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Syntheses are reported for new bolaform ionic liquids **2a-f** containing the cyanometallate anions $[Ag(CN)_2]^{-}$ (**2a**), $[Ni(CN)_4]^{2-}$ (**2b**), $[Pt(CN)_4]^{2-}$ (**2c**), $[Co(CN)_6]^{3-}$ (**2d**), $[Fe(CN)_6]^{3-}$ (**2e**) and $[Fe(CN)_6]^{4-}$ (**2f**), respectively, associated with a bis(imidazolium) dication. Except for those containing the square-planar nickelate and platinite anions, all the compounds displayed thermotropic behaviour, exhibiting lamellar smectic A phases. The mesomorphic behavior and phase transition temperatures were investigated by polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and small-angle X-ray scattering (SAXS). To investigate the nature anion influence on its interactions with the cation, crystal structures from single crystal X-Ray diffraction have been obtained for both $[Ag(CN)_2]^{-}$ and $[Ni(CN)_4]^{2-}$ derivatives. These studies showed that the square planar Ni anion disrupts the lateral cohesion of the ionic layers. This may explain the loss of liquid crystal behavior in this case and Pt salt.

Introduction

Over the past decade, extensive studies of ionic liquids (ILs) have revealed their many useful properties such as extremely low volatility, high thermal stability, non-flammability, high chemical and radiochemical stability, high ionic conductivity and wide electrochemical window.¹⁻³ These have led to their use, for example, as new reaction media, increasing the yields of many syntheses and eliminating the hazards associated with some conventional solvents.⁴ Changes in both the cation and its counter anion can be used to fine-tune properties such as viscosity. melting point, polarity and hydrophilicity/hydrophobicity.1 Important emerging applications include those in separation and extraction processes, in catalysis and in various electrochemical devices,^{2,} ^{5, 6} such as lithium ion batteries,⁷ solar cells,^{8, 9} as well as capacitors.2

Liquid crystals are characterized by both mobility and selforganization at the macroscopic level.¹⁰ Almost all such mesomorphic materials are based on molecules combining two antagonistic units consisting of rigid (aromatic) and flexible (alkyl) or hydrophilic (polar heads) and hydrophobic (alkyl chains) parts. The subtle balance of these effects governs the formation of a multitude of supramolecular architectures depending on the temperature (thermotropic liquid crystals)

and/or the solvent (lyotropic liquid crystals). In the case of thermotropic liquid crystals the organizations give rise to nematic phases (molecules are aligned along a particular axis), smectic phases (orientational /positional order with formation of layers) and columnar phases (orientational/positional order with formation of columns arranged in a two-dimensional lattice). The lyotropic compounds display not only lamellar and columnar organization but also hierarchical self-assembly into spheres (micelles), ribbons and fibres. These unique properties have led to applications ranging from display technology through templating media for synthesis to biological activity (targeting and transportation of drugs and gene materials).¹¹ The vast majority of liquid crystal molecules are made up of a rigid part functionalized by alkyl tails. For example, the mesomorphic molecules known as liquid crystal oligomers (particularly dimers) has been widely studied as model compounds for the technologically important semi-flexible main chain liquid crystal polymers. Here, the molecular structure is formed by linking standard mesogenic components with flexible alkyl chains.¹²

Full convergence of the ionic liquid and liquid crystal fields could provide a vast range of materials (Ionic liquid crystals, ILCs) with novel and tuneable characteristics such as those of ordered and oriented hybrid compound semiconductors exhibiting both electronic and ionic conductivity.¹³⁻¹⁵ In that matter, the imidazolium unit is an excellent platform that can be designed to promote liquid crystalline phases and easily varied with a large diversity of anions.¹⁶⁻¹⁹

Despite growing interest in ionic liquids properties based on imidazolium compounds, very little is known about bolaamphiphile species, which may form liquid crystals. Ionic liquid crystal dimers (bolaform) will be defined as consisting of

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molecules composed by charged semi-rigid mesogenic units connected via flexible spacers (Scheme 1). In contrast, the Gemini form with lateral alkyl tails starts to be well reported.²⁰⁻²⁸ For such multiply-charged species, the charge on the counterion plays a crucial role in inducing specific properties or



