



Electronic Supporting Information

Bolaamphiphilic Liquid Crystals based on Bis-imidazolium Cations

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General Synthetic Methods

Reagents and solvents were purchased from commercial sources (Aldrich, Acros, Fluka) and used without further purification unless otherwise specified. Dichloromethane (CH_2Cl_2) was distilled from CaH_2 under argon. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under argon. Thin layer chromatography (TLC) was performed on Polygram Aluminium oxide 0.2 mm N/UV₂₅₄ with visualization by UV light or staining. Flash column chromatography was performed using Aluminium Oxid 90 standardized from Merck. ^1H (300.13 MHz) and ^{13}C NMR (75.48 MHz) spectra were recorded on a Bruker Avance 300 spectrometer. Chemical shifts (δ) are given in parts per million (ppm) referenced to residual protonated solvent (CDCl_3 : δ_{H} 7.27 ppm, δ_{C} 77.00 ppm; $\text{DMSO}-d_6$: δ_{H} 2.50 ppm, δ_{C} 39.50 ppm; $\text{methanol}-d_4$: δ_{H} 3.35 ppm, δ_{C} 49.00 ppm). Abbreviations used are s (singlet), d (doublet), t (triplet), quin (quintet), br (broad), and m (multiplet). FT-IR spectra were recorded on IR Digilab FTS 3000 spectrophotometer. Frequencies are given in cm^{-1} . UV spectra were recorded on a Perkin Elmer Precisly Lambda 950 UV/Vis Spectrometer. Wavelengths are given in nm and the molar absorption coefficient in $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. Elemental Analyses were performed by the Institute Charles Sadron (ICS). The transition temperatures and enthalpies were measured by differential scanning calorimetry with a DSC Q1000 from TA Instruments operated at heating/cooling rate of $5^\circ\text{C}/\text{min}$. The device was calibrated with indium (156.6°C , $28.4\text{ J}\cdot\text{g}^{-1}$) and gallium (29.8°C) as the standards. The TGA measurements were carried out on a SDTQ 600 at scanning rate of $10^\circ\text{C}\cdot\text{min}^{-1}$. The optical texture of the mesophases were studied with a Leitz Orthoplan polarizing microscope equipped with a Mettler FP80 hot-stage and an FP80 central processor. XRD measurements were recorded by curve counter (CPS120 model from INEL). Samples were directly filled in Lindemann capillaries of 0.5 mm diameter.

General Procedures for the preparation of compounds 1 to 4

dimethyl 4,4'-(dodecane-1,12-diylbis(oxy))dibenzoate (1).

To a mixture of 4-hydroxybenzoic acid (24.34 g, 160 mmol) and potassium carbonate (31.54 g, 229 mmol) stirred during 2 h in DMF (300 mL), was added dibromododecane (25.00 g, 76 mmol) and the resulting white suspension was heated at 80°C for 16 h. The reaction mixture was then filtered and washed with water (100 mL). The white solid was diluted with CH_2Cl_2 and water until all solids were dissolved. The organic phase was extracted with CH_2Cl_2 . All organics were combined and washed successively with saturated aqueous NaHCO_3 , water, and brine. The methylene chloride layer was dried over MgSO_4 , filtered and concentrated in vacuum to give **1** (35.85 g, quantitative) as a white pure solid. ^1H NMR (CDCl_3 ; 300 MHz): δ 1.31 (12H, br s, CH_2 aliphatic chain), 1.41–1.48 (4H, m, CH_2 aliphatic chain), 1.80 (4H, quin, $J = 6.6\text{ Hz}$, $\text{CH}_2\text{--CH}_2\text{--O}$), 3.88 (6H, s, $\text{CH}_3\text{--O}$), 4.00 (4H, t, $^3J = 6.6\text{ Hz}$, $\text{CH}_2\text{--O}$), 6.88–6.93 (4H, m, aromatic, BB' system, 9.6 Hz), 7.96–8.00 (4H, m, aromatic, AA' system, 9.6 Hz). ^{13}C NMR (CDCl_3 ; 75 MHz): δ_{C} 25.94, 29.08, 29.30, 29.49 (CH_2 aliphatic chain), 51.75 ($\text{CH}_3\text{--O}$),

68.15 (CH₂-O), 114.02 (CH phenyl), 122.30 (C phenyl), 131.51(CH phenyl), 162.92 (C phenyl), 166.85 (C=O ester). IR (KBr, cm⁻¹): ν_{max} = 2920 (C-H aliphatic), 2850 (C-H aliphatic), 1723 (C=O ester), 1508 (C=C aromatic), 1281 (C-O ester), 1256 (C-O aromatic ether), 849 (C-H aromatic).

1,12-bis(4-(hydroxymethyl)phenoxy)dodecane (2).

