Supporting Information

X-shaped polyphilics: Liquid crystal honeycombs with single-molecule walls

Robert Kieffer,[a] Marko Prehm,[a,b] Benjamin Glettner,[a] Karsten Pelz,[b] Ute Baumeister,[b] Feng Liu,[c] Xiangbing Zeng,[c] Goran Ungar*,[c] and Carsten Tschierske*,[a]

Martin-Luther-University Halle-Wittenberg, Institute of Chemistry, [a]Organic Chemistry, Kurt-Mothes Str. 2, D-06120 Halle, [b]Physical Chemistry, Mühlpforte 1, D-06108 Halle, Germany; [c]Department of Engineering Materials, University of Sheffield, Mappin Street, Sheffield S1 3JD, Great Britain.

1. Additional Figures and Tables

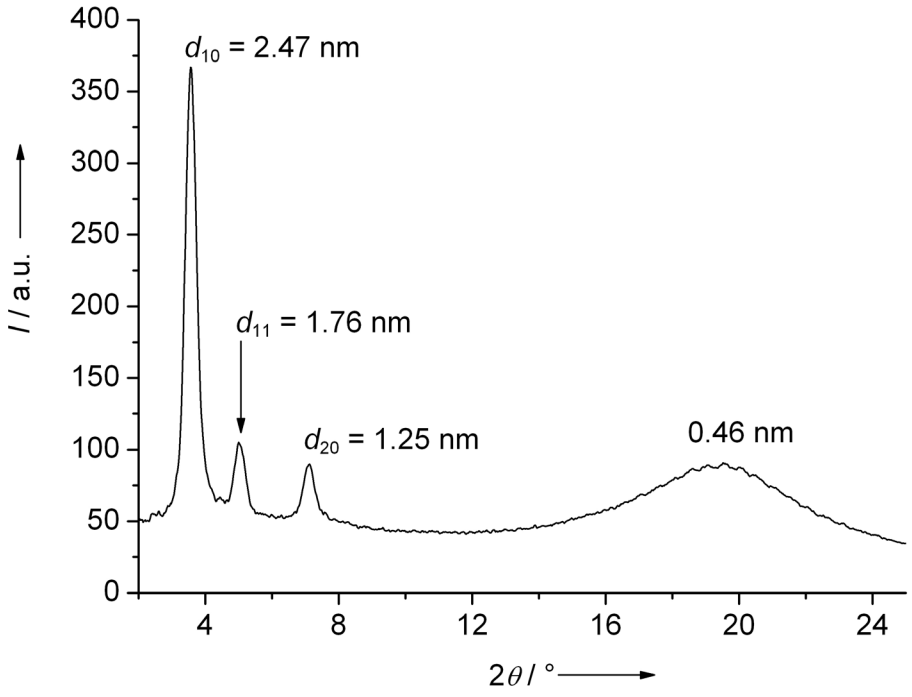


Figure S1. Powder diffraction pattern of the Col_{squ}-phase of **A1** at T = 55 °C with d values for the observed reflections and for the maximum of the diffuse outer scattering.

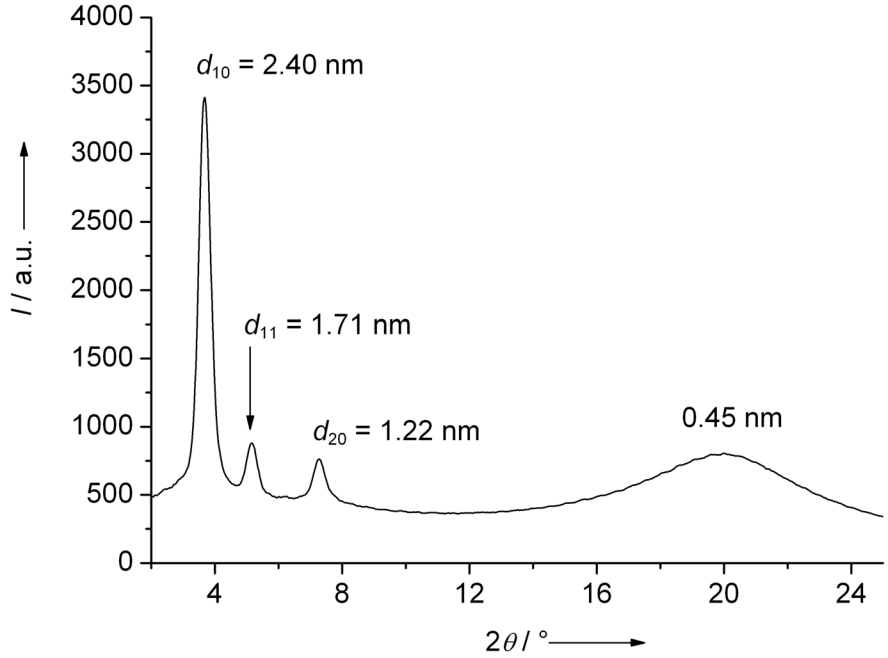


Figure S2. Powder diffraction pattern of the Col_{squ}-phase of **B2** at T = 28 °C with d values for the observed reflections and for the maximum of the diffuse outer scattering.

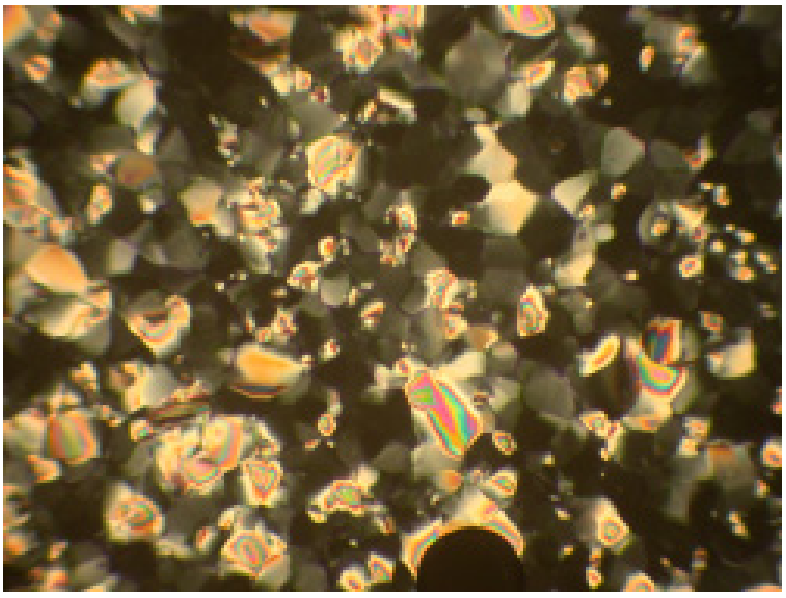


Figure S3: Texture of the Col_{hex}/*p6mm* phase of compound **C2** at T = 80 °C.

