{cybC} phase a) at 100 °C; b) 70 °C and c) at 45 °C; d) CybC phase at 40 °C; the left row shows the original wide angle-patterns, the middle row shows the wide angle patterns after subtraction of the scattering in the isotropic liquid state (at T = 115 °C); the right row shows the small angle patterns.

Table S4. Crystallographic data of compound **1/7**.

	Small angle scattering			Wide angle scattering	
T / °C	θ / °	*d*/nm	$\Delta\chi/2$ / °	θ / °	*d*/nm
100	1.213	3.641	27.3	9.609	0.462
90	1.191	3.708	27.3	9.663	0.459
70	1.177	3.752	26.1	9.771	0.454
50	1.181	3.742	25.0	9.884	0.449
45	1.189	3.717	24.8	9.911	0.448
40	1.196	3.694	20.4	9.942	0.447

1.5 Compound 1/8



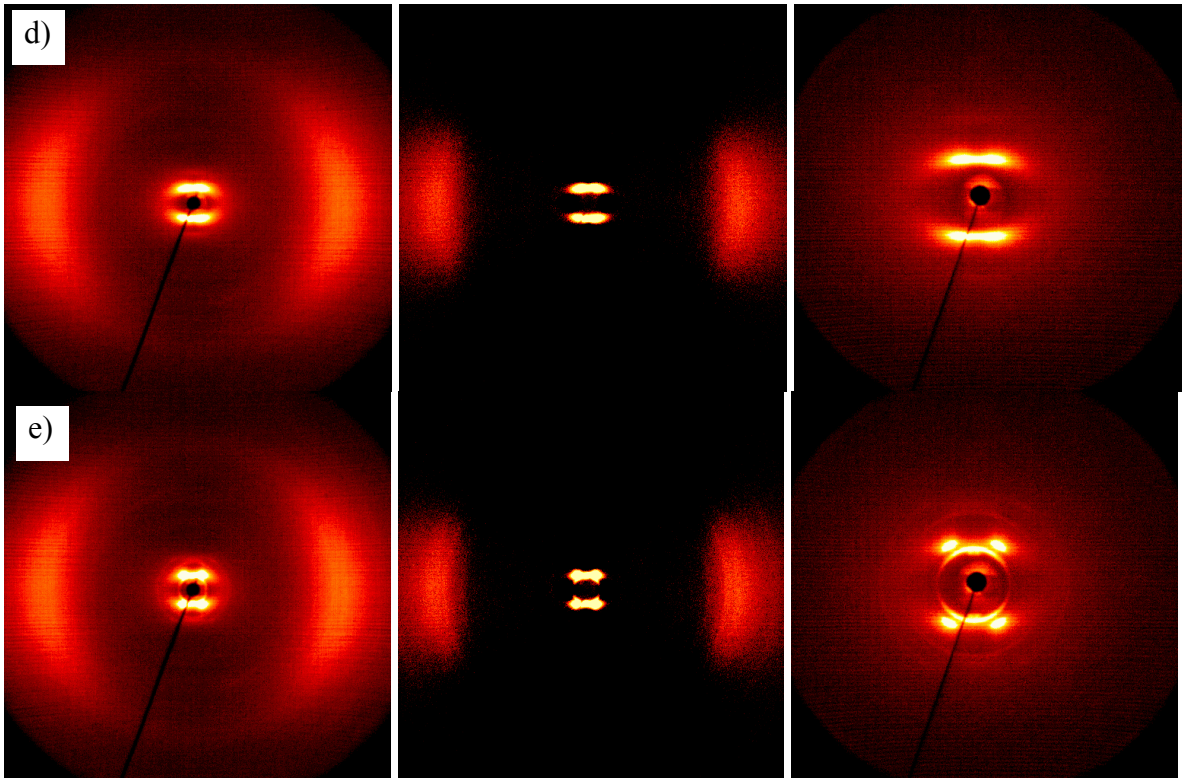


Figure S7: X-ray diffraction patterns of an oriented sample of compound **1/8** under a magnetic field; a-d) N_{cybC} phase a) at 90 °C; b) 70 °C; c) at 50 °C and d) at 45 °C; e) CybC phase at 40 °C (with partial crystallization); the left row shows the original wide angle patterns, the middle row shows the same patterns after subtraction of the scattering in the isotropic liquid state (at T = 105 °C); the right row shows the small angle patterns.

Table S5. Crystallographic data of compound **1/8**.

	Small angle scattering			Wide angle scattering	
T / °C	θ / °	d/nm	$\Delta\chi/2$ / °	θ / °	d/nm
90	1.135	3.893	25.0	9.643	0.460
70	1.108	3.987	22.5	9.768	0.454
50	1.106	3.994	21.0	9.882	0.449
45	1.112	3.973	20.9	9.908	0.448

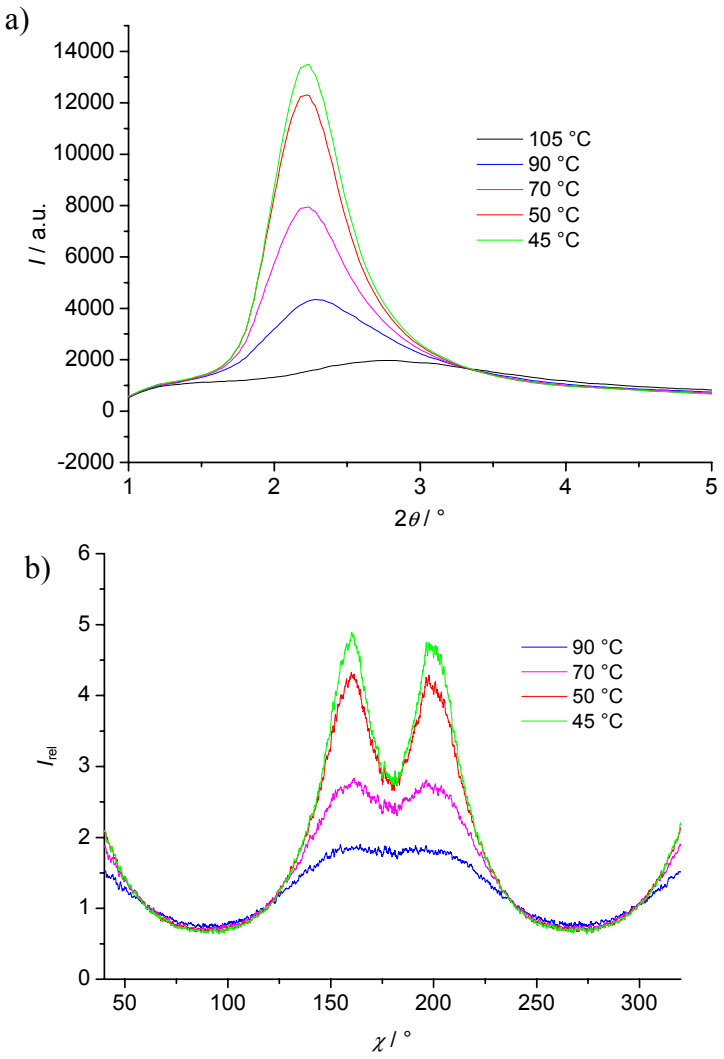
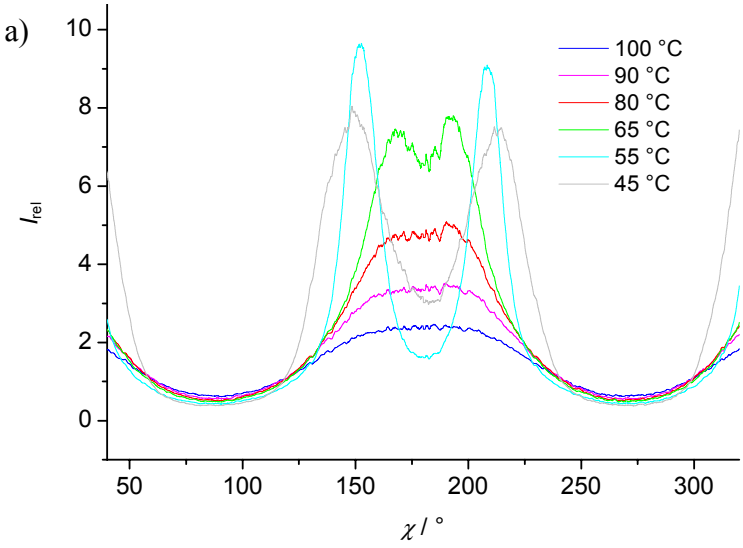


Figure S8: a) θ–scans and b) χ–scans over the diffuse small angle scattering (for 2θ = 1.5-3.5°) of compound **1/8** at different temperatures, $I_{rel} = I(T) / I(105\ °C, Iso)$.

1.6 Compound 1/9



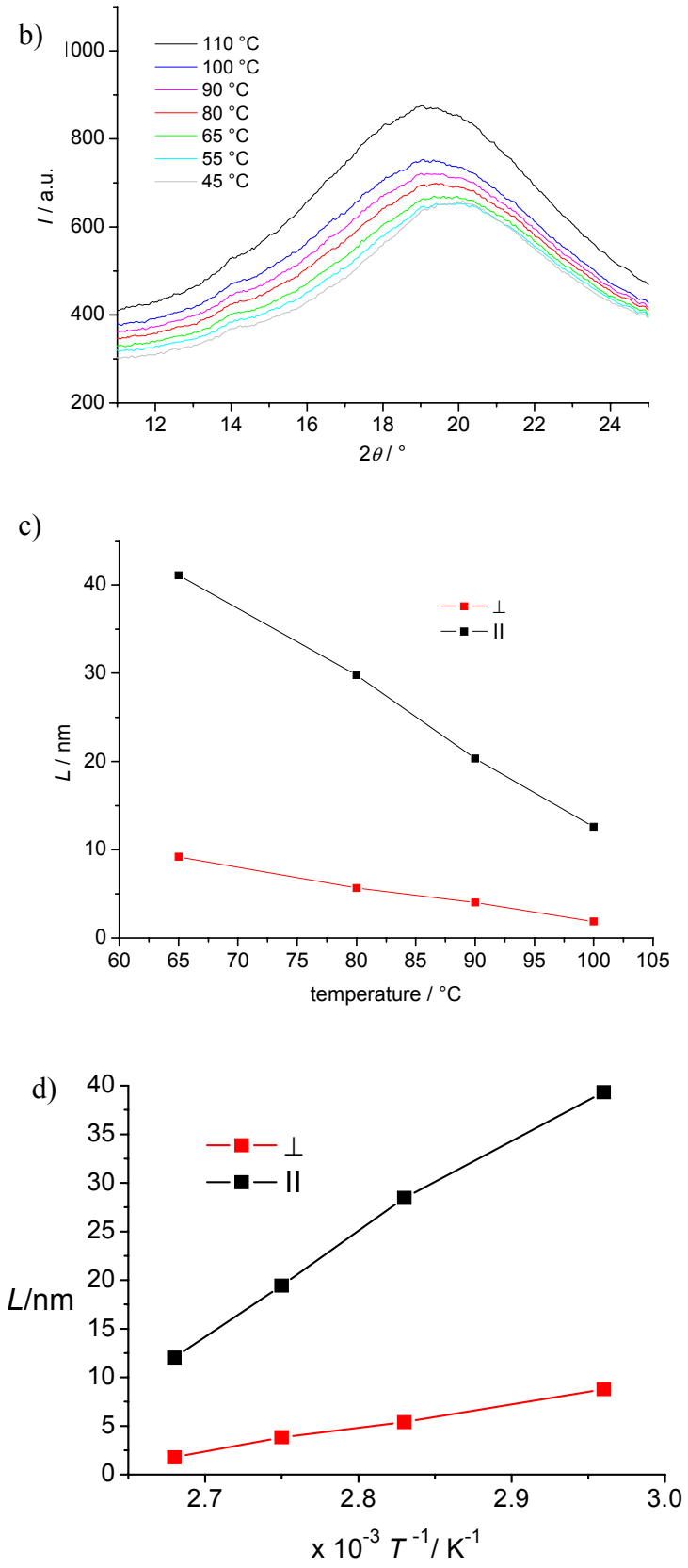


Figure S9. a) χ–scans over the diffuse small angle scattering (for 2θ = 1.5-3.5°, I_{rel} = I(T) / I(110 °C, iso. liqu.); b) θ–scans over the diffuse wide angle scattering of compound **1/9** in the distinct phases; c) longitudinal ($L_{\parallel}$) and transversal cluster size ($L_{\perp}$) as estimated using the Scherrer equation;[S1] cluster size ($L_{\parallel\perp}$) plotted against 1/T.

Table S6. Crystallographic data of compound **1/9** at different temperatures.

	Small angle scattering					Wide angle scattering	
T / °C	θ / °	*d*/nm	$\Delta\chi/2$ / °	$\Delta q_{\perp}^{FWHM}$/Å^{-1}	$\Delta q_{\parallel}^{FWHM}$/Å^{-1}	θ / °	*d*/nm
100	1.114	3.965	23.9	0.3372	0.0499	9.653	0.460
90	1.078	4.099	20.4	0.1565	0.0309	9.721	0.457
80	1.056	4.185	16.9	0.1108	0.0211	9.782	0.454
65	1.043	4.236	14.6	0.0682	0.0153	9.867	0.450
55	1.159	3.811	28.0			9.922	0.447
45	1.256	3.516	31.6			9.979	0.445

1.7 Compound 1/10

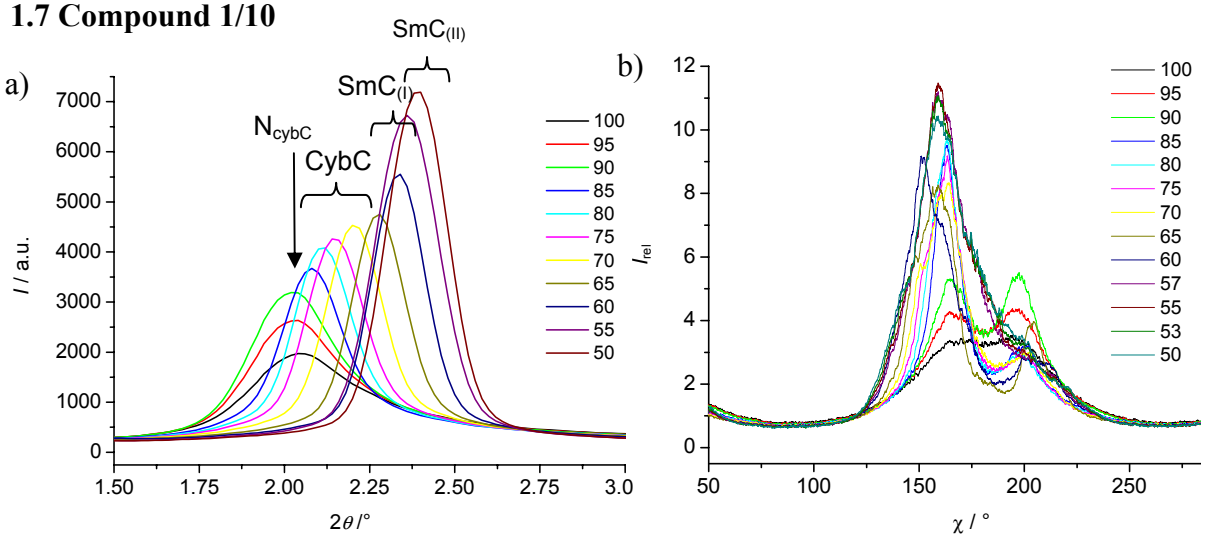


Figure S10. a) Position and shape of the small angle scattering (θ-scans) depending on temperature and b) χ–scans over the diffuse small angle scattering (for 2θ = 1.5-3.5°) of compound **1/10** at different temperatures, $I_{rel} = I(T) / I(115\ °C, Iso.)$

Table S7. Crystallographic data of compound **1/10** at different temperatures.

