Supplementary Material (ESI) for *Journal of Materials Chemistry*

Electronic Supporting Information

Liquid Crystals Based on Semiperfluorinated Imines and Salicylaldimato Metal Complexes. A Comparative Study of Alkyl, Alkoxy and Polyether Substituents

Belkız Bilgin-Eran[a], Çiğdem Yörür[a], Carsten Tschierske[b], Marko Prehm[b] and Ute Baumeister[c]

[a]Department of Chemistry, Yıldız Technical University, Davutpaşa Yerleşim Birimi, TR-34210 Esenler, Istanbul, Turkey
[b]Institute of Organic Chemistry, Martin-Luther University Halle-Wittenberg, Kurt Mothes-Str. 2, D-06120 Halle, Germany
[c]Institute of Physical Chemistry, Martin-Luther University Halle-Wittenberg, Mühlpforte 1, D-06118 Halle, Germany

1. Experimental conditions for X-ray scattering and supporting X-ray data

Powder X-ray investigations were carried out with a Guinier film camera and a Guinier Goniometer (Huber Diffraktionstechnik, Germany). 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 $Pb(NO_3)_2$. 2D patterns for aligned samples on a glass plate on a temperature-controlled heating stage (alignment at the sample – glass or at the sample – air interface) were recorded with a 2D detector (HI-STAR, Siemens) using CuK_α radiation monochromatized by a Ni filter.

Table S1. X-ray data from Guinier powder patterns (θ_{obs}: experimental scattering angle; d_{obs}: experimental and d_{calc}: d spacing calculated from the layer distance d; n: order of reflection; d: layer distance with an error in the order of 0.1 nm).

Compound	T (°C)	Phase	θ_{obs} (°)	d_{obs} (nm)	n	d_{calc} (nm)	d_{obs}- d_{calc} (nm)	d (nm)
3b	150	SmA	1.296	3.40	1	3.40	0.00	3.40
			2.585	1.71	2	1.70	0.01	
	130		1.266	3.48	1	3.48	0.00	3.48
			2.537	1.74	2	1.74	0.00	
	120		1.269	3.48	1	3.48	0.00	3.48
			2.547	1.73	2	1.74	-0.01	
	110		1.272	3.47	1	3.47	0.00	3.47
			2.549	1.73	2	1.74	-0.01	
	100		1.274	3.46	1	3.46	0.00	3.46
			2.549	1.73	2	1.73	0.00	
	90	SmC	1.319	3.35	1	3.34	0.01	3.34
			2.652	1.66	2	1.67	-0.01	
6b	80	SmA	1.175	3.76	1	3.76	0.00	3.76
			2.350	1.88	2	1.88	0.00	
	90		1.181	3.74	1	3.74	0.00	3.74
			2.363	1.87	2	1.88	-0.01	
	100		1.188	3.72	1	3.73	-0.01	3.73
			2.363	1.87	2	1.86	0.01	
	110		1.188	3.72	1	3.72	0.00	3.72
			2.375	1.86	2	1.86	0.00	
	120		1.200	3.68	1	3.68	0.00	3.68
			2.400	1.84	2	1.84	0.00	
	130		1.212	3.64	1	3.65	-0.01	3.65
			2.412	1.83	2	1.82	0.01	
	140		1.212	3.64	1	3.64	0.00	3.64
			2.425	1.82	2	1.82	0.00	

Table S1. (cont.)

Compound	T (°C)	Phase	θ_{obs} (°)	d_{obs} (nm)	n	d_{calc} (nm)	d_{obs}- d_{calc} (nm)	d (nm)
5b*	72	SmA	1.170	3.78				
	45		1.145	3.86				
11a	170	SmA	1.397	3.16	1	3.16	0.00	3.16
			2.789	1.58	2	1.58	0.00	
	150		1.373	3.22	1	3.20	0.02	3.20
			2.776	1.59	2	1.60	-0.01	
	130		1.362	3.24	1	3.24	0.00	3.24
			2.724	1.62	2	1.62	0.00	
	110	SmX	1.353	3.26	1	3.26	0.00	3.26
			2.710	1.63	2	1.63	0.00	
	90		1.353	3.26	1	3.26	0.00	3.26
			2.714	1.63	2	1.63	0.00	
11b	120	SmX	2.720	1.63	2	1.64	-0.01	3.28
			3.990	1.11	3	1.09	0.02	
	130		2.739	1.61	2	1.64	-0.03	3.28
			3.955	1.12	3	1.09	0.03	
	140		2.752	1.60	2	1.64	-0.04	3.28
			3.955	1.12	3	1.09	0.03	
	150	SmA	2.768	1.60	2	1.63	-0.03	3.25
			3.942	1.12	3	1.08	0.04	
	160		2.787	1.58	2	1.63	-0.05	3.25
			3.925	1.13	3	1.08	0.05	

* Data from 2D patterns (Fig. S4)

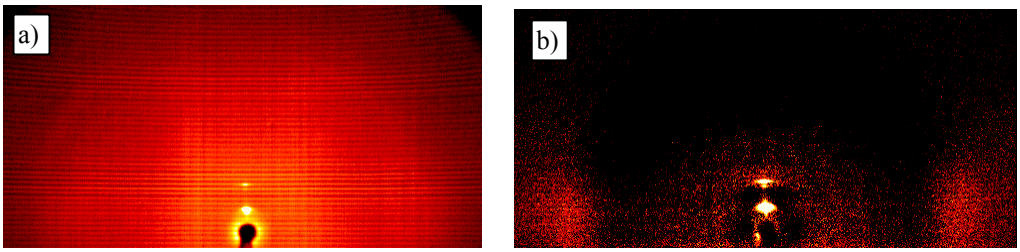

Fig. S1 X-ray diffraction of the SmA phase of **3b**: a) original 2D pattern of an aligned sample at 120 °C, b) as a), but the scattering of the isotropic liquid has been subtracted from that at 120 °C to show the enhancement of the outer diffuse scattering at the equator of the pattern more clearly (The lower part of the patterns is shadowed by the heating stage).