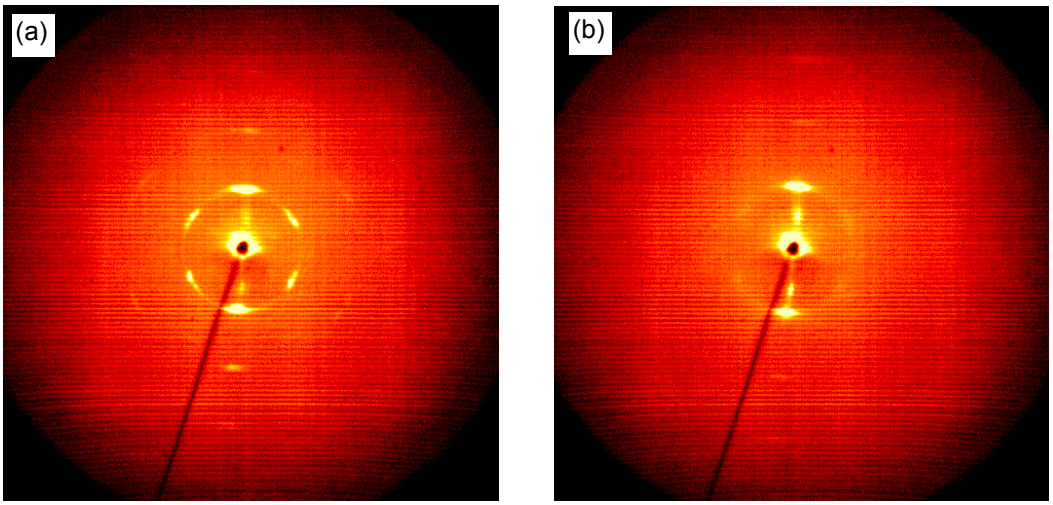


Figure S4. X-ray diffraction patterns (small angle region) obtained from mesophases of the surface-aligned sample **C3**: (a) Col_{hex}/*p6mm*-phase at $T = 81$ °C; (b) Lam_{Iso}-phase at $T = 113$ °C.

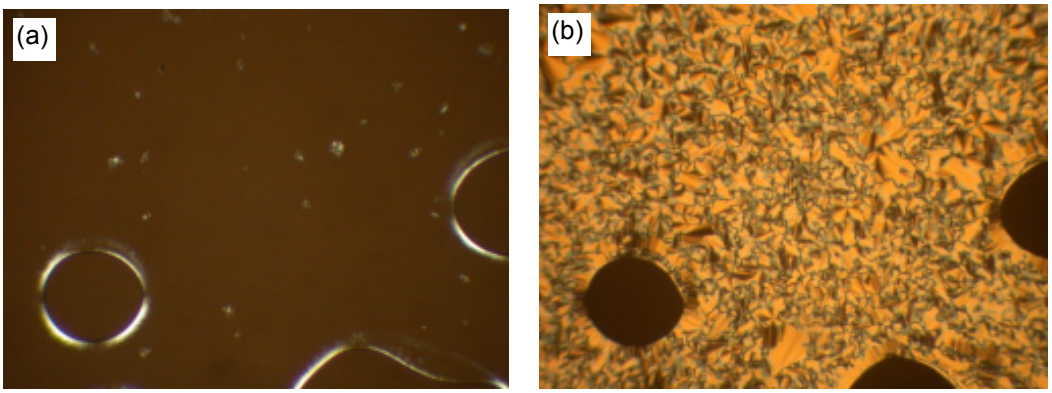


Figure S5. Texture of compound **C3** in the (a) Lam_{Iso} phase at $T = 113$ °C and (b) Col_{hex}/*p6mm* phase at $T = 80$ °C.

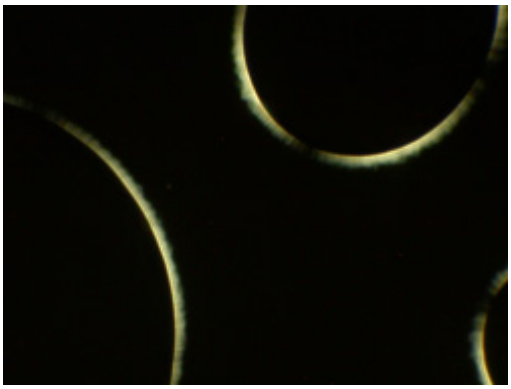


Figure S6. Texture of the Lam_{Iso} phase of compound **C4** at $T = 140$ °C (birefringence is seen only around the air bubbles, the dark area outside the air bubbles is the hometropically aligned Lam_{Iso} phase.

Table S1. Crystallographic data of the LC compounds **A-D** .[a]

Comp.	*T*/°C	Phase plane Group	θ_{obs}/°	d_{obs}/nm	*hk*/*n*	d_{calc}/nm	d_{obs}- d_{calc}/ nm	Parameters used/nm
A1	55	Col_{squ}	1.785	2.47	10	2.48	-0.01	*a* = 2.48
		p4mm	2.515	1.76	11	1.75	0.01	
			3.550	1.25	20	1.24	0.01	
B1	50	Col_{squ}	1.818	2.43	10	2.43	0.00	*a* = 2.43
		p4mm	2.568	1.72	11	1.72	0.00	
			3.620	1.22	20	1.22	0.00	
B2	28	Col_{squ}	1.841	2.40	10	2.42	-0.02	*a* = 2.42
		p4mm	2.578	1.71	11	1.71	0.00	
			3.638	1.22	20	1.21	0.01	
C1	65	Col_{squ}	1.694	2.61	10	2.61	0.00	*a* = 2.61
		p4mm						
C2	67	Col_{hex}	1.320	3.35	10	3.35	0.00	*a* = 3.87
		p6mm	2.635	1.68	20	1.68	0.00	
			3.965	1.11	30	1.12	-0.01	
C3	81	Col_{hex}	1.273	3.47	10	3.47	0.00	*a* = 4.01
		p6mm	2.508	1.76	20	1.74	0.02	
	113	Lam_{Iso}	1.347	3.28	1	3.28	0.00	*d* = 3.28
			2.707	1.63	2	1.64	-0.01	
C4	110	Lam_{Iso}	1.241	3.56	1	3.56	0.00	*d* = 3.56
			2.465	1.79	2	1.78	0.01	
			3.683	1.20	3	1.19	0.01	
D	170	Col_{hex}	1.204	3.67	10	3.67	0.00	*a* = 4.24
		p6mm	2.421	1.82	20	1.84	-0.02	
			3.151	1.40	21	1.39	0.01	
			3.580	1.23	30	1.22	0.01	

[a] (θ_{obs}: experimental scattering angle; d_{obs}: experimental and d_{calc}: calculated d spacing; *hk*/*n*: assigned indices for 2D phases (Col_{squ}, Col_{hex})/ order of reflection for Lam_{Iso} phases, Parameter used: Lattice parameters or *d* values used to calculate d_{calc} with an error of the calculated parameters in the order of 0.1 nm).