Results and discussion

Synthesis and characterisation

Herein, we report the synthesis of a bolaform bis(imidazolium) species (Scheme 2) designed to give liquid crystal behavior and to facilitate study of the influence of the counteranion on the mesomorphism. Compound **1**, 1,1'-(4,4'-(dodecane-1,12-diylbis(oxy))bis(4,1-phenylene)) bis(methylene)bis(3-methyl-1*H*-imidazol-3-ium) bromide was prepared in a three-step procedure in 72 % yield overall



Scheme 2: Synthesis of the bromide **1**. Reaction conditions: (i) DMF, K_2CO_3 , 100 °C, overnight ; (ii) LiAlH₄, THF, 4 h ; (iii) SOBr₂, DCM; dry THF, two equivalents of methylimidazole under an inert atmosphere.

The bromide salt **1** is air stable and was purified by flash chromatography (gradient 100/0 to 95/5: $CH_2Cl_2/MeOH$). Distinctive signals of the CH (1*H*-imidazolium) group appear in the ¹H and ¹³C NMR spectra at 9.06 ppm and at 137.67 ppm, respectively.



Scheme 3: Precipitation of **2a-f** from water/methanol in presence of 2 equivalents of $M(CN)_{x}^{n}$, RT, 10 days.

In order to investigate the influence of the form and charge of the counteranion, dication derivatives with [Ag(CN)₂]⁻ (2a), $[Ni(CN)_4]^{2-}$ (2b), $[Pt(CN)_4]^{2-}$ (2c), $[Co(CN)_6]^{3-}$ (2d), $[Fe(CN)_6]^{3-}$ (2e) and [Fe(CN)₆]⁴⁻ (2f) were synthesized. All were obtained in excellent yield by mixing the dication bromide in a methanolic solution with an aqueous solution of the cyanometallate potassium salt respectively. The very water-insoluble precipitates were simply washed well with water and then dried in vacuum to obtain the pure materials. All these compounds were fully characterized by the by standard methods (NMR, FT-IR, UV and elemental analysis). The IR spectra show typical anion vibrations of $v_{CN} = 2127 \text{ cm}^{-1}$ (2a), 2119 cm⁻¹ (**2b**), 2124 cm⁻¹ (**2c**), 2134 cm⁻¹ (**2d**), 2106 cm⁻¹ (**2e**) and 2044 cm⁻¹ (2f). The UV spectrum displays in MeOH for all the compounds two typical transitions charge transfer (n- π^* and π - π *) at 230 (ϵ > 10 000 M⁻¹. cm⁻¹) and 270 nm (ϵ > 5000 M⁻¹. cm⁻¹) generated by the aromatic parts. Moreover, it's difficult to determine d-d transition due to the poor solubility of such complexes. However, we succeeded to measure with a poor precision for the Fe(II) **2e** (420 nm, $\varepsilon \approx 85 \text{ M}^{-1}$. cm⁻¹) and Fe(III) **2f** (425 nm, $\varepsilon \approx 55 \text{ M}^{-1}$. cm⁻¹). The chemical shift for the proton CH (1H-imidazolium) is very dependent upon the anion, being found at δ = 8.92 ppm (2a), 9.12 ppm (2d) and 7.94 ppm (2e). For the compounds 2b, 2c, 2f, this signal was not observed due to proton/deuteron exchange with the solvent.^{29, 30} Thermogravimetric analysis of compounds 1 and 2a-f showed them to be stable up to 200°C (see scheme 3). Below 100°C, weight loss consistent with dehydration was observed. Hydration was confirmed by elemental analyses and thus the compounds must be regarded as deliguescent.





Single-Crystal X-ray Diffraction Studies

Single crystals of **2a** and **2b** suitable for X-ray diffraction measurements were obtained by slow diffusion of an aqueous cyanometallate solution into a solution of **1** in methanol. The

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stoichiometric unit found in the lattice of **2a** is shown in Figure 1 and a partial view of the lattice is given in Figure 2.



Figure 1: ORTEP view, with partial labeling, of the asymmetric unit of **2a** showing both types of weak CH interactions. The CH- π interactions are represented as contacts to the centroid of the phenyl ring. The displacement probability ellipsoids are shown at the 50 % level. Symmetry codes for equivalent positions: 'x, y-1, z' '' : 1+x, 1+y, z. lmidazolium-CH/N-cyano hydrogen bond C4 H4...N3'' : 0.9498 Å' : 2.2856 Å' : 3.182(4) Å; 157° CH- π interaction: centroid of C6_C11 phenyl ring and H13' : 2.9821 Å ; 167°; 3.954(3) Å.

