Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

From tectons to luminescent supramolecular ionic liquid crystals

Pierre Dechambenoit[a,c], Sylvie Ferlay[a*], Bertrand Donnio[b], Daniel Guillon[b] and Mir Wais Hosseini[a*]

Physical measurements

Polarized optical microscopy (POM), differential scanning calorimetry (DSC), and small-angle X-ray scattering (SAXS).

Small-angle X-ray scattering (SAXS)

The XRD patterns were obtained with two different experimental set-ups. In all cases, a linear monochromatic Cu-Kα_1 beam (λ = 1.5405 Å) was obtained using a sealed-tube generator (900 W) equipped with a bent quartz monochromator. In the first set, the transmission Guinier geometry was used, whereas a Debye-Scherrer-like geometry was used in the second experimental set-up. In all cases, the crude powder was filled in Lindemann capillaries of 1 mm diameter and 10 μm wall thickness. An initial set of diffraction patterns was recorded on an image plate; periodicities up to 80 Å can be measured, and the sample temperature controlled to within ± 0.3 °C from 20 to 350 °C. The second set of diffraction patterns was recorded with a curved Inel CPS 120 counter gas-filled detector linked to a data acquisition computer; periodicities up to 60 Å can be measured, and the sample temperature controlled to within ± 0.05 °C from 20 to 200 °C. In each case, exposure times were varied from 1 to 24 h.

Differential scanning calorimetry (DSC)

The transition temperatures and enthalpies were measured by differential scanning calorimetry with a TA Instruments DSC-Q1000 instrument operated at scanning rates of 2-to-10 °C min^{-1} on heating and on cooling. TG measurements were carried out on a SDTQ 600 apparatus at a scanning rate of 10 °C min^{-1} from RT to 300°C, in air.

Polarized optical microscopy (POM)

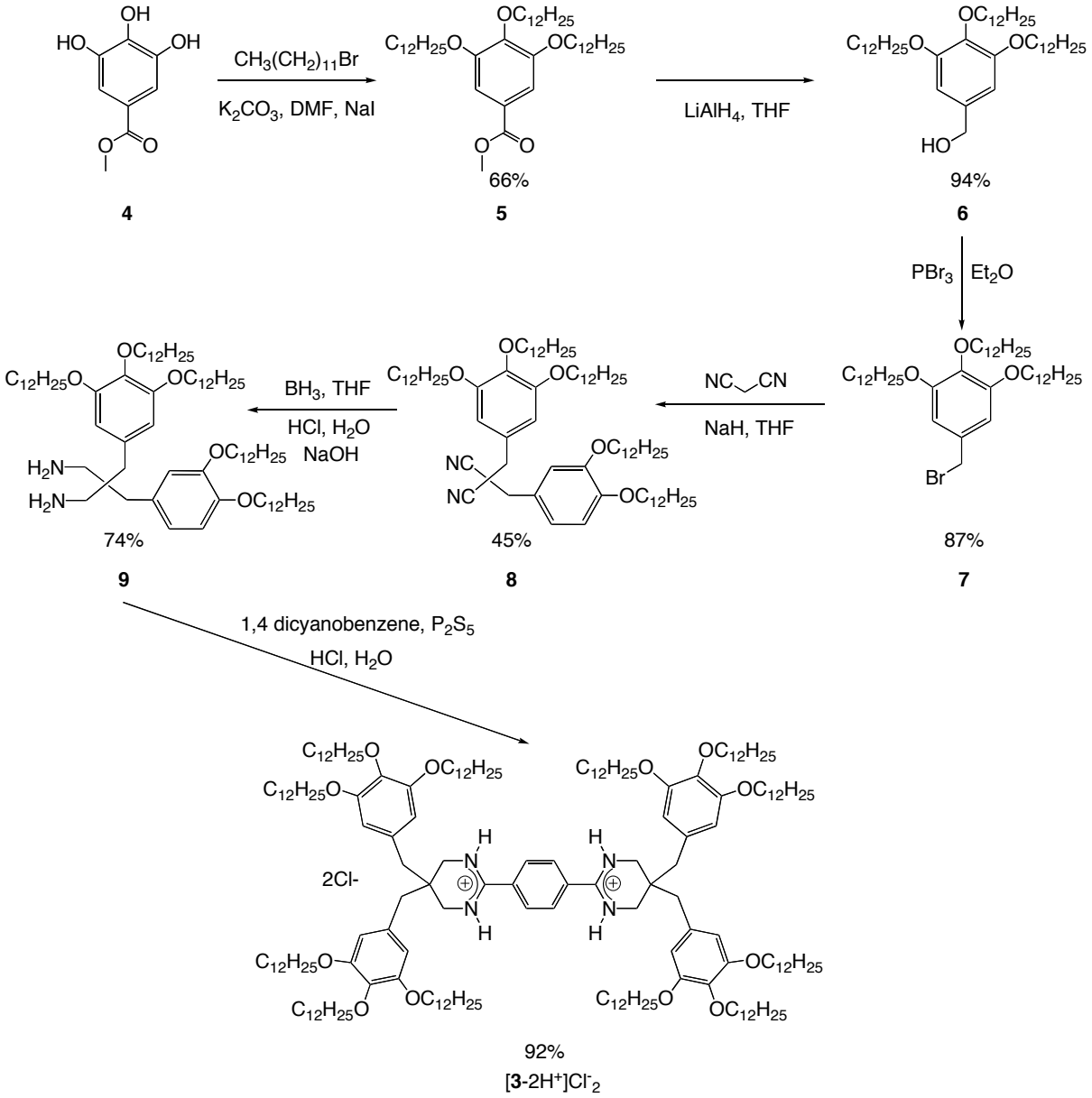
The optical textures of the mesophases were studied with a Leitz polarizing microscope equipped with a Mettler FP80 hot-stage and a FP80 central processor.