Table S2. Transition temperatures (*T*/°C), transition enthalpy values (ΔH/kJ mol^{-1}, lower lines in italics), calculation of molecular volume (V_{mol}), volume of the hypothetical unit cell (V_{cell}) and number of molecules in these unit cells (n_{cell}) and in the walls separating the columns (n_{wall}).[a]

Comp.	*T* /°C [ΔH /kJ/mol]	*a,d*/ nm	A_{cell}/ nm^2	V_{cell}/ nm^3	V_{mol}/ nm^3	$n_{cell,cr}$	$n_{cell,liq}$	n_{cell}	n_{wall}	f_R
A1	Cr 86 (Col_{squ} 64) Iso *42.4 1.2*	2.48	6.15	2.77	1.13	2.45	1.93	2.19	1.09	0.54
B1	Cr 58 Col_{squ} 67 Iso *21.2 3.8*	2.43	5.90	2.66	1.08	2.46	1.93	2.20	1.10	0.52
B2	Cr_1 46 Cr_2 90 (Col_{squ} 37) Iso *24.4 37.5 2.4*	2.42	5.86	2.64	1.08	2.44	1.92	2.18	1.09	0.52
C1	Cr 64 Col_{squ} 92 Iso *10.0 3.9*	2.61	6.81	3.07	1.13	2.70	2.12	2.41	1.20	0.54
C2	Cr 79 Col_{hex} 98 Iso *1.5 3.2*	3.87	12.97	5.84	1.28	4.55	3.57	4.06	1.35	0.59
C3	Cr 44 Col_{hex} 106 Lam_{Iso} 116 Iso *5.6 0.7 1.3*	4.01 3.28[b]	13.93	6.27	1.43	4.38	3.45	3.91	1.30	0.64
C4	Cr 71 Lam_{Iso} 158 Iso *0.8 2.8*	3.56								0.69
D	Cr 87 Col_{hex} 229 Iso *9.3 10.7*	4.24	15.57	7.01	0.973	7.20	5.66	6.43	2.14	0.47

[a] V_{cell} = volume of the unit cell defined by the dimensions *a* x *b* x 0.45 nm for rectangular phases and $a^2\sin(60°)$ x 0.45 nm for hexagonal phases; V_{mol} = volume for a single molecule as calculated using the crystal volume increments;[S1] $n_{cell,cr}$ = number of molecules in the unit cell, calculated according to $n_{cell} = V_{cell}/V_{mol}$ (average packing coefficient in the crystal is $k = 0.7$;[S2] $n_{cell,liq}$ = number of molecules in the unit cell of an isotropic liquid with an average packing coefficient $k = 0.55$, calculated according to $n_{cell,liq} = 0.55/0.7 \times n_{cell,cr}$; n_{cell} = number of molecules in the unit cell in the LC phase estimated as the average of that in the $n_{cell,cr}$ and $n_{cell,liq}$; n_{wall} = number of molecules in the cross section of the cylinder walls as calculated from n_{cell}; f_R = volume fraction of the lateral chains (calculated using crystal volume increments[1]); [b] *d*-value of the Lam_{Iso} phase.

2. Conditions for X-ray scattering

2.1 X-ray scattering on powder-like and aligned samples

X-ray investigations on powder samples were carried out with a Guinier film camera (Huber), samples in glass capillaries (∅ 1 mm) in a temperature-controlled heating stage, quartz-monochromatized CuK_α radiation, 30 to 60 min exposure time, calibration with the powder pattern of $Pb(NO_3)_2$. Aligned samples were obtained on a glass plate. Alignment was achieved upon slow cooling (rate: 1 K·min^{-1} – 0.01 K·min^{-1}) of a small droplet of the sample and takes place at the sample–glass or at the sample–air interface, with domains fiber-like disordered

around an axis perpendicular to the interface. The aligned samples were held on a temperature-controlled heating stage and the diffraction patterns were recorded with a 2D detector (HI-STAR, Siemens).

2.2 Synchrotron X-ray diffraction and electron density reconstruction

High-resolution small-angle powder diffraction experiments were recorded at Beamline ID02 of the European Synchrotron Radiation Facility. Samples were held in evacuated 1 mm capillaries. A modified Linkam hot stage was used, with a hole for the capillary drilled through the silver heating block and mica windows attached to it on each side. CCD detectors were used simultaneously for both small and wide angle scattering, Q calibration and linearization were verified using silver behenate. Diffraction intensities were Lorentz and multiplicity corrected. Fourier reconstruction of the electron density is carried out using the general formula for columnar phases (2-dimensional order):

$$\rho(xy) = \Sigma_{hk} F(hk) \exp[2\pi i(hx+ky)] = \Sigma_{hk} \sqrt{I(hk)} \exp[2\pi i(hx+ky) + i\phi(hk)]$$

Here $\phi(hk)$ is the phase of the (hk) reflection and I is the corrected intensity.

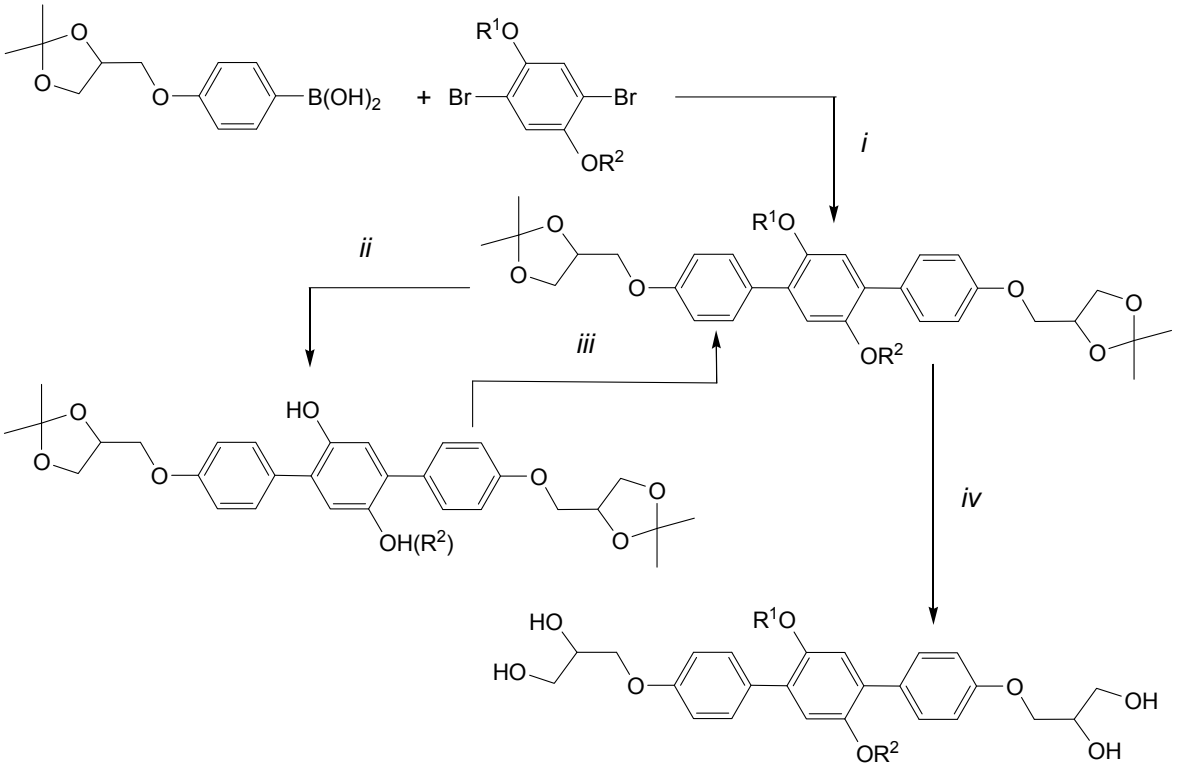
Table S3. d-spacings, (d_{obs} = experimental, d_{calc} = calculated) intensities and phases of reflections used to reconstruct the electron densities for the $Col_{squ}/p4mm$ phase of compound **B1** at T = 50 ^{o}C; all intensities values are Lorentz corrected with correction for multiplicity.