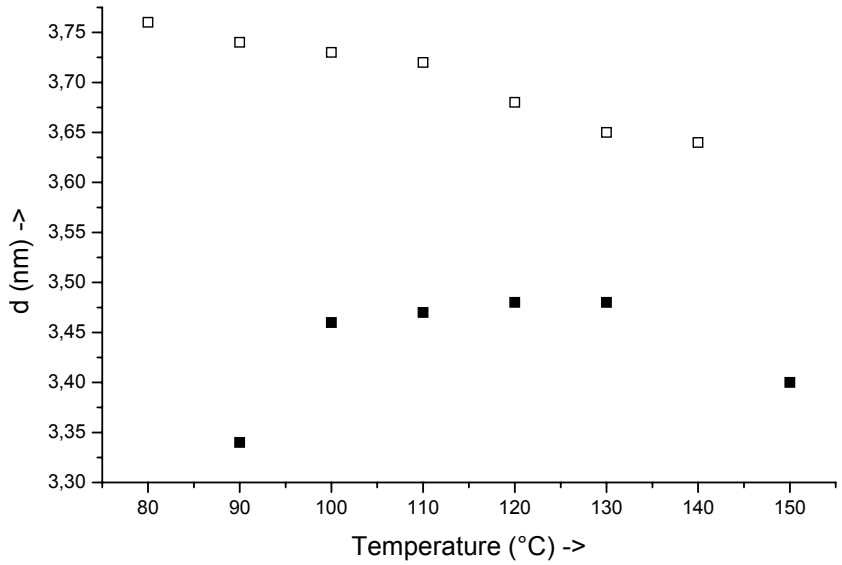

Fig. S2 Temperature dependence of the layer spacings for **3b** (full squares) and **6b** (open squares).

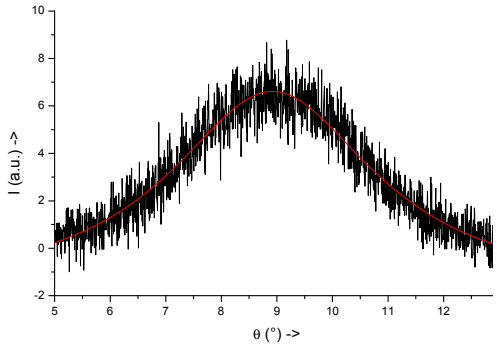

Fig. S3 X-ray diffraction of the SmA phase of **6b**: intensity profile of the outer diffuse scattering as measured from a powder-like sample with Lorentzian fit.

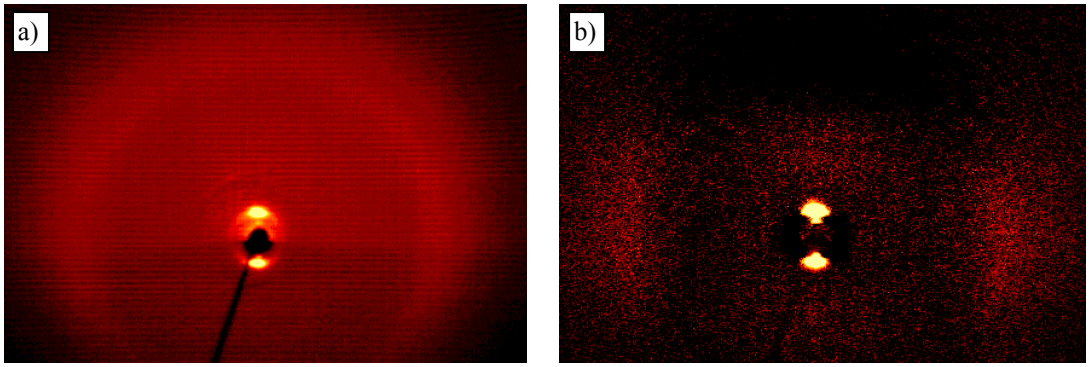

Fig. S4 X-ray diffraction of the SmA phase of **5b**: a) original 2D pattern of an aligned sample at 72 °C, b) as a), but the scattering of the isotropic liquid has been subtracted from that at 72 °C to show the enhancement of the outer diffuse scattering at the equator of the pattern more clearly.

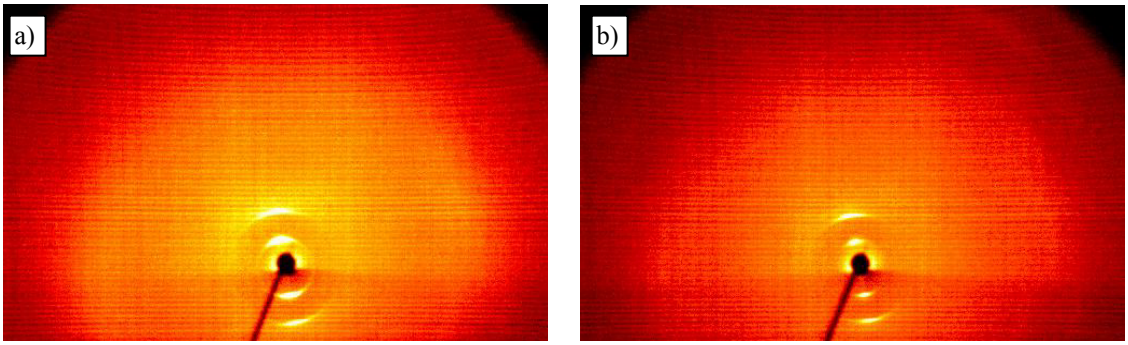

Fig. S5 2D diffraction patterns for partially surface-aligned samples of **11a** in the SmA phase at 170 °C on cooling and of **11b** in the SmX phase at 130 °C on heating. (The lower part of the patterns is shadowed by the heating stage).

