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Synthesis, characterization, and tuning of the liquid crystal properties of ionic materials based on the cyclic polyoxothiometalate $[\{Mo_4O_4S_4(H_2O)_3(OH)_2\}_2(P_8W_{48}O_{184})]^{36-}$.

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Supporting Information

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I Synthetic details of organic cations

Synthesis of 1-methyl-3-alkylimidazolium bromides, mimC_nBr (n = 12, 14, 16, 18, 20). 10^{-2} mole of 1-methyl imidazole and 1.2×10^{-2} mole of C_nH_{2n+1}Br were dissolved in acetonitrile (5 mL for n = 12-16, 15 mL for n = 18, 20). The resulting solution was refluxed for 24 hrs. After it was cooled down in an ice bath, a precipitate appeared. The latter was isolated by filtration and washed with diethyl ether.

mimC₁₂Br. IR/cm⁻¹, (ATR diamond, ATR correction applied): 3475 (ms), 3427 (ms), 3082 (s), 3062 (s), 2950 (m), 2915 (vs), 2870 (mw), 2850 (s), 1668 (w), 1627 (m), 1572 (s), 1472 (s), 1426 (mw), 1382 (w), 1177 (vs), 861 (ms), 791 (s), 741 (w), 716 (ms), 662 (m), 622 (s), 503 (s), 472 (s), 444 (s), 419 (s), 400 (s). ¹H NMR (δ / ppm / CDCl₃): 10.44 (s., 1H), 7.41 (s. br., 1H), 7.30 (s. br., 1H), 4.32 (t., 2H), 4.13 (s., 3H), 2.13 (m, 2H), 1.92 (m, 2H), 1.35-1.20 (m, 16H), 0.88 (t., 3H).

mimC₁₄Br. IR/cm⁻¹, (ATR diamond, ATR correction applied): 2954 (m), 2920 (vs), 2870 (m), 2851 (s), 1639 (mw), 1467 (m), 1135 (m), 1078 (m), 1022 (w), 939 (s), 879 (m), 792 (s), 723 (s). ¹H NMR (δ / ppm / CDCl₃): 10.52 (s., 1H), 7.39 (s. br., 1H), 7.28 (s. br., 1H), 4.32 (t., 2H), 4.13 (s., 3H), 1.92 (m, 2H), 1.85 (m, 2H), 1.35-1.20 (m, 20H), 0.88 (t., 3H).

mimC₁₆Br. IR/cm⁻¹, (ATR diamond, ATR correction applied): 2954 (m), 2920 (vs), 2870 (m), 2851 (s), 1639 (mw), 1467 (m), 1135 (m), 1078 (m), 1022 (w), 939 (s), 879 (m), 792 (s), 723 (s). ¹H NMR (δ / ppm / CDCl₃): 10.60 (s., 1H), 7.35 (s. br., 1H), 7.25 (s. br., 1H), 4.32 (t., 2H), 4.14 (s., 3H), 1.92 (m, 2H), 1.83 (s. br., 2H), 1.35-1.20 (m, 24H), 0.88 (t., 3H).

mimC₁₈Br. IR/cm⁻¹, (ATR diamond, ATR correction applied): 2954 (m), 2920 (vs), 2870 (m), 2851 (s), 1639 (mw), 1467 (m), 1135 (m), 1078 (m), 1022 (w), 939 (s), 879 (m), 792 (s), 723 (s). ¹H NMR (δ / ppm / CDCl₃): 10.57 (s., 1H), 7.33 (s. br., 1H), 7.26 (s. br., 1H), 4.32 (t., 2H), 4.14 (s., 3H), 1.92 (m, 2H), 1.76 (s. br., 2H), 1.35-1.20 (m, 28H), 0.88 (t., 3H).

mimC₂₀Br. IR/cm⁻¹, (ATR diamond, ATR correction applied): 2954 (m), 2920 (vs), 2870 (m), 2851 (s), 1639 (mw), 1467 (m), 1135 (m), 1078 (m), 1022 (w), 939 (s), 879 (m), 792 (s), 723 (s). ¹H NMR (δ / ppm / CDCl₃): 10.62 (s., 1H), 7.25 (s. br., 1H), 7.22 (s. br., 1H), 4.33 (t., 2H), 4.14 (s., 3H), 1.93 (t, 2H), 1. (s. br., 2H), 1.35-1.20 (m, 32H), 0.89 (t., 3H).