	Small angle scattering			Wide angle scattering	
T / °C	θ / °	*d*/nm	$\Delta\chi/2$ / °	θ / °	*d*/nm
100	1.063	4.156	16.0	9.577	0.463
95	1.050	4.209	15.2	9.603	0.462
90	1.045	4.228	15.5	9.630	0.461
85	1.073	4.117	18.0	9.659	0.460
80	1.086	4.067	18.5	9.685	0.458
75	1.100	4.014	19.1	9.712	0.457
70	1.125	3.928	20.1	9.742	0.456
65	1.158	3.814	23.7	9.770	0.454
60	1.180	3.742	25.3	9.796	0.453
57	1.184	3.731	23.9	9.814	0.452
55	1.191	3.708	24.0	9.823	0.452
53	1.197	3.690	24.2	9.833	0.451
50	1.205	3.667	24.3	9.848	0.451

1.8 Compound 1/11

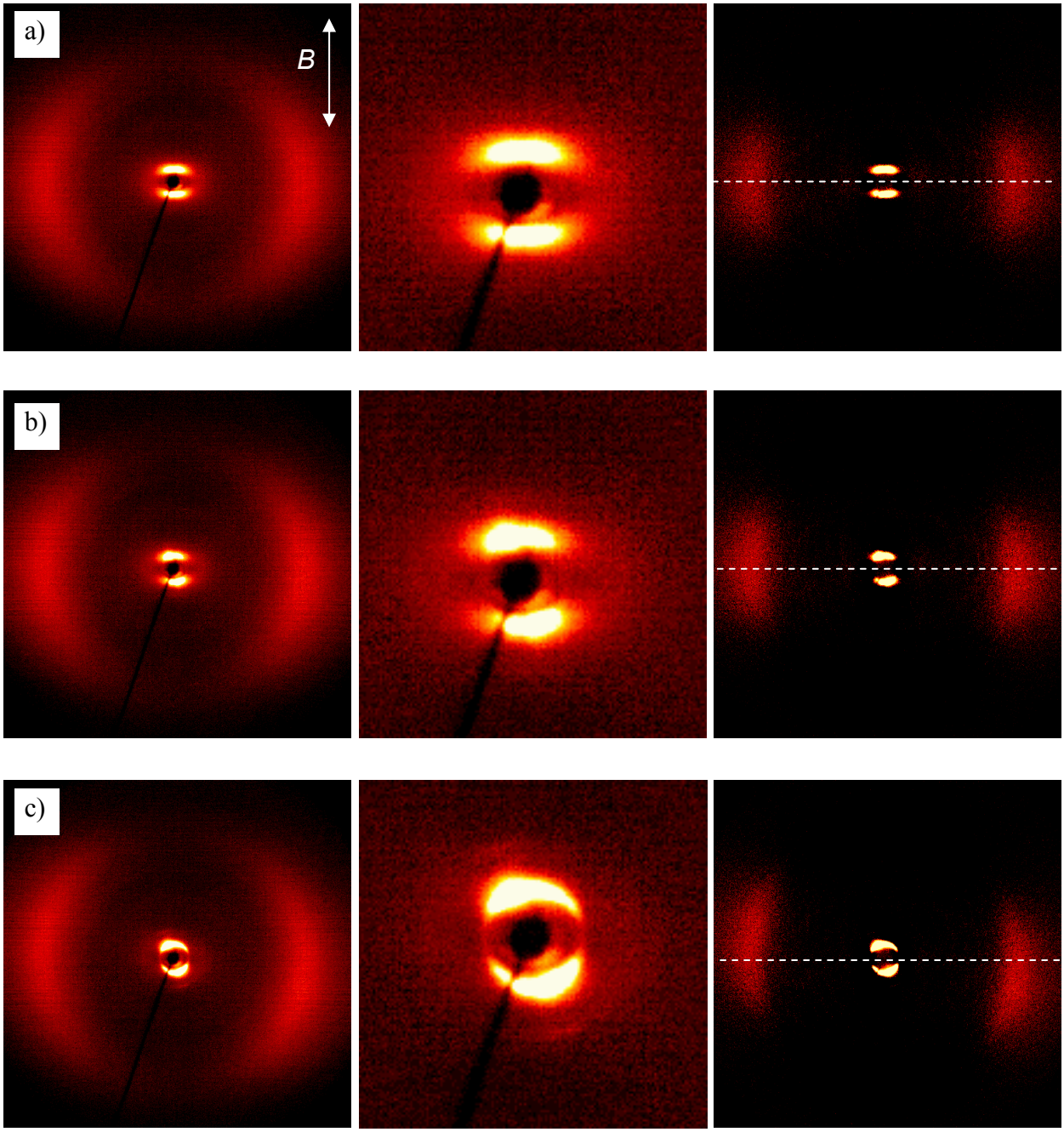


Figure S11: X-ray diffraction patterns of an oriented sample of compound **1/11** under a magnetic field; a) N_{cyb} phase at 100 °C; b) CybC phase at 80 °C and c) $SmC_{(II)}$ phase at 60 °C; the left row shows the original patterns, the second row the enlarged small angle regions and in the patterns at the right the scattering of the isotropic liquid state (at T = 153 °C) was subtracted from the original diffraction patterns in order to enhance the visibility of the position of the maximum of the diffuse wide angle scattering.

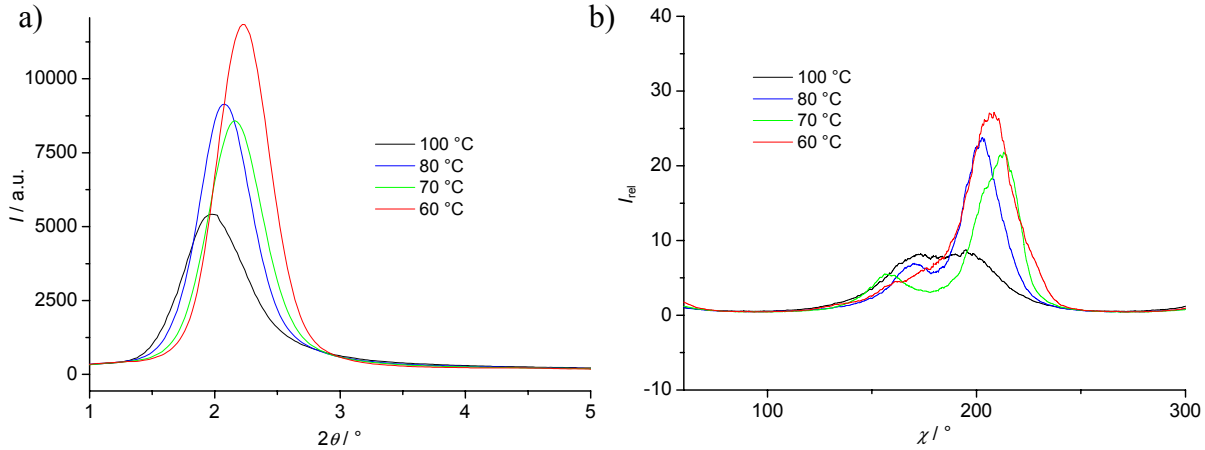
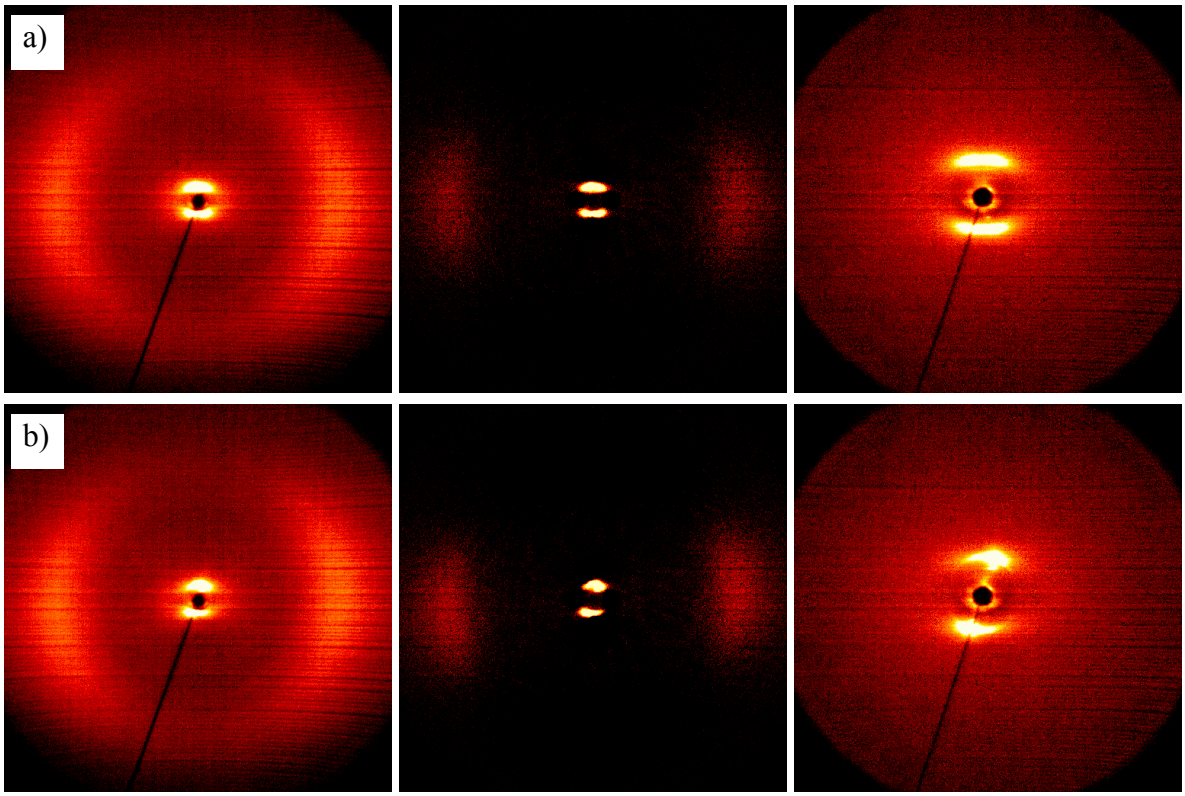


Figure S12. a) θ–scans and b) χ–scans over the diffuse small angle scattering (for 2θ = 1.5-3.5°) of compound **1/11** at different temperatures, $I_{rel} = I(T) / I(115\ °C, Iso.)$.

Table S8. Crystallographic data of compound **1/11** at different temperatures.

	Small angle scattering		Wide angle scattering		tilt angle
T / °C	θ / °	d/nm	θ / °	d/nm	β / °
100	1.000	4.419	9.534	0.465	14
80	1.043	4.235	9.653	0.460	22
70	1.084	4.077	9.716	0.457	31
60	1.116	3.958	9.785	0.454	33

1.9 Compound 1/12



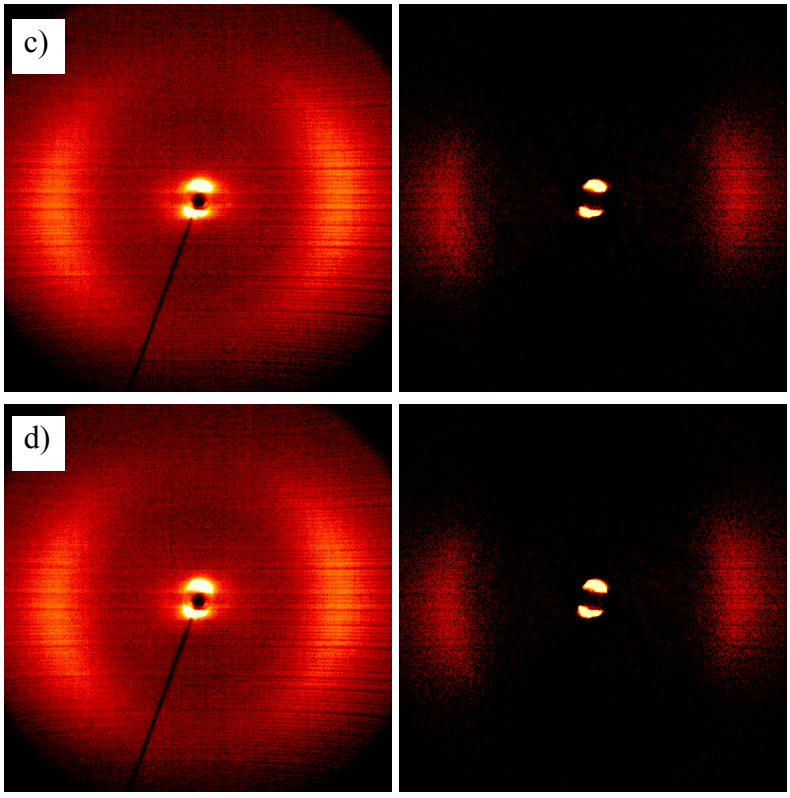


Figure S13: X-ray diffraction patterns of an oriented sample of compound **1/12** under a magnetic field; a) N_{cyb} phase at 106 °C; b-d) CybC phase at 95 °C, c) at 82 °C and d) at 75 °C; the left row shows the original wide angle patterns, the middle row the same patterns after subtraction of the scattering in the isotropic liquid state (at T = 115 °C), the right row in a,b) shows the small angle patterns.