2. Synthesis and analytical data of compounds 1-12

The characterization of the synthesized compounds presented here are based on various spectroscopic data, e.g. ^{1}H-, ^{13}C-NMR (Varian Unity 500 and Varian Unity 400 spectrometers, in CDCl3 solutions) with tetramethylsilane as internal standard, MS [AMD 402 (electron impact, 70 eV)]. Microanalyses were performed using a Leco CHNS-932 elemental analyzer. Only structurally relevant resonances are given in the NMR data.
Transition temperatures were measured using a Leitz Laborlux 12 Pol polarizing microscope, equipped with a Linkam THMS 600 hot stage and a Linkam TMS93 temperature controller or a Mettler FP 82 HT hot stage and control unit in conjunction with a Nikon Optiphot 2 polarizing microscope. DSC-thermograms were recorded on a Perkin-Elmer DSC-7, heating and cooling rate: 10 K min-1.

The preparation procedures and spectroscopic datas for compounds **1**, **2** and **9** are given in Ref.[16a] and,[25] respectively. The compound **9H** and **10H** were also reported from Lee et.al[26a] and Lai et.al,[26b] respectively. The preparation procedures for semiperfluorinated aldehydes,[16a] (S)-2-hydroxy-4-(2-methylbutoxy)benzaldehyde,[30] 2-hydroxy-4-butoxybenzaldehyde,[ia] 2-hydroxy-4-hexyloxybenzaldehyde,[ib] 2-hydroxy-4-decyloxybenzaldehyde,[ic] 2-hydroxy-4-tetradecyloxy-benzaldehyde,[id] 2-hydroxy-4-octadecyloxybenzaldehyde[ib] and 3,4-didecyloxybenzaldehyde[ii] were as in the literature.

Synthesis of the imine compounds:

The new compounds **3-8** and **10** were prepared from the corresponding alkyloxybenzaldehydes (2.5 mmol) by the usual[iii] p-toluenesulfonic acid (40 mg) catalyzed condensation reactions with the corresponding aniline (4-hexylaniline (commercially available), 3,4-didecyloxyaniline[iva] and 4-(1,4,7,10-tetraoxaundecyl)aniline[ivb] (3 mmol) in 25 ml toluene under argon atmosphere at reflux for 4-6 h. The crude products were purified by column chromatography on basic aluminum oxide using petroleum ether / ethyl acetate (20:1 to 5:1) as eluent or by crystallization from acetone/methanol. The transition temperature of the mesogenic compounds **1-3**, **4-6**, **7** and **8-10** are presented in Table 1, 2, 3 and 4, respectively.

*Compounds **3a***: Yield: 1.06 g (71 %) of yellow crystals. ^{1}H-NMR: δ =13.88 (s; OH), 8.50 (s; HC=N), 7.23, 7.19, 7.16 (3d; $J \approx 8.7$ Hz each; 1, 2 and 2 arom. H, respectively), 6.47-6.43 (m; 2 arom. H), 3.99 (t, $J \approx 6.3$ Hz; OCH_2), 2.60 (t, J ≈ 7.8 Hz; α-CH_2). ^{13}C-NMR: δ = 164.01, 163.23, 145.87, 141.37, 113.13 (5s; 5 arom. C), 160.50 (d, HC=N), 133.27 129.26, 120.73, 107.39, 101.60 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 67.89 (t; OCH_2), 35.55 (t; α-CH_2). MS (EI): m/z (%) = 599 (100) [M^+], 297 (40) [M^+-$C_{10}H_{12}F_9$]. $C_{29}H_{34}F_9NO_2$ (599.6); Anal. Calc.: C, 58.09; H, 5.72; N, 2.34. Found: C, 58.04; H, 5.93; N 2.31%.

*Compounds **3b***: Yield: 1.12 g (66 %) of yellow crystals. ^{1}H-NMR: δ =13.85 (s; OH), 8.51 (s; HC=N), 7.24, 7.20, 7.17 (3d; $J \approx 8.6$ Hz each; 1, 2 and 2 arom. H, respectively), 6.49-6.44 (m; 2 arom. H), 4.03 (t, $J \approx 5.9$ Hz; OCH_2), 2.61 (t, J ≈ 7.7 Hz; α-CH_2). ^{13}C-NMR: δ = 164.45, 162.82, 145.66, 141.50, 113.37 (5s; 5 arom. C), 160.32 (d, HC=N), 133.41 129.27, 120.78, 107.54, 101.10 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 67.40 (t; OCH_2), 35.54 (t; α-CH_2). MS (EI): m/z (%) = 671 (100) [M^+], 297 (30) [M^+-$C_{10}H_8F_{13}$]. $C_{29}H_{30}F_{13}NO_2$ (671.6); Anal. Calc.: C, 51.86; H, 4.50; N, 2.08. Found: C, 51.85; H, 4.41; N 2.24%.

*Compounds **4a***: Yield: 2.18 g (67 %) of yellow oil. ^{1}H-NMR: δ = 8.71 (s; HC=N), 7.82, 7.15, 6.91, 6.72 (4d, $J \approx 8.9$ Hz each; 1, 2, 2 and 1 arom. H, respectively), 4.12, 3.85 (2t, $J \approx 4.9$ Hz each; 2 OCH_2), 4.07, 4.02, 3.98 (3t, $J \approx 6.4$ Hz each; 3 OCH_2), 3.75-3.72, 3.69-3.63, 3.55-3.53 (3m; 1, 2 and 1 OCH_2, respectively), 3.36 (s; OCH_3). ^{13}C-NMR: δ = 157.24, 154.28, 153.91, 145.87, 141.19, 123.42 (6s; 6 arom. C), 155.89 (d, HC=N), 122.38, 122.05, 115.12, 108.76 (4d; 1, 2, 2 and 1 arom. CH, respectively), 74.60, 73.37, 71.95, 70.85, 70.68, 70.58, 69.78, 68.50, 67.70 (9t; 9 OCH_2), 59.01 (q; OCH_3).