A solution of **1** (35.85 g, 76.18 mmol) dissolved in dry THF (150 mL) under inert condition was cooled at 0 °C. Then, lithium aluminium hydride (1.0M in THF – 76.18 mL) was slowly added to the stirring solution and the resulting mixture was stirred under argon for 20 h at room temperature. It was then quenched with EtOH (50 mL), followed by water (25 mL) and the remaining residue was acidified with concentrated HCl to pH=1. The organic phase was extracted with CH₂Cl₂ and washed successively with saturated aqueous NaHCO₃, water, and brine. The organic was dried over MgSO₄, filtered and evaporated to dryness to afford **2** (29.92 g, 95%) as a pure white solid. ¹H NMR (DMSO; 300 MHz): δ 1.26 (12H, br s, CH₂ aliphatic chain), 1.36–1.38 (4H, m, CH₂ aliphatic chain), 1.67 (4H, quin, J = 6.6 Hz, CH₂-CH₂-O), 3.91 (4H, t, ³ J = 6.6 Hz, CH₂-O), 4.38 (4H, d, CH₂-OH, ³ J = 5.22 Hz), 5.01 (2H, t, HO-CH₂, ³ J = 5.49 Hz), 6.83–6.86 (4H, m, aromatic, BB' system, 8.49 Hz), 7.17–7.20 (4H, m, aromatic, AA' system, 8.52 Hz). ¹³C NMR (DMSO; 75 MHz): δ_c 25.46, 28.65, 28.71, 28.90, 28.93 (CH₂ aliphatic chain), 62.52 (CH₂-OH), 67.33 (CH₂-O), 113.96 (CH phenyl), 127.84 (CH phenyl), 134.33(C phenyl), 157.52 (C phenyl). IR (KBr, cm⁻¹): ν_{max} = 3331 (OH) 2919 (C-H aliphatic), 2851 (C-H aliphatic), 1510 (C=C aromatic), 1252 (C-O aromatic ether), 817 (C-H aromatic).

1,12-bis(4-(bromomethyl)phenoxy)dodecane (3).

To a solution of **2** (4.00 g, 9.65 mmol) in dry THF (30 mL) was added dropwise thionyl bromide (2.01 g, 9.65 mmol) under inert condition. The orange mixture was stirred during 2 h at room temperature under argon. The reaction mixture was quenched with saturated NaHCO₃ and diluted with CH₂Cl₂. The organic layer was extracted with CH₂Cl₂ and washed with NaHCO₃, dried over MgSO₄, filtered and evaporated in vacuum to give **3** (5.07 g, 97%) as a crude pure white solid. ¹H NMR (CDCl₃; 300 MHz): δ 1.31 (12H, br s, CH₂ aliphatic chain), 1.41–1.48 (4H, m, CH₂ aliphatic chain), 1.79 (4H, quin, J = 6.6 Hz, CH₂-CH₂-O), 3.96 (4H, t, ³ J = 6.6 Hz, CH₂-O), 4.51 (4H, s, CH₂-Br), 6.84–6.89 (4H, m, aromatic, BB' system, 8.79 Hz), 7.29–7.34 (4H, m, aromatic, AA' system, 8.79 Hz). ¹³C NMR (CDCl₃; 75 MHz): δ_c 26.00, 29.19, 29.34, 29.52 (CH₂ aliphatic chain), 34.05 (CH₂-Br), 68.08 (CH₂-O), 114.75 (CH phenyl), 129.69 (C phenyl), 130.38 (CH phenyl), 159.27 (C phenyl). IR (KBr, cm⁻¹): ν_{max} = 2917 (C-H aliphatic), 2850 (C-H aliphatic), 1513 (C=C aromatic), 1256 (C-O aromatic ether), 821 (C-H aromatic), 602 (C-Br).

3,3'-(4,4'-(dodecyloxybenzyl)bis(3-methyl-1H-imidazol-3-ium) dodecane bromide (4).

A mixture of methylimidazole (0.32 g, 3.89 mmol) and **3** (1.00 g, 1.85 mmol), dried separately under vacuum overnight, was heated at 80 °C and stirred for 20 h in a sealed tube. After cooling to room temperature, the sealed tube was broken and the resulting solid was dissolved with dichloromethane and methanol. The reaction mixture was concentrated under vacuum and purified via column chromatography (gradient 100/0 to 95/10: CH₂Cl₂/methanol) to furnish **4** (1.05 g, 81%) as a white solid. ¹H NMR (MeOD; 300 MHz): δ 1.40 (12H, br s, CH₂ aliphatic chain), 1.49–1.56 (4H, m, CH₂ aliphatic chain), 1.83 (4H, quin, J = 6.57 Hz, CH₂-CH₂-O), 3.99 (6H, s, N-CH₃), 4.04 (4H, t, ³ J = 6.6 Hz, CH₂-O), 5.41 (4H, s, N-CH₂-O), 7.00–7.05 (4H, m, aromatic, BB' system, 8.79 Hz), 7.43–7.48 (4H, m, aromatic, AA' system, 8.79 Hz), 7.63 (2H, t, ³ J = 1.92 Hz, MeN-CH imidazolium), 7.66 (2H, t, ³ J = 1.92 Hz, CH-NCH₂ imidazolium), 9.06 (s, 2H, N-CH-N imidazolium). ¹³C NMR (MeOD; 75 MHz): δ_c