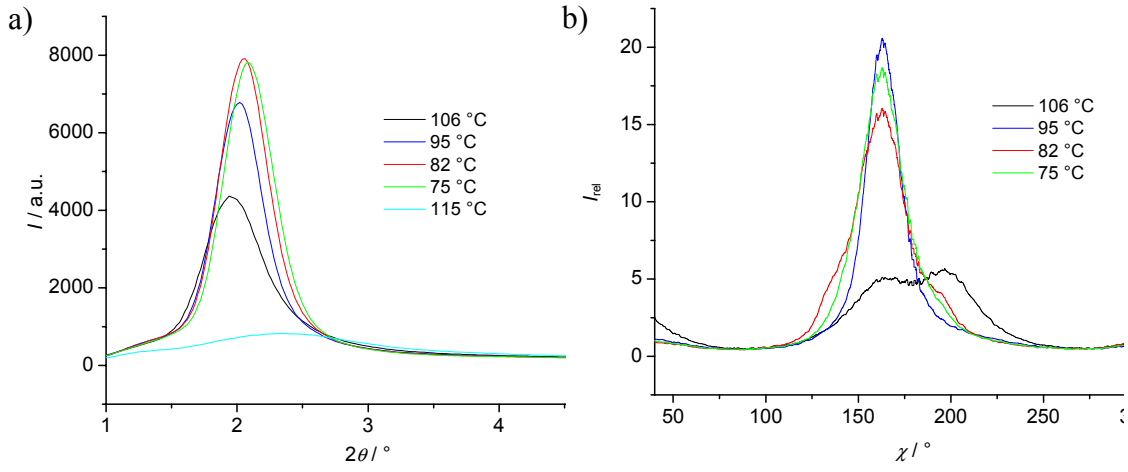
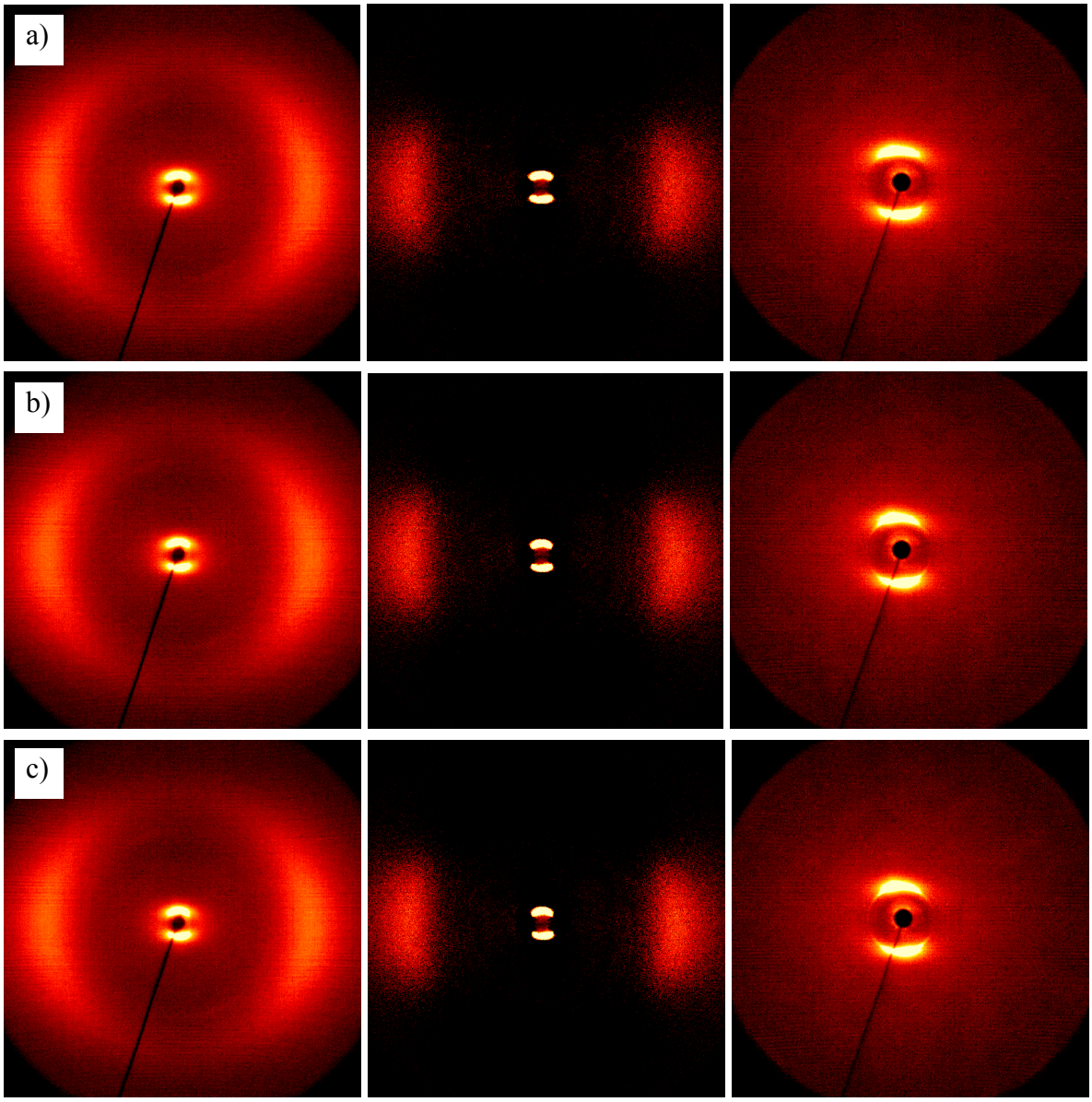


Figure S14. a) θ–scans and b) χ–scans over the diffuse small angle scattering (for 2θ = 1-3°) of compound **1/12** at different temperatures, $I_{rel} = I(T) / I(115\ °C, Iso.)$.

Table S9. Crystallographic data of compound **1/12** at different temperatures.

	Small angle scattering		Wide angle scattering		tilt angle
T / °C	θ / °	*d*/nm	θ / °	*d*/nm	β / °
106	0.978	4.517	9.327	0.476	17.9
95	1.009	4.378	9.400	0.472	24.5
82	1.027	4.301	9.473	0.468	21.9
75	1.046	4.225	9.523	0.466	22.3

1.10 Compound 1/14



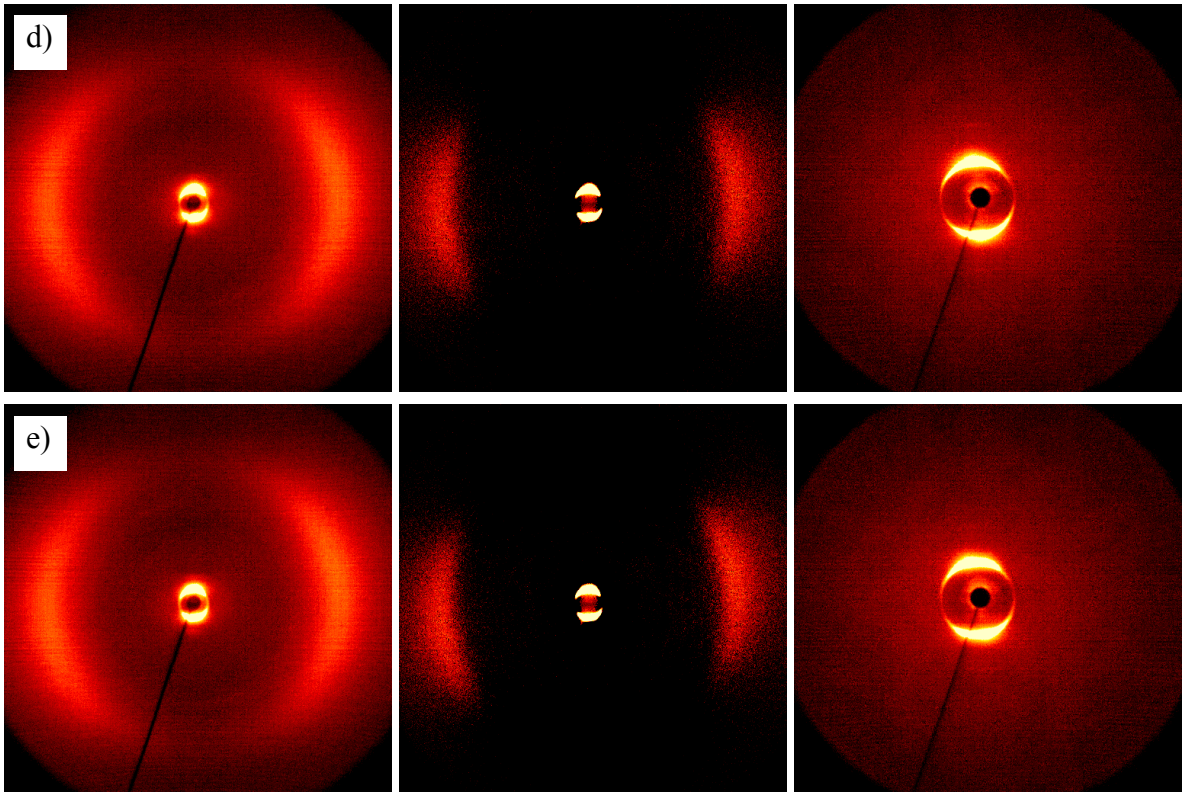


Figure S15. X-ray diffraction patterns of an oriented sample of compound **1/14** under a magnetic field; a) N_{cyb} phase at 115 °C; b,c) CybC phase, b) at 113 °C, c) at 80 °C; d) $SmC_{(I)}$ phase at 75 °C; e) $SmC_{(II)}$ phase at 70 °C; the left row shows the original wide angle patterns, the middle row the same patterns after subtraction of the scattering in the isotropic liquid state (at T = 120 °C), the right row shows the small angle patterns.

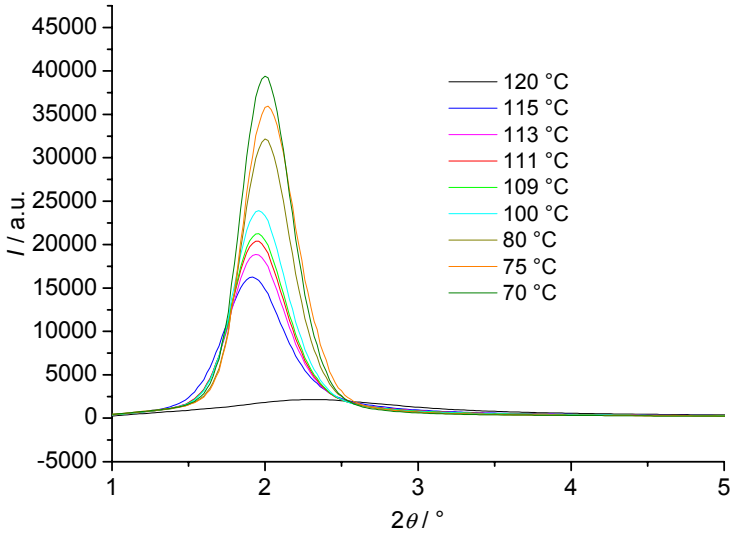
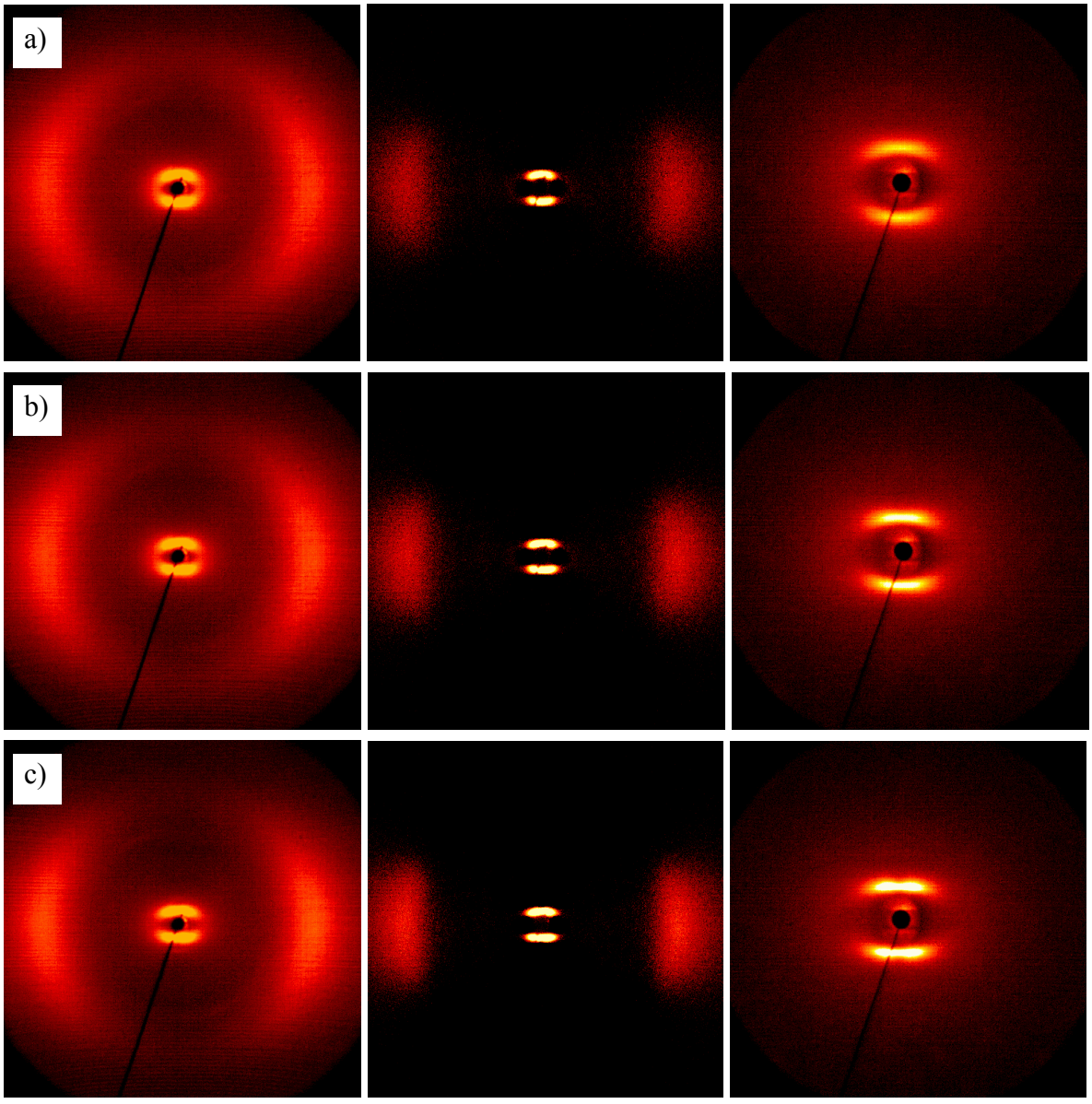


Figure S16 a) θ–scans over the diffuse small angle scattering of compound **1/14** at different temperatures.

Table S10. Crystallographic data of compound **1/14** at different temperatures.