*Compounds **4b***: Yield: 3.31 g (87 %) of yellow oil. ^{1}H-NMR: δ = 8.69 (s; HC=N), 7.85, 7.16, 6.91, 6.75 (4d, $J \approx 8.9$ Hz each; 1, 2, 2 and 1 arom. H, respectively), 4.12, 3.85 (2t, $J \approx 4.9$ Hz each; 2 OCH_2), 4.07 (t, $J \approx 5.09$ Hz; OCH_2), 4.04-3.99, 3.75-3.72, 3.69-3.63, 3.55-3.53 (4m; 1, 1, 2 and 1 OCH_2, respectively), 3.36 (s; OCH_3). ^{13}C-NMR: δ = 157.29, 153.64, 152.88, 145.61, 141.04, 123.63 (6s; 6 arom. C), 155.46 (d, HC=N), 122.74, 121.03, 115.16, 108.96 (4d; 1, 2, 2 and 1 arom. CH, respectively), 74.22, 72.93, 71.96, 70.87, 70.69, 70.59, 69.79, 68.13, 65.75 (9t; 9 OCH_2), 59.02 (q; OCH_3).

*Compounds **5H***: Yield: 1.46 g (89 %) of white crystals. ^{1}H-NMR: δ = 8.33 (s; HC=N), 7.54, 7.24 (2s, broad; 2 arom. H), 7.16 (d, $J \approx 8.7$ Hz; 2 arom. H), 6.93-6.88 (m; 3 arom. H), 4.13, 4.08, 4.04, 3.85 (4t, $J \approx 4.9$ Hz, $J \approx 6.6$ Hz, $J \approx 6.6$ Hz and $J \approx 4.9$ Hz, respectively; 4 OCH_2), 3.75-3.72, 3.69-3.64, 3.55-3.53 (3m; 1, 2 and 1 OCH_2, respectively), 3.37 (s; OCH_3). ^{13}C-

NMR: δ = 158.36 (d, HC=N), 157.14, 151.98, 149.47, 145.43, 129.57 (5s; 5 arom. C), 123.87, 121.99, 115.13, 112.50, 111.22 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 71.94, 70.84, 70.67, 70.57, 69.79, 69.17, 69.12, 67.71 (8t; 8 OCH_2), 59.02 (q; OCH_3). MS (EI): m/z (%) = 655 (100) [M^+], 509 (37) [M^+ - $C_7H_{15}O_3$], 368 (6) [M^+-$C_7H_{15}O_3$–$C_{10}H_{21}$], 228 (10) [M^+ - $C_7H_{15}O_3$–2x $C_{10}H_{21}$], $C_{40}H_{65}NO_6$ (655.9); Anal. Calc.: C, 73.24; H, 9.99; N, 2.14. Found: C, 73.25; H, 9.86; N 1.95%.

Compounds ***5a***: Yield: 2.11 g (86 %) of white crystals. ^{1}H-NMR: δ = 8.34 (s; HC=N), 7.55, 7.24 (2s, broad; 2 arom. H), 7.16 (d, $J \approx$ 8.7 Hz; 2 arom. H), 6.93-6.88 (m; 3 arom. H), 4.13, 4.09, 4.04, 3.85 (4t, $J \approx$ 4.9 Hz, $J \approx$ 6.4 Hz, $J \approx$ 6.4 Hz and $J \approx$ 4.9 Hz, respectively; 4 OCH_2), 3.75-3.72, 3.69-3.64, 3.55-3.53 (3m; 1, 2 and 1 OCH_2, respectively), 3.37 (s; OCH_3). ^{13}C-NMR: δ = 158.09 (d, HC=N), 157.23, 151.80, 149.38, 145.42, 129.88 (5s; 5 arom. C), 123.93, 121.98, 115.22, 112.63, 111.33 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 71.99, 70.89, 70.71, 70.61, 69.83, 68.88, 68.83, 67.83 (8t; 8 OCH_2), 59.02 (q; OCH_3). $C_{40}H_{47}F_{18}NO_6$ (979.8); Anal. Calc.: C, 49.03; H, 4.83; N, 1.43. Found: C, 49.09; H, 4.56; N 1.24%.

Compounds ***5b***: Yield: 2.24 g (80 %) of white crystals. ^{1}H-NMR: δ = 8.34 (s; HC=N), 7.56, 7.24 (2s, broad; 2 arom. H), 7.16 (d, $J \approx$ 8.7 Hz; 2 arom. H), 6.93-6.88 (m; 3 arom. H), 4.15-4.11 (m; 2 OCH_2), 4.07, 3.85 (2t, $J \approx$ 5.7 Hz and $J \approx$ 4.9 Hz, respectively; 2 OCH_2), 3.75-3.72, 3.69-3.64, 3.55-3.53 (3m; 1, 2 and 1 OCH_2, respectively), 3.37 (s; OCH_3). ^{13}C-NMR: δ = 157.99 (d, HC=N), 157.26, 151.47, 149.14, 145.31, 130.04 (5s; 5 arom. C), 124.13, 122.02, 115.17, 112.40, 110.91 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 71.96, 70.86, 70.69, 70.59, 69.80, 68.34, 68.30, 67.73 (8t; 8 OCH_2), 59.04 (q; OCH_3). $C_{40}H_{39}F_{26}NO_6$ (1123.7); Anal. Calc.: C, 42.76; H, 3.50; N, 1.25. Found: C, 42.79; H, 3.74; N 1.10%.