Synthesis

Chemicals purchased from commercial sources were used without further purification.

Synthesis of $\boldsymbol{3}^{2+}$ *salts*

For the synthesis of $\mathbf{3}^{+}$ (scheme 1), the starting material was methyl gallate **4**. The reaction of the latter with 1-bromodecane in DMF in the presence of K_2CO_3 and catalytic amounts of NaI afforded **5** in 66 % yield. The reduction of the latter into the alcohol **6** using $LiAlH_4$ in dry THF was achieved in 94 % yield. The activation of the alcohol **6** into the bromo derivative **7** was achieved in 87 % yield upon treatment with PBr_3 in Et_2O. The condensation of **7** with malonitrile in THF using NaH afforded **8** in 45 % yield. The latter was reduced into **9** in 74 % yield by reaction with BH_3 in refluxing dry THF. Finally, the condensation at 150 °C of **9** with 1,4-dicyanobenzene in the presence of P_2S_5 afforded the free base which was converted quantitatively into $[\mathbf{3}^{2+}][Cl^-]_2$ upon treatment with HCl. The $[\mathbf{3}^{2+}][Ag(CN)_2^-]_2$ salt was prepared by anion metathesis in the solid state upon grinding a mixture of $[\mathbf{3}^{2+}][Cl^-]_2$ and $KAg(CN)_2$ followed by extraction of the desired compound into CH_2Cl_2.



Scheme S1

*Synthesis of **5***

The synthesis was adapted from a procedure described in the literature.[1]

In 120 ml of dry DMF, 1.5 g (8.15 mmol) of methyl gallate **4**, 10.15 g (40.7 mmol) of 1-bromododecane, 3.9 g (28.5 mmol) of K_2CO_3 and 176 mg of NaI were added under Ar and the mixture was heated to 80 °C for 48 h. After evaporating the solvent, the residue was dissolved in 80 ml of water and extracted with CH_2Cl_2 (2 x 100 ml). The organic phase was dried over $MgSO_4$ and the solvent removed under vacuum affording a residue which was purified by column chromatography (SiO_2, $C_6H_{12}\rightarrow CH_2Cl_2$). Compound **5** was obtained in 66 %yield as a pure solid. ^{1}H-NMR ($CDCl_3$, δ ppm): 0.87 (t, 9H, ^{3}J = 6.6 Hz, C*H*$_3$), 1.26 (m, 48H, CH_3-(C*H*$_2$)$_8$), 1.46 (m, 6H, CH_3-(CH$_2$)$_8$-C*H*$_2$), 1.79 (m, 6H, C*H*$_2$-CH$_2$-O), 3.88 (s, 3H, OC*H*$_3$), 4.00 (t, 6H, ^{3}J = 6.6 Hz, C*H*$_2$-O), 7.25 (s, 2H, C*H* arom); ^{13}C-NMR ($CDCl_3$, δ ppm): 14.1 (CH_3), 22.7, 26.1, 29.3, 29.4, 29.6, 29.6, 29.7, 30.3, 31.9 (CH_2), 52.1 (OCH_3), 69.1 (CH_2-O positions 3,5), 73.4 (CH_2-O position 4), 107.9 (CH arom.), 124.6 (C arom.-CO_2Me), 142.3 (C arom.-O position 4), 152.8 (C arom.-O positions 3,5), 166.9 (CO_2Me).