	Small angle scattering		Wide angle scattering		tilt angle
T / °C	θ / °	*d*/nm	θ / °	*d*/nm	β / °
115	0.965	4.580	9.510	0.467	14.6
113	0.977	4.522	9.537	0.465	14.3
111	0.979	4.512	9.551	0.465	13.8
109	0.980	4.509	9.559	0.464	13.5
100	0.984	4.488	9.613	0.462	13.0
80	1.003	4.404	9.726	0.456	27.0
75	1.013	4.360	9.759	0.455	20.6
70	1.003	4.402	9.795	0.453	30.2

1.11 Compound 2



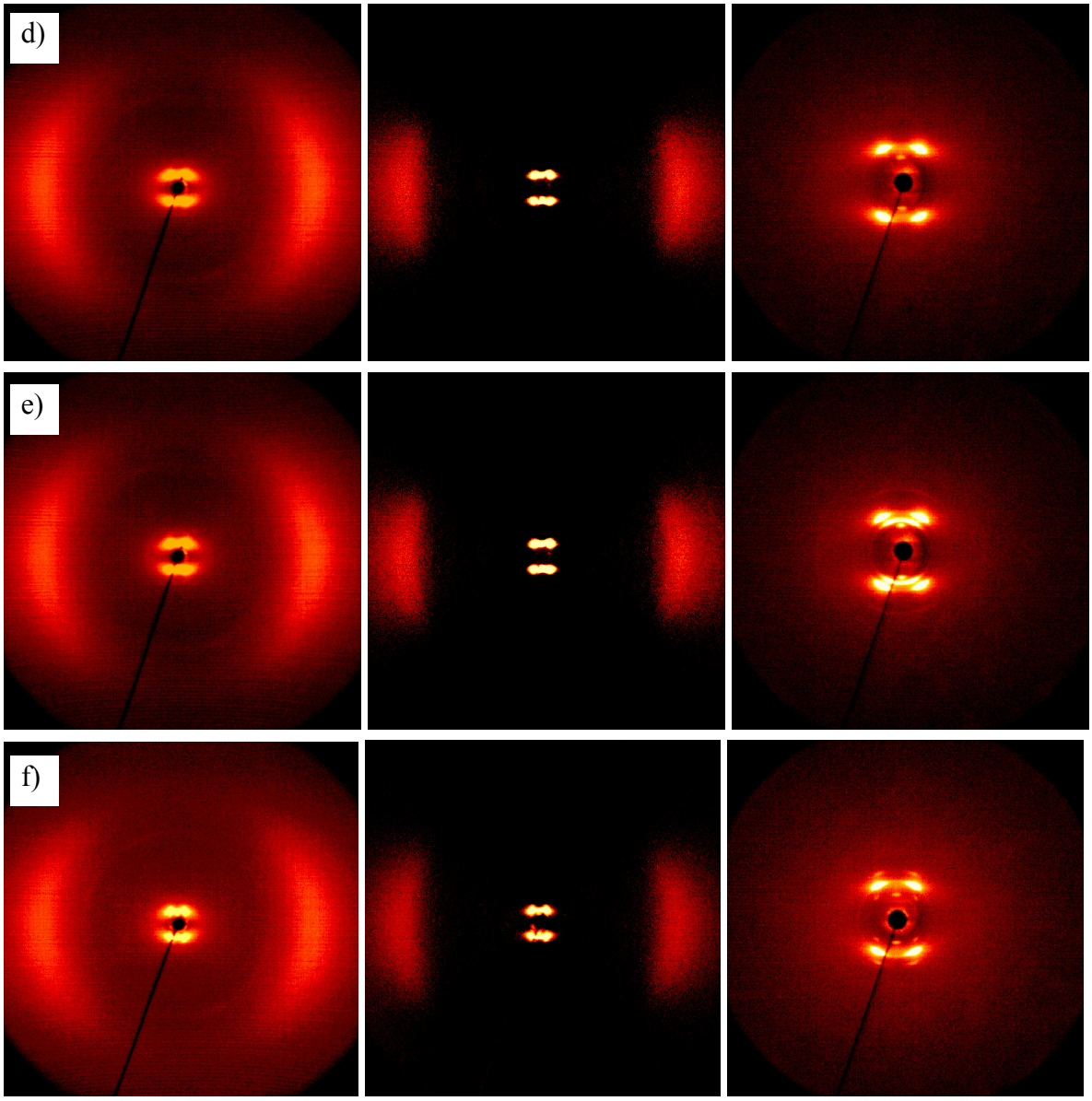


Figure S17. X-ray diffraction patterns of an oriented sample of compound **2** under a magnetic field; a-c) N_{cyb} phase a) at 100 °C, b) at 90 °C and c) at 60 °C; d-f) CybC phase, d) at 50 °C, e) at 45 °C (with partial crystallization) and f) at 45 °C (different sample); the left row shows the original wide angle patterns, the middle row the same patterns after subtraction of the scattering in the isotropic liquid state (at T = 110 °C), the right row shows the small angle patterns.

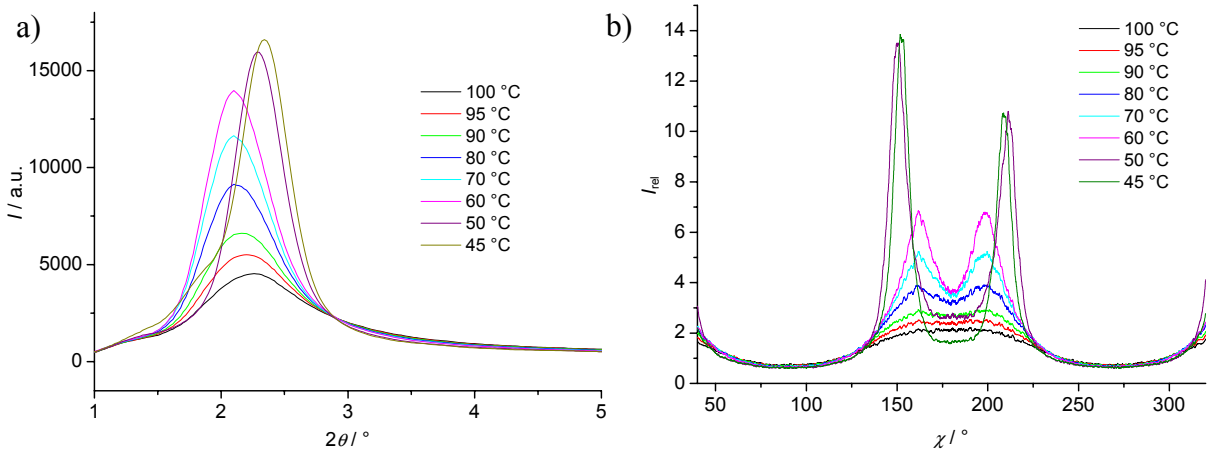


Figure S18. a) θ–scans and b) χ–scans over the diffuse small angle scattering (for 2θ = 1-3°) of compound **2** at different temperatures, $I_{rel} = I(T) / I(110\ °C, Iso)$.

Table S11a. Crystallographic data of compound **2** for the nematic, CybC and SmC phases at different temperatures.

	Small angle scattering			Wide angle scattering	
T / °C	θ / °	d/nm	$\Delta\chi/2$ / °	θ / °	d/nm
100	1.128	3.917	22.1	9.560	0.464
95	1.106	3.993	22.0	9.590	0.463
90	1.090	4.051	21.5	9.619	0.461
80	1.071	4.126	20.3	9.673	0.459
70	1.060	4.169	19.4	9.727	0.456
60	1.062	4.159	18.9	9.785	0.454
50	1.149	3.844	29.8	9.842	0.451
45	1.170	3.775	28.2	9.865	0.450

Table S11b. Crystallographic data for the 2D-lattice in the CybC phase of compound **2** at 45 °C.

θ / °	d/nm	hk	d_{calc}	d_{obs}-d_{calc}
0.715	6.182	01	6.181	0.00
0.853	5.176	10	5.179	0.00
1.406	3.141	11	3.141	0.00

Col_{ob}: a = 6.51 nm;
b = 7.77 nm; γ = 127.3°

V_{cell} = 18.1 nm^3 (volume of the unit cell defined by the dimensions a x b x sin(γ) x 0.45 nm);
V_{mol} = 1.15 nm^3 (volume for a single molecule as calculated using the crystal volume increments[S2]);
$n_{cell,cryst}$ = 15.8 (number of molecules in the unit cell, calculated according to $n_{cell} = V_{cell}/V_{mol}$ with average packing coefficient in the crystal is k = 0.7[S3]);
$n_{cell,liqu}$ = 12.4 (number of molecules in the unit cell of an isotropic liquid with an average packing coefficient k = 0.55, calculated according to $n_{cell,liqu} = 0.55/0.7$ x $n_{cell,cryst}$);
n_{cell} = 14.1 (number of molecules in the unit cell in the LC phase estimated as the average of that in the $n_{cell,liqu}$ and $n_{cell,liqu}$).

2. Additional textures

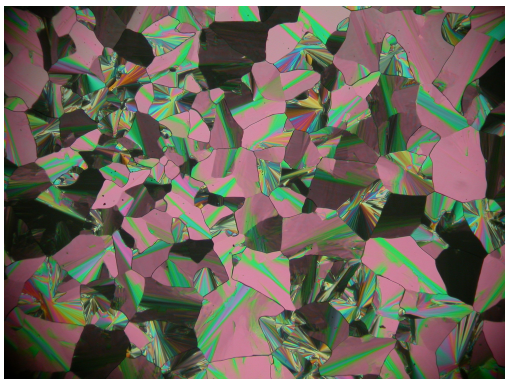


Figure S19. Texture of the B1 phase of compound **6**/6 at T = 54 °C.

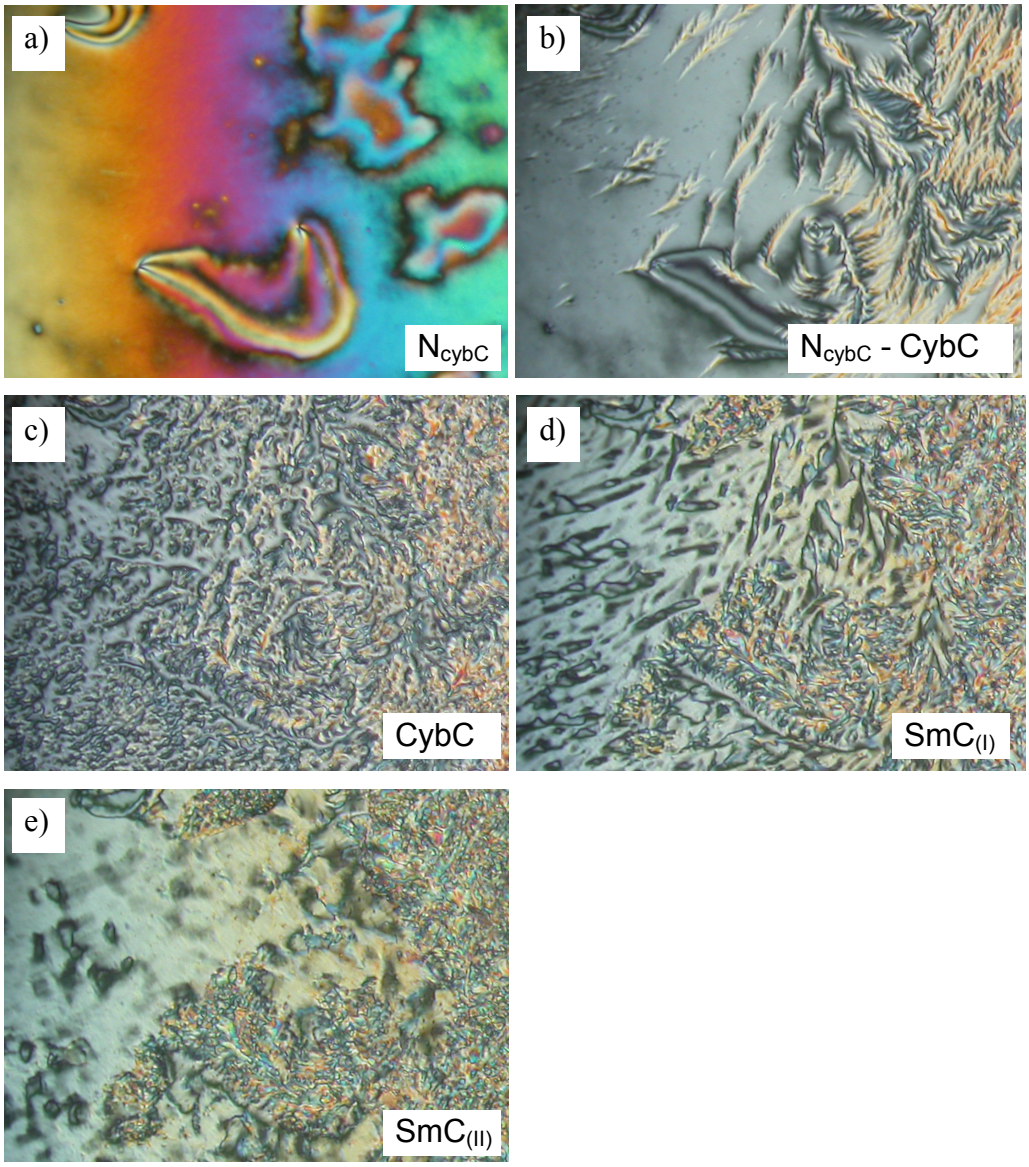


Figure S20. Textures showing the distinct mesophases of compound **1/10** as observed on cooling between crossed polarizers (same region, direction of the polarizers is horizontal and

vertical, respectively): a) N_{cyb} phase at T = 90 °C; b) N_{Cyb} to CybC transition at T = 86 °C; c) CybC phase at T = 70 °C; d) $SmC_{(I)}$ phase at T = 60 °C and e) $SmC_{(II)}$ phase at T = 50 °C.

3. Molecular lengths

Table S12. Molecular lengths of compounds **1/*n*** as measured with CPK models assuming a V-shaped conformation (see Figure 3d) with a 140° bending angle and extended all-trans conformation of the alkyl chains.

Comp.	L_{mol} /nm
1/2	3.5
1/4	3.9
1/6	4.3
1/7	4.5
1/8	4.8
1/9	5.0
1/10	5.2
1/11	5.5
1/12	5.7
1/14	6.2

4. Syntheses and analytical data

2,4-Dihydroxybenzaldehyde (Alfa Aesar), 5-cyanoresorcinol (Alfa Aesar), 4-chlororesorcinol (Sigma Aldrich), 4,6-dichlororesorcinol (Sigma Aldrich), 4-methylresorcinol (Sigma Aldrich) and 4-benzyloxy-2-hydroxybenzaldehyde (ABCR) were obtained from commercial sources and were used as obtained. 4-(4-*n*-alkylbenzoyloxy)benzoic acids[S4] were prepared according to reported standard procedures.

4.1 General procedure for the synthesis of compounds 1/*n* and 3/*n*-6/*n*

The corresponding 4-substituted benzoic acid (1 eq.), 4-cyanoresorcinol[S5] (synthesis of compounds **1/*n*** and **3/*n***), 5-cyanoresorcinol (synthesis of compounds **4/*n***), 4-chlororesorcinol (synthesis of compound **5/12**), 4,6-dichlororesorcinol (synthesis of compounds **6/*n***) or 4-methylresorcinol (synthesis of compound **7/6**) (0.5 eq.), DCC (1.1 eq.) and DMAP (cat.) were dissolved in anhydrous CH_2Cl_2 (ca. 20 ml/mmol benzoic acid) and stirring is continued for 24 hrs. The reaction mixture is then filtered to remove solids, evaporated and purified by column chromatography.

4.2 Data of compounds 1/*n* and 3/*n*-6/*n*

1/2 Prepared from 4-cyanoresorcinol (0.25 g, 1.85 mmol), 4-(4-ethylbenzoyloxy)benzoic acid (1.05 g, 3.89 mmol), DCC (0.84 g, 4.07 mmol), DMAP (20 mg) in dry CH_2Cl_2 (50 ml), purified by column chromatography (silica gel, CH_2Cl_2, R_f: 0.33), followed by crystallisation from CH_2Cl_2/Ethanol (1:9) to yield 0.60 g (0.94 mmol, 51 %).^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.32 (d, 2H, *J* 8.7, Ar-H), 8.30 (d, 2H, *J* 8.9, Ar-H), 8.12 (d, 2H, *J* 8.3 Ar-H), 8.11 (d, 2H, *J* 8.3, Ar-H), 7.79 (d, 1H, *J* 8.5, Ar-H), 7.53 (d, 1H, *J* 2.3, Ar-H), 7.40 (d, 2H, *J* 8.7, Ar-H), 7.40 (d, 2H, *J* 8.7, Ar-H), 7.34 (d, 2H, *J* 8.3, Ar-H), 7.31 (dd, 1H, *J* 8.5, *J* 2.1, Ar-H), 2.75 (q, 4H, *J* 7.7, Ar-CH_2), 1.28 (t, 6H, *J* 7.7, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 164.49, 163.24,

162.86, 155.97, 155.83, 154.78, 153.47, 151.15, 151.09, 133.95, 132.28, 132.03, 130.48, 130.46,128.26, 128.24, 126.42, 125.86, 125.47, 122.37, 122.32, 120.02, 117.40, 114.75, 104.31, 29.14, 15.23.