Synthesis of 1,2-dimethyl-3-alkylimidazolium bromides, dmimC_nBr (n = 12, 16)The same procedure was employed except that 10^{-2} mole of 1,2-dimethylimidazole was used.

dmimC₁₂Br. IR/cm⁻¹, (ATR diamond, ATR correction applied): 2954 (m), 2920 (vs), 2870 (m), 2851 (s), 1639 (mw), 1467 (m), 1135 (m), 1078 (m), 1022 (w), 939 (s), 879 (m), 792 (s), 723 (s). ¹H NMR (δ / ppm / CDCl₃): 7.64 (s. br., 1H), 7.37 (s. br., 1H), 4.20 (t., 2H), 3.99 (s., 3H), 2.78 (t, 3H), 1.78 (m, 2H), 1.35-1.20 (m, 18H), 0.87 (t., 3H).

dmimC₁₆Br. IR/cm⁻¹, (ATR diamond, ATR correction applied): 2954 (m), 2920 (vs), 2870 (m), 2851 (s), 1639 (mw), 1467 (m), 1135 (m), 1078 (m), 1022 (w), 939 (s), 879 (m), 792 (s), 723 (s). ¹H NMR (δ / ppm / CDCl₃): 7.73 (d. br., 1H), 7.43 (d. br., 1H), 4.18 (t., 2H), 4.04 (s., 3H), 2.82 (t, 3H), 1.84 (m, 2H), 1.35-1.20 (m, 26H), 0.88 (t., 3H).

II FT-IR characterizations

The FT-IR spectra of materials and of their precursors were room temperature on a 6700 FT-IR recorded at Nicolet spectrophotometer, using diamond ATR technique. The spectra were recorded on pure compounds and ATR correction was applied (Figures S1 to S9). For some selected compounds, the FT-IR spectra were recorded in the 20-300 °C temperature range. The variable temperature FT-IR spectra were recorded on an IRTF Nicolet iS10 spectrometer in Diffuse Reflectance mode by using High temperature Diffuse Reflectance Environmental Chamber. The background was recorded on dry KBr at 150 $\,^{\circ}\text{C}.$ The samples were diluted into a KBr matrix and the resulting mixtures containing about 10% of compound were ground before being heated. The FT-IR spectra were recorded in the 20-300 °C temperature range under air heating rate of 2 °C/minute. The spectra were recorded with a resolution of 0.4 cm⁻¹ (Figures S1 to S12).



Figure S1. FT-IR spectra of DODACl (green), NaK-1 (red) and DODA₁₉-1 (blue)



Figure S2.FT-IR spectra of $\text{TMAC}_{16}\text{Cl}(\text{green})$, NaK-1 (red) and (TMAC₁₆)₁₈-1 (blue)



Figure S3. FT-IR spectra of $mimC_{12}Br$ (green), NaK-1 (red) and $(mimC_{12})_{25}-1$ (blue)



Figure S4. FT-IR spectra of $mimC_{14}Br$ (green), NaK-1 (red) and $(mimC_{14})_{26}-1$ (blue)



Figure S5. FT-IR spectra of $mimC_{16}Br$ (green), NaK-1 (red) and $(mimC_{16})_{23}-1$ (blue)



Figure S7. FT-IR spectra of $mimC_{20}Br$ (green), NaK-1 (red) and $(mimC_{20})_{24}-1$ (blue)



Figure S9. FT-IR spectra of $dmimC_{16}Br$ (green), NaK-1 (red) and $(dmimC_{16})_{20}-1$ (blue)



Figure S11. Selected FT-IR spectra recorded at various temperatures for compound (mimC₁₆)₂₃-1 in air.



Figure S12. Selected FT-IR spectra recorded at various
 temperatures for compound (mimC₁₈)₂₄-1 in air.

III Thermo-Gravimetric Analyses, TGA.

Water content and thermal stability were determined by thermal gravimetric analysis with a Seiko TG/DTA 320 thermogravimetric balance (5°C min⁻¹, under O_2).



Figure S14. TGA curve of (TMAC₁₆)₁₈-1 under O₂.