27.09, 30.26, 30.43, 30.63 (CH_2 aliphatic chain), 36.58 ($\text{CH}_3\text{-N}$), 53.73 ($\text{N-CH}_2\text{-Ph}$), 69.15 ($\text{CH}_2\text{-O}$), 116.25 (CH phenyl), 123.45 (N-CH imidazolium), 125.13 (N-CH imidazolium), 126.75 (C phenyl), 131.40 (CH phenyl), 137.67 (N-CH-N imidazolium), 161.37 (C phenyl). IR (KBr, cm^{-1}): $\nu_{\text{max}} = 3081$ (C-H imidazolium), 2922 (C-H aliphatic), 2854 (C-H aliphatic), 1608 (C=N imidazolium), 1517 (C=C aromatic), 1252 (C-O aromatic ether), 836 (C-H aromatic). UV-vis (MeOH): $\lambda(\epsilon) = 231(5568)$, 271(2811), 280(2541). Elem anal calcd (%) for $\text{C}_{34}\text{H}_{48}\text{Br}_2\text{N}_4\text{O}_2 \cdot 0.75\text{H}_2\text{O}$: C, 56.87; H, 6.95; N, 7.80. Found: C, 56.90; H, 6.94; N, 7.54.

General procedure for compounds 5 to 10: anion metathesis of 4.

A solution of potassium cyanometallate dissolved in water (4 mL) was added to a solution of compound 4 dissolved in methanol (6 mL). The solution was stirred at room temperature during ten days. The resulting precipitate was filtered and washed with water. Then, the solid was dried under reduced pressure. No further purification is required.

3,3'-(4,4'-(dodecyloxybenzyl)bis(3-methyl-1H-imidazol-3-ium) dodecane dicyanoargentate(I) (5).

Prepared from compound 4 (100 mg, 0.142 mmol) and potassium dicyanoargentate(I) (57 mg, 0.284 mmol) according to the general procedure to yield 5 as a pure white solid (107 mg, 87%). ^1H NMR (MeOD/ CD_2Cl_2 :1/1; 300 MHz): δ 1.38 (12H, br s, CH_2 aliphatic chain), 1.47–1.52 (4H, m, CH_2 aliphatic chain), 1.84 (4H, quin, $J = 6.57$ Hz, $\text{CH}_2\text{-CH}_2\text{-O}$), 3.97 (6H, s, N-CH_3), 4.04 (4H, t, $^3J = 6.57$ Hz, $\text{CH}_2\text{-O}$), 5.34 (4H, s, $\text{N-CH}_2\text{-O}$), 7.01–7.05 (4H, m, aromatic, BB' system, 8.79 Hz), 7.38–7.40 (4H, m, aromatic, AA' system, 8.79 Hz), 7.54 (4H, br s, MeN-CH imidazolium and CH-NCH_2 imidazolium), 8.92 (2H, br s, N-CH-N imidazolium). ^{13}C NMR (MeOD/ CD_2Cl_2 :1/1; 75 MHz): δ_c 26.72, 29.89, 30.11, 30.29, 30.90, 30.91 (CH_2 aliphatic chain), 36.57 ($\text{CH}_3\text{-N}$), 52.85 ($\text{N-CH}_2\text{-Ph}$), 69.02 ($\text{CH}_2\text{-O}$), 116.08 (CH phenyl), 123.15 (N-CH imidazolium), 124.76 (N-CH imidazolium), 125.50 (C phenyl), 131.02 (CH phenyl), 161.13 (C phenyl). IR (KBr, cm^{-1}): $\nu_{\text{max}} = 3104$ (C-H imidazolium), 2923 (C-H aliphatic), 2853 (C-H aliphatic), 2127 ($\text{C}\equiv\text{N}$), 1607 (C=N imidazolium), 1516 (C=C aromatic), 1253 (C-O aromatic ether), 832 (C-H aromatic). UV-vis (MeOH): $\lambda(\epsilon) = 235(14432)$, 273(5243), 280(4811). Elem anal calcd (%) for $\text{C}_{38}\text{H}_{48}\text{Ag}_2\text{N}_8\text{O}_2$: C, 52.79; H, 5.60; N, 12.96. Found: C, 52.79; H, 5.62; N, 12.63.

3,3'-(4,4'-(dodecyloxybenzyl)bis(3-methyl-1H-imidazol-3-ium) dodecane tetracyanonickelate(II) (6).

Prepared from compound 4 (100 mg, 0.142 mmol) and potassium tetracyanonickelate(II) (35 mg, 0.142 mmol) according to the general procedure to yield 6 as a pure white solid (89 mg, 89%). ^1H NMR (MeOD/ CD_2Cl_2 :1/1; 300 MHz): δ 1.27 (12H, br s, CH_2 aliphatic chain), 1.28–1.51 (4H, m, CH_2 aliphatic chain), 1.83 (4H, quin, $J = 6.33$ Hz, $\text{CH}_2\text{-CH}_2\text{-O}$), 4.00 (6H, s, N-CH_3), 4.04 (4H, t, $^3J = 6.33$ Hz, $\text{CH}_2\text{-O}$), 5.39 (4H, s, $\text{N-CH}_2\text{-O}$), 7.01–7.04 (4H, m, aromatic, BB' system, 8.79 Hz), 7.43–7.46 (4H, m, aromatic, AA' system, 8.49 Hz), 7.54 (4H, m, MeN-CH and CH-NCH_2 imidazolium). ^{13}C NMR (MeOD/ CD_2Cl_2 :1/1; 75 MHz): δ_c 26.60, 29.80, 29.84, 29.86, 30.02, 30.09 (CH_2 aliphatic chain), 36.75 ($\text{CH}_3\text{-N}$), 53.89 ($\text{N-CH}_2\text{-Ph}$), 68.92 ($\text{CH}_2\text{-O}$), 116.06 (CH phenyl), 123.06 (N-CH imidazolium), 124.86 (N-CH imidazolium), 125.83 (C phenyl), 131.21 (CH phenyl), 133.69 (N-CH-N imidazolium), 161.02 (C phenyl). IR (KBr, cm^{-1}): $\nu_{\text{max}} = 3104$ (C-H imidazolium), 2923 (C-H aliphatic), 2854 (C-H aliphatic), 2119 ($\text{C}\equiv\text{N}$), 1607 (C=N imidazolium), 1516 (C=C aromatic), 1255 (C-O aromatic ether), 837 (C-H aromatic). UV-vis (MeOH): $\lambda(\epsilon) = 237(12540)$, 267(16973), 279(7081), 312(1297). Elem anal calcd (%) for $\text{C}_{42}\text{H}_{48}\text{Ni}_2\text{N}_{12}\text{O}_2 \cdot 0.5\text{H}_2\text{O}$: C, 63.70; H, 6.89; N, 15.64. Found: C, 63.79; H, 6.88; N, 15.36.