Compounds ***6H***: Yield: 0.92 g (71 %) of yellow crystals. ^{1}H-NMR: δ = 13.84 (s, broad; OH) 8.47 (s; HC=N), 7.21 (d, $J \approx$ 8.3 Hz; 1 arom. H), 7.19, 6.92 (2d, $J \approx$ 8.9 Hz each; 4 arom. H), 6.47-6.43 (m; 2 arom. H), 4.13, 3.85 (2t, $J \approx$ 4.8 Hz each; 2 OCH_2), 3.97 (t, $J \approx$ 6.6 Hz; 1 OCH_2), 3.74-3.72, 3.69-3.63, 3.55-3.52 (3m; 1, 2 and 1 OCH_2, respectively), 3.36 (s; OCH_3). ^{13}C-NMR: δ = 163.72, 163.26, 157.58, 141.56, 113.03 (5s; 5 arom. C), 159.64 (d, HC=N), 133.12, 121.92, 115.33, 107.40, 101.57 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 71.93, 70.84, 70.66, 70.57, 69.73, 68.20, 67.75 (7t; 7 OCH_2), 59.01 (q; OCH_3). MS (EI): m/z (%) = 515 (100) [M^+], 369 (18) [M^+-$C_7H_{15}O_3$], 228 (55) [M^+-$C_7H_{15}O_3$–$C_{10}H_{21}$]. $C_{30}H_{45}NO_6$ (515.7); Anal. Calc.: C, 69.87; H, 8.79; N, 2.72. Found: C, 69.83; H, 8.74; N 2.58%.

Compounds ***6a***: Yield: 1.48 g (87 %) of yellow crystals. ^{1}H-NMR: δ = 13.85 (s, broad; OH) 8.48 (s; HC=N), 7.22 (d, $J \approx$ 8.3 Hz; 1 arom. H), 7.20, 6.93 (2d, $J \approx$ 8.9 Hz each; 4 arom. H), 6.47-6.43 (m; 2 arom. H), 4.13, 3.85 (2t, $J \approx$ 4.8 Hz each; 2 OCH_2), 3.98 (t, $J \approx$ 6.3 Hz; 1 OCH_2), 3.74-3.72, 3.69-3.63, 3.55-3.53 (3m; 1, 2 and 1 OCH_2, respectively), 3.36 (s; OCH_3). ^{13}C-NMR: δ = 163.77, 163.15, 157.69, 141.61, 113.21 (5s; 5 arom. C), 159.64 (d, HC=N), 133.17, 121.95, 115.41, 107.35, 101.62 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 71.98, 70.88, 70.69, 70.59, 69.76, 67.87, 67.84 (7t; 7 OCH_2), 59.00 (q; OCH_3). MS (EI): m/z (%) = 677 (100) [M^+], 531 (65) [M^+-$C_7H_{15}O_3$], 228 (54) [M^+-$C_7H_{15}O_3$–$C_{10}H_{12}F_9$]. $C_{30}H_{36}F_9NO_6$ (677.6); Anal. Calc.: C, 53.17; H, 5.35; N, 2.06. Found: C, 53.34; H, 5.34, N 1.84%.

Compounds ***6b***: Yield: 1.32 g (70 %) of yellow crystals. ^{1}H-NMR: δ = 13.88 (s, broad; OH) 8.49 (s; HC=N), 7.22 (d, $J \approx$ 8.3 Hz; 1 arom. H), 7.20, 6.93 (2d, $J \approx$ 8.9 Hz each; 4 arom. H),

6.46-6.43 (m; 2 arom. H), 4.14, 3.86 (2t, $J \approx 4.8$ Hz each; 2 OCH_2), 4.02 (t, $J \approx 5.5$ Hz; 1 OCH_2), 3.74-3.72, 3.69-3.63, 3.55-3.53 (3m; 1, 2 and 1 OCH_2, respectively), 3.36 (s; OCH_3). ^{13}C-NMR: δ = 163.63, 162.71, 157.61, 141.48, 113.31 (5s; 5 arom. C), 159.51 (d, HC=N), 133.13, 121.91, 115.34, 107.22, 101.55 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 71.97, 70.88, 70.70, 70.60, 69.76, 67.81, 67.35 (7t; 7 OCH_2), 59.04 (q; OCH_3). MS (EI): m/z (%) = 749 (100) [M^+], 603 (35) [M^+-$C_7H_{15}O_3$], 228 (28) [M^+-$C_7H_{15}O_3$–$C_{10}H_8F_{13}$]. $C_{30}H_{32}F_{13}NO_6$ (749.6); Anal. Calc.: C, 48.07; H, 4.30; N, 1.87. Found: C, 48.03; H, 4.26, N 2.02%.

Compounds ***7c***: Yield: 0.76 g (68 %) of yellow crystals. ^{1}H-NMR: δ= 13.83 (s, broad; OH), 8.47 (s; HC=N), 7.24-7.17 (m; 3 arom. H), 6.92 (d, $J \approx 8.9$ Hz; 2 arom. H), 6.46-6.43 (m; 2 arom. H), 4.13 (t, $J \approx 4.7$ Hz; OCH_2), 3.86-3.52 (m; 6 OCH_2), 3.36 (s; OCH_3). ^{13}C-NMR: δ= 163.62, 163.35, 157.53, 141.62, 113.04 (5s; 5 arom. C) 159.60 (d; HC=N), 133.04, 121.89, 115.30, 107.36, 101.61 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 73.01, 71.96, 70.87, 70.68, 70.59, 69.76, 67.81 (7t; 7 OCH_2), 59.03 (q; OCH_3). MS (EI): m/z (%) = 445 (100) [M^+], 299 (12) [M^+-$C_7H_{15}O_3$], 229 (35) [M^+-$C_7H_{15}O_3$–C_5H_{11}]. $C_{25}H_{35}NO_6$ (445.6); Anal. Calc.: C, 67.39; H, 7.92; N, 3.14. Found: C, 67.44; H, 7.87; N, 2.96%.