Figure S16. TGA curve of $(mimC_{14})_{26}-1$ under O_2 .







Figure S18. TGA curve of $(\mbox{mim} C_{18})_{24} \mbox{--} 1$ under $\mbox{O}_2 \mbox{.}$



Figure S20. TGA curve of $(dmimC_{12})_{18}-1$ under O₂.



Figure S21. TGA curve of $(\texttt{dmimC}_{16})_{20}\text{--}1$ under $\text{O}_2\text{-}$

IV ¹H NMR studies in solution

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Figure S24. ¹H NMR spectra of mimC₁₈Br (black) and $(mimC_{18})_{24}-1$ (red) in CDCl₃.

Figure S25. ¹H MAS (500.13 MHz, 20 kHz) NMR spectrum of (TMAC₁₆)₁₈-1. Experimental spectrum in black, deconvolved spectra in red and complete simulated spectrum in blue.

Figure S26. $^{13}\mathrm{C}$ CPMAS NMR spectra of $(\mathrm{TMAC_{16}})_{18}\text{--1}$ (a) and $\mathrm{TMAC_{16}C1}$ (b).

Figure S27. ¹³C{¹H} HETCOR CPMAS NMR spectrum of $(TMAC_{16})_{18}-1$. The ¹³C NMR signals at 67 and 55 ppm are assigned to the -CH₂and the three CH₃ groups attached to the ammonium head, respectively. These correlations confirm that the ¹H NMR lines at 3.3-3.5 ppm belong to these groups.

Figure S28. ¹³C{¹H} HETCOR MAS NMR spectrum of $(mimC_{18})_{24}-1$.

Figure S29. $^{13}\mathrm{C}$ CPMAS NMR spectra of $(\text{DODA})_{19}\text{--}1$ (a) and <code>DODACl</code> (b).

Figure S30. ³¹P NMR spectrum of the precursor compound 1 in aqueous medium containing LiCl 1M as a function of the counter cations. (a) crystals of a potassium salt: the central peak corresponds to the trans isomer whereas the peripheral peaks refer to the *cis* isomer; (b) a mixed Na^+/K^+ salt: both isomers are also present with different chemical shifts and the signal of the *trans* isomer is broadened; (c) crystalline powder mainly containing Na^+ as counter ions which was employed as precursor in this study.

Figure S31. SA-XRD patterns recorded at 200°C for compound (mimC₁₂)₂₅-1.

Figure S32. SA-XRD patterns recorded at 200°C for compound $(mimC_{14})_{26}-1$.

Figure S33. SA-XRD patterns recorded at 200°C for compound (mimC₁₈)₂₄-1.

Figure S34. SA-XRD patterns recorded at 200°C for compound $(mimC_{20})_{24}-1$.

Figure S35. SA-XRD patterns recorded at 200°C for compound DODA₁₉-1.

<u>Table S1.</u> Indexation at a Given Temperature for the Reflections Detected in the Liquid-Crystalline Phase by SA-XRD for **DODA₁₉-1**. Values are Given for the Second Heating and Cooling.

	-			. 0	
T ∕°C	$d_{hkl (mes)} / { m \AA}$	<i>I</i> /a.u.	001	d_{hkl} (calc) /Å	
180°C	39.94	VS(Sh)	001	39.97	h = 39.97 Å
Cooling	_	-	003		a _{Hex} - 55.05 A
	13.5 11.4	W(Br) W(Br)			
	_*	_			
160°C	39.76	VS(Sh)	001	39.89	h = 39.89 Å
Cooling	20.01	S(Sh) -	002 003	19.95	$a_{Hex} = 33.87$ A
_	13.5	W(Br) W(Br)			
	_* _*	W(BL) -			
140°C	39.75	VS(Sh)	001	39.92	h = 39.92 Å
Cooling	20.04	S(Sh) -	002 003	19.96	<i>a_{Hex}</i> = 33.86 Å
	13.5	W(Br)			
	*	W(BL) -			
120°C	40.25	VS(Sh)	001	40.33	h = 40.33 Å
Cooling	20.20	S(Sh) _	002	20.16	<i>a_{Hex}</i> = 33.68 Å
00011119	13.5	W(Br)	000		
	⊥⊥.4 _*	W(Br) -			
100°C	40.02	VS(Sh)	001	40.17	h = 40.17 Å
Cooling	20.16	S(Sh) _	002	20.09	<i>a_{Hex}</i> = 33.75 Å
COOTING	13.5	W(Br)	000		
	11.4 _*	W(Br) -			
80°C	40.19	VS(Sh)	001	40.30	h = 40.30 Å
Caaling	20.20	S(Sh)	002	20.15	<i>a_{Hex}</i> = 33.7 Å
COOLING	_ 13.5	- W(Br)	003	_	
	11.4 _*	W(Br) -			
60°C	40 21	VS (Sh)	001	40 32	h = 40.32 Å
00 C	20.21	S (Sh)	002	20.16	a_{Hex} = 33.69 Å
Cooling	_ 13.5	- W(Br)	003	_	