3,3'-(4,4'-(dodecyloxybenzyl)bis(3-methyl-1H-imidazol-3-ium) dodecane tetracyanoplatinate(II) (7).

Prepared from compound **4** (100 mg, 0.142 mmol) and potassium tetracyanoplatinate (II) (66 mg, 0.142 mmol) according to the general procedure to yield **7** as a pure white solid (109 mg, 87%). ¹H NMR (MeOD/CD₂Cl₂:1/1; 300 MHz): δ 1.37 (12H, br s, CH₂ aliphatic chain), 1.49–1.51 (4H, m, CH₂ aliphatic chain), 1.83 (4H, quin, *J* = 6.57 Hz, CH₂–CH₂–O), 4.00 (6H, s, N–CH₃), 4.04 (4H, t, ³*J* = 6.57 Hz, CH₂–O), 5.39 (4H, s, N–CH₂–O), 7.01–7.04 (4H, m, aromatic, BB' system, 8.79 Hz), 7.43–7.45 (4H, m, aromatic, AA' system, 8.49 Hz), 7.49 (2H, d, ³*J* = 1.92 Hz, MeN–CH imidazolium), 7.52 (2H, d, ³*J* = 1.86 Hz, CH–NCH₂ imidazolium). ¹³C NMR (MeOD/CD₂Cl₂:1/1; 75 MHz): δ_c 26.54, 29.73, 29.80, 29.96, 30.03 (CH₂ aliphatic chain), 36.78 (CH₃–N), 53.71 (N–CH₂–Ph), 68.87 (CH₂–O), 116.00 (CH phenyl), 123.03 (N–CH imidazolium), 124.73 (N–CH imidazolium), 125.57 (C phenyl), 131.20 (CH phenyl), 160.91 (C phenyl). IR (KBr, cm⁻¹): ν_{max} = 2922 (C–H aliphatic), 2852 (C–H aliphatic), 2124 (C≡N), 1613 (C=N imidazolium), 1516 (C=C aromatic), 1254 (C–O aromatic ether), 835 (C–H aromatic). Elem anal calcd (%) for C₃₈H₄₈PtN₈O₂: C, 54.08; H, 5.73; N, 13.28. Found: C, 54.15; H, 5.75; N, 12.78.

3,3'-(4,4'-(dodecyloxybenzyl)bis(3-methyl-1H-imidazol-3-ium) dodecane hexacyanocobaltate(III) (8).

Prepared from compound **4** (100 mg, 0.142 mmol) and potassium hexacyanocobaltate(III) (32 mg, 0.095 mmol) according to the general procedure to yield **8** as a pure white solid (91 mg, 93%). ¹H NMR (MeOD/CD₂Cl₂:1/1; 300 MHz): δ 1.37 (12H, br s, CH₂ aliphatic chain), 1.42–1.52 (4H, m, CH₂ aliphatic chain), 1.81 (4H, quin, *J* = 6.57 Hz, CH₂–CH₂–O), 4.00 (4H, t, ³*J* = 6.57 Hz, CH₂–O), 4.06 (6H, s, N–CH₃), 5.44 (4H, s, N–CH₂–O), 6.95–7.00 (4H, m, aromatic, BB' system, 8.52 Hz), 7.42 (2H, t, ³*J* = 1.92 Hz, MeN–CH imidazolium), 7.43–7.46 (4H, m, aromatic, AA' system, 8.79 Hz), 7.49 (2H, t, ³*J* = 1.92 Hz, CH–NCH₂ imidazolium), 9.12 (2H, s, N–CH–N imidazolium). ¹³C NMR (MeOD/CD₂Cl₂:1/1; 75 MHz): δ_c 26.47, 29.68, 29.80, 29.92 (CH₂ aliphatic chain), 36.95 (CH₃–N), 53.60 (N–CH₂–Ph), 68.78 (CH₂–O), 115.84 (CH phenyl), 122.63 (N–CH imidazolium), 124.64 (N–CH imidazolium), 126.15 (C phenyl), 131.20 (CH phenyl), 137.14 (N–CH–N imidazolium), 160.69 (C phenyl). IR (KBr, cm⁻¹): ν_{max} = 2921 (C–H aliphatic), 2854 (C–H aliphatic), 2134 (C≡N), 1605 (C=N imidazolium), 1516 (C=C aromatic), 1254 (C–O aromatic ether), 833 (C–H aromatic). UV–vis (MeOH): λ(ε) = 235(10811), 273(5730), 280(5405). Elem anal calcd (%) for C₁₁₄H₁₄₄Co₂N₂₄O₆·3.75H₂O: C, 64.22; H, 7.16; N, 15.77. Found: C, 64.31; H, 7.18; N, 15.49.