Compounds ***7d***: Yield: 0.82 g (76 %) of yellow crystals. ^{1}H-NMR: δ= 13.84 (s, broad; OH), 8.48 (s; HC=N), 7.23-7.17 (m; 3 arom. H), 6.92 (d, $J \approx 8.9$; Hz; 2 arom. H), 6.47–6.42 (m; 2 arom. H), 4.13, 3.98, 3.85 (3t, $J \approx 4.7$ Hz, $J \approx 6.5$ Hz and $J \approx 4.7$ Hz, respectively; 3 OCH_2) 3.74–3.51 (m; 4 OCH_2), 3.36 (s; OCH_3). ^{13}C-NMR: δ= 163.70, 163.26, 157.60, 141.64, 113.07 (5s; 5 arom. C) 159.67 (d, HC=N), 133.12, 121.94, 115.33, 107.38, 101.56 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 71.94, 70.85, 70.67, 70.57 69.74, 67.87, 67.76 (7t; 7 OCH_2), 59.02 (q; OCH_3). MS (EI): m/z (%) = 431 (100) [M^+], 285 (34) [M^+-$C_7H_{15}O_3$], 228 (27) [M^+-$C_7H_{15}O_3$-C_4H_9]. $C_{24}H_{33}NO_6$ (431.5); Anal. Calc.: C, 66.81; H, 7.71; N, 3.25. Found: C, 66.95; H, 7.49; N, 3.25%.

Compounds ***7e***: Yield: 0.85 g (74 %) of yellow crystals. ^{1}H-NMR: δ= 13.84 (s, broad; OH), 8.47 (s; HC=N), 7.22-7.17 (m; 3 arom. H), 6.92 (d, $J \approx 8.9$ Hz; 2 arom. H), 6.46–4.43 (m; 2 arom. H), 4.13, 3.97, 3.85 (3t, $J \approx 4.8$ Hz, $J \approx 6.6$ Hz and $J \approx 4.8$ Hz, respectively; 3 OCH_2), 3.74–3.52 (m; 4 OCH_2), 3.36 (s; OCH_3). ^{13}C-NMR: δ= 163.60, 163.16, 157.52, 141.58, 113.04 (5s; 5 arom. C) 159.57 (d, HC=N), 133.05, 121.87, 115.31, 107.32, 101.57 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 71.94, 70.85, 70.67, 70.59, 69.74, 68.19, 67.79 (7t; 7 OCH_2), 59.00 (q; OCH_3). MS (EI): m/z (%) = 459 (100) [M^+], 313 (24) [M^+-$C_7H_{15}O_3$], 228 (14) [M^+-$C_7H_{15}O_3$-C_6H_{13}]. $C_{26}H_{37}NO_6$ (459.6); Anal. Calc.: C, 67.95; H, 8.11; N, 3.05. Found: C, 68.21; H, 7.95; N, 3.06%.

Compounds ***7f***: Yield: 1.23 g (86 %) of cream crystals. ^{1}H-NMR: δ= 13.84 (s, broad; OH), 8.48 (s; HC=N), 7.22-7.17 (m; 3 arom. H), 6.92 (d, $J \approx 8.9$ Hz; 2 arom. H), 6.47–6.42 (m; 2 arom. H), 4.13, 3.97, 3.85 (3t, $J \approx 4.9$ Hz, $J \approx 6.5$ Hz and $J \approx 4.9$ H respectively; 3 OCH_2), 3.74–3.51 (m; 4 OCH_2), 3.36 (s; OCH_3). ^{13}C-NMR: δ= 163.64, 163.20, 157.54, 141.56, 113.02 (5s; 5 arom. C) 159.60 (d, HC=N), 133.08, 121.89, 115.28, 107.31, 101.52 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 71.89, 70.80, 70.61, 70.52 69.69, 68.14, 67.70 (7t; 7 OCH_2), 58.96 (q; OCH_3). MS (EI): m/z (%) = 571 (100) [M^+], 425 (16) [M^+-$C_7H_{15}O_3$], 375 (22) [M^+-$C_{14}H_{29}$], 228 (20) [M^+-$C_7H_{15}O_3$–$C_{14}H_{29}$]. $C_{34}H_{53}NO_6$ (571.8); Anal. Calc.: C, 71.42; H, 9.34; N, 2.44. Found: C, 71.43; H, 9.12; N, 2.28%.

Compounds ***7g***: Yield: 1.31 g (84 %) of cream crystals. ^{1}H-NMR: δ= 13.84 (s, broad; OH), 8.48 (s; HC=N), 7.22-7.18 (m; 3 arom. H), 6.92 (d, $J \approx 8.9$ Hz; 2 arom. H), 6.47-6.43 (m; 2 arom. H), 4.13, 3.97, 3.86 (3t, $J \approx 4.9$, $J \approx 6.5$ and $J \approx 4.9$ Hz, respectively; 3 OCH_2), 3.74–

3.52 (m; 4 OCH_2), 3.36 (s; OCH_3). ^{13}C-NMR: δ= 163.70, 163.26, 157.60, 141.64, 113.07 (5s; 5 arom. C), 159.67 (d, HC=N), 133.12, 121.94, 115.34, 107.39, 101.57 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 71.94, 70.85, 70.66, 70.57 69.75, 68.21, 67.76 (7t; 7 OCH_2), 59.02 (q; OCH_3). MS (EI): m/z (%) = 627 (100) [M^+], 481 (6) [M^+ - $C_7H_{15}O_3$], 375 (15) [M^+ - $C_{18}H_{37}$], 228 (12) [M^+-$C_5H_7O_3$-$C_{18}H_{37}$]. $C_{38}H_{61}NO_6$ (627.9); Anal. Calc.: C, 72.69; H, 9.79; N, 2.23. Found: C, 72.94; H, 9.59; N, 2.46%.