*Synthesis of **6***

The synthesis of **6** was adapted from a procedure described in the literature.[2]

In 25 ml of freshly distilled THF, 110 mg (2.89 mmol) of $LiAlH_4$ and 2.70 g (3.92 mmol) of **5** were added and the mixture stirred at room temperature during 3 h. 2 ml of H_2O was added carefully and the mixture was filtered. After washing with THF, the solvent was evaporated affording compound **6** as a white solid (94 % yield). ^{1}H-NMR ($CDCl_3$, δ ppm): 0.88 (t, 9H, ^{3}J = 6.1 Hz, C*H*$_3$); 1.26 (m, 48H, CH_3-(C*H*$_2$)$_8$), 1.45 (m, 6H, CH_3-(CH$_2$)$_8$-C*H*$_2$), 1.80 (m, 6H, C*H*$_2$-CH$_2$-O), 3.94 (t, 2H, ^{3}J = 6.8 Hz, C*H*$_2$-O position 4), 3.97 (t, 4H, ^{3}J = 7.0 Hz, C*H*$_2$-O positions 3,5), 4.59 (s, 2H, C*H*$_2$OH); 6.56 (s, 2H, CH arom.); ^{13}C-NMR ($CDCl_3$, δ ppm): 14.0 (CH_3), 22.6, 26.1, 29.4, 29.6, 30.3, 31.9 (CH_2), 65.4 (CH_2-OH), 69.0 (CH_2-O positions 3,5), 73.4 (CH_2-O position 4), 105.1 (CH arom.), 136.2, 137.5 (C arom.-CH_2OH et C arom.-O position 4), 153.1 (C arom.-O positions 3,5) .

*Synthesis of **7***

The synthesis of **7** was adapted from a procedure described in the literature.[3]

In 70 ml of freshly distilled Et_2O, 4.81 g (6.98 mmol) of **6** was dissolved before 2.1 ml (21 mmol) of PBr_3 was drop wise added. The mixture thus obtained was stirred at room temperature for 1.5 h. The solution was cooled to 0°C and 70 ml of an aqueous solution (5 % of $NaHCO_3$) was added drop wise while stirring. The desired compound was extracted into Et_2O (3 x 50 ml) and the combined organic phases were dried over $MgSO_4$. Removal of the solvent afforded the pure compound **7** as a white solid in 87 % yield. ^{1}H-NMR ($CDCl_3$, δ ppm): 0.88 (t, 9H, ^{3}J = 6.6 Hz, C*H*$_3$), 1.26 (m, 48H, CH_3-(C*H*$_2$)$_8$), 1.46 (m, 6H, CH_3-(CH$_2$)$_8$-C*H*$_2$), 1.77 (m, 6H, C*H*$_2$-CH$_2$-O), 3.94 (t, 2H, ^{3}J = 6.9 Hz, C*H*$_2$-O position 4), 3.96 (t, 4H, ^{3}J = 6.6 Hz, C*H*$_2$-O positions 3,5), 4.43 (s, 2H, C*H*$_2$Br), 6.57 (s, 2H, CH arom.); ^{13}C-NMR ($CDCl_3$, δ ppm): 14.1 (CH_3), 22.7, 26.1, 29.4, 29.4 29.6, 29.6, 29.7, 29.7, 30.3, 31.9 (CH_2), 34.6 (CH_2-Br), 69.1 (CH_2-O positions 3,5), 73.4 (CH_2-O position 4), 107.5 (CH arom.), 132.5 (C arom.-CH_2Br), 138.4 (C arom.-O position 4), 153.1 (C arom.-O positions 3,5).

*Synthesis of **8***

At 0 °C, to a suspension of NaH (264 mg, 11.0 mmol) in dry THF (120 ml), a THF (dry) solution (25 ml) of malonitrile (661 mg, 10.0 mmol) was added drop wise and the mixture was stirred for 30 minutes. To the mixture, 5 mg of KI and a THF (dry) solution (30 ml) of **7**

[1] Johansson, G.; Percec, V.; Ungar, G.; Abramic, D. *J. Chem. Soc. Perkin Trans.1,* **1994**, 447-459.
[2] Balagurusamy, V. S. K.; Ungar, G.; Percec, V.; Johansson, G. *J. Am. Chem. Soc.*, **1997**, *119*, 1539-1555.
[3] Hammond, S. R.; Zhou, W.-J.; Gin, D. L.; Avlyanov, J. K.*Liq. Cryst.*, **2002**, *29*,. 1151-1159.