3,3'-(4,4'-(dodecyloxybenzyl)bis(3-methyl-1H-imidazol-3-ium) dodecane hexacyanoferrate(III) (9).

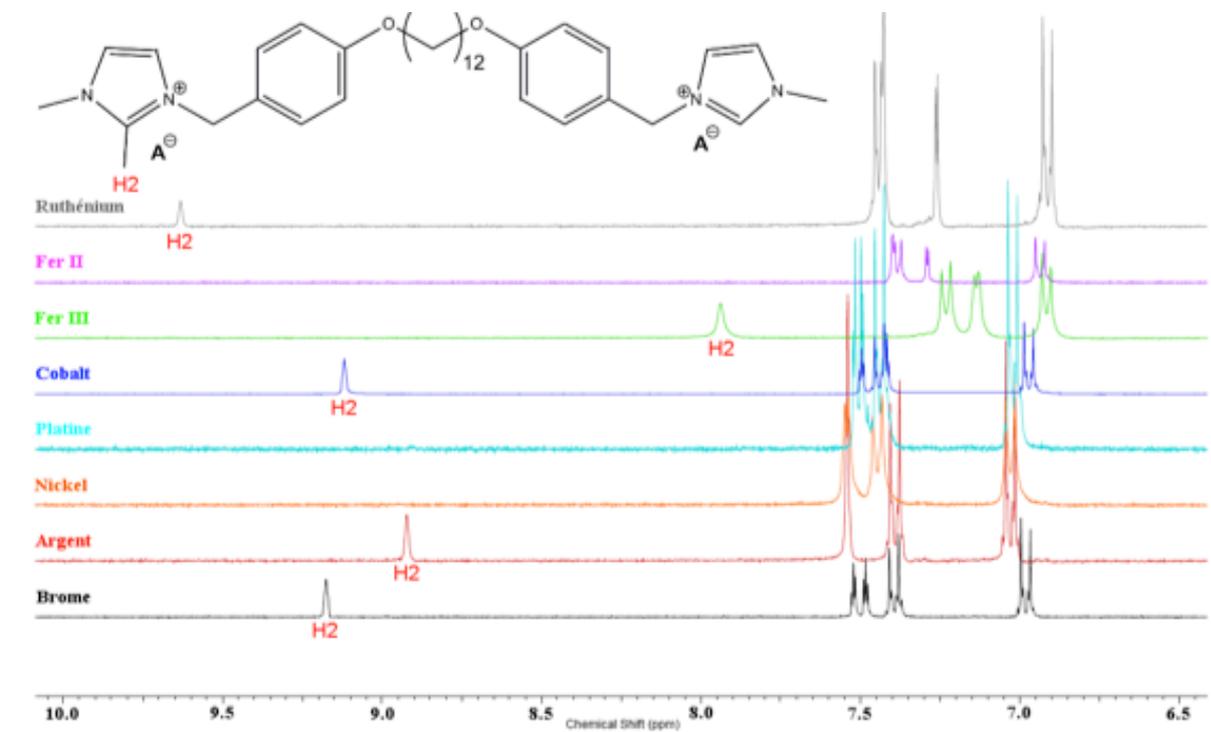
Prepared from compound **4** (100 mg, 0.142 mmol) and potassium hexacyanoferrate (III) (32 mg, 0.095 mmol) according to the general procedure to yield **9** as a pure dark yellow solid (91 mg, 94%). ¹H NMR (MeOD/CD₂Cl₂:1/1; 300 MHz): δ 1.37 (12H, br s, CH₂ aliphatic chain), 1.42–1.52 (4H, m, CH₂ aliphatic chain), 1.80 (4H, quin, *J* = 6.57 Hz, CH₂–CH₂–O), 3.59 (6H, s, N–CH₃), 3.99 (4H, t, ³*J* = 6.57 Hz, CH₂–O), 5.01 (4H, s, N–CH₂–O), 6.90–6.93 (4H, m, aromatic, BB' system, 8.22 Hz), 7.13–7.14 (4H, m, MeN–CH imidazolium and CH–NCH₂ imidazolium), 7.22–7.24 (4H, m, aromatic, AA' system, 8.25 Hz), 7.94 (2H, br s, N–CH–N imidazolium). ¹³C NMR (MeOD/CD₂Cl₂:1/1; 75 MHz): δ_c 26.55, 29.76, 29.89, 30.00 (CH₂ aliphatic chain), 40.00 (CH₃–N), 55.59 (N–CH₂–Ph), 68.83 (CH₂–O), 115.94 (CH phenyl), 123.45 (N–CH imidazolium), 125.55 (N–CH imidazolium), 126.06 (C phenyl), 131.67 (CH phenyl), 141.06 (N–CH–N imidazolium), 160.74 (C phenyl). IR (KBr, cm⁻¹): ν_{max} = 2919 (C–H aliphatic), 2851 (C–H aliphatic), 2106 (C≡N), 1612 (C=N imidazolium), 1516 (C=C