(hk)	$d_{obs.}$ –spacing/nm	$d_{cal.}$ –spacing/nm	*intensity*	*phase*
(10)	2.43	2.43	100.0	π
(11)	1.72	1.72	26.2	π
(20)	1.22	1.22	34.5	0
a = 2.43 nm				

3. Molecular dynamics simulation

Annealing dynamics runs were carried out using the Universal Force Field (Material Studio, Accelrys). The structure in Figure 2c was obtained with two molecules in a square prism box with the side equal to the unit cell length and a height of 0.45nm, with 3d periodic boundary conditions. 30 temperature cycles of NVT dynamics were run between 300 and 500 K, with a total annealing time of 30 ps.

4. Synthesis and analytical data



Scheme S1. Synthesis of compounds **A-C**: *Reagents and conditions*: *i*) $Pd[PPh_3]_4$, $NaHCO_3$, glyme, H_2O, reflux[S3] (R^1 = Bn or *n*-alkyl; R^2 = Bn or *n*-alkyl); *ii*) for R^1 = Bn, R^2 = *n*-alkyl or for R^1, R^2 = Bn: H_2, Pd/C, EtOAc, 3.2 bar, 45 °C (R^2 = *n*-alkyl); *iii*) RBr (R = *n*-alkyl or $-(CH_2)_6-C_nF_{2n+1}$), K_2CO_3, DMF, 80 °C, 8 h (R^1, R^2 = *n*-alkyl or R^1, R^2 = $-(CH_2)_6-C_nF_{2n+1}$); *iv*) 10 % HCl, MeOH, reflux, 6h (R^1, R^2 = *n*-alkyl or R^1, R^2 = $-(CH_2)_6-C_nF_{2n+1}$).

4.1 Compounds A

4,4´´-Bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2',5'-didodecyloxy-p-terphenyl: A mixture of 1,4-didodecyloxy-2,5-dibromobenzene[S4] (130 mg, 0.22 mmol), 4-(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)benzeneboronic acid[S5] (120 mg, 0.47 mmol), $Pd(PPh_3)_4$ (10 mg, 0.009 mmol), glyme (30 ml) and saturated $NaHCO_3$ solution (30 ml) was refluxed for 10 h under an argon atmosphere. After cooling to room temperature, the solvent was evaporated and the residue was dissolved in $CHCl_3$ (150 ml). The resulting solution was filtered through a plug of silica gel and then washed with water and brine (100 ml each). After separation and drying over Na_2SO_4 the solvent was evaporated. The product was purified by column chromatography with $CHCl_3$ as solvent (R_F = 0.77, eluent: $CHCl_3$/MeOH = 10:0.1, v/v). Yield: 97 mg (52.5 %); colourless solid; mp: 78-82 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, ^3J = 8.7 Hz, 4H, Ar-H), 6.94 (d, ^3J = 8.7 Hz, 4H, Ar-H), 6.91 (s, 2H, Ar-H), 4.52-4.46 (m, 2H, OCH), 4.19-4.15 (m, 2H, OCH_2), 4.11-4.08 (m, 2H, OCH_2), 3.99-3.89 (m, 4H, OCH_2), 3.87 (t, ^3J = 6.5 Hz, 4H, OCH_2), 1.69-1.56 (m, 4H, $OCH_2\mathbf{CH_2}$), 1.46 (s, 6H, CH_3), 1.40 (s, 6H, CH_3), 1.35-1.23 (m, 36H, CH_2), 0.86 (t, ^3J = 6.9 Hz, 6H, CH_3).

A1: A mixture of 4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2',5'-didodecyloxy-p-terphenyl (92 mg, 0.11 mmol) and 10% HCl (10 ml) in MeOH (50 ml) was refluxed for 6 h. After cooling to room temperature, the solvent was evaporated and the residue was dissolved in EtOAc (100 ml). The organic phase was washed with saturated $NaHCO_3$ solution (2x 50 ml), water and brine (50 ml each). After drying over Na_2SO_4 the solvent was evaporated. The crude product was purified by crystallisation from MeOH. Yield: 65 mg (77.9 %); colourless solid; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.54 (d, ^3J = 8.9 Hz, 4H, Ar-H), 6.99 (s, 2H, Ar-H), 6.97 (d, ^3J = 8.9 Hz, 4H, Ar-H), 4.14-4.07 (m, 4H, OCH, OCH_2), 4.04-3.99 (m, 4H, OCH_2), 3.94 (t, ^3J = 6.3 Hz, 4H, OCH_2) 3.78-3.63 (m, 6H, OCH_2, OH), 1.70-1.63 (m, 4H, $OCH_2\mathbf{CH_2}$), 1.41-1.37 (m, 4H, $OCH_2CH_2\mathbf{CH_2}$),1.26-1.21 (m, 32H, CH_2), 0.86 (t, ^3J = 6.9 Hz, 6H, CH_3); ^{13}C-NMR (100 MHz, acetone-d_6): δ = 158.95 (2C), 151.06 (2C), 131.76 (2C), 131.20 (4C), 130.69 (2C), 116.76 (4C), 114.74 (2C), 71.42 (2C), 71.31 (2C), 70.44, 70.07 (OCH_2), 64.22, 64.09 (2C), 32.63, 30.40, 30.36, 30.33, 30.31, 30.24, 26.86, 23.33 (CH_2), 14.36 (CH_3); anal. calcd. for $C_{48}H_{74}O_8$: C 74.00, H 9.57; found: C 73.91, H 9.67.

A2: Synthesized and purified in an analogues way as **A1** from 4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2',5'-ditetradecyloxy-p-terphenyl (200 mg, 0.22 mmol). Yield: 151 mg (82.7 %), colourless solid; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.54 (d, ^3J = 8.7 Hz, 4H, Ar-H), 6.99 (s, 2H, Ar-H), 6.97 (d, ^3J = 8.7 Hz, 4H, Ar-H), 4.12-4.08 (m, 4H, OCH, OCH_2), 4.07-3.99 (m, 4H, OCH_2), 3.94 (t, ^3J = 6.4 Hz, 4H, OCH_2) 3.77-3.64 (m, 6H, OCH_2, OH), 1.70-1.63 (m, 4H, $OCH_2\mathbf{CH_2}$), 1.41-1.36 (m, 4H, $OCH_2CH_2\mathbf{CH_2}$),1.32-1.22 (m, 40H, CH_2), 0.86 (t, ^3J = 6.7 Hz, 6H, CH_3); ^{13}C-NMR (100 MHz, acetone-d_6): δ = 158.95 (2C), 151.06 (2C), 131.75 (2C), 131.20 (4C), 130.69 (2C), 116.75 (4C), 114.74 (2C), 71.42 (2C), 71.30 (2C), 70.44, 70.07 (OCH_2), 64.21, 64.08 (2C), 32.63, 30.35, 30.32, 30.30, 30.23, 26.86, 23.33 (CH_2), 14.36 (CH_3); anal. calcd. for $C_{52}H_{82}O_8$: C 74.78, H 9.90; found: C 74.76, H 9.96.