The solid array is formed by ionic double layers containing the imidazolium dimer and argentate species separated by strongly tilted (65.5°) $(CH_2)_{12}$ spacers. This arrangement is supported by two types of CH interactions: 1) imidazolium-CH with the counter anion and 2) CH- π interactions between the phenyl ring and the CH₂ in beta-position in the chains.



Figure 2: Complex 2a packing diagram in the (a,c) plane projection

Unlike that of **2a**, the ionic double layer of **2b** contains water molecules involved in the CH bond networks. As well, the tilting of the spacers is slightly smaller (62.3°) than in the crystal of **2a**. CH- π interactions with the aromatic units occur again but involve methylene groups in the \mathbb{D} and \mathbb{D} positions of the spacer chains.







Figure 4: Complex ${\bf 2b}$ lattice partial view. The arrow point to the main intermolecular CH- π interactions.

Contacts consistent with the different H-bonding interactions are gathered in Tables 1 and 2.

Donor	н	Acceptor_code	D-H	НА	DA	D - HA	
03	H1	N7_\$1	0.79(4)	2.18(4)	2.966(3)	173(4)	
03	Н5	N8	0.90(4)	1.99(4)	2.850(3)	159(3)	
C2	H2	03_\$2	0.9493	2.4370	3.085(3)	125.32	
C3	H4	N7_\$3	0.9500	2.5651	3.497(3)	166.84	
C5	H5B	N6_\$3	0.9896	2.5053	3.484(2)	170.04	
C32	H32	N8_\$4	0.9498	2.5326	3.363(3)	146.08	
C34	H34B	03_\$4	0.9798	2.4187	3.385(4)	168.69	
Table 1: <u>H-bonding contacts in the complex 2b lattice</u> . Symmetry codes for equivalent positions: $\$1 = 1-x, -1-y, -z; \$2 = -x, -y, -z; \$3 = -1+x, 1+y, z; \$4 = 3-x, -1-y, -1-z; \$4 = 3-x, -1-z; *1-z; *1-$							

ХН	CX_CY_ring_code	HCg	X-HCg	XCg		
C23H23A	C9_C11_\$1	2.7954	145.24	3.6519(19)		
C16H16B	C24_C29_\$5	2.8697	143.61	3.7129(18)		
Table 2: <u>Shortest X-HCg(π-Ring) contacts in the complex 2b lattice.</u> Symmetry codes for equivalent positions: $\$1 = 1-x, -1-y, 1-z; \$5 = 2-x, -2-y, 1-z$.						

Mesomorphic properties.

For all the compounds, the mesomorphic behavior and phase transition temperatures were investigated by polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and small-angle X-ray scattering (SAXS). To avoid possible effects of the material hydration, all were dried under vacuum at 50°C overnight before measurements. The phase transition and the corresponding enthalpy changes derived for the compounds are compiled in Table 3.

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Ref.	Anion	Transitions ^a	T(°C)⁵	ΔH (kJ.mol ⁻¹) ^c
2	Br	Cr ->PPPA	82	44
		SmA → Iso	127	1.8
2a	Ag(CN)2	Cr ➔ SmA	78	12
		SmA ➔ Iso	124	1.2
2b	Ni(CN) ₄ ²⁻	Cr1 → Cr2	98	7
		Cr2 🗲 Iso	147	33
2c	Pt(CN)42-	Cr ➔ Iso	149	50
2d	Co(CN) ₆ ³⁻	Cr ➔ SmA	91	28
		SmA → d	>230	
_	Fe(CN) ₆ ³⁻	Cr 🗲 SmA	91	12
2e		SmA → d	>210	
	Fe(CN) ₆ ⁴⁻	Cr ➔ SmA	68	36
2f		SmA → d	>220	
Table 3. Phase	e transition ter	norature (T) and	corresponding	enthalpies (DH)

Table 3: Phase transition temprature (T) and corresponding enthalpies (DH) determined from the 1st heating cycle. – ^a Abbreviations: Cr), Cr1), Cr2) crystalline phases; SmA) smectic A phase; Iso) isotropic liquid phase; d) decomposition. All the transition temperatures listed in this table. Correspond to peak maximums in heating run DSC traces. Calculated for 1 mole Bis(imidazolium) units and stoichiometric amount of counter-ions.