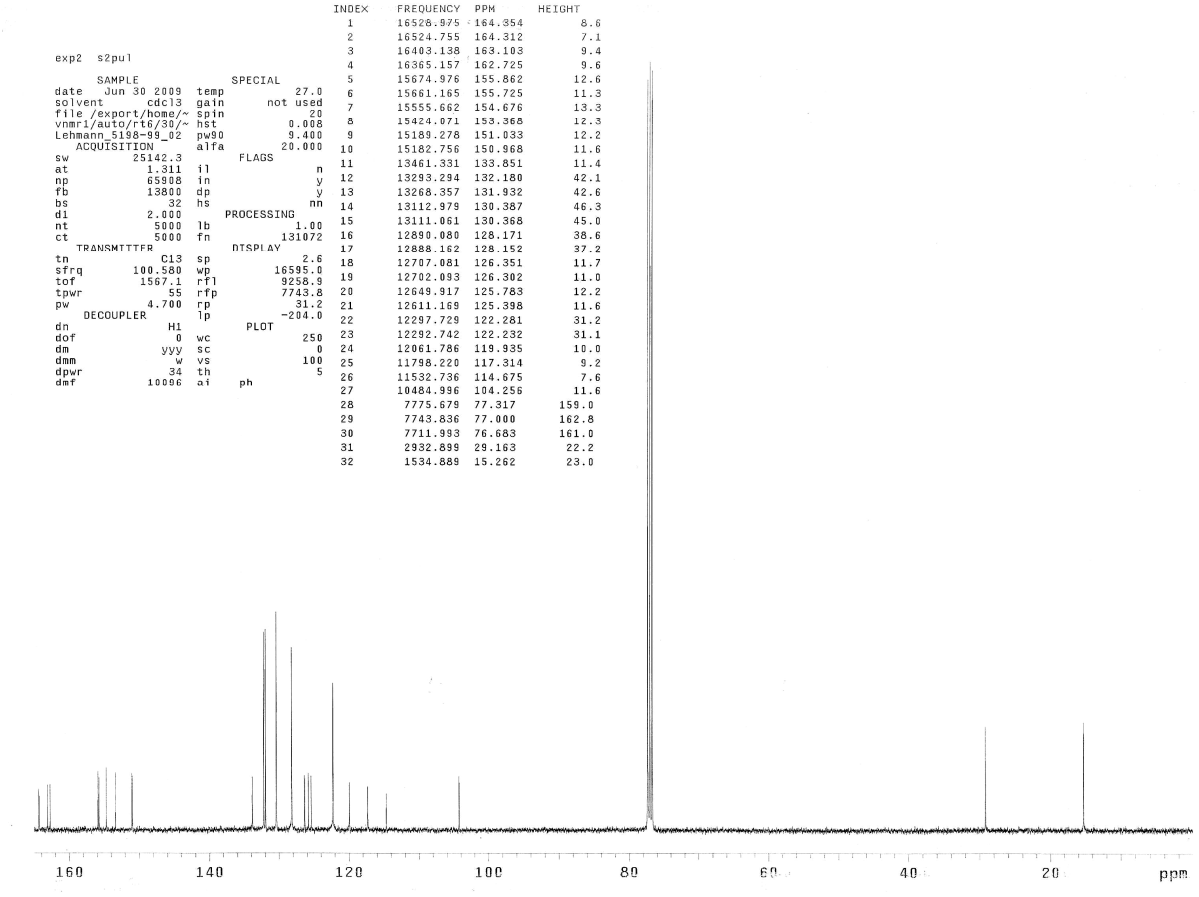


Figure S21. ^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of compound **1/2**.

1/3 Prepared from 4-cyanoresorcinol (0.2 g, 1.5 mmol), 4-(4-propylbenzoyloxy)benzoic acid (0.82 g, 3.0 mmol), DCC (0.64 g, 3.1 mmol), DMAP (20 mg) in dry CH_2Cl_2 (50 ml), purified by column chromatography (silica gel, $CHCl_3$, R_f: 0.08), followed by crystallisation from CH_2Cl_2/Ethanol (1:9) to yield 0.42 g (0.63 mmol, 42 %).^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.32 (d, 2H, *J* 8.7, Ar-H), 8.26 (d, 2H, *J* 8.9 Ar-H), 8.12 (d, 2H, *J* 8.3, Ar-H), 8.10 (d, 2H, *J* 8.3, Ar-H), 7.78 (d, 1H, *J* 8.5, Ar-H), 7.52 (d, 1H, *J* 2.3, Ar-H), 7.40 (d, 2H, *J* 8.7, Ar-H), 7.38 (d, 2H, *J* 8.9, Ar-H), 7.31 (m, 5H, Ar-H), 2.68 (t, 4H, *J* 7.6, Ar-CH_2), 1.69 (m, 4H, CH_2), 0.96 (t, 6H, *J* 7.4, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 164.34, 164.32, 163.11, 162.74, 155.90, 155.77, 154.71, 153.41, 149.53, 149.46, 133.84, 132.18, 131.93, 130.30, 130.28, 128.77, 128.75, 125.82, 125.43, 122.27, 122.23, 119.92, 117.31, 114.66, 104.29, 76.68, 38.22, 24.27, 13.81.

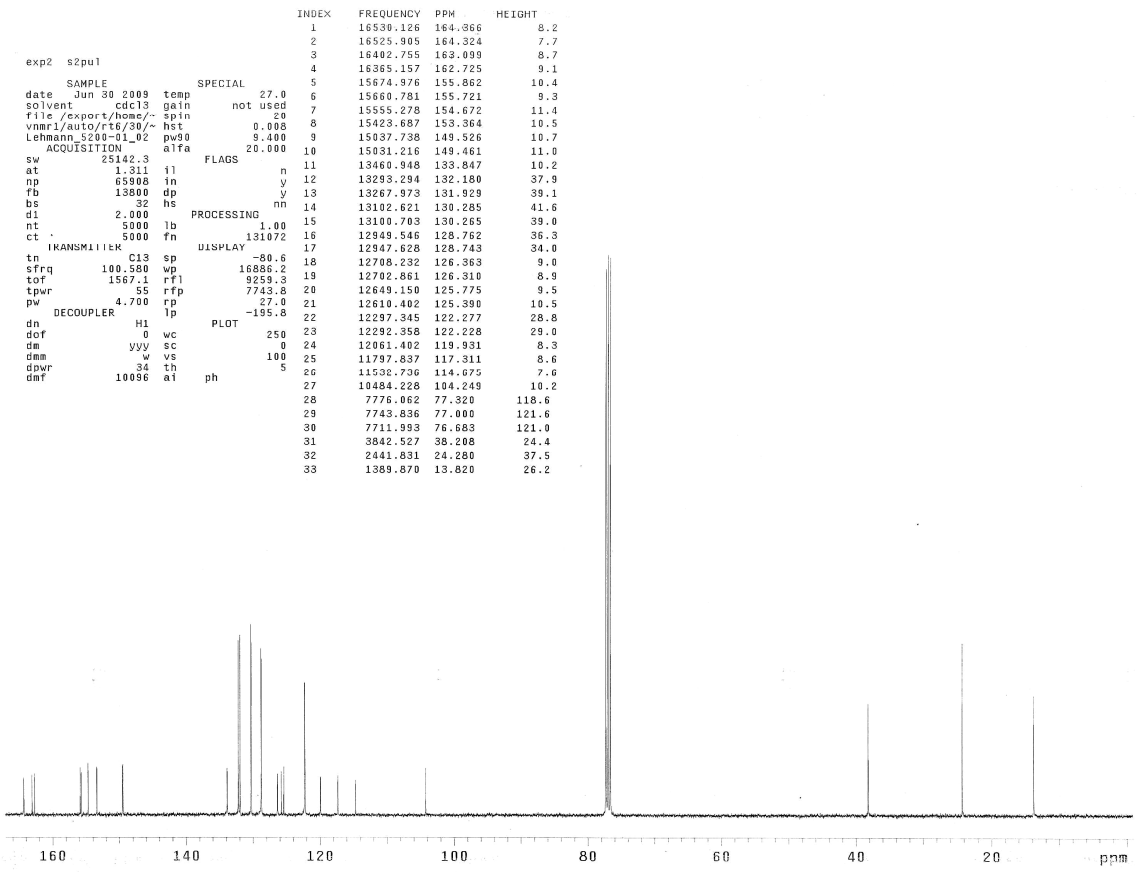


Figure S22. ^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of compound **1/3**.

1/4 Prepared from 4-cyanoresorcinol (0.2 g, 1.5 mmol), 4-(4-butylbenzoyloxy)benzoic acid (0.92 g, 3.0 mmol), DCC (0.64 g, 3.1 mmol), DMAP (20 mg) (50 ml), purified by column chromatography (silica gel, $CHCl_3$, R_f: 0.08)), followed by crystallisation from CH_2Cl_2/Ethanol (1:9) to yield 0.24 g (0.34 mmol, 23 %). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.31 (d, 2H, J 8.5, Ar-H), 8.25 (d, 2H, J 8.7 Ar-H), 8.11 (d, 2H, J 8.3, Ar-H), 8.09 (d, 2H, J 8.3, Ar-H), 7.78 (d, 1H, J 8.5, Ar-H), 7.52 (d, 1H, J 2.1, Ar-H), 7.40 (m, 4H, Ar-H), 7.36 (m, 5H, Ar-H), 2.70 (t, 4H, J 7.8, Ar-CH_2), 1.64 (m, 4H, CH_2), 1.37 (m, 4H, CH_2), 0.93 (t, 6H, J 7.4, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 164.37, 164.32, 163.11, 162.74, 155.90, 155.77, 154.71, 153.41, 149.80, 149.72, 133.85, 132.19, 131.94, 130.60, 130.31, 130.29, 128.85, 128.72, 128.70, 126.37, 125.81, 125.43, 122.28, 122.23, 119.92, 117.31, 114.67, 104.29, 76.68, 35.89, 33.28, 22.41, 13.97. EA, calc. for $C_{43}H_{37}O_8N$, 695.7605 g/mol:, C 74.23 H 5.36, N 2.01, found: C 73.93, H 5.40, N 1.90

1/5 Prepared from 4-cyanoresorcinol (0.2 g, 1.5 mmol), 4-(4-pentylbenzoyloxy)benzoic acid (0.97 g, 3.0 mmol), DCC (0.64 g, 3.1 mmol), DMAP (20 mg) in dry CH_2Cl_2 (50 ml), purified by column chromatography (silica gel, $CHCl_3$, R_f: 0.08), followed by crystallisation from CH_2Cl_2/Ethanol (1:9) to yield 0.11 g (0.15 mmol, 10 %). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.32 (d, 2H, *J* 8.8, Ar-H), 8.25 (d, 2H, *J* 8.9 Ar-H), 8.11 (d, 2H, *J* 8.3, Ar-H), 8.10 (d, 2H, *J* 8.3, Ar-H), 7.78 (d, 1H, *J* 8.5, Ar-H), 7.51 (d, 1H, *J* 2.3, Ar-H), 7.39 (d, 2H, *J* 8.7, Ar-H), 7.38 (d, 2H, *J* 8.7, Ar-H), 7.31 (m, 5H, Ar-H), 2.70 (t, 4H, *J* 7.8, Ar-CH_2), 1.66 (m, 4H, CH_2), 1.33 (m, 8H, CH_2), 0.89 (t, 6H, J 6.9, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 164.48, 164.43, 163.22, 162.85, 155.99, 155.85, 155.64, 154.79, 153.73, 153.49, 150.37, 149.92, 149.85, 133.93, 132.30, 132.26, 132.05, 132.01, 131.95, 131.93, 130.67, 130.43, 130.38, 130.36, 128.92, 128.85, 128.79, 128.77, 126.83, 126.41, 126.36, 126.11, 125.87, 125.48, 122.35, 122.29,

122.24, 122.19, 119.99, 119.78, 117.37, 114.72, 104.32, 77.21, 76.30, 53.40, 40.42, 36.13, 34.04, 31.46, 30.78, 29.76, 27.78, 22.53, 14.00 EA, calc. for $C_{45}H_{41}O_8N$, 723.8141 g/mol:, C 74.67, H 5.71, N 1.95, found: C 74.44, H 5.88, N 1.73

1/6 Prepared from 4-cyanoresorcinol (0.2 g, 1.5 mmol), 4-(4-hexylbenzoyloxy)benzoic acid (1.01 g, 3.0 mmol), DCC (0.64 g, 3.1 mmol), DMAP (20 mg) in dry CH_2Cl_2 (50 ml), purified by column chromatography (silica gel, $CHCl_3$, R_f: 0.08), followed by crystallisation from CH_2Cl_2/Ethanol (1:9) to yield 0.31 g (0.41 mmol, 27 %) of the product. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.32 (d, 2H, *J* 8.9, Ar-H), 8.26 (d, 2H, *J* 8.3 Ar-H), 8.10 (m, 4H, Ar-H), 7.78 (d, 1H, *J* 8.7, Ar-H), 7.52 (d, 1H, *J* 1.9, Ar-H), 7.40 (d, 2H, *J* 8.7, Ar-H), 7.39 (d, 2H, *J* 8.7, Ar-H), 7.32 (m, 5H, Ar-H), 2.70 (t, 4H, *J* 7.7, Ar-CH_2), 1.63 (m, 4H, CH_2), 1.36-1.24 (m, 12H, CH_2), 0.88 (t, 6H, *J* 6.4, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 164.42, 163.21, 162.83, 155.99, 155.85, 154.79, 153.48, 149.92, 149.84, 133.91, 132.25, 132.00, 128.77, 128.75, 126.41, 125.86, 122.33, 122.28, 119.97, 117.36, 114.71, 104.31, 77.21, 104.31, 53.39, 36.16, 31.68, 31.07, 28.94, 22.60, 14.07. EA, calc. for $C_{47}H_{45}O_8N$, 751.8677 g/mol:, C 75.08, H 6.03, N 1.86, found: C 75.04, H 6.09, N 1.75