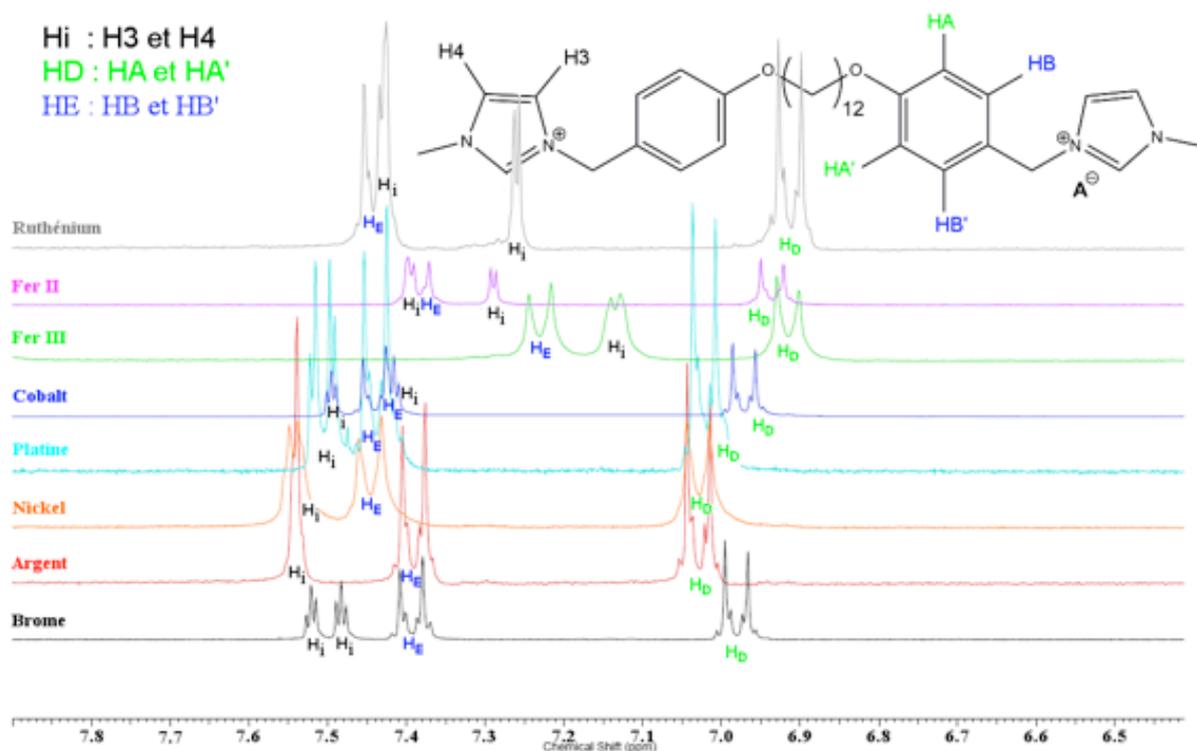
aromatic), 1250 (C–O aromatic ether), 836 (C–H aromatic). UV–vis (MeOH): $\lambda(\epsilon) = 234(11351), 273(3514), 280(3081), 421(649)$. Elem anal calcd (%) for $C_{114}H_{144}Fe_2N_{24}O_6 \cdot 3.75H_2O$: C, 64.41; H, 7.18; N, 15.81. Found: C, 64.19; H, 7.19; N, 15.39.

3,3'-(4,4'-(dodecyloxybenzyl)bis(3-methyl-1H-imidazol-3-ium) dodecane hexacyanoferrate (II) (10).

Prepared from compound **4** (100 mg, 0.142 mmol) and potassium hexacyanoferrate (II) (30 mg, 0.071 mmol) according to the general procedure to yield **10** as a pure yellow solid (83 mg, 90%). 1H NMR (MeOD/ CD_2Cl_2 :1/1; 300 MHz): δ 1.37 (12H, br s, CH_2 aliphatic chain), 1.43–1.52 (4H, m, CH_2 aliphatic chain), 1.81 (4H, quin, $J = 6.87$ Hz, CH_2-CH_2-O), 3.99 (4H, t, $^3J = 6.87$ Hz, CH_2-O), 3.99 (6H, s, N– CH_3), 5.40 (4H, s, N– CH_2-O), 6.92–6.95 (4H, m, aromatic, BB' system, 8.49 Hz), 7.29 (2H, d, $^3J = 1.92$ Hz, MeN– CH imidazolium), 7.37–7.39 (4H, m, aromatic, AA' system, 5.76 Hz), 7.40 (2H, br s, $CH-NCH_2$ imidazolium). ^{13}C NMR (MeOD/ CD_2Cl_2 :1/1; 75 MHz): δ_c 25.66, 28.88, 29.00, 29.11 (CH_2 aliphatic chain), 37.13 (CH_3-N), 53.21 (N– CH_2-Ph), 67.96 (CH_2-O), 114.98 (CH phenyl), 121.69 (N– CH imidazolium), 123.86 (N– CH imidazolium), 125.43 (C phenyl), 130.46 (CH phenyl), 159.95 (C phenyl). IR (KBr, cm^{-1}): $\nu_{max} = 2922$ (C–H aliphatic), 2854 (C–H aliphatic), 2044 (C \equiv N), 1607 (C=N imidazolium), 1517 (C=C aromatic), 1256 (C–O aromatic ether), 835 (C–H aromatic). UV–vis (MeOH): $\lambda(\epsilon) = 235(9189), 273(3730), 280(3405), 424(1621)$. Elem anal calcd (%) for $C_{74}H_{96}FeN_{14}O_4 \cdot 2H_2O$: C, 66.45; H, 7.54; N, 14.66. Found: C, 66.32; H, 7.50; N, 15.45.