Only the compounds containing tetracyano-nickelate and platinite anions do not show thermotropic behavior. The optical textures observed by POM for **1** during slow cooling from isotropic melts displayed the emergence of typical smectic A phase. The mesophase appears as Batônnet rods (figure 5 left) and turn into a wide fan like focal-conic texture (figure 5 right).



Figure 5: (left) Smetic A phase emergence from the isotropic liquid at 124°C. (right) Typical Smetic A phase texture at 110°C.

A diffuse band at 4.6 Å (wide angle) found in compound 1, Xray pattern recorded at 110°C shows clearly that the alkyl spacers have liquid-like structure (Figure 6). The layer thickness in the smectic A phase was determined from the position of the sharp reflection in the small angle region (1 d = 28.5 Å at 110 °C).

Monocatenary liquid crystals series containing methylimidazolium with bromide and other singly-charged counterions have been previously investigated.³¹⁻³³ The polymorphism evolution in the series could be well described by using the molecular area, obtained as the ratio of the molecular volume measured by dilatometry to the layer spacing obtained from SAXS patterns. In agreement with single-crystal X-ray diffraction for another monocatenar analogue,³⁴ the molecular area in the crystalline phase is determined by the flat ionic double layer and is more than twice that of the strongly tilted aliphatic tails. Melting to the smectic A phase causes ruffling of the ionic layers and the molecular area drastically increases to an intermediate value between the flat of ionic layer lattice and the extended aliphatic chains. At higher temperatures in the mesophase, the molecular area decreases again and continuously up to the isotropization. Since the thermal expansion and softening of the aliphatic tails sets the compromise molecular area to a lower ruffling degree of the ionic layers. Remarkably, the evolution of the smectic A polymorphism in the salt series follows mainly the counter-ion size variation: the mesophase exists in a similar molecular area range throughout the series, but the molecular area close to the isotropization is reached earlier in the case of bigger counter-ions.

The bolaamphiphiles cationic moiety, investigated here, is considered as a dimer formed by connecting the tails of these previously studied compounds, called "monomers" hereafter. Another variation concerns the anions: besides the singlycharged, spherical bromide and the singly-charged linear shaped Ag[CN]₂ (2a), the bolaamphiphiles series includes also multi-charged cyanometallates of different geometries. All compounds exhibiting smectic A ranges were characterized by SAXS. The molecular volume variation of the dimer bromide was directly measured by dilatometry and used to calculate the volume variations of the other terms of the series as described previously.33 Molecular areas in the mesophase were finally obtained from the ratio of these molecular volumes and of the layer spacings and compared to the values in the crystalline state from single-crystal structures (see previous section).

One may expect that the bonding of the tails in the aliphatic layers stabilizes the layering and reduces the fluidity, shifting melting and isotropization temperatures upward, as found for other systems.^{35, 36} However, comparison of the polymorphism (see Figure 6 and ref.)³³ indicates that the transition temperature shift is small or nonexistent here (a more precise answer is not possible, since the polymorphism is strongly chain length dependent and the monomer bromide series starts with octyl tails, i.e. still more than the half dimer spacer length corresponding to hexyl). Moreover, mesophase molecular areas (see Figure 7) do not differ significantly between dimer and monomer (this comparison is more reliable because the chain length dependence is very weak, as found for the monomer bromide series).³³ Molecular areas are also similar in crystalline phases, as shown for Ag[CN]2⁻ dimer (2a) and monomer (43.6 and 46.7 Å², respectively). Actually, essential identity in the crystalline phase was expected, since the molecular area is then determined by the flat ionic layers and thus the natural size of ionic species. The apparent identity in the mesophase is more surprising and means that the degree of ruffling of the ionic layers is not significantly modified between monomers and dimers. Since this degree of ruffling is directly related to the degree of folding of the aliphatic chains and it is perhaps surprising that these characteristics of the packing are not significantly influenced by the chain ends buried in the aliphatic layer.

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Figure 6: (Left) DSC runs of liquid-crystalline Bis(imidazolium salts (ramps of 5°C/Min, endotherm up); Cr: crystalline phase; SmA: smectic A phase; Iso: isotropic liquid phase. Both monovalent anion salts (2: Br-; 2a: Ag[CN]2-) show similar melting and isotropization temperature, i.e of ca. 80°C and 125°C, whereas hexacyanometalate salts SmA phases stay up to degradation above 200°C. Behaviors are also different on cooling: crystallization occurs for the former salts and supercooling of the SMA phase for the latter.