A3: Synthesized and purified in an analogues way as **A1** from 4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2',5'-dihexadecyloxy-p-terphenyl (135 mg, 0.14 mmol). Yield: 103 mg (83.2 %), colourless solid; mp.: 71°C; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.54 (d, ^3J = 8.7 Hz, 4H, Ar-H), 6.99 (s, 2H, Ar-H), 6.97 (d, ^3J = 8.7 Hz, 4H, Ar-H), 4.14-3.99 (m, 8H, OCH, OCH_2), 3.94 (t, ^3J = 6.3 Hz, 4H, OCH_2) 3.76-3.63 (m, 6H, OCH_2, OH), 1.70-1.63 (m, 4H, $OCH_2\mathbf{CH_2}$), 1.41-1.37 (m, 4H, $OCH_2CH_2\mathbf{CH_2}$), 1.35-1.22 (m, 48H, CH_2), 0.86 (t, ^3J = 6.7 Hz, 6H, CH_3); ^{13}C-NMR (100 MHz, acetone-d_6): δ = 158.95 (2C), 151.06 (2C), 131.75 (2C), 131.20 (4C), 130.68 (2C), 116.75 (4C), 114.74 (2C), 71.42 (2C), 71.30 (2C), 70.44, 70.07 (OCH_2), 64.21, 64.09 (2C), 32.63, 30.40, 30.32, 30.30, 30.24, 30.06, 26.86, 23.32 (CH_2), 14.35 (CH_3); anal. calcd. for $C_{56}H_{90}O_8$: C 75.46, H 10.18; found: C 75.25, H 10.22.

A4: Synthesized and purified in an analogues way as **A1** from 4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2',5'-dioctadecyloxy-p-terphenyl (250 mg, 0.24 mmol). Yield: 170 mg (73.8 %), colourless solid; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.54 (d, ^3J = 8.9 Hz, 4H, Ar-H), 6.99 (s, 2H, Ar-H), 6.97 (d, ^3J = 8.7 Hz, 4H, Ar-H), 4.12-3.99 (m, 8H, OCH, OCH_2), 3.94 (t, ^3J = 6.3 Hz, 4H, OCH_2) 3.75-3.64 (m, 6H, OCH_2, OH), 1.70-1.64 (m, 4H, $OCH_2\mathbf{CH_2}$), 1.41-1.37 (m, 4H, $OCH_2CH_2\mathbf{CH_2}$), 1.35-1.22 (m, 56H, CH_2), 0.86 (t, ^3J = 6.9 Hz, 6H, CH_3); ^{13}C-NMR (100 MHz, acetone-d_6): δ = 158.95 (2C), 151.06 (2C), 131.76 (2C), 131.20 (4C), 130.69 (2C), 116.75 (4C), 114.74 (2C), 71.42 (2C), 71.30 (2C), 70.44, 70.07 (OCH_2), 64.21, 64.09 (2C), 32.63, 30.40, 30.36, 30.33, 30.30, 30.24, 30.06, 26.86, 23.33 (CH_2), 14.36 (CH_3); anal. calcd. for $C_{60}H_{98}O_8$: C 76.06, H 10.43; found.: C 75.77, H 10.24.

4.2 Compounds B

4,4´´-Bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2'-tetradecyloxy-5'-octyloxy-p-terphenyl: Synthesized and purified in an analogues way as 4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2',5'-didodecyloxy-p-terphenyl from 1-tetradecyloxy-4-octyloxy-2,5-dibromo-benzene[S6] (700 mg, 1.29 mmol), 4-(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)benzeneboronic acid (713 mg, 2.83 mmol), $Pd(PPh_3)_4$ (75 mg, 0.065 mmol), glyme (50 ml), saturated $NaHCO_3$ solution (50 ml). Yield: 448 mg (41.9 %), colourless solid; mp: 70-73 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, ^3J = 8.7 Hz, 4H, Ar-H), 6.94 (d, ^3J = 8.7 Hz, 4H, Ar-H), 6.92 (s, 2H, Ar-H), 4.53-4.47 (m, 2H, OCH), 4.20-4.16 (m, 2H, OCH_2), 4.12-4.08 (m, 2H, OCH_2), 3.99-3.86 (m, 8H, OCH_2), 1.69-1.63 (m, 4H, $OCH_2\mathbf{CH_2}$), 1.47 (s, 6H, CH_3), 1.41 (s, 6H, CH_3), 1.36-1.24 (m, 32H, CH_2), 0.87 (t, ^3J = 6.9 Hz, 6H, CH_3).

B1: Synthesized and purified in an analogues way as **A1** from 4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2'-tetradecyloxy-5'-octyloxy-p-terphenyl (350 mg, 0.42 mmol). Yield: 284 mg (89.8 %), colourless solid; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.54 (d, ^3J = 8.7 Hz, 4H, Ar-H), 6.99 (s, 2H, Ar-H), 6.98 (d, ^3J = 8.9 Hz, 4H, Ar-H), 4.14-4.07 (m, 4H, OCH, OCH_2), 4.04-3.97 (m, 4H, OCH_2), 3.94 (t, ^3J = 6.4 Hz, 4H, OCH_2) 3.77-3.63 (m, 6H, OCH_2, OH), 1.70-1.63 (m, 4H, $OCH_2\mathbf{CH_2}$), 1.41-1.37 (m, 4H, $OCH_2CH_2\mathbf{CH_2}$),1.35-1.23 (m, 28H, CH_2), 0.87-0.84 (m, 6H, CH_3); ^{13}C-NMR (100 MHz, acetone-d_6): δ = 158.94 (2C), 151.05 (2C), 131.74 (2C), 131.19 (4C), 130.67 (2C), 116.73 (4C), 114.72 (2C), 71.41 (2C), 71.29 (2C), 70.43, 70.06 (OCH_2), 64.21, 64.08 (2C), 32.62, 32.52, 30.34, 30.32, 30.29, 30.23, 30.05, 26.86, 23.30 (CH_2), 14.37, 14.35 (CH_3); anal. calcd. for $C_{46}H_{70}O_8$: C 73.56, H 9.39; found: C 73.53, H 9.36.