	11.4 _*	W(Br) -			
40°C Cooling	40.17 20.20 	VS(Sh) S(Sh) - W(Br) W(Br)	001 002 003	40.29 20.14 -	h = 40.29 Å a _{Hex} = 33.7Å
60°C Heating	-* 40.26 20.21 - 13.5 11.4 -*	- S(Sh) - W(Br) W(Br) -	001 002 003	40.34 20.17 -	h = 40.34 Å a _{Hex} = 33.68 Å
80°C Heating	40.41 20.27 - 13.5 11.4 -*	VS(Sh) S(Sh) - W(Br) W(Br) -	001 002 003	40.48 20.24 -	h = 40.48 Å a _{Hex} = 33.62Å
100°C Heating	40.28 20.20 - 13.5 11.4 -*	VS(Sh) S(Sh) - W(Br) W(Br) -	001 002 003	40.34 20.17 -	h = 40.34 Å a _{Hex} = 33.68 Å
120°C Heating	40.12 20.16 - 13.5 11.4 -*	VS(Sh) S(Sh) - W(Br) W(Br) -	001 002 003	40.22 20.11 -	h = 40.22 Å a _{Hex} = 33.73Å
140°C Heating	39.94 20.04 - 13.5 11.4 -*	VS(Sh) S(Sh) - W(Br) W(Br) -	001 002 003	40.01 20.01 -	h = 40.01 Å a _{Hex} = 33.82 Å
160°C Heating	39.74 19.91 _ 13.5 11.4 _*	VS(Sh) S(Sh) - W(Br) W(Br) -	001 002 003	39.78 19.89 -	h = 39.78 Å a _{Hex} = 33.92 Å
180°C Heating	39.30 19.88 -	VS(Sh) S(Sh) -	001 002 003	39.53 19.77 -	h = 39.53 Å a _{Hex} = 34.02 Å

13.5	W(Br)
11.4	W(Br)
_*	_

 $d_{hkl \ (mes)}$ and $d_{hkl \ (calc)}$ are the measured and calculated diffraction spacing ; *h* is the lattice parameter of the smectic phase ; *I* corresponds to the intensity of the reflections (VS : very strong. S : strong. W : weak ; br and sh stand for broad and sharp) ; *h* and $d_{hkl \ (calc)}$ are respectively calculated according the formula : $h = 1/3 (d_{001(exp)} + 2d_{002\ (exp)} + 3d_{003\ (exp)})$ and $d_{hkl \ (calc)} = h/l$; a_{Hex} is the local hexagonal organization within the layers calculated with eq. 1 of the main text. * The reflection corresponding to the molten aliphatic chains (usually ~ 4.5 Å) is too broad to be measured.