(Center and Right) SAXS patterns in the SmA phase at 100°C, only displaying the first order reflection (001) of the lamellar periodicity and a broad wide-angle scattering signal from overlapping lateral distances betwee molten chains (h_{ch}) and mesogenic moieties (h_{mes}). The low-quality patterns obtained for Co and Fecontaining samples are due to absorption of CuK_{at} radiation and fluorescence emission.

In marked contrast with this low influence of the dimerization on the molecular organization, the variation of the anion resulted in a huge evolution of the polymorphism within the temperature range. The smectic phase vanishes on the contrary with the doubly-charged and square-planar $[Ni(CN)_4]^{2^-}$ (**2b**), but reappears over an extended temperature range with the octahedral multiply-charged hexacyanometallates.



The molecular areas in the mesophase and crystal structures might elucidate the variation within the anion series. In fact, molecular areas in the mesophase dimer are about 10 percent greater with $[Ag(CN)_2]$ ⁻ (2a) than with bromide (see Figure 7), in agreement with the discrepancy found between crystalline phases of corresponding monomers (46.7 Å² with $[Ag(CN)_2]$ ⁻ (2a) and 42.6 Å² with Br⁻ (1)). This is in in accordance with the slightly larger overall size of the cyanometallate, but implies

series (see figure 6). Thus, the dimer derivatives containing the singly-charged anion, i.e. the spherical Br- or the linear $[Ag(CN)_2]^-$ (2a), exhibit the smectic A phase over a similar that the anion's main axis is strongly tilted with respect to the normal layer, in order to project a large area in the plane layer. Indeed the crystalline lattice contains an alternation of rows of imidazolium cations and rows of the anions, with a 6.42 Å spacing within rows and with the anions'axis tilted by about 60° with respect to the layer normal. This large tilt angle draws the negative charges borne by the cyano groups back into the interior of the layer. Still larger tilt angles are excluded since they would expand the imidazolium rows and therefore reduce the ionic layer compactness. This organization is probably preserved on the local range in the ruffled layers of the smectic phase, as suggested by the similar ratios of molecular areas in both phases between the $[Ag(CN)_2]^{-}$ (2a) and Br⁻ (1) derivatives.

The $[Ni(CN)_4]^{2-}$ (**2b**) derivative melts directly in the isotropic phase without crossing a smectic phase with ruffled ionic layers. Reasons for this singularity in the metallocyanate series can be found in the structure of the low-temperature crystalline phase. Thus, one may have expected that the four negatively charged cyano groups of the square-planar complex would just intercalate between the imidazolium rows in the interior of the ionic layers. However the real structure consist in an alternation of two rows of imidazoliums and of one row of anions, with 8.84 Å spacing within rows and with a strongly tilted orientation of the plane of the complex anion with respect to the layer plane. More precisely, one diagonal of the [Ni(CN)₄]²⁻ square is tilted by about 85° from the layer normal, burying two cyano groups in the ionic layer, while the other diagonal is tilted by about 45°, posing the two other cyano groups at the ionic layer boundaries. The flat shape of the

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complex is obviously the reason for this tilted orientation since it optimizes the space filling between the imidazolium rows. An explanation of the absence of a mesophase may be that the cyano groups, at the layer boundaries, are less strongly retained in position by ionic bonds than the ones buried inside the layer. Therefore contribute weakly to the lateral cohesion of the ionic layers. After melting, mobility and disorder are introduced in the packing, the long range ordered piling of segregated sublayers then collapse rather than being preserved with ruffled ionic layers as in the case of the anions with other geometries.