(4.40 g, 6.08 mmol) was added drop wise before it was refluxed during 2.5 h. The mixture was allowed to cool to room temperature and 5 ml of distilled water was added to quench the excess of sodium hydride. The removal of solvents under reduced pressure left a residue which was dissolved in 100 ml of water and extracted with CH_2Cl_2 (2 x 100 ml). The organic layers were combined and further washed with 50 ml of distilled water, dried over $MgSO_4$, and evaporated to dryness affording a mixture of mono and disubstituted derivatives which was purified by column chromatography (cyclohexane/CH_2Cl_2 6/4 → 4/6; Rf : 0.25). The pure compound **8** was obtained in 45 % yield as a colorless oil that solidified upon standing. Mp: 41 °C (decomposition at 300 °C).^{1}H-NMR ($CDCl_3$, δ ppm): 0.88 (t, 18H, ^{3}J = 6.6Hz, C*H*$_3$), 1.26 (m, 96H, CH_3-(C*H*$_2$)$_8$), 1.44 (m, 12H, CH_3-(CH_2)$_8$-C*H*$_2$), 1.76 (m, 12H, C*H*$_2$-CH_2-O), 3.11 (s, 4H, C*H*$_2$-C(CN)$_2$), 3.96 (t, 12H, ^{3}J = 6.6 Hz, C*H*$_2$-O), 6.54 (s, 4H, CH arom.) ; ^{13}C-NMR ($CDCl_3$, δ ppm): 14.1 (CH_3), 22.7, 26.1, 29.4, 29.4, 29.6, 29.7, 29.8, 30.4, 31.9 (CH_2), 41.1 ($C(CN)_2$) 43.8 (CH_2-$C(CN)_2$), 69.2 (CH_2-O positions 3,5), 73.4 (CH_2-O position 4), 108.6 (CH arom.), 115.4 (CN), 126.8 (C-CH_2), 138.5 (C arom.-O position 4), 153.3 (C arom.-O positions 3,5). Calc. for $C_{89}H_{158}N_2O_6$: C = 79.05 %, H = 11.78 %, N = 2.07 %. Found: C = 78.71 %, H = 12.25 %, N = 2.09 %. IR: $\nu_{C\equiv N}$ = 2247 cm^{-1}.

*Synthesis of **9***

Under Ar, 1.71 g (1.26 mmol) of **8** was dissolved in 30 ml of dry THF. To this solution, 15 ml of BH_3 (1M in THF) was added and the mixture was refluxed for 18 h. The excess of BH_3 was quenched with 8 ml of water and the solvents were evaporated under reduced pressure. To the solid thus obtained, 150 ml of a mixture of MeOH (40 %), $CHCl_3$ (40 %), H_2O (5 %), and aqueous HCl (12N, 15 %) was added and the mixture refluxed overnight. After cooling to room temperature, the solvents were evaporated to dryness and the residue obtained was suspended in water and the pH was adjusted to 13 using an aqueous NaOH solution. The desired compound **9** was extracted into CH_2Cl_2 (3 x 40 ml). The organic layers were combined and further washed with 10 ml of water, dried over $MgSO_4$ and evaporated under reduced pressure. The mixture thus obtained was purified by column chromatography (Al_2O_3, CH_2Cl_2/MeOH 99/1 → 95/5) affording **9** as a viscous liquid in 74 % yield. ^{1}H-NMR ($CDCl_3$, δ ppm): 0.88 (t, 18H, ^{3}J = 6.6Hz, C*H*$_3$), 1.26 (m, 96H, CH_3-(C*H*$_2$)$_8$), 1.46 (m, 12H, CH_3-(CH_2)$_8$-C*H*$_2$), 1.75 (m, 12H, C*H*$_2$-CH_2-O), 2.56, 2.61 (2s, 2x4H, C*H*$_2$-CH et C*H*$_2$-N), 3.93 (t, 12H, ^{3}J = 6.9 Hz, C*H*$_2$-O), 6.39 (s, 4H, CH arom.); ^{13}C-NMR ($CDCl_3$, δ ppm): 14.1 (CH_3), 22.7, 26.1, 29.4, 29.5, 29.7, 29.8, 30.4, 31.9 (CH_2), 41.2, 45.9 (CH_2N et CH_2-$C(CH_2N)_2$); 43.5 (C-(CH_2N)$_2$); 69.2 (CH_2-O positions 3,5); 73.4 (CH_2-O position 4), 109.1 (CH arom.), 133.5, 136.8 (C-CH_2 et C arom.-O position 4), 152.7 (C arom.-O positions 3,5). Calc. for $C_{89}H_{166}N_2O_6$: C = 78.58 %, H = 12.30 %, N = 2.06 %. Found: C = 78.36 %, H = 12.21 %, N = 1.88 %.