5'-Benzyloxy-4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2'-hexadecyloxy-p-terphenyl: Synthesized and purified in an analogues way as 4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2',5'-didodecyloxy-p-terphenyl from 4-benzyloxy-2,5-dibromo-1-hexadecyloxybenzene[S7] (1.45 g, 2.49 mmol), 4-(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-benzene boronic acid (1.38 g, 5.48 mmol), $Pd(PPh_3)_4$ (89 mg, 0.076 mmol), glyme (50 ml), saturated $NaHCO_3$ solution (30 ml). Yield: 1.63 g (78.2 %); colourless solid; mp: 85 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, ^3J = 8.9 Hz, 2H, Ar-H), 7.48 (d, ^3J = 8.9 Hz, 2H, Ar-H), 7.30-7.26 (m, 5H, Ar-H), 6.99 (s, 1H, Ar-H), 6.96-6.92 (m, 5H, Ar-H), 4.96 (s, 2H, Ph-CH_2), 4.52-4.48 (m, 2H, OCH), 4.20-4.16 (m, 2H, OCH_2), 4.12-4.08 (m, 2H, OCH_2), 4.00-3.95 (m, 2H, OCH_2), 3.94-3.87 (m, 4H, OCH_2), 1.69-1.65 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.47 (s, 6H, CH_3), 1.41 (s, 6H, CH_3), 1.36-1.24 (m, 26H, CH_2), 0.86 (t, ^3J = 6.9 Hz, 3H, CH_3).

4,4´´-Bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-5'-hexadecyloxy-p-terphenyl-2'-ol: 5'-benzyloxy-4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2'-hexadecyloxy-p-terphenyl (820 mg, 0.98 mmol) was dissolved in EtOAc (50 ml) under an Ar atmosphere. Pd/C (0.1g, 10 % Pd) was added and after rinsing with H_2 (3x) the hydrogen pressure was set to 3.2 bar and the temperature was set to 45 °C. After 6 h the solution was filtered and the filtrate was washed with hot EtOAc (200 ml). Finally the solvent was evaporated. Yield: 635 mg (86.8 %); colourless solid; mp: 78 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, ^3J = 8.9 Hz, 2H, Ar-H), 7.42 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.02 (d, ^3J = 8.7 Hz, 2H, Ar-H), 6.93 (s, 1H, Ar-H, overlapped by $CHCl_3$), 6.93 (d, ^3J = 8.7 Hz, 2H, Ar-H), 6.81 (s, 1H, Ar-H), 4.53-4.46 (m, 2H, OCH), 4.20-4.15 (m, 2H, OCH_2), 4.12-4.08 (m, 2H, OCH_2), 4.00-3.95 (m, 2H, OCH_2), 3.93-3.90 (m, 2H, OCH_2), 3.84 (t,

^3J = 6.5 Hz, 2H, OCH_2), 1.69-1.62 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.47 (s, 6H, CH_3), 1.40 (s, 6H, CH_3), 1.35-1.24 (m, 26H, CH_2), 0.86 (t, ^3J = 6.9 Hz, 3H, CH_3).

4,4´´-Bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2'-hexadecyloxy-5'-hexyloxy-p-terphenyl: A solution of 4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-5'-hexadecyloxy-p-terphenyl-2'-ol (150 mg, 0.2 mmol), 1-bromohexane (37 mg, 0.22 mmol), K_2CO_3 (280 mg, 2 mmol), Bu_4NI (20 mg) in dry DMF (40 ml) was heated to 80 °C for 8 hours under an Ar atmosphere. After cooling to room temperature water (100 ml) was added and the mixture was extracted with EtOAc (3x 70 ml). The combined organic phases were washed with a saturated LiCl solution (2x 50 ml), water and brine (50 ml each). After drying over Na_2SO_4 the solvent was evaporated. The crude product was purified by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$). Yield: 158 mg (94.7 %); colourless solid; mp: 71-75 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, ^3J = 8.7 Hz, 4H, Ar-H), 6.94 (d, ^3J = 8.7 Hz, 4H, Ar-H), 6.91 (s, 2H, Ar-H), 4.52-4.46 (m, 2H, OCH), 4.19-4.16 (m, 2H, OCH_2), 4.12-4.08 (m, 2H, OCH_2), 3.99-3.90 (m, 4H, OCH_2), 3.87 (t, ^3J = 6.5 Hz, 4H, CH_3), 1.69-1.62 (m, 4H, $OCH_2\mathbf{CH_2}$), 1.47 (s, 6H, CH_3), 1.40 (s, 6H, CH_3), 1.38-1.24 (m, 32H, CH_2), 0.88-0.83 (m, 6H, CH_3).

B2: Synthesized and purified in an analogues way as **A1** from 4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2'-hexadecyloxy-5'-hexyloxy-p-terphenyl (157 mg, 0.19 mmol). Yield: 115 mg (81.1 %), colourless solid; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.54 (d, ^3J = 8.1 Hz, 4H, Ar-H), 6.99 (s, 2H, Ar-H), 6.97 (d, ^3J = 8.7 Hz, 4H, Ar-H), 4.14-4.07 (m, 4H, OCH, OCH_2), 4.04-3.97 (m, 4H, OCH_2), 3.94 (t, ^3J = 6.4 Hz, 4H, OCH_2) 3.77-3.63 (m, 6H, OCH_2, OH), 1.70-1.63 (m, 4H, $OCH_2\mathbf{CH_2}$), 1.43-1.35 (m, 4H, $OCH_2CH_2\mathbf{CH_2}$), 1.31-1.22 (m, 28H, CH_2), 0.87-0.84 (m, 6H, CH_3); ^{13}C-NMR (100 MHz, acetone-d_6): δ = 158.94 (2C), 151.05 (2C), 131.74 (2C), 131.19 (4C), 130.67 (2C), 116.73 (4C), 114.72 (2C), 71.40 (2C), 71.29 (2C), 70.42, 70.05 (OCH_2), 64.19, 64.07 (2C), 32.62, 32.23, 30.34, 30.32, 30.29, 30.05, 26.86, 26.55, 23.32, 23.27 (CH_2), 14.35, 14.29 (CH_3); anal. calcd. for $C_{46}H_{70}O_8$: C 73.56, H 9.39; found: C 73.35, H 9.56.

B3: Synthesized and purified in an analogues way as **A1** from 4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-5'-butyloxy-2'-octadecyloxy-p-terphenyl (150 mg, 0.18 mmol). Yield: 105 mg (77.5 %), colourless solid; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.54 (d, ^3J = 8.7 Hz, 4H, Ar-H), 6.99 (s, 2H, Ar-H), 6.97 (d, ^3J = 8.9 Hz, 4H, Ar-H), 4.14-3.99 (m, 8H, OCH, OCH_2), 3.97-3.93 (m, 4H, OCH_2), 3.77-3.63 (m, 6H, OCH_2, OH), 1.70-1.62 (m, 4H, $OCH_2\mathbf{CH_2}$), 1.46-1.36 (m, 4H, $OCH_2CH_2\mathbf{CH_2}$), 1.27-1.21 (m, 28H, CH_2), 0.90-0.84 (m, 6H, CH_3);^{13}C-NMR (100 MHz, acetone-d_6): δ = 158.93 (2C), 151.03 (2C), 131.72 (2C), 131.18 (4C), 130.64 (2C), 116.68 (4C), 114.72 (2C), 71.40 (2C), 71.29 (2C), 70.41, 70.05 (OCH_2), 69.74, 64.18, 64.05 (2C), 32.62, 32.35, 30.34, 30.32, 30.29, 30.22, 30.04, 26.85, 23.31, 19.99 (CH_2), 14.35, 14.09 (CH_3); anal. calcd. for $C_{46}H_{70}O_8$: C 73.56, H 9.39; found: C 73.31, H 9.42.