The dimer derivatives containing an octahedral multiplycharged hexacyanometallate all exhibit the smectic A phase over an extended temperature range, up to their degradation temperature about 100°C above that of the isotropization of the dimer bromide (see Figure 6). Indeed, the comparison with the bromide is more relevant than for the other cyanometallates, as the octahedral shape is closer to spherical and the area projected in the layer plane defining the molecular area changes little with the orientation of the anion. Based on that spherical shape approximation, the contribution of all hexacyanometallates to the molecular area was deduced from partial volumes in reference salts. By assuming that the ionic layers of all dimer hexacyanometallates exhibit the same degree of ruffling as the dimer bromide, the molecular areas for both salts of the triply-charged complexes $([Co(CN)_6]^{3-}$ (2d) and $[Fe(CN)_6]^{3-}$ (**2e**)) would be similar and 3.5 Å² greater than that of the Br (1) while the salt of the quadruply-charged complex $[Fe(CN)_6]^{4-}$ (2f) would be 3 Å² smaller. Exact molecular areas can indeed not be predicted with these approximations (see Figure 8), but the sequence of molecular areas is respected and the order of magnitude for the discrepancies is correct, justifying nonetheless that the ruffled-layer model developed for the mono-charged anions is also relevant for the hexacyanometallates. Particularities of the hexacyanometallate derivatives consist in the enlarged smectic ranges and in the less steep variation with temperature of the molecular areas, revealing the reinforced lateral interactions between the imidazolium rows and the multi-charged anions. Confirmation and a more detailed investigation of the



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Figure 8: Variation with temprature of the molecular area in the smectic A phase for the bolaamphiphile series with various counter-ions.

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molecular organization would necessitate crystal structure determinations but none of these salts could be obtained in a suitable form.

Conclusions

We report the full characterisation of new mesomorphic bolaforms based on bis(imidazolium) units. The cation-anion organization has been determined in the solid state in two different cases by Single-Crystal X-ray diffraction and for the whole series in the mesophase by Small-Angle X-ray Scattering. The bis-imidazolium, "dimer" cation appears to be a versatile smectogenic platform which promotes mesomorphic behavior with different mono- and poly-charged cyanometallates of linear or octahedral geometry as in $[Ag(CN)_2]^{-}$ (2a), $[Co(CN)_6]^{3-}$ (2d), $[Fe(CN)_6]^{3-}$ (2e) and $[Fe(CN)_6]^{4-}$ (2f). Square planar $[Ni(CN)_4]^{2-}$ (2b) and $[Pt(CN)_4]^{2-}$ (2c) are not conducive to the emergence of liquid crystal properties. All the metallomesogens display lamellar self-organization (Smectic A phase). We have investigated the temperature dependence of the layer thickness of the Smectic A phase as a function of the temperature and different anions and we are now attempting to introduce different lateral tails to obtain room-temperature ionic liquid crystals.

Materials and methods

General Synthetic Methods. Reagents and solvents were purchased from commercial sources (Aldrich, Acros, Fluka) and used without further purification unless otherwise specified. Dichloromethane (CH₂Cl₂) was distilled from CaH₂ under argon. Tetrahyfrofuran (THF) was distilled from sodium/benzophenone under argon. Flash column chromatography was performed using Merck Aluminium oxide ¹H (300.13 MHz) and ¹³C NMR (75.48 MHz) spectra 90. were recorded on a Bruker Avance 300 spectrometer. Chemical shifts (δ) are given in parts per million (ppm) referenced to residual protonated solvent (CDCl₃: δ_H 7.27 ppm, $δ_{\rm C}$ 77.00 ppm; DMSO- $d_{\rm 6}$: $\delta_{\rm H}$ 2.50 ppm, $\delta_{\rm C}$ 39.50 ppm; methanol- d_4 : δ_H 3.35 ppm, δ_C 49.00 ppm). Abbreviations used are s (singlet), d (doublet), t (triplet), br (broad) and m (multiplet). FT-IR spectra were recorded on IR Digilab FTS 3000 spectrophotometer. Frequencies are given in cm⁻¹. Abbreviations used are br (broad), s (strong), m (medium) and w (weak). UV spectra were recorded on a Perkin Elmer Lambda 950 UV/Visible Spectrophotometer. Wavelengths are given in nm and the molar absorption coefficient in L mol⁻¹ 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°C/min. The device was calibrated with indium (156.6 °C, 28.4 J g^{-1}) and gallium (29.8 °C) as the standards. The TGA measurements were carried out on a SDTQ 600 apparatus at

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scanning rate of 10 °C min⁻¹. Polarized optical microscopy studies: 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. SAXS measurements were recorded either on a curved counter (CPS120 model from INEL) or on image plates (scanned by STORM 820 from Molecular Dynamics with 50 µm resolution). The setup consists in a transmission Guinier-like geometry, the linear focalized monochromatic Cu K α 1 beam (λ = 1.54056 Å) being obtained with a sealed-tube generator equipped with a bent quartz monochromator. For our compounds, the sample was directly filled in Lindemann capillaries of 0.5 mm diameter.