Compounds ***8a***: Yield: 3.07 g (85 %) of white crystals. ^{1}H-NMR: δ = 8.72 (s; HC=N), 7.81 (d, $J \approx$ 8.7 Hz; 1 arom. H), 6.86, 6.83 (2d, $J \approx$ 8.5 Hz and $J \approx$ 2.3 Hz, respectively; 2 arom. H), 6.74-6.71 (m; 2 arom. H), 4.09-3.96 (m; 5 OCH_2). ^{13}C-NMR: δ = 155.75, 153.77, 149.53, 147.52, 146.19, 141.11, 123.34 (7s; 7 arom. C), 154.11 (d, HC=N), 122.31, 114.44, 111.97, 108.77, 108.26 (5d; 5 arom. CH), 74.64, 73.40, 69.78, 69.29, 68.57 (5t; 5 OCH_2). $C_{63}H_{84}F_{27}NO_5$ (1448.3); Anal. Calc.: C, 52.25; H, 5.85; N, 0.97. Found: C, 52.03; H, 5.98; N 0.79%.

Compounds ***8b***: Yield: 3.19 g (77 %) of white crystals. ^{1}H-NMR: δ = 8.69 (s; HC=N), 7.84, 6.75 (2d, $J \approx$ 8.9 Hz each; 2 arom. H), 6.86, 6.83 (2d, $J \approx$ 8.5 Hz and $J \approx$ 2.3 Hz, respectively; 2 arom. H), 6.73 (dd, $J \approx$ 8.5 Hz and $J \approx$ 2.3 Hz; 1 arom. H), 4.09-4.06, 4.02-3.97 (2m; 2 and 3 OCH_2, respectively). ^{13}C-NMR: δ = 155.49, 153.63, 149.66, 147.72, 146.09, 141.07, 123.65 (7s; 7 arom. C), 153.66 (d, HC=N), 122.76, 114.55, 111.97, 109.00, 108.29 (5d; 5 arom. CH), 74.27, 72.95, 69.78, 69.30, 68.16 (5t; 5 OCH_2). $C_{63}H_{72}F_{39}NO_5$ (1664.2); Anal. Calc.: C, 45.47; H, 4.36; N, 0.84. Found: C, 45.44; H, 4.62; N 0.75%.

Compounds ***10H***: Yield: 1.10 g (66 %) of yellow crystals. ^{1}H-NMR: δ = 13.85 (s, broad; OH), 8.46 (s; HC=N), 7.22 (d, $J \approx$ 8.5 Hz; 1 arom. H), 6.87, 6.78 (2d, $J \approx$ 8.3 Hz and $J \approx$ 2.4 Hz, respectively; 2 arom. H), 6.81 (dd, $J \approx$ 8.3 Hz and $J \approx$ 2.4 Hz; 1 arom. H), 6.49-6.44 (m; 2 arom. H), 4.03-3.96 (m; 3 OCH_2). ^{13}C-NMR: δ = 163.80, 163.32, 149.89, 148.10, 141.91, 113.03 (6s; 6 arom. C), 159.56 (d, HC=N), 133.12, 114.60, 112.65, 107.49, 107.44, 101.66 (6d; 6 arom. CH), 69.82, 69.44, 68.27 (3t; 3 OCH_2). MS (EI): m/z (%) = 665 (100) [M^+], 524 (10) [M^+-$C_{10}H_{21}$], 384 (16) [M^+-2x $C_{10}H_{21}$], 244 (10) [M^+-3x $C_{10}H_{21}$]. $C_{43}H_{71}NO_4$ (666.0); Anal. Calc.: C, 77.55; H, 10.75; N, 2.10. Found: C, 77.33; H, 10.75; N 2.01%.

Compounds ***10a***: Yield: 1.78 g (86 %) of yellow crystals. ^{1}H-NMR: δ = 13.88 (s, broad; OH), 8.47 (s; HC=N), 7.22 (d, $J \approx$ 8.3 Hz; 1 arom. H), 6.87, 6.82 (2d, $J \approx$ 8.3 Hz and $J \approx$ 2.3 Hz, respectively; 2 arom. H), 6.79 (dd, $J \approx$ 8.3 Hz and $J \approx$ 2.3 Hz; 1 arom. H), 6.46-6.43 (m; 2 arom. H), 4.03-3.97 (m; 3 OCH_2). ^{13}C-NMR: δ = 163.75, 163.05, 149.83, 148.08, 141.83, 113.15 (6s; 6 arom. C), 159.50 (d, HC=N), 133.10, 114.51, 112.64, 107.44, 107.31, 101.59 (6d; 6 arom. CH), 69.78, 69.41, 67.87 (3t; 3 OCH_2). MS (EI): m/z (%) = 827 (100) [M^+], 687 (8) [M^+-$C_{10}H_{21}$], 546 (18) [M^+-2x $C_{10}H_{21}$], 244 (10) [M^+-2x $C_{10}H_{21}$–$C_{10}H_{12}F_9$]. $C_{43}H_{62}F_9NO_4$ (827.9); Anal. Calc.: C, 62.38; H, 7.55; N, 1.69. Found: C, 62.35; H, 7.38; N 1.58%.

Compounds ***10b***: Yield: 1.65 g (73 %) of yellow crystals. ^{1}H-NMR: δ = 13.90 (s, broad; OH), 8.48 (s; HC=N), 7.23 (d, $J \approx$ 8.3 Hz; 1 arom. H), 6.87, 6.83 (2d, $J \approx$ 8.3 Hz and $J \approx$ 2.3 Hz, respectively; 2 arom. H), 6.80 (dd, $J \approx$ 8.3 Hz and $J \approx$ 2.3 Hz; 1 arom. H), 6.46-6.41 (m; 2 arom. H), 4.04-3.98 (m; 3 OCH_2). ^{13}C-NMR: δ = 163.76, 162.77, 149.84, 148.13, 141.77, 113.31 (6s; 6 arom. C), 159.46 (d, HC=N), 133.15, 114.50, 112.67, 107.44, 107.24, 101.60 (6d; 6 arom. CH), 69.78, 69.43, 67.36 (3t; 3 OCH_2). MS (EI): m/z (%) = 899 (100) [M^+], 759 (8) [M^+ - $C_{10}H_{21}$], 618 (22) [M^+ - 2x $C_{10}H_{21}$], 244 (6) [M^+ - 2x $C_{10}H_{21}$ – $C_{10}H_8F_{13}$].