Characterization RMN 1H for 1, 2a-f





XRD experimental data

Table A-2: Indexation of the reflections detected in the liquid-crystalline phase by SAXS/WAXS for different anions at a given temperature.

Compounds	T ($^{\circ}\text{C}$)	$d_{00l(mes)}$ (\AA)	I (shape)	00l	
Bromide	80 heating	29.2	S (sh)	001	
		4.4	W (br)		
30.6		S (sh)	001		
4.7		W (br)			
Silver (I)	90 Heating	28.8	S (sh)	001	
		4.4	W (br)		
30.4		S (sh)	001		
4.7		W (br)			
Bromide	100 Heating	28.5	S (sh)	001	
		4.4	W (br)		
30.1		S (sh)	001		
4.7		W (br)			
Silver (I)		110 Heating	28.3	S (sh)	001
			4.9	W (br)	
27.8			S (sh)	001	
4.9			W (br)		
Cobalt (III)	110 Heating	30.3	S (sh)	001	
		4.9	W (br)		
28.0		S (sh)	001		
4.4		W (br)			
Silver (I)	110 Heating	29.8	S (sh)	001	
		4.7	W (br)		
28.2		S (sh)	001		
4.9		W (br)			
Cobalt (III)	110 Heating	27.6	S (sh)	001	
		4.9	W (br)		
27.6		S (sh)	001		
4.9		W (br)			

		4.9	W (br)	
Iron (II)		30.0	S (sh)	001
		4.9	W (br)	
Cobalt (III)	120 Heating	28.2	S (sh)	001
		4.9	W (br)	
Iron (III)		27.6	S (sh)	001
		4.9	W (br)	
Iron (II)		29.9	S (sh)	001
		4.9	W (br)	
Cobalt (III)	130 Heating	28.1	S (sh)	001
		4.9	W (br)	
Iron (III)		27.5	S (sh)	001
		4.9	W (br)	
Iron (II)		29.8	S (sh)	001
		4.9	W (br)	
Cobalt (III)	140 heating	28.1	S (sh)	001
		4.9	W (br)	
Iron (III)		27.5	S (sh)	001
		4.9	W (br)	
Iron (II)		29.8	S (sh)	001
		4.9	W (br)	
Cobalt (III)	150 heating	28.1	S (sh)	001
		4.9	W (br)	
Iron (III)		27.4	S (sh)	001
		4.9	W (br)	
Iron (II)		29.6	S (sh)	001
		4.9	W (br)	

$d_{hkl (mes)}$ is the measured diffraction spacing, I corresponds to the intensity of the reflections (S : strong; W : weak; br and sh stand for broad and sharp)

Complements to figure 8

The molecular packing inside lamellar mesophases can be probed with the concept of molecular area. The emergence of multi-layered lamellae implies that molecules cover the same statistical layer portion in all sublayers, i.e. the same molecular area $S = V_{Mol}/d$, defined as the ratio of molecular volume V_{Mol} and lamellar periodicity d .

The position of the (001) reflection in SAXS patterns provided all d -values.

The variation of V_{Mol} with temperature for derivative **1** was directly measured with our home-developed dilatometry instrument and comes down to the following equation in the 20-140°C temperature range, with accuracy of 0.01% on relative volume variations and of 0.15% on absolute volumes:

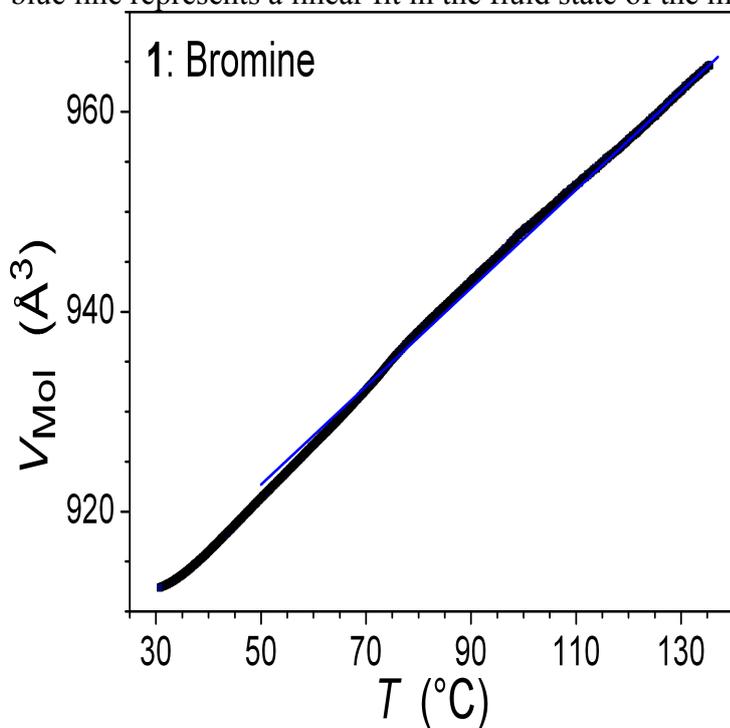
$$V_{Mol} = 898 + 0.49 T, \text{ where } T \text{ is the temperature in } ^\circ\text{C}.$$