1/7 Prepared from 4-cyanoresorcinol (0.27 g, 2.0 mmol), 4-(4-heptylbenzoyloxy)benzoic acid (1.39 g, 4.1 mmol), DCC (0.86 g, 4.2 mmol), DMAP (20 mg) in dry CH_2Cl_2 (50 ml), purified by column chromatography (silica gel, $CHCl_3$, R_f: 0.08), followed by crystallisation from CH_2Cl_2/Ethanol (1:9) to yield 0.38 g (0.48 mmol, 24 %). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.32 (d, 2H, *J* 8.7, Ar-H), 8.26 (d, 2H, *J* 8.7 Ar-H), 8.10 (d, 2H, *J* 8.3, Ar-H), 8.09 (d, 2H, *J* 8.3, Ar-H), 7.78 (d, 1H, *J* 8.7, Ar-H), 7.53 (d, 1H, *J* 1.9, Ar-H), 7.40 (d, 2H, *J* 8.7, Ar-H), 7.38 (d, 2H, *J* 8.9, Ar-H), 7.31 (m, 5H, Ar-H), 2.70 (t, 4H, *J* 7.7, Ar-CH_2), 1.67 (m, 4H, CH_2), 1.33-1.28 (m, 16H, CH_2), 0.88 (t, 6H, *J* 6.8, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 164.47, 164.42, 163.20, 162.83, 155.99, 155.85, 154.79, 153.48, 149.92, 149.85, 133.91, 132.25, 132.00, 130.37, 130.35, 128.77, 128.75, 126.36, 125.86, 125.47, 122.33, 122.28, 119.97, 117.36, 114.71, 104.31, 76.68, 36.16, 31.80, 31.11, 29.24, 29.14, 22.66, 14.08. EA, calc. for $C_{49}H_{49}O_8N$, 779.92 g/mol:, C 75.46, H 6.33, N 1.79, found: C 75.44, H 6.38, N 1.56

1/8 Prepared from 4-cyanoresorcinol (0.27 g, 2.0 mmol), 4-(4-octylbenzoyloxy)benzoic acid (1.45 g, 4.1 mmol), DCC (0.86 g, 4.2 mmol), DMAP (20 mg) in dry CH_2Cl_2 (50 ml), purified by column chromatography (silica gel, $CHCl_3$, R_f: 0.08), followed by crystallisation from CH_2Cl_2/Ethanol (1:9) to yield 0.1 g (0.13 mmol, 6.5 %). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.32 (d, 2H, *J* 8.7, Ar-H), 8.26 (d, 2H, *J* 8.7 Ar-H), 8.10 (m, 4H, Ar-H), 7.78 (d, 1H, *J* 8.5, Ar-H), 7.52 (d, 1H, *J* 2.1, Ar-H), 7.40 (d, 2H, *J* 8.5, Ar-H), 7.38 (d, 2H, *J* 8.7, Ar-H), 7.32 (m, 5H, Ar-H), 2.70 (t, 4H, *J* 7.7, Ar-CH_2), 1.65 (m, 4H, CH_2), 1.26 (m, 20H, CH_2), 0.87 (t, 6H, *J* 6.7, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 164.38, 163.13, 155.72, 154.92, 154.63, 153.62, 153.34, 150.29, 150.13, 149.84, 133.81, 132.17, 131.92, 130.59, 130.35, 130.29, 128.84, 128.78, 128.72, 126.27, 125.82, 125.41, 122.27, 122.22, 119.73, 117.36, 114.77, 104.29, 77.21, 36.21, 31.93, 31.17, 31.12, 29.50, 29.34, 29.29, 22.74, 14.18. EA, calc. for $C_{51}H_{53}O_8N$, 807.97 g/mol:, C 75.81, H 6.61, N 1.73, found: C 75.71, H 6.64, N 1.65

1/9 Prepared fropm 4-cyanoresorcinol (0.27 g, 2.0 mmol), 4-(4-nonylbenzoyloxy)benzoic acid (1.51 g, 4.1 mmol), DCC (0.86 g, 4.2 mmol), DMAP (20 mg) in dry CH_2Cl_2 (50 ml), purified by column chromatography (silica gel, $CHCl_3$, R_f: 0.08) to yield 0.1 g (0.11 mmol, 5.5 %), ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.32 (d, 2H, *J* 8.7, Ar-H), 8.25 (d, 2H, *J* 8.5 Ar-H), 8.10 (m, 4H, Ar-H), 7.78 (d, 1H, *J* 8.5, Ar-H), 7.52 (d, 1H, *J* 2.1, Ar-H), 7.40 (d, 2H, *J* 8.7, Ar-H), 7.38 (d, 2H, *J* 8.7, Ar-H), 7.32 (m, 5H, Ar-H), 2.70 (t, 4H, *J* 7.7, Ar-CH_2), 1.65 (m, 4H, CH_2), 1.49 (m, 16H, CH_2), 1.27 (m, 16H, CH_2), 0.87 (t, 6H, *J* 6.7, CH_3). ^{13}C-NMR

($CDCl_3$, 100 MHz): δ 164.35, 164.30, 163.09, 162.72, 155.89, 155.75, 154.69, 153.39, 149.82, 149.76, 133.83, 132.17, 131.92, 130.30, 130.28, 128.71, 128.69, 126.34, 126.29, 125.80, 125.41, 122.27, 122.22, 119.91, 117.30, 114.26, 36.19, 31.94, 31.15, 29.58, 29.53, 29.36, 29.32, 22.74, 14.17; EA, calc. for $C_{53}H_{57}O_8N$, 836.0285 g/mol:, C 76.14, H 6.87, N 1.67, found: C 76.18, H 6.86, N 1.44

1/10 Prepared from 4-cyanoresorcinol (0.27 g, 2.0 mmol), 4-(4-decylbenzoyloxy)benzoic acid (1.51 g, 4.1 mmol), DCC (0.86 g, 4.2 mmol), DMAP (20 mg) in dry CH_2Cl_2 (50 ml) purified by column chromatography (silica gel, $CHCl_3$, R_f: 0.08), followed by crystallisation from CH_2Cl_2/Ethanol (1:9) to yield 0.22 g (0.25 mmol, 12.7 %). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.32 (d, 2H, *J* 8.9, Ar-H), 8.25 (d, 2H, *J* 8.7 Ar-H), 8.11 (d, 2H, *J* 8.5, Ar-H), 8.09 (d, 2H, *J* 8.3, Ar-H), 7.78 (d, 1H, *J* 8.5, Ar-H), 7.53 (d, 1H, *J* 2.3, Ar-H), 7.40 (d, 2H, *J* 8.7, Ar-H), 7.38 (d, 2H, *J* 8.7, Ar-H), 7.31 (m, 5H, Ar-H), 2.69 (t, 4H, *J* 7.7, Ar-CH_2), 1.65 (m, 4H, CH_2), 1.29 (m, 38H, CH_2), 0.87 (t, 6H, *J* 6.8, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 164.48, 164.43, 163.21, 162.83, 155.96, 155.82, 154.76, 153.45, 149.93, 149.86, 133.93, 132.25, 132.00, 130.36, 130.34, 128.78, 128.76, 126.35, 126.30, 125.83, 125.44, 122.34, 122.29, 119.99, 117.37, 114.73, 104.28, 36.16, 31.92, 31.12, 29.62, 29.58, 29.48, 29.34, 29.28, 22.71, 14.13.

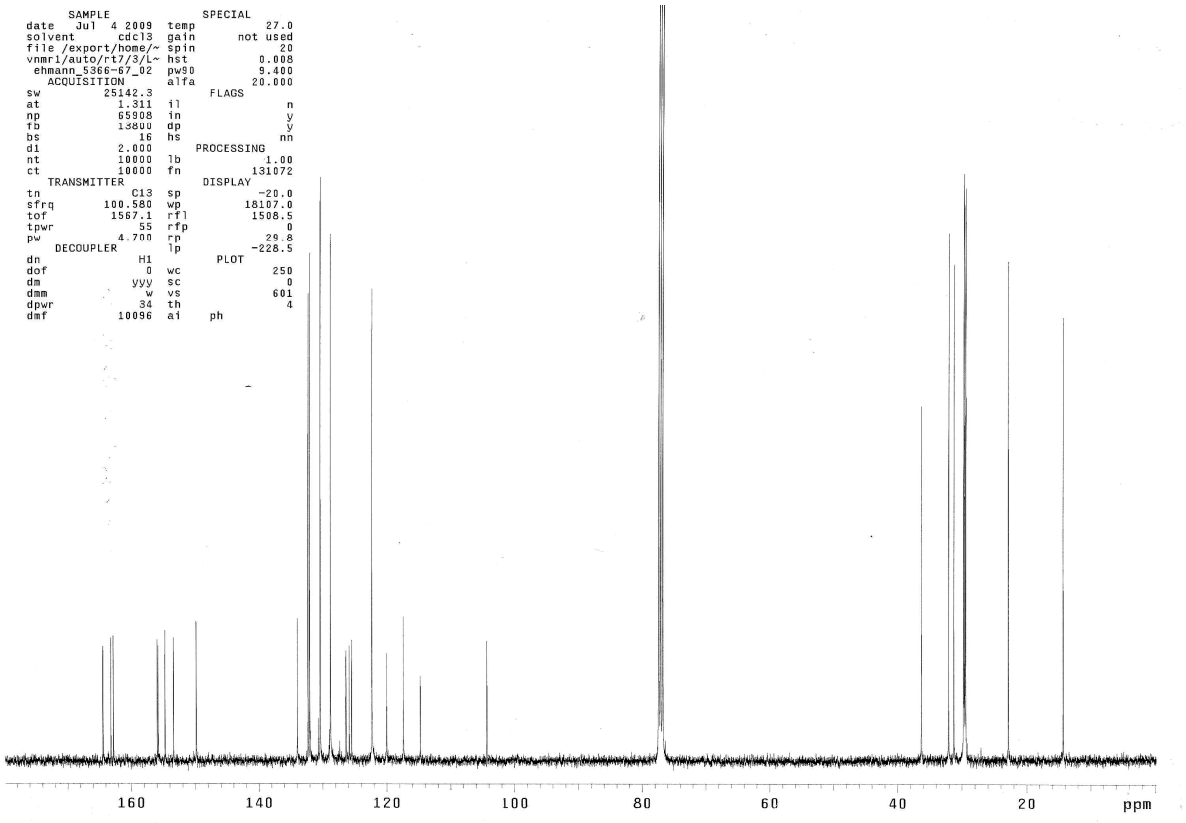


Figure S23. ^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of compound **1/10**.

1/11 4-cyanoresorcinol (0.27 g, 2.0 mmol), 4-(4-undecylbenzoyloxy)benzoic acid (1.57 g, 4.1 mmol), DCC (0.86 g, 4.2 mmol), DMAP (20 mg) in dry CH_2Cl_2 (50 ml), purified by column chromatography (silica gel, $CHCl_3$, R_f: 0.08) to yield 0.6 g (0.67 mmol, 34 %), ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.32 (d, 2H, *J* 8.5, Ar-H), 8.25 (d, 2H, *J* 8.7 Ar-H), 8.12 (d, 2H, *J* 8.3, Ar-H), 8.10 (d, 2H, *J* 8.3, Ar-H), 7.78 (d, 1H, *J* 8.7, Ar-H), 7.52 (d, 1H, *J* 2.3, Ar-H), 7.39 (d, 2H, *J* 8.5, Ar-H), 7.38 (d, 2H, *J* 8.5, Ar-H), 7.31 (m, 5H, Ar-H), 2.70 (t, 4H, *J* 7.8, Ar-CH_2), 1.65 (m, 4H, CH_2), 1.31 (m, 8H, CH_2), 1.25 (m, 24H, CH_2), 0.87 (t, 6H, *J* 6.8, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 164.37, 164.33, 163.11, 162.73, 155.89, 155.74, 154.69, 153.38,

149.84, 149.77, 133.85, 132.18, 131.93, 130.30, 130.29, 128.71, 128.70, 126.33, 126.27, 125.79, 125.40, 122.28, 122.23, 119.93, 117.31, 114.68, 104.27, 77.20, 36.20, 31.99, 31.16, 29.71, 29.69, 29.63, 29.53, 29.41, 29.33, 22.77, 14.19. EA, calc. for $C_{57}H_{65}O_8N$, 892.1357 g/mol:, C 76.74, H 7.39, N 1.57, found: C 76.70, H 7.37, N 1.43

1/12 Prepared from 4-cyanoresorcinol (0.27 g, 2.0 mmol), 4-(4-dodecylbenzoyloxy)benzoic acid (1.62 g, 4.1 mmol), DCC (0.86 g, 4.2 mmol), DMAP (20 mg) in dry CH_2Cl_2 (50 ml), purified by column chromatography (silica gel, $CHCl_3$, R_f: 0.08) to yield 0.9 g (0.98 mmol, 49%) of the product. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.32 (d, 2H, *J* 8.9, Ar-H), 8.27 (d, 2H, *J* 8.7 Ar-H), 8.12 (d, 2H, *J* 8.3, Ar-H), 8.10 (d, 2H, *J* 8.3, Ar-H), 7.78 (d, 1H, *J* 8.5, Ar-H), 7.52 (d, 1H, *J* 2.3, Ar-H), 7.37 (m, 4H, Ar-H), 7.31 (m, 5H, Ar-H), 2.70 (t, 4H, *J* 7.7, Ar-CH_2), 1.65 (m, 4H, CH_2), 1.29 (m, 36H, CH_2), 0.87 (t, 6H, *J* 6.8, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 164.37, 164.32, 163.11, 162.74, 155.90, 155.77, 154.71, 153.41, 149.84, 149.77, 133.84, 132.18, 131.93, 130.31, 130.29, 128.72, 128.70, 126.36, 126.31, 125.81, 125.43, 122.28, 122.23, 119.92, 117.31, 104.29, 36.21, 32.00, 31.15, 29.74, 29.71, 29.64, 29.53, 29.42, 29.34, 22.77, 14.18 EA, calc. for $C_{59}H_{69}O_8N$, 920.1893 g/mol:, C 77.01, H 7.56, N 1.52, found: C 76.92, H 7.57, N 1.41

1/14 Prepared from 4-cyanoresorcinol (0.27 g, 2.0 mmol), 4-(4-tetradecylbenzoyloxy)benzoic acid (1.69 g, 4.1 mmol), DCC (0.86 g, 4.2 mmol), DMAP (20 mg) in dry CH_2Cl_2 (50 ml), purified by column chromatography (silica gel, $CHCl_3$, R_f: 0.08) to yield 0.7 g (0.72 mmol, 36 %) of the product. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.32 (d, 2H, *J* 8.7, Ar-H), 8.26 (d, 2H, *J* 8.7 Ar-H), 8.12 (d, 2H, *J* 8.3, Ar-H), 8.10 (d, 2H, *J* 8.3, Ar-H), 7.78 (d, 1H, *J* 8.5, Ar-H), 7.53 (d, 1H, *J* 2.3, Ar-H), 7.39 (d, 2H, *J* 8.7, Ar-H), 7.38 (d, 2H, *J* 8.7, Ar-H), 7.32 (m, 5H, Ar-H), 2.70 (t, 4H, *J* 7.7, Ar-CH_2), 1.65 (m, 4H, CH_2), 1.31 (m, 8H, CH_2), 1.25 (m, 36H, CH_2), 0.87 (t, 6H, *J* 6.8, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 164.37, 164.32, 163.11, 162.73, 155.89, 155.75, 154.70, 153.39, 149.84, 149.77, 133.85, 132.18, 131.93, 130.30, 130.29, 128.72, 128.70, 126.33, 126.28, 125.80, 125.41, 122.28, 122.23, 119.93, 117.31, 104.27, 77.20, 36.21, 32.01, 31.17, 29.77, 29.74, 29.64, 29.53, 29.43, 29.34, 22.77, 14.19. EA, calc. for $C_{63}H_{77}O_8N$, 976.2965 g/mol:, C 77.51, H 7.95, N 1.43, found: C 77.50, H 7.95, N 1.43

3/6 Prepared from 5-cyanoresorcinol (0.2 g, 1.5 mmol), 4-(4-hexylbenzoyloxy)benzoic acid (1.01 g, 3.1 mmol), DCC (0.64 g, 3.1 mmol), DMAP (20 mg) in dry CH_2Cl_2 (50 ml), purified by column chromatography (silica gel, $CHCl_3$, R_f: 0.60), followed by crystallisation from CH_2Cl_2/Ethanol (1:9) to yield 0.404 g (0.537 mmol, 49 %). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.25 (d, 4H, *J* 8.7, Ar-H), 8.10 (d, 4H, *J* 8.3 Ar-H), 7.51 (m, 2H, Ar-H), 7.38 (d, 4H, *J* 8.7, Ar-H), 7.32 (d, 4H, *J* 8.3, Ar-H), 7.25 (s, 1H, Ar-H), 2.70 (t, 4H, *J* 7.7, Ar-CH_2), 1.65 (m, 4H, CH_2), 1.31 (m, 12H, CH_2), 0.88 (t, 6H, *J* 6.9, CH_3); EA, calc. for $C_{47}H_{45}O_8N$, 751.86 g/mol:, C 75.08, H 6.03 N 1.86, found: C 74.91, H 5.92, N 1.78.