T ∕°C	dhkl (mag)	I	001	$d_{\rm hbl}$ (and a) $/{\rm \AA}$	
	/ Å	(2 11		Carc) / 1	
	/A	/a.u.			0 - 1 - °
200°C	35.01	VS(Sh)	001	35.15	$h = 35.15 A_{0}$
	22.15	W(Sh)			a _{Hex} =32.75 Å
Cooling	17.64	S(Sh)	002	17.57	h′ = 22.15 Å
-	13	W(Br)			
	11	$W(\mathbf{B}\mathbf{r})$			
	± ±	W(DI)			
	- ^	-			
2					٥
180°C	35.46	VS(Sh)	001	35.55	h = 35.55 A
	22.36	W(Sh)			a _{Hex} = 32.57 Å
Cooling	17.82	S(Sh)	002	17.78	h′ = 22.36 Å
2	13	W(Br)			
	11	W (Br)			
	± ± +	W(DL)			
	- ^	_			
					<u>_</u>
160°C	35.52	VS(Sh)	001	35.59	h = 35.59 Å
	21.99	W(Sh)			a _{Hex} = 32.55 Å
Cooling	17.83		002	17.80	h' = 21.99 Å
		S(Sh)			
	1 0				
	13	W(BL)			
	11	W(Br)			
	-*	-			
140°C	35.47	VS(Sh)	001	35.63	h = 35.63 Å
	22.00	W(Sh)			$a_{\rm max} = 32.53$ Å
Cooling	17 89	S (Sh)	002	17 81	h' = 22 00 Å
COOLING	12		002	17.01	M = 22.00 R
	13	W(BL)			
		W(Br)			
	_*	-			
120°C	35.58	VS(Sh)	001	35.69	h = 35.69 Å
	21.98	W(Sh)			a _{Hey} = 32.5 Å
Cooling	17 90	S (Sh)	002	17 85	h' = 21.98 Å
COOLING	12		002	1,.00	11 21.90 11
	13	W(DL)			
		W(Br)			
	_*	_*			
100°C	35.62	VS(Sh)	001	35.57	h = 35.57 Å
	21.82	W(Sh)			$a_{max} = 32.56$ Å
Cooling	17 76	R (Sh)	002	17 79	$h_{Hex} = 21.82$
COULTING	10	5 (511) H (D)	002	11.15	m = 21.02 A
	13	W(Br)			
	11	W(Br)			
	_*	-			
80°C	35.73	VS(Sh)	001	35.75	h = 35.75 Å
	22.01	W(Sh)			$a_{\rm max} = 32.47$ Å
Cooling	17 99	C (Ch)	002	17 97	h' = 22.01 Å
COOTTING	100	S (SII)	UUZ	11.01	II = 22.01 A
	13	w(Br)			

<u>Table S2.</u> Indexation at a Given Temperature for the Reflections Detected in the Liquid-Crystalline Phase by SA-XRD for $(\min C_{12})_{25}$ -1. Values are Given for the Second Cooling.

	11 _*	W(Br) -			
60°C	35.38 22.62	VS(Sh) W(Sh)	001	35.59	h = 35.59 Å a _{Hex} = 32.55 Å
Cooling	17.90 13 11 -*	S(Sh) W(Br) W(Br) -	002	17.80	h' = 22.62 Å
40°C	35.27 21.98	VS(Sh) W(Sh)	001	35.30	h = 35.30 Å a _{Hex} = 32.68Å
Cooling	17.66 13 11 -*	S(Sh) W(Br) W(Br) -	002	17.65	h' = 21.98 Å

 $d_{hkl \ (mes)}$ and $d_{hkl \ (calc)}$ are the measured and calculated diffraction spacing ; *h* is the lattice parameter of the smectic phase ; *I* corresponds to the intensity of the reflections (VS : very strong. S : strong. W : weak. VW : very weak ; br and sh stand for broad and sharp) ; *h* and $d_{hkl \ (calc)}$ are respectively calculated according the formula : $h = 1/2 (d_{001(exp)} + 2d_{002\ (exp)})$ and $d_{hkl \ (calc)} = h/l$; a_{Hex} is the local hexagonal organization within the layers calculated with eq. 1 of the main text. * The reflection corresponding to the molten aliphatic chains (usually ~ 4.5 Å) is too broad to be measured.