*Synthesis of [**3**$^{2+}$][Cl$^-$]$_2$*

Under Ar, a mixture of **9** (2.31 g, 1.70 mmol), P_2S_5 (15 mg) and 1,4-dicyanobenzene (109 mg, 0.85 mmol) was stirred and heated at 125 °C during 3 h, then at 150°C during 2 h. After cooling, the mixture was purified by column chromatography (Al_2O_3, CH_2Cl_2/MeOH 99/1 → 97/3) affording the desired free base as a yellow solid in 44 % yield. 591 mg (0.206 mmol) of the latter was dissolved in 8 ml Et_2O before 3 ml of an HCl 0.5N aqueous solution was added and the mixture is stirred during 10 minutes. The mixture was washed with 3 ml of distilled water and the organic phase was dried over $MgSO_4$, filtered and evaporated to dryness. The residue thus obtained was purified by chromatography (SiO_2, CH_2Cl_2/MeOH 99/1 → 96/4) affording [**3**$^{2+}$][Cl$^-$]$_2$ as a gummy solid in 92% yield. Mp = -12 °C. ^{1}H-NMR ($CDCl_3$, δ ppm): 0.86 (t, 36H, J = 6.6 Hz, C*H*$_3$), 1.24 (m, 192H, CH_3-(C*H*$_2$)$_8$), 1.44 (m, 24H, CH_3-(CH_2)$_8$-C*H*$_2$), 1.73 (m, 24H, C*H*$_2$-CH_2-O), 2.55 (br, 8H, C arom.-C*H*$_2$-C quat.), 3.38 (br, 8H, C*H*$_2$-N), 3.89

(t, 8H, ^{3}J = 6.6 Hz, C*H*$_2$-O position 4), 3.93 (t, 16H, ^{3}J = 6.6 Hz, C*H*$_2$-O positions 3,5), 6.25 (s, 8H, CH arom.), 7.86 (s, 4H, CH arom.), 10.57 (4H, NH); ^{13}C-NMR ($CDCl_3$, δ ppm): 14.3 (**C**H$_3$), 22.9, 26.4, 26.4, 29.6, 29.8, 29.9, 30.0, 30.6, 32.1 (**C**H$_2$ n-dodecyle), 42.0, 46.5 (**C**H$_2$-C(CH$_2$N)$_2$ and **C**H$_2$-N);, 69.7 (**C**H$_2$-O positions 3,5), 73.6 (**C**H$_2$-O position 4), 109.5 (**C**H arom.), 128.9 (**C**H arom.), 130.3, 131.4, 137.6 (**C** arom.-CH$_2$, **C** arom.-CN$_2$ et **C** arom.-O position 4), 153.2 (**C** arom.-O positions 3,5), 157.7 (N=**C**-N). Calc. for $C_{186}H_{332}Cl_2N_4O_{12}$: C = 77.37 %, H = 11.59 %, N = 1.94 %. Found: C = 77.47 % , H = 11.75 %, N = 1.83 %.

*Synthesis of [**3**$^{2+}$][Ag(CN)$_2^-$]$_2$*

A solid mixture of [**3**$^{2+}$][Cl$^-$]$_2$ (30 mg, 0.01 mmol) and KAg(CN)$_2$ (4.8 mg, 0.02 mmol) was carefully ground. The residue thus obtained was taken up in CH_2Cl_2 (30 ml) and washed with distilled water (3 x 10 ml). The organic phase was dried over $MgSO_4$ and evaporated to dryness affording the desired compounds [**3**$^{2+}$][Ag(CN)$_2^-$]$_2$ as a gummy solid in quantitative yield. Calc. for $C_{190}H_{332}N_8O_{12}Ag_2$: C = 72.76 %, H = 10.67 %, N = 3.57 %. Found: C = 72.56 %, H = 11.03 %, N = 3.54 %. IR: $\nu_{C\equiv N}$ = 2137 cm^{-1}.