4.3 Compounds C

4,4´´-Bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2',5'-dibenzyloxy-p-terphenyl:
Synthesized and purified in an analogues way as 4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2',5'-didodecyloxy-p-terphenyl from 1,4-dibenzyloxy-2,5-dibromobenzene[S8] (3.0 g, 6.7 mmol) and 4-(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)benzeneboronic acid (3.71 g, 14.7 mmol), $Pd(PPh_3)_4$ (230 mg, 0.2 mmol), glyme (100 ml), saturated $NaHCO_3$ solution (100 ml). Yield: 2.65 g (56.3 %), colourless solid; mp: 143-146 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, ^3J = 8.7 Hz, 4H, Ar-H), 7.33-7.25 (m, 10H, Ar-H), 7.01 (s, 2H, Ar-H), 6.95 (d, ^3J = 8.7 Hz,

4H, Ar-H), 4.99 (s, 4H, Ph-CH_2), 4.53-4.47 (m, 2H, OCH), 4.20-4.16 (m, 2H, OCH_2), 4.12-4.08 (m, 2H, OCH_2), 4.00-3.90 (m, 4H, OCH_2), 1.47 (s, 6H, CH_3), 1.41 (s, 6H, CH_3).

4,4´´-Bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-p-terphenyl-2',5'-diol: Synthesized and purified in an analogues way as 4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-5'-hexadecyloxy-p-terphenyl-2'-ol from 4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2',5'-dibenzyloxy-p-terphenyl (1.5 g, 2.1 mmol), Pd/C (10% Pd, 200 mg), in EtOAc (100 ml). Yield: 0.78 g (69.9 %), orange solid, mp: 201-205 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, ^3J = 8.5 Hz, 4H, Ar-H), 7.02 (d, ^3J = 8.5 Hz, 4H, Ar-H), 6.83 (s, 2H, Ar-H), 4.84 (s, 2H, OH), 4.52-4.47 (m, 2H, OCH), 4.20-4.16 (m, 2H, OCH_2), 4.11-4.08 (m, 2H, OCH_2), 4.00-3.96 (m, 2H, OCH_2), 3.93-3.90 (m, 2H, OCH_2), 1.47 (s, 6H, CH_3), 1.40 (s, 6H, CH_3).

4,4´´-Bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2',5'-bis(7,7,8,8,9,9,10,10,10-nonafluorodecyloxy)-p-terphenyl: Synthesized and purified in an analogues way as 4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2'-hexadecyloxy-5'-hexyloxy-p-terphenyl from 4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-p-terphenyl-2',5'-diol (150 mg, 0.29 mmol), 10-bromo-1,1,1,2,2,3,3,4,4-nonafluorodecane (231 mg, 0.6 mmol), K_2CO_3 (400 mg, 2.9 mmol), Bu_4NI (100 mg), DMF (50 ml). Yield: 190 mg (58.7 %), colourless solid, mp: 97-99 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.49 (d, ^3J = 8.9 Hz, 4H, Ar-H), 6.94 (d, ^3J = 8.9 Hz, 4H, Ar-H), 6.91 (s, 2H, Ar-H), 4.50-4.46 (m, 2H, OCH), 4.18-4.15 (m, 2H, OCH_2), 4.10-4.07 (m, 2H, OCH_2), 3.98-3.87 (m, 8H, OCH_2), 2.03-1.95 (m, 4H, $\mathbf{CH_2}CF_2$), 1.70-1.65 (m, 4H, $OCH_2\mathbf{CH_2}$), 1.57-1.51 (m, 4H, $OCH_2CH_2\mathbf{CH_2}$), 1.46 (s, 6H, CH_3), 1.40-1.24 (m, 14H, CH_2, CH_3); ^{19}F-NMR (188 MHz, $CDCl_3$): δ = -81.49 (t, ^3J = 9.9 Hz, 6F, CF_3), -114.88-(-115.04) (m, 4F, CH_2CF_2), -124.83-(-124.88) (m, 4F, CF_2), -126.39-(-126.50) (m, 4F, $\mathbf{CF_2}CF_3$).

C1: Synthesized in an analogues way as **A1** from 4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2',5'-bis(7,7,8,8,9,9,10,10,10-nonafluorodecyl-oxy)-p-terphenyl (188 mg, 0.17 mmol). Purification: preparative centrifugal thin layer chromatography (eluents: $CHCl_3$/MeOH = 10:0.3, v/v). Yield: 138 mg (79.0 %), colourless solid; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.54 (d, ^3J = 8.7 Hz, 4H, Ar-H), 6.99 (s, 2H, Ar-H), 6.98 (d, ^3J = 8.7 Hz, 4H, Ar-H), 4.15-4.08 (m, 2H, OCH), 4.04-3.96 (m, 10H, OCH, OCH_2), 3.73-3.62 (m, 6H, OCH_2, OH), 2.24-2.11 (m, 4H, CH_2CF_2), 1.74-1.67 (m, 4H, $OCH_2\mathbf{CH_2}$), 1.63-1.55 (m, 4H, $\mathbf{CH_2}CH_2CF_2$), 1.51-1.42 (m, 8H, CH_2); ^{13}C-NMR (100 MHz, acetone-d_6): δ = 159.03 (2C), 151.08 (2C), 131.74 (2C), 131.22 (4C), 130.79 (2C), 116.83 (4C), 114.76 (2C), 71.43 (2C), 71.32 (2C), 70.45, 69.97 (OCH_2), 64.20, 64.08 (2C), 31.43, 31.21, 30.99, 30.43, 30.24, 30.05, 29.85, 29.32, 26.54, 20.91 (CH_2); ^{19}F-NMR (188 MHz, acetone-d_6): δ = -82.36 (t, ^3J = 9.9 Hz, 6F, CF_3), -115.30 (s, 4F, CH_2CF_2), -125.36 (s, 4F, CF_2), -127.03-(-127.15) (m, 4F, $\mathbf{CF_2}CF_3$); anal. calcd. for $C_{44}H_{48}F_{18}O_8$*0.25 H_2O : C 50.27, H 4.65; found: C 50.46, H 4.98.