X-ray single crystal structure determinations of 2a and 2b

The selected crystals have been mounted on a Nonius Kappa-CCD area detector diffractometer (Mo K α , λ =0.71073 Å). The complete conditions of data collection (Denzo software) 37 and structure refinements are given in the corresponding cif file. The cell parameters were determined from reflections taken from one set of ten frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved using direct methods (SHELXS97)³⁸ and refined against F2 using the SHELXL97 software. The absorption was not corrected. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereo-chemistry and refined using a riding model in SHELXL97, excepted for water molecules in 2b. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as Supplementary publication CCDC reference numbers (2a: 1496539 and 2b: 1496540). This material is available free of charge via the Internet at http://www.ccdc.cam.ac.uk.

Crystal data and structure refinement details summary (T=173 K):

2a: colorless crystal; crystal dimension: $0.15 \times 0.11 \times 0.08 \text{ mm}^3$; $C_{34}H_{48}N_4O_2$, $2(AgCN_2)$, $M=864.58 \text{ g.mol}^{-1}$; triclinic; space group P-1; a = 6.420(1) Å; b = 6.924(1) Å; c = 22.131(2) Å; α = 95.130(2)°; β = 92.580(2)°; γ = 100.820(3)°; Z = 1; Dc = 1.495 g.cm⁻³; μ (Mo K α)= 1.063 mm⁻¹; a total of 8953 reflections; 1.85°< θ <30.03°, 5559 independent reflections with 4694 having I > 2 σ (I); 226 parameters; Final results: R1= 0.0507; wR2= 0.1229, Goof=1.047, maximum residual electronic density = 0.9 e⁻Å⁻³.

2b: colorless crystal; crystal dimension: $0.13 \times 0.10 \times 0.07 \text{ mm}^3$; $C_{34}H_{48}N_4O_2$, H_2O , Ni(CN)₄, M=725.57 g.mol⁻¹; triclinic; space group P-1; a = 8.8400(3) Å; b = 9.3130(4) Å; c = 24.9890(5) Å; α = 90.611(2)°; β = 99.078(2)°; γ = 108.8990(13)°; Z = 2; \square c = 1.256 g.cm⁻³; μ (Mo K α)= 0.552 mm⁻¹; a total of 18343 reflections; 1.65°< θ <30.03°, 11122 independent reflections with 8181 having I > 2 σ (I); 459 parameters; Final results: R1= 0.0669; wR2= 0.1277, Goof=1.043, maximum residual electronic density = 0.667 e⁻Å⁻³.

Synthetic procedures

Synthesis of Dimethyl 4,4'-(dodecane-1,12diylbis(oxy))dibenzoate. With continuous stirring, dibromododecane (25.00 g, 76 mmol) was added to a mixture of methyl 4-hydroxybenzoate (24.34 g, 160 mmol) and potassium carbonate (31.54 g, 229 mmol) in DMF (300 mL)

over 2 h and the resulting white suspension was then heated at 80 °C for 16 h. After cooling, the precipitate was collected by filtration and washed with water (100 mL). It was then treated with a mixture of CH₂Cl₂ and water until all solids had dissolved. The organic phase was separated and the aqueous solution was extracted with CH_2Cl_2 . All organics were combined and washed successively with saturated aqueous NaHCO₃, water, and brine. The CH₂Cl₂ layer was dried over MgSO₄, filtered and dried under vacuum to give a pure white solid (35.85 g, quantitative). ¹H NMR (CDCl₃; 300 MHz): δ 1.31 (br s, 12H, CH₂ aliphatic chain), 1.45 (m, 4H, J = 6.72 Hz, CH₂ aliphatic chain), 1.80 (m, 4H, J = 6.59 Hz, CH2- CH2-O), 3.88 (s, 6H, CH_3 -O), 4.00 (t, 4H, ³J = 6.59 Hz, CH_2 -O), 6.90 (m, 4H, aromatic, BB' system, J = 8.78 Hz), 7.98 (m, 4H, aromatic, AA' system, J = 8.78 Hz). ¹³C NMR (CDCl₃; 75 MHz): δ_c 25.94, 29.08, 29.30, 29.49 (CH₂ aliphatic chain), 51.75 (CH₃-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): v_{max} = 2920 (m, C-H aliphatic), 2850 (m, C-H aliphatic), 1723 (s, C=O ester), 1607 (m, C=C aromatic), 1507 (m, C=C aromatic), 1109 (m, C-O ester), 768 (m, C-H aromatic).