Figures

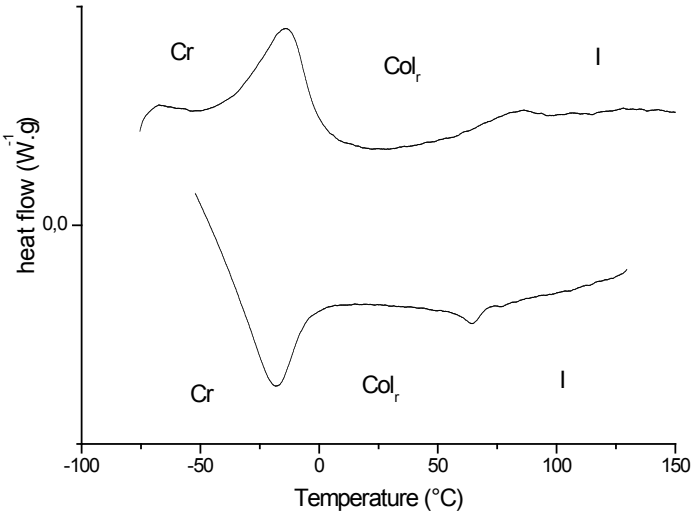


Figure S1: DSC traces of [**3**$^{2+}$][Cl$^-$]$_2$ (second heating, top curve, first cooling, bottom curve).

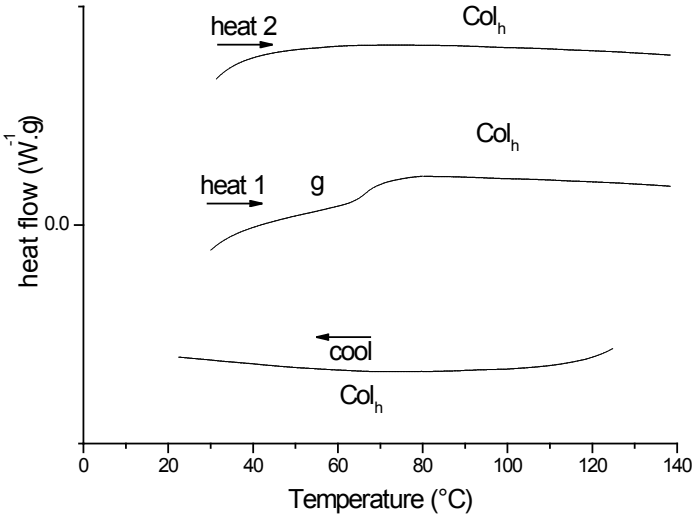


Figure S2: DSC traces of $[\mathbf{3}^{2+}][Ag(CN)_2^-]_2$ (second heating, top curve, , first heating, middle curve, and first cooling, bottom curve). A glass transition is detected during the first heating; the transition to the isotropic liquid is broad and not detectable. On subsequent cooling and heating cycles, the DSC traces are silent (both isotropic liquid-to-mesophase and mesophase-to-vitreous state are broad, likely due to the viscosity of the system.

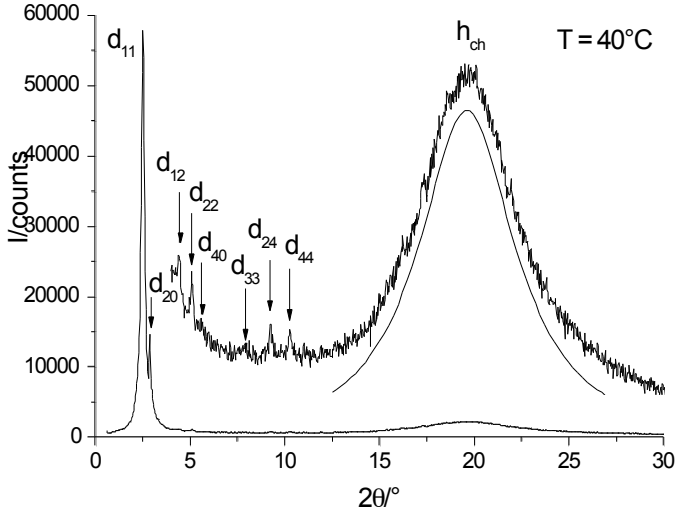


Figure S3: Small-angle XRD diffraction pattern and peaks indexation for $[\mathbf{3}^{2+}][Cl^-]_2$, recorded at 313 K (the diffuse scattering halo is fitted by a Gaussian function in agreement with the short-range order of the chains in their melted conformation).