C2: Synthesized in an analogues way as **A1** from 4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2',5'-bis(7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluorododecyloxy)-p-terphenyl (170 mg, 0.13 mmol). Purification: preparative centrifugal thin layer chromatography (eluents: $CHCl_3$/MeOH = 10:0.3, v/v). Yield: 107 mg (67.0 %), colourless solid; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.55 (d, ^3J = 8.7 Hz, 4H, Ar-H), 7.01 (s, 2H, Ar-H), 6.99 (d, ^3J = 8.7 Hz, 4H, Ar-H), 4.12-4.10 (m, 2H, OCH), 4.04-3.97 (m, 10H, OCH, OCH_2), 3.72-3.67 (m, 6H, OCH_2, OH), 2.26-2.13 (m, 4H, CH_2CF_2), 1.74-1.70 (m, 4H, $OCH_2\mathbf{CH_2}$), 1.62-1.58 (m, 4H, $\mathbf{CH_2}CH_2CF_2$), 1.47-1.44 (m, 8H, CH_2); ^{13}C-NMR (100 MHz, acetone-d_6): δ = 159.03 (2C), 151.08 (2C), 131.74 (2C), 131.23 (4C), 130.78 (2C), 116.83 (4C), 114.76 (2C), 71.43 (4C), 70.44, 69.97 (OCH_2),

64.20 (2C), 31.53, 31.32, 31.10, 30.24, 30.04, 29.34, 26.54, 20.95 (CH_2); ^{19}F-NMR (188 MHz, acetone-d_6): δ = -82.12 (t, ^3J = 9.3 Hz, 6F, CF_3), -114.89-(-115.22) (m, 4F, CH_2CF_2), -122.86 (s, 4F, CF_2), -123.83 (s, 4F, CF_2), -124.40 (s, 4F, CF_2), -127.06-(-127.25) (m, 4F, $\mathbf{CF_2}CF_3$); anal. calcd. for $C_{48}H_{48}F_{26}O_8$: C 46.24, H 3.88; found.: C 46.01, H 3.95.

C3: Synthesized and purified in an analogues way as **A1** from 4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2',5'-bis(7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluorotetradecyloxy)-p-terphenyl (146 mg, 0.10 mmol). Yield: 127 mg (91.8 %), colourless solid; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.54 (d, ^3J = 8.9 Hz, 4H, Ar-H), 6.99 (s, 2H, Ar-H), 6.98 (d, ^3J = 8.9 Hz, 4H, Ar-H), 4.16-4.09 (m, 2H, OCH), 4.04-3.96 (m, 10H, OCH, OCH_2), 3.74-3.62 (m, 6H, OCH_2, OH), 2.25-2.12 (m, 4H, CH_2CF_2), 1.74-1.68 (m, 4H, $OCH_2\mathbf{CH_2}$), 1.63-1.56 (m, 4H, $\mathbf{CH_2}CH_2CF_2$), 1.50-1.44 (m, 8H, CH_2); ^{13}C-NMR (100 MHz, acetone-d_6): δ = 159.04 (2C), 151.09 (2C), 131.75 (2C), 131.23 (4C), 130.80 (2C), 116.85 (4C), 114.77 (2C), 71.43 (2C), 71.32 (2C), 70.45, 69.98 (OCH_2), 64.21, 64.08 (2C), 31.55, 31.33, 31.11, 30.24, 30.05, 29.85, 29.34, 26.55, 20.95 (CH_2); ^{19}F-NMR (188 MHz, acetone-d_6): δ = -82.13 (t, ^3J = 9.9 Hz, 6F, CF_3), -114.96-(-115.14) (m, 4F, CH_2CF_2), -122.86 (s, 12F, CF_2), -123.83 (s, 4F, CF_2), -124.39 (s, 4F, CF_2), -127.06-(-127.22) (m, 4F, $\mathbf{CF_2}CF_3$); anal. calcd. for $C_{52}H_{48}F_{34}O_8$: C 43.17, H 3.34; found: C 43.37, H 3.52.

C4: Synthesized and purified in an analogues way as **A1** from 4,4´´-bis(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)-2',5'-bis(7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-heneicosafluorohexadecyloxy)-*p*-terphenyl (250 mg, 0.14 mmol). Yield: 229 mg (96.1 %), colourless solid; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.55 (d, ^3J = 8.7 Hz, 4H, Ar-H), 7.01 (s, 2H, Ar-H), 6.99 (d, ^3J = 8.7 Hz, 4H, Ar-H), 4.12-4.10 (m, 2H, OCH), 4.04-3.97 (m, 10H, OCH, OCH_2), 3.71-3.65 (m, 6H, OCH_2, OH), 2.20-2.15 (m, 4H, CH_2CF_2), 1.72-1.70 (m, 4H, $OCH_2\mathbf{CH_2}$), 1.63-1.56 (m, 4H, $\mathbf{CH_2}CH_2CF_2$), 1.47-1.44 (m, 8H, CH_2); ^{13}C-NMR (100 MHz, acetone-d_6): δ = 158.26 (2C), 150.24 (2C), 130.88 (2C), 130.46 (2C), 129.86 (2C), 115.85 (2C), 113.87 (2C), 70.50 (4C), 69.46 , 68.93 (OCH_2), 29.48, 29.35, 29.29, 29.19, 29.04, 28.43, 28.34, 25.58 (CH_2); ^{19}F-NMR (188 MHz, acetone-d_6): δ = -82.05 (t, ^3J = 9.9 Hz, 6F, CF_3), -115.02 (s, 4F, CH_2CF_2), -122.63 (s, 20F, CF_2), -123.58 (s, 4F, CF_2), -124.33 (s, 4F, CF_2), -127.06 (s, 4F, $\mathbf{CF_2}CF_3$); anal. calcd. for $C_{56}H_{48}F_{42}O_8$: C 40.84, H 2.94; found: C 40.83, H 3.20.

4.4 Compound D

D: Details of the synthesis will be reported in another manuscript dealing with related monosubstituted terphenyls. Purification by column chromatography (eluent: $CHCl_3$) and crystallisation from MeOH. Yield: 36.2 %; colourless solid; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, ^3J = 8.9 Hz, 2H, Ar-H), 7.50 (d, ^3J = 8.9 Hz, 2H, Ar-H), 7.33 (d, ^3J = 7.9 Hz, 1H, Ar-H), 7.16 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, Ar-H), 7.33 (d, ^4J = 1.5 Hz, 1H, Ar-H), 6.98 (d, ^3J = 8.7 Hz, 2H, Ar-H), 6.94 (d, ^3J = 8.7 Hz, 2H, Ar-H), 4.14-4.08 (m, 6H, OCH, OCH_2), 4.01 (m, 2H, OCH_2), 3.88-3.71 (m, 4H, OCH_2), 2.07-1.95 (m, 2H, CH_2CF_2), 1.75 (quin, ^3J = 6.6 Hz, 2H, $OCH_2\mathbf{CH_2}$), 1.38-1.65 (m, 6H, CH_2); ^{13}C-NMR (100 MHz, acetone-d_6): δ = 159.76, 159.03, 157.22, 141.58, 134.10, 131.74, 131.44, 131.28, 129.66, 128.66, 119.69, 115.75, 114.77, 111.79, 71.43, 70.55, 70.39, 68.99, 64.17, 31.27, 29.30, 26.54, 20.91 (CH_2); ^{19}F-NMR (200 MHz, $CDCl_3$): δ = -81.16 (t, ^3J = 9.2 Hz, 3F, CF_3), -114.66 (m, 2F, CH_2CF_2), -122.23 (m, 6F, CF_2), -123.06 (s, 2F, CF_2), -123.84 (s, 2F, CF_2), -126.45 (s, 2F, $\mathbf{CF_2}CF_3$); anal. calcd. for $C_{38}H_{37}F_{17}O_7$: C 49.15, H 4.02; found: C 49.27, H 4.13.

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