The other samples could not be produced in sufficient quantity for dilatometry experiments; however absolute volumes can be obtained with 1 % accuracy using the partial molecular additivity rule, as relevant for liquids and mesophases (e.g., see C. de Gracia Lux, Bertrand Donnio, Benoît Heinrich, Marie Pierre Krafft, *Langmuir*, (2013), **29**, 5325-5336.). Hence volumes of compounds **2a-f** were calculated from **1** and partial volume differences between Br- and other anions, determined from reference salts (T=100°C; $V_{Mol} = 947$ (Bromide), 1076

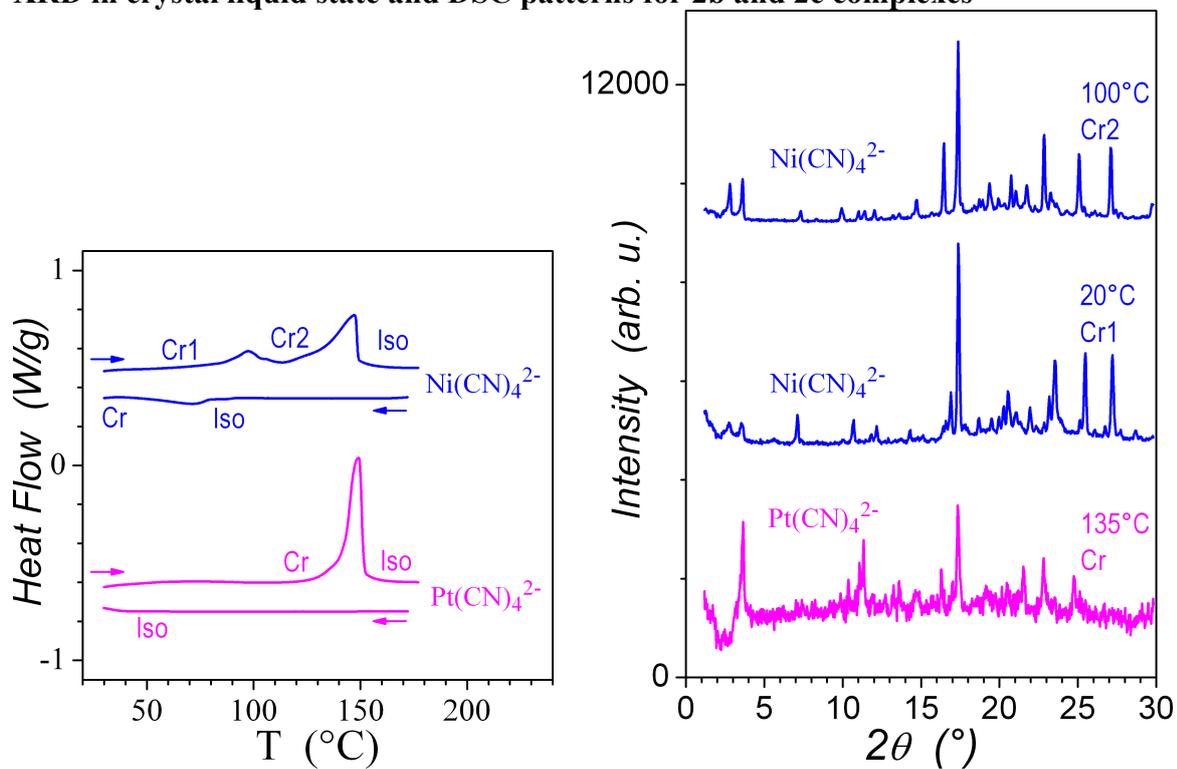
(Silver (I)), 976 (Cobalt (III)), 974 (Iron (III)), 925 (Iron (II)) \AA^3). Molecular areas at 100°C: $S = 33.3$ (Bromide), 35.7 (Silver (I)), 34.4 (Cobalt (III)), 35.1 (Iron (III)), 30.6 (Iron (II)) \AA^2 .

Dilatometry experimental data

Dilatometry curve for sample 1 (Bromide), acquired on cooling from SmA phase (5°C/h). The blue line represents a linear fit in the fluid state of the mesophase.



XRD in crystal liquid state and DSC patterns for 2b and 2c complexes



Left: DSC runs of the tetracyanometalate Bis(imidazolium) salts (ramps of 5°/Min, endotherm up); Cr, Cr1, Cr2: crystalline phases; Iso: isotropic liquid phase. None is mesomorphous.
Right: SAXS patterns in the three crystalline phases with only sharp reflections, distributed in the whole angular range, which definitively proves their crystalline nature.