T /°C	d _{hkl (mes)}	I	001	d _{hkl (calc)} /Å	
	/Å	/a.u.			
200°C	38.39	VS(Sh)	001	38.44	h = 38.44 Å
Cooling	19.24 13 11 -*	- S(Sh) W(Br) W(Br) -	002	19.22	<i>d_{Hex}</i> = 32.10 A
180°C	38.25	VS(Sh)	001	38.28	h = 38.28 Å
Cooling	19.15 13 11 -*	S(Sh) W(Br) W(Br) -	002	19.14	a _{Hex} 52.17 H
160°C	38.51	VS(Sh)	001	38.44	h = 38.44 Å
Cooling	19.18 13 11 -*	S(Sh) W(Br) W(Br) -	002	19.22	a _{Hex} - 52.10 A
140°C	38.32	VS(Sh) -	001	38.24	h = 38.24 Å
Cooling	19.08 13 11 -*	S(Sh) W(Br) W(Br) -	002	19.12	Chex Clille II
120°C	38.17	VS(Sh)	001	38.14	h = 38.14 Å
Cooling	19.05 13 11 -*	S(Sh) W(Br) W(Br) -	002	19.07	a _{Hex} S2.22 II
100°C	37.95	VS(Sh)	001	37.95	h = 37.95 Å
Cooling	18.97 13 11 -*	S(Sh) W(Br) W(Br) -	002	18.97	SHOX SEIST II
80°C	37.91	VS(Sh) -	001	37.98	h = 37.98 Å $a_{\text{Hex}} = 32.29 \text{ Å}$
Cooling	19.02 13	S(Sh) W(Br)	002	18.99	10A

<u>Table S3.</u> Indexation at a Given Temperature for the Reflections Detected in the Liquid-Crystalline Phase by SA-XRD for $(\min C_{14})_{26}$ -1. Values are Given for the Second Cooling.

	11 _*	W(Br) -			
60°C	37.74	VS(Sh) -	001	37.67	h = 37.67 Å $a_{\text{Hex}} = 32.43 \text{ Å}$
Cooling	18.80 13 11 -*	S(Sh) W(Br) W(Br) -	002	18.84	a _{Hex} = 32.43 A
40°C	37.12	VS(Sh) -	001	37.06	h = 37.06 Å $a_{\text{Hex}} = 32.69 \text{ Å}$
Cooling	18.50 13 11 -*	S(Sh) W(Br) W(Br) -	002	18.53	

 $d_{hkl \ (mes)}$ and $d_{hkl \ (calc)}$ are the measured and calculated diffraction spacing ; *h* is the lattice parameter of the smectic phase ; *I* corresponds to the intensity of the reflections (VS : very strong. S : strong. W : weak. VW : very weak ; br and sh stand for broad and sharp) ; *h* and $d_{hkl \ (calc)}$ are respectively calculated according the formula : $h = 1/2 (d_{001(exp)} + 2d_{002\ (exp)})$ and $d_{hkl \ (calc)} = h/l$; a_{Hex} is the local hexagonal organization within the layers calculated with eq. 1 of the main text. * The reflection corresponding to the molten aliphatic chains (usually ~ 4.5 Å) is too broad to be measured.

T /°C	d _{hkl (mes)}	I	001	d_{hkl} (calc) /Å	
	/Å	/a.u.			
200°C	41.09	VS(Sh)	001	40.96	h = 40.96 Å
Cooling	20.41 12 -*	S(Sh) W(Br) -	002	20.48	a _{Hex} = 30.97 A
180°C	40.09	VS(Sh)	001	40.46	h = 40.46 Å
Cooling	20.41 12 -*	S(Sh) W(Br) -	002	20.23	a _{Hex} of for
160°C	40.09	VS(Sh)	001	40.46	h = 40.46 Å
Cooling	20.41 12 -*	S(Sh) W(Br) -	002	20.23	a _{Hex} - 51.10 A
140°C	40.09	VS(Sh)	001	40.41	h = 40.41 Å
Cooling	20.36 12 -*	S(Sh) W(Br) -	002	20.20	a _{Hex} of for
120°C	40.09	VS(Sh)	001	40.41	h = 40.41 Å
Cooling	20.36 12 -*	S(Sh) W(Br) -	002	20.20	a _{Hex} of to h
100°C	40.71	VS(Sh) -	001	40.67	h = 40.67 Å
Cooling	20.31 12 -*	S(Sh) W(Br) -	002	20.33	-nex
80°C	40.52	VS(Sh) -	001	40.48	h = 40.48 Å
Cooling	20.22 12 -*	S(Sh) W(Br) -	002	20.24	Snex 01.10 II
60°C	40.34	VS(Sh) -	001	40.34	h = 40.34 Å $a_{\rm max} = 31.20$ Å
Cooling	20.17	S(Sh)	002	20.17	CHEX CI.ZO II

<u>Table S4.</u> Indexation at a Given Temperature for the Reflections Detected in the Liquid-Crystalline Phase by SA-XRD for $(\min C_{16})_{23}$ -1. Values are Given for the Second Cooling.