3/12 Prepared from 5-cyanoresorcinol (0.2 g, 1.5 mmol), 4-(4-dodecylbenzoyloxy)benzoic acid (1.25 g, 3.15 mmol), DCC (0.68 g, 3.3 mmol), DMAP (20 mg) in dry CH_2Cl_2 (50 ml), purified by column chromatography (silica gel, $CHCl_3$, R_f: 0.60), followed by crystallisation from CH_2Cl_2/Ethanol (1:9) to yield 0.42 g (0.46 mmol, 42 %). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.25 (d, 4H, *J* 8.7, Ar-H), 8.10 (d, 4H, *J* 8.3 Ar-H), 7.51 (m, 2H, Ar-H), 7.39 (d, 4H, *J* 8.7, Ar-H), 7.32 (d, 4H, *J* 8.5, Ar-H), 7.25 (s, 1H, Ar-H), 2.70 (t, 4H, *J* 7.7, Ar-CH_2), 1.65 (m, 4H, CH_2), 1.31 (m, 8H, CH_2), 1.25 (m, 28H, CH_2), 0.87 (t, 6H, *J* 6.9, CH_3); EA, calc. for $C_{59}H_{69}O_8N$, 920.18 g/mol:, C 77.01, H 7.56 N 1.52, found: C 76.67, H 7.44, N 1.54.

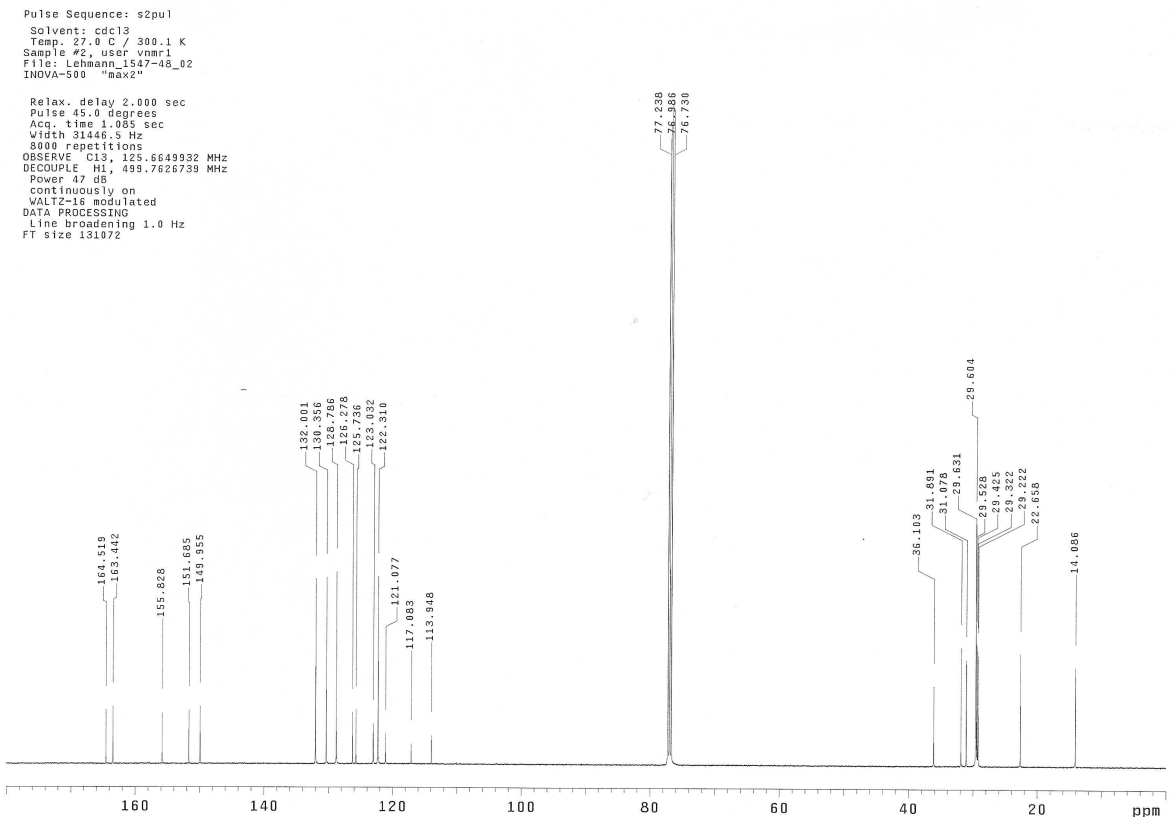


Figure S24. ^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of compound **3/12**.

4/12 Prepared from 4-chlororesorcinol (0.158 g, 1.1 mmol), 4-(4-dodecylbenzoyloxy)benzoic acid (0.927 g, 2.34 mmol), DCC (0.51 g, 2.5 mmol), DMAP (15 mg) in dry CH_2Cl_2 (30 ml), purified by column chromatography (silica gel, $CHCl_3$, R_f: 0.66) to yield 0.545 g (0.55 mmol, 50 %). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.30 (d, 2H, *J* 8.9, Ar-H), 8.25 (d, 2H, *J* 8.9, Ar-H), 8.11 (d, 2H, *J* 8.3 Ar-H), 8.10 (d, 2H, *J* 8.3, Ar-H), 7.53 (d, 1H, *J* 8.7, Ar-H), 7.38 (d, 2H, *J* 8.9, Ar-H), 7.36 (d, 2H, *J* 8.9, Ar-H), 7.31 (d, 4H, *J* 8.1, Ar-H), 7.28 (d, 1H, *J* 2.5, Ar-H), 7.16 (dd, 1H, *J* 8.7, *J* 2.5, Ar-H), 2.69 (t, 4H, *J* 7.5, Ar-CH_2), 1.65 (m, 4H, CH_2), 1.30 (m, 8H, CH_2), 1.25 (m, 28H, CH_2), 0.87 (t, 6H, *J* 7.1, CH_3). EA, calc. for $C_{58}H_{69}O_8Cl$, 929.62 g/mol:, C 74.87, H 7.48, found: C 74.87, H 7.47.

5/6 Prepared from 4, 6-dichlororesorcinol (0.2 g, 1.1 mmol), 4-(4-hexylbenzoyloxy)benzoic acid (0.76 g, 2.34 mmol), DCC (0.51 g, 2.5 mmol), DMAP (20 mg) in dry CH_2Cl_2 (50 ml), purified by column chromatography (silica gel, $CHCl_3$, R_f: 0.7), followed by crystallisation from CH_2Cl_2/Hexane (1:9) to yield 0.45 g (0.52 mmol, 47 %). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.28 (d, 4H, *J* 8.7, Ar-H), 8.10 (d, 4H, *J* 8.3, Ar-H), 7.64 (s, 1H, Ar-H), 7.38 (d, 4H, *J* 8.7, Ar-H), 7.37 (s, 1H, Ar-H), 7.31 (d, 4H, *J* 8.3, Ar-H), 2.70 (t, 4H, *J* 7.6, Ar-CH_2), 1.64 (m, 4H, CH_2), 1.31 (m, 12H, CH_2), 0.88 (t, 6H, *J* 6.7, CH_3).

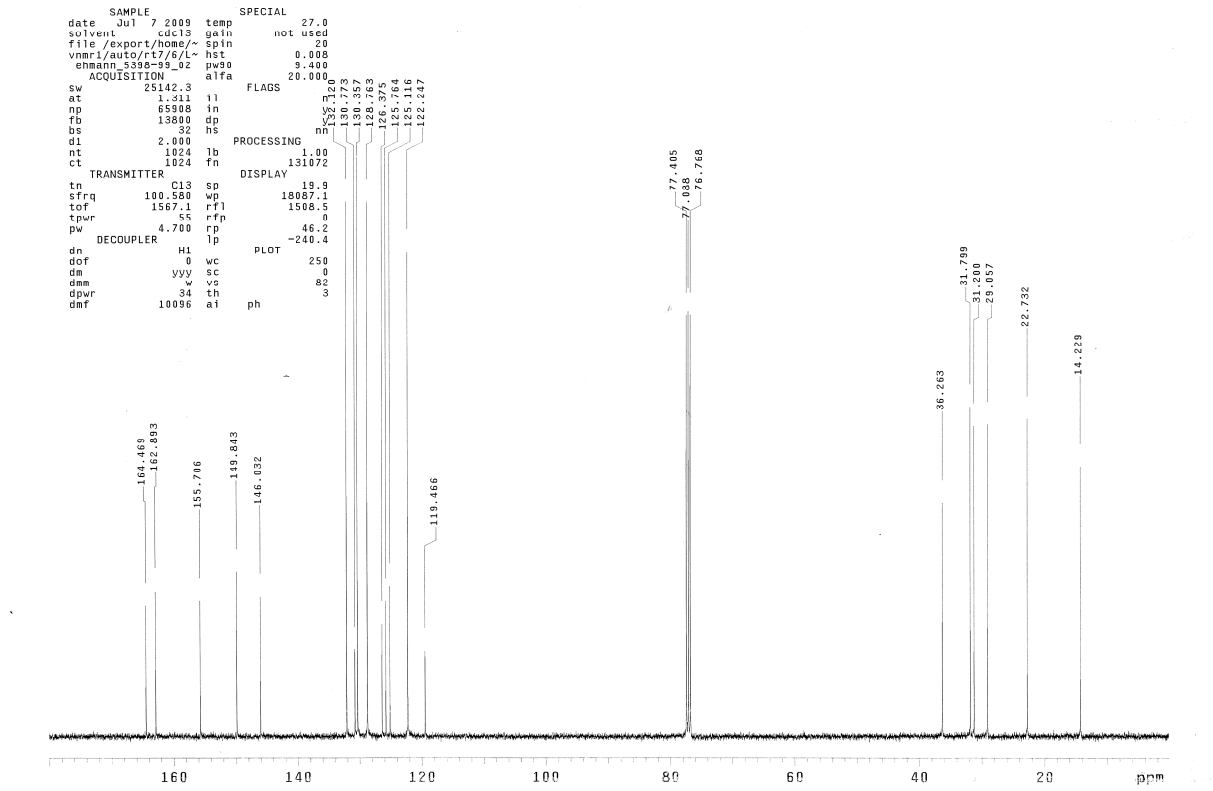


Figure S25. ^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of compound **5/6**.

5/12 Prepared from 4, 6-dichlororesorcinol (0.2 g, 1.1 mmol), 4-(4-dodecylbenzoyloxy)benzoic acid (0.927 g, 2.34 mmol), DCC (0.51 g, 2.5 mmol), DMAP (20 mg) in dry CH_2Cl_2 (40 ml), purified by column chromatography (silica gel, $CHCl_3$, R_f: 0.76), followed by crystallisation from CH_2Cl_2/Hexane (1:9) to yield 0.51 g (0.49 mmol, 45 %).
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.29 (d, 4H, *J* 8.9, Ar-H), 8.10 (d, 4H, *J* 8.3, Ar-H), 7.64 (s, 1H, Ar-H), 7.38 (d, 4H, *J* 8.5, Ar-H), 7.37 (s, 1H, Ar-H), 7.31 (d, 4H, *J* 8.3, Ar-H), 2.70 (t, 4H, *J* 7.7, Ar-CH_2), 1.63 (m, 4H, CH_2), 1.30 (m, 36H, CH_2), 0.87 (t, 6H, *J* 6.8, CH_3).