$C_{43}H_{58}F_{13}NO_4$ (899.9); Anal. Calc.: C, 57.39; H, 6.50; N, 1.56. Found: C, 57.45; H, 6.28; N 1.37%.

*Synthesis of the copper(II) complexes **11** and **12**:*

A suspension of 0.5 mmol appropriate ligand in absolute ethanol (5 ml) was added 0.5 mmol of potassium hydroxyde dissolved in 10 ml of absolute ethanol and 0.25 mmol of copper(II) acetate dihydrate. The mixture was stirred at room temperature under an argon atmosphere for 24 h; the greenish or greenish brown solid formed was filtered and recrystallized from chloroform/ethanol. The transition temperature of the copper(II) complexes **11b** and **11c** are given in Table 5.

*Compounds **11a***: Yield: 0.26 g (83%) of brown crystals. $C_{58}H_{66}CuF_{18}N_2O_4$ (1260.7); Anal. Calc.: C, 55.26; H, 5.28; N, 2.22. Found: C, 55.50; H, 5.14; N 2.04%.

*Compounds **11b***: Yield: 0.31 g (88%) of brown crystals. $C_{58}H_{58}CuF_{26}N_2O_4$ (1404.6); Anal. Calc.: C, 49.60; H, 4.16; N, 1.99. Found: C, 49.47; H, 4.03; N 1.84%.

*Synthesis of the palladium complexe **12b**:*

A suspension of 0.5 mmol of the compound **3b** and 0.5 mmol of bis(benzonitrile)-palladium(II) chloride in 10 ml of dry ethanol and in 5 ml of dry dichloromethane was stirred under Ar atmosphere for 2 day at room temperature. The resulting yellow-brown solid was filtered off, suspended in chloroform and the suspension filtered through a short Celite column. The solvent was evaporated under reduced pressure. The compound **12b** was purified by several crystallizations from methanol/dichloromethane. The transition temperatures of the palladium compound **12 b** are given in Table 5.

*Compounds **12b***: Yield: 0.23 g (64%) of rot-brown crystals. **^{1}H-NMR**: δ = 7.56 (s; 2 HC=N), 7.21, 7.17 (2d; $J \approx 8.5$ Hz each; 4 arom. H), 7.01 (d; $J \approx 8.9$; 2 arom. H), 6.11 (dd, $J \approx 8.9$ Hz and $J \approx 2.3$ Hz; 2 arom. H), 5.52 (d, $J \approx 2.3$ Hz; 2 arom. H), 3.79 (t, $J \approx 5.6$ Hz; 2 OCH_2), 2.62 (t, J ≈ 7.8 Hz; 2 α-CH_2). **^{13}C-NMR**: δ = 166.87, 164.54, 147.44, 140.77, 114.84 (5s; 10 arom. C), 161.01 (d, 2 HC=N), 135.49, 127.86, 124.66, 106.34, 101.97 (5d; 2, 2, 4, 4 and 2 arom. CH, respectively), 66.71 (t; 2 OCH_2), 35.61 (t; 2 α-CH_2). **$C_{58}H_{58}F_{26}N_2O_4Pd$** (1447.5); Anal. Calc.: C, 48.13; H, 4.04; N, 1.94. Found: C, 47.87; H, 4.26; N 1.70%.

3. References

[i] (a) Yoshitaka, O., *Chem. Pharm. Bulletin*, 1984, **32**, 4260; (b) I. Aiello, M. Ghedini, M. La Deda, D. Pucci, O. Francescangeli, *Eur. J. Inorg. Chem.*, 1999, 1367; (c) R. M. Claramunt, I. Forfar, P. Cabildo, J. Lafuente, J. Barbare, R. Gimenez, J. Elguero, *Heterocycles*, 1999, **51**, 751; (d) K. Binnemans, Y.G. Galyametdinov, D. Rik Van, D.W. Bruce, S.R. Collinson, P. Polishckuk, I. Bickhantaev, W. Haase, V. Prosvirin, L. Tinchurina, I. Litvinow, A. Goubajdullin, A. Rackmatullin, R. Uytterhoeven, L.V. Meervelt, *J. Am. Chem. Soc.*, 2000, **122**, 4335.

[ii] (a) J.M. Elliott, J.R. Chipperfield, S. Clark, E. Sinn, *Inorg. Chem.,* 2001, **40**, 6390; (b) D. Pez, I. Leal, F. Zuccotto, C. Boussard, R. Brun, S. L.Croft, V. Yardley, L. M.Ruiz Perez, D. Gonzalez Pacanowska, I. H.Gilbert, *Bioorganic &Medicinal Chemistry*, 2003, **11**, 4693.

[iii] (a) K. Praefcke, D. Singer, B. Gündogan, *Mol. Cryst. Liq. Cryst.* 1992, **223**, 181. (b) B. Bilgin Eran, D. Singer, K. Praefcke, *Eur. J. Inorg. Chem.*, 2001, 111; (c) B. Bilgin Eran, D. Singer, J. Pickardt, K. Praefcke, *J. Organometallic Chem.,* 2001, **620**, 249.

[iv] (a) W. Bradley, J.D. Thompson, *Chimia*, 1961, **15**, 147; (b) J.L. Bahr, J. Yang, D.V. Kosynkin, M.J. Bronikowski, R.E. Smalley, J.M. Tour, *J. Am. Chem. Soc.*, 2001, **123**, 6536.