	12 _*	W(Br) -			
40°C	40.16	VS(Sh)	001	40.16	h = 40.16 Å
Cooling	20.08 12 -*	S(Sh) W(Br) -	002	20.08	a _{Hex} 01.20 H
20°C	39.44	VS(Sh)	001	39.31	h = 39.31 Å
Cooling	19.59 12 -*	S(Sh) W(Br) -	002	19.66	a _{Hex} - 51.10 A
10°C	38.92	VS(Sh)	001	38.54	h = 38.54 Å
Cooling	19.08 12 -*	S(Sh) W(Br) -	002	19.27	a _{Hex} - 51.95 K
0°C	38.58	VS(Sh)	001	38.29	h = 38.29 Å a _{Hex} = 32.03 Å
Cooling	_ 19.00 12 _*	- S(Sh) W(Br) -	002	19.15	
-10°C	38.58	VS(Sh)	001	38.29	h = 38.29 Å
Cooling	_ 19.00 12 _*	- S(Sh) W(Br) -	002	19.15	$a_{Hex} = 32.03$ A
-20°C	38.58	VS(Sh)	001	38.29	h = 38.29 Å
Cooling	19.00 12 _*	S(Sh) W(Br) -	002	19.15	<i>a_{Hex}</i> = 32.03 A
-30°C	38.58	VS(Sh)	001	38.29	h = 38.29 Å
Cooling	_ 19.00 12 _*	- S(Sh) W(Br) -	002	19.15	$a_{Hex} = 32.03$ A
-40°C	38.58	VS(Sh)	001	38.29	h = 38.29 Å
Cooling	_ 19.00 12 _*	- S(Sh) W(Br) -	002	19.15	a _{Hex} = 32.03 A

 $d_{hkl (mes)}$ and $d_{hkl (calc)}$ are the measured and calculated diffraction spacing; *h* is the lattice parameter of the smectic phase; *I* corresponds to the intensity of the reflections (VS : very strong. S : strong. W : weak. VW : very weak; br and sh stand for broad and sharp); *h* and

 $d_{hkl\ (calc\)}$ are respectively calculated according the formula : $h = 1/2 (d_{001(exp)} + 2d_{002\ (exp)})$ and $d_{hkl\ (calc)} = h/l$; a_{Hex} is the local hexagonal organization within the layers calculated with eq. 1 of the main text. * The reflection corresponding to the molten aliphatic chains (usually ~ 4.5 Å) is too broad to be measured.

T /°C	d _{hkl (mes)}	I	001	d _{hkl (calc)} /Å	
	/Å	/a.u.			
200°C	43.30	VS(Sh)	001	43.28	h = 43.28 Å
Cooling	21.63 12 -*	- S(Sh) W(Br) -	002	21.64	$a_{Hex} = 30.81$ A
180°C	43.21	VS(Sh)	001	43.25	h = 43.25 Å
Cooling	21.64 12 -*	S(Sh) W(Br) -	002	21.62	a _{Hex} - 52.02 A
160°C	43.25	VS(Sh)	001	43.23	h = 43.23 Å
Cooling	21.60 12 -*	S(Sh) W(Br) -	002	21.61	a _{Hex} 50.05 H
140°C	43.72	VS(Sh)	001	43.76	h = 43.76 Å
Cooling	21.90 12 -*	S(Sh) W(Br) -	002	21.88	a _{Hex} solution
120°C	43.73	VS(Sh)	001	43.70	h = 43.70 Å
Cooling	21.83 12 -*	S(Sh) W(Br) -	002	21.85	anex correction
100°C	43.55	VS(Sh) -	001	43.58	h = 43.58 Å $a_{\rm max} = 30.7$ Å
Cooling	21.80 12 -*	S(Sh) W(Br) -	002	21.79	Thex of the second
80°C	43.62	VS(Sh) -	001	43.59	h = 43.59 Å
Cooling	21.78 12 -*	S(Sh) W(Br) -	002	21.80	-nex COULT
60°C	43.60	VS(Sh) -	001	43.52	h = 43.52 Å $a_{\mu_e} = 30.72$ Å
Cooling	21.72 12	S(Sh) W(Br)	002	21.76	

<u>Table S5.</u> Indexation at a Given Temperature for the Reflections Detected in the Liquid-Crystalline Phase by SA-XRD for $(\min C_{18})_{24}$ -1. Values are Given for the Second Cooling.