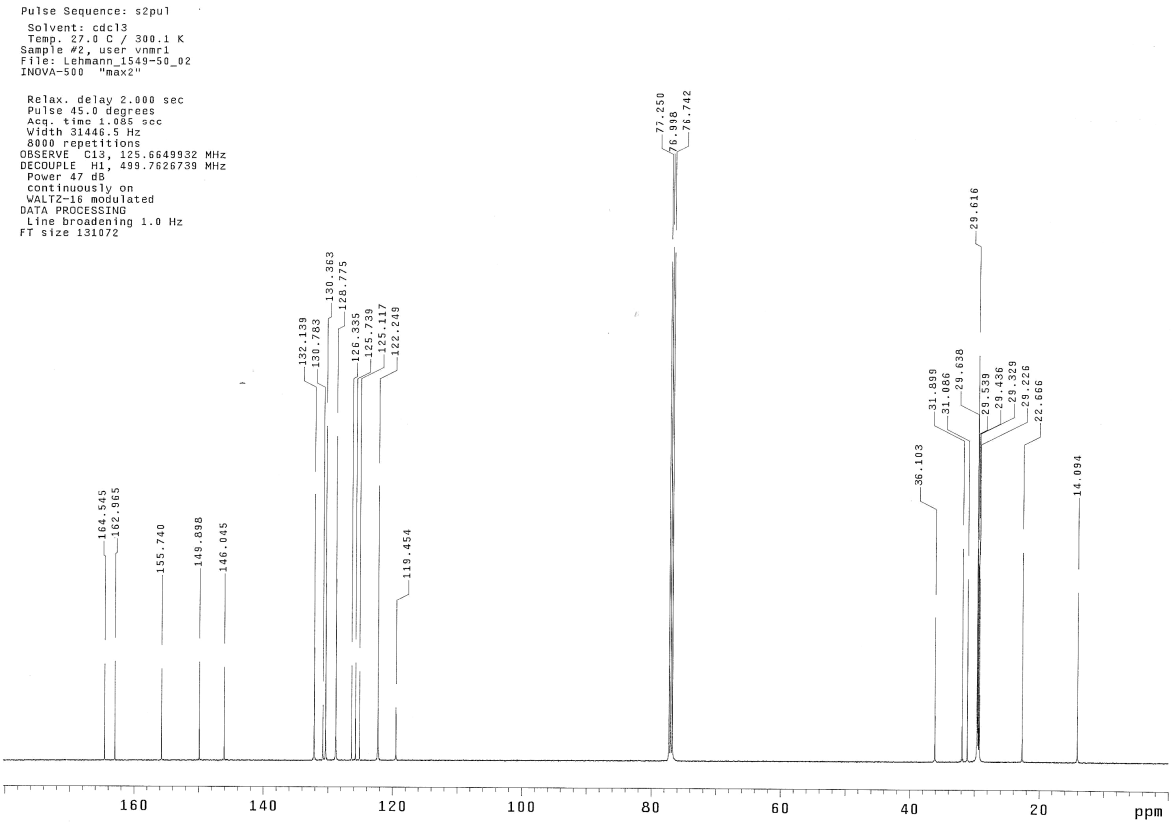
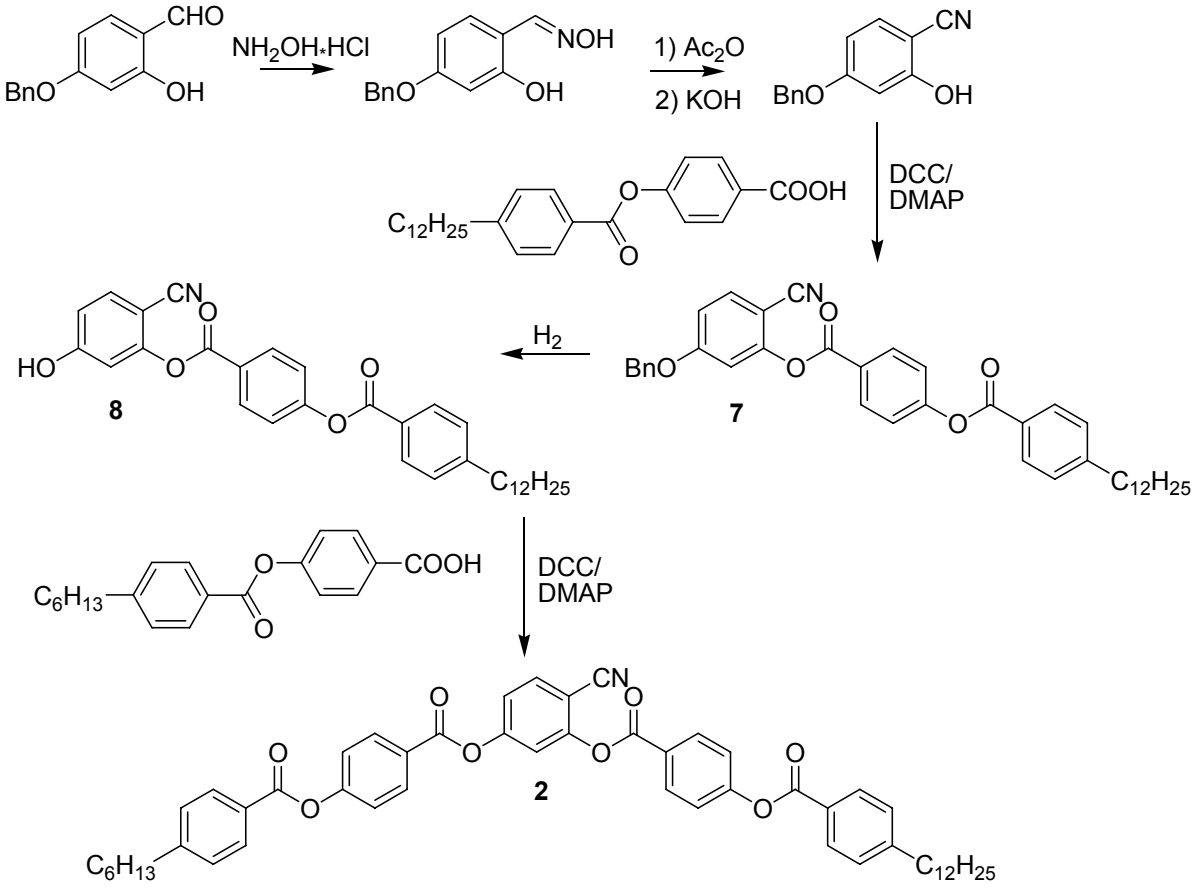


Figure S26. ^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of compound **5/12**.

6/6 Prepared from 4-methylresorcinol (0.09 g, 0.725 mmol), 4-(4-hexylbenzoyloxy)benzoic acid (0.497 g, 1.52 mmol), DCC (0.33 g, 1.60 mmol), DMAP (15 mg) in dry CH_2Cl_2 (40 ml), purified by column chromatography (silica gel, CH_2Cl_2, R_f: 0.39), followed by crystallisation from CH_2Cl_2/Ethanol (1:9) to yield 0.242 g (0.33 mmol, 45 %). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.28 (d, 2H, *J* 8.5, Ar-H), 8.23 (d, 2H, *J* 8.7, Ar-H), 8.11 (d, 2H, *J* 8.1 Ar-H), 8.10 (d, 2H, *J* 8.1, Ar-H), 7.38-7.31 (m, 9H, Ar-H), 7.12 (d, 1H, *J* 2.2, Ar-H), 7.09 (dd, 1H, *J* 8.3, *J* 2.4, Ar-H), 2.70 (t, 4H, *J* 7.7, Ar-CH_2), 2.25 (s, 3H, Ar-CH_3), 1.65 (m, 4H, CH_2), 1.31 (m, 12H, CH_2), 0.88 (t, 6H, *J* 6.8, CH_3). EA, calc. for $C_{47}H_{48}O_8$, 740.88 g/mol:, C 76.19, H 6.53, found: C 75.86, H 6.17.

4.3 Synthesis of compound 2

The non-symmetric compound **2** was prepared analogously to that reported by Kosata et al.[S6] for cyano-substituted twin molecules as shown in Scheme S1.



Scheme S1. Syntheis of compound **2**.

4-Benzyloxy-2-hydroxybenzonitrile A Solution of 4-benzyloxy-2-hydroxybenzaldehyde (10 g, 0.044 mol) in 150 ml ethanol was treated with a concentrated aqueous solution of hydroxylamine hydrochloride (4.6 g, 0.066 mol) followed by slow addition of a concentrated aqueous solution of Na_2CO_3 (6.96 g, 0.066 mol). After stirring for 30 min, the solvent was removed in vacuo, followed by extraction with diethyl ether (4 x 50 ml). The combined organic phases were washed with water (3 x 50 ml) and brine. After drying over Na_2SO_4 the solvent was removed in vacuo to give 10.2 g (96%) of the 4-benzyloxy-2-hydroxybenzaldoxime. The crude product was dissolved in 150 ml acetic anhydride and refluxed for 3 h. The solvent was evaporated followed by extraction with dichloromethane. After washing the combined organic phases with a saturated solution of $NaHCO_3$ (3 x 50 ml) and drying over Na_2SO_4 the solvent is removed in vacuo to give 10.1 g (80%) of the acetylated intermediate. This product was treated with a concentrated aqueous solution of KOH (7.2 g, 0.13 mol) followed by stirring for 3 days at room temperature. After acidification (pH 2) with H_2SO_4 (20 vol%) the solution was extracted with diethyl ether (3 x 50 ml). The combined organic phases were washed with a saturated solution of $NaHCO_3$, water and brine, followed by drying over Na_2SO_4 . After evaporating of the solvent the crude product was purified by flash chromatography (silica gel, $CHCl_3$, R_f: 0.14) to yield 8.52 g

(0.038 mol, 86%) of 4-Benzyloxy-2-hydroxybenzonitrile. Mp.: 141-143 °C. ^{1}H-NMR (CD_3OD, 400 MHz): δ 7.41-7.31 (m, 6H, Ar-H), 6.58 (dd, 1H, *J* 2.3, *J* 8.7, Ar-H), 6.51 (d, 1H, *J* 2.3, Ar-H), 5.09 (s, 2H, OCH_2Ph).

2-Cyano-5-benzyloxyphenyl-4-(4-dodecylbenzoyloxy)benzoate (7) Prepared from 4-Benzyloxy-2-hydroxybenzonitrile (1 g, 4.44 mmol), 4-(4-dodecylbenzoyloxy)benzoic acid (2.01 g, 4.88 mmol), DCC (1.01 g, 4.88 mmol), DMAP (40 mg) in dry CH_2Cl_2 (50 ml), purified by column chromatography (silica gel, $CHCl_3$/PE 4:1, R_f: 0.36) to yield 2.15 g (3.48 mmol, 78%) of the product. Mp.: 81-83 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.30 (d, 2H, *J* 8.7, Ar-H), 8.10 (d, 2H, *J* 8.3 Ar-H), 7.60 (d, 1H, *J* 8.7, Ar-H), 7.40-7.35 (m, 7H, Ar-H), 7.32 (d, 2H, *J* 8.3 Ar-H), 7.09 (d, 1H, *J* 2.3, Ar-H), 6.93 (dd, 1H, *J* 2.5, *J* 8.7, Ar-H), 5.12 (s, 2H, OCH_2Ph), 2.69 (t, 2H, *J* 7.5, Ar-CH_2), 1.65 (m, 2H, CH_2), 1.31-1.25 (m, 18H, CH_2), 0.87 (t, 3H, *J* 7.1, CH_3).

2-Cyano-5-hydroxyphenyl-4-(4-dodecylbenzoyloxy)benzoate (8) A suspension of compound **7** (2.15 g, 3.48 mmol) and Pd/C (10% Pd, 0.3 g) in 80 ml THF was flushed with hydrogen. The mixture was shaked at 45 °C and 3 bar for 48 h, followed by filtration off the catalyst and evaporation of the solvent. The crude product was purified by flash chromatography (silica gel, $CHCl_3$/PE 7:3, $CHCl_3$, $CHCl_3$/EtOH 9:1, R_f: 0.5) to give 2.05 g (3.89 mmol, 70%) of 2-Cyano-5-hydroxyphenyl-4-(4-dodecylbenzoyloxy)benzoate. Mp.: 185-187 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.28 (d, 2H, *J* 8.7, Ar-H), 8.10 (d, 2H, *J* 8.3 Ar-H), 7.53 (d, 1H, *J* 8.5, Ar-H), 7.37 (d, 2H, *J* 8.7 Ar-H), 7.32 (d, 2H, *J* 8.1 Ar-H), 6.94 (d, 1H, *J* 2.3, Ar-H), 6.76 (dd, 1H, *J* 2.3, *J* 8.5, Ar-H), 2.69 (t, 2H, *J* 7.7, Ar-CH_2), 1.65 (m, 2H, CH_2), 1.31-1.25 (m, 18H, CH_2), 0.87 (t, 3H, *J* 7.1, CH_3).

2 Prepared from compound **8** (0.25 g, 0.474 mmol), 4-(4-hexylbenzoyloxy)benzoic acid (0.162 g, 0.5 mmol), DCC (0.24 g, 1.16 mmol), DMAP (30 mg) in dry CH_2Cl_2 (30 ml), purified by column chromatography (silica gel, Hex/EE 9:1, R_f: 0.42), followed by crystallisation from CH_2Cl_2/Ethanol (1:9) to yield 0.06 g (0.072 mmol, 15 %) of the product. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.32 (d, 2H, *J* 8.7, Ar-H), 8.25 (d, 2H, *J* 8.7, Ar-H), 8.10 (d, 2H, *J* 8.3 Ar-H), 8.10 (d, 2H, *J* 8.3, Ar-H), 7.78 (d, 1H, *J* 8.5, Ar-H), 7.52 (d, 1H, *J* 2.3, Ar-H), 7.39 (d, 2H, *J* 8.9, Ar-H), 7.38 (d, 2H, *J* 8.7, Ar-H), 7.33-7.30 (m, 5H, Ar-H), 2.69 (t, 4H, *J* 7.5, Ar-CH_2), 1.65-1.62 (m, 4H, CH_2), 1.31-1.25 (m, 22H, CH_2), 0.86 (t, 6H, *J* 7.1, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 164.45, 164.40, 163.18, 162.80, 155.93, 155.79, 154.74, 153.43, 149.90, 149.84, 133.92, 132.25, 132.00, 130.37, 130.34, 128.78, 128.76, 126.36, 126.31, 125.83, 125.45, 122.35, 122.30, 120.00, 117.39, 114.74, 104.32, 36.26, 32.10, 31.79, 31.23, 31.19, 29.80, 29.77, 29.70, 29.59, 29.48, 29.39, 29.05, 22.84, 22.72, 14.26, 14.21.

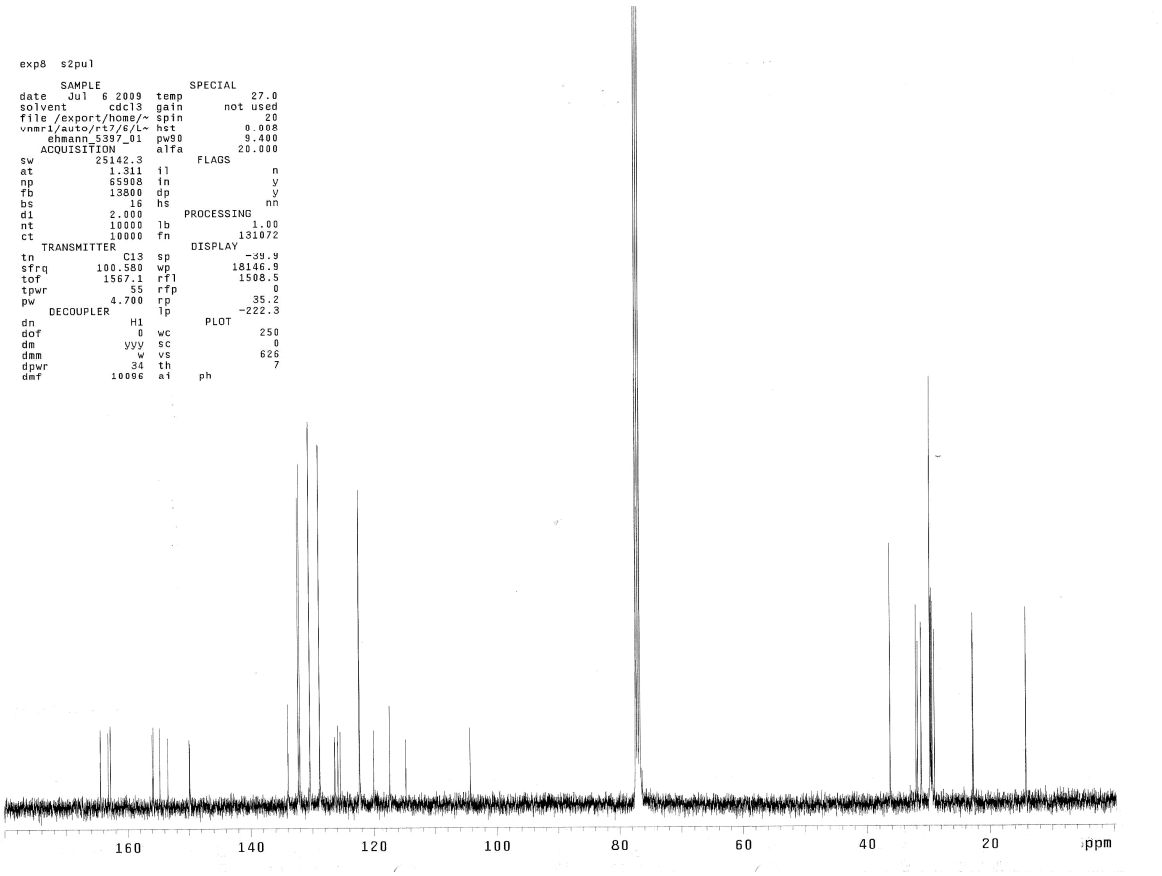


Figure S27. ^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of compound **6/12**.

5. References

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