	_ *	-			
40°C	43.57	VS(Sh) -	001	43.63	h = 43.63 Å
Cooling	21.84 12 -*	S(Sh) W(Br) -	002	21.84	a _{Hex} 50.05 m

 $d_{hkl \ (mes)}$ and $d_{hkl \ (calc)}$ are the measured and calculated diffraction spacing ; *h* is the lattice parameter of the smectic phase ; *I* corresponds to the intensity of the reflections (VS : very strong. S : strong. W : weak. VW : very weak ; br and sh stand for broad and sharp) ; *h* and $d_{hkl} \ (calc)$ are respectively calculated according the formula : $h = 1/2 \ (d_{001(exp)} + 2d_{002\ (exp)})$ and $d_{hkl} \ (calc) = h/l$; a_{Hex} is the local hexagonal organization within the layers calculated with eq. 1 of the main text. * The reflection corresponding to the molten aliphatic chains (usually ~ 4.5 Å) is too broad to be measured.

T /°C	d _{hkl (mes)}	I	001	d_{hkl} (calc.) /Å	
	/Å	/a.u.			
200°C	15 10	S (Sh)	0.01	15 03	b - 15 03 λ
200 C	-	-	001	40.05	a_{Hex} = 30.68 Å
Cooling	22.48 12 -*	S(Sh) W(Br) -	002	22.52	
180°C	45.67	S(Sh) -	001	45.64	h = 45.64 Å $a_{mm} = 30.47 \text{ Å}$
Cooling	22.80 12 -*	S(Sh) W(Br) -	002	22.82	a _{Hex} oo Ir I
160°C	45.78	S(Sh)	001	45.81	h = 45.81 Å
Cooling	22.92 12 -*	S(Sh) W(Br) -	002	22.91	a _{Hex} Solit II
140°C	46.28	S(Sh) _	001	46.30	h = 46.30 Å
Cooling	23.16 12 -*	S(Sh) W(Br) -	002	23.15	a _{Hex} oo.20 H
120°C	46.32	S(Sh) _	001	46.34	h = 46.34 Å
Cooling	23.18 12 -*	S(Sh) W(Br) -	002	23.17	Shex Collin
100°C	46.10	S(Sh) -	001	46.07	h = 46.07 Å $a_{ver} = 30.33 \text{ Å}$
Cooling	23.02 12 -*	S(Sh) W(Br) -	002	23.02	nex
80°C	46.85	S(Sh) _	001	46.42	h = 46.42 Å
Cooling	22.99 12 -*	S(Sh) W(Br) -	002	23.21	-nex coller in
60°C	46.21	S(Sh) -	001	46.12	h = 46.12 Å $a_{\text{Hex}} = 30.31 \text{ Å}$
Cooling	23.01 12	S(Sh) W(Br)	002	23.06	

<u>Table S6.</u> Indexation at a Given Temperature for the Reflections Detected in the Liquid-Crystalline Phase by SA-XRD for $(\min C_{20})_{24}$ -1. Values are Given for the Second Cooling.

	- ^	-			
40°C	43.72	VS(Sh) -	001	43.70 21.85	h = 43.70 Å $a_{Hex} = 31.14$ Å
Cooling	21.84 12 -*	S(Sh) W(Br) -	002		

 $d_{hkl \ (mes)}$ and $d_{hkl \ (calc)}$ are the measured and calculated diffraction spacing ; *h* is the lattice parameter of the smectic phase ; *I* corresponds to the intensity of the reflections (VS : very strong. S : strong. W : weak. VW : very weak ; br and sh stand for broad and sharp) ; *h* and $d_{hkl} \ (calc)$ are respectively calculated according the formula : $h = 1/2 \ (d_{001(exp)} + 2d_{002\ (exp)})$ and $d_{hkl} \ (calc) = h/l$; a_{Hex} is the local hexagonal organization within the layers calculated with eq. 1 of the main text. * The reflection corresponding to the molten aliphatic chains (usually ~ 4.5 Å) is too broad to be measured.