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

A solution of 1 (35.85 g, 76.18 mmol) dissolved in dry THF (150 mL) under argon was cooled to 0 ºC. Lithium aluminium hydride (1.0M in THF - 76.18 mL) was slowly added to the stirred 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 mixture formed was acidified with concentrated HCl to pH=1. It was next extracted with CH₂Cl₂ and the combined organic extracts washed successively with saturated aqueous NaHCO₃, water, and brine. They were finally dried over MgSO₄, filtered and evaporated to dryness to afford a pure white solid (29.92 g, 95%). ¹H NMR (DMSO; 300 MHz): δ 1.26 (br s, 12H, CH₂ aliphatic chain), 1.38 (m, 4H, CH₂ aliphatic chain), 1.67 (m, 4H, $J = 6.04 \text{ Hz}, CH_2 - CH_2 - O), 3.91 (t, 4H, {}^3J = 6.59 \text{ Hz}, CH_2 - O), 4.38$ (d, 4H, J = 5.21 Hz, CH_2 –OH), 5.01 (t, 2H, HO–CH₂, ³J = 5.49 Hz), 6.84 (d, 4H, aromatic, J = 8.51 Hz), 7.19 (d, 4H, aromatic, J = 8.51 Hz). ^{13}C 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): v_{max} = 3331 (br, OH), 2919 (s, C-H aliphatic), 2851 (s, C-H aliphatic), 1611 (m, C=C aromatic), 1510 (s, C=C aromatic), 1252 (s, methyl alkyl), 1028 (s, C-O alcohol), 817 (m, C-H aromatic).

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

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 argon. The orange mixture was stirred for 2 h at room temperature under argon. The reaction mixture was quenched with saturated NaHCO_3 and extracted with $\mathsf{CH}_2\mathsf{Cl}_2.$ The combined extracts were washed with NaHCO3, dried over MgSO₄, and evaporated in vacuum to give a crude white solid (5.07 g, 97%). ¹H NMR (CDCl₃; 300 MHz): δ 1.31 (br s, 12H, CH₂ aliphatic chain), 1.45 (m, 4H, CH₂ aliphatic chain), 1.79 (m, 4H, $J = 6.59 \text{ Hz}, CH_2 - CH_2 - O), 3.96 (t, 4H, {}^{3}J = 6.59 \text{ Hz}, CH_2 - O), 4.51$ (s, 4H, CH₂-Br), 6.86 (m, 4H, aromatic, BB' system, J = 9.06 Hz), 7.32 (m, 4H, aromatic, AA' system, J = 8.78 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): $v_{max} = 2917$ (m, C–H aliphatic), 2850 (m, C–H

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aliphatic), 1611 (m, C=C aromatic), 1513 (s, C=C aromatic), 1256 (s, methyl alkyl), 821 (m, C–H aromatic), 602 (s, C–Br). Procedures for the mesogenic materials preparation:

Synthesis of 3,3'-(((dodecane-1,12-diylbis(oxy))bis(4,1phenylene))bis(methylene))bis(1-methyl-1H-imidazol-3-ium) bromide (1).

A mixture of methylimidazole (0.32 g, 3.89 mmol) and 1,12bis(4-(bromomethyl)phenoxy)dodecane (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 to a small volume under reduced pressure and purified via column chromatography (gradient 100/0 to 95/10: CH_2Cl_2 /methanol) to furnish 1 (1.05 g, 1.46mmol, 79%) as a white solid. ¹H NMR (MeOD; 300 MHz): δ 1.40 (br s, 12H, CH₂ aliphatic chain), 1.52 (m, 4H, CH₂ aliphatic chain), 1.83 (m, 4H, J = 6.57 Hz, CH₂-CH₂-O), 3.99 (s, 6H, N-CH₃), 4.30 (t, 4H, ${}^{3}J$ = 6.60 Hz, CH₂-O), 5.41 (s, 4H, N-CH₂-Ph), 7.03 (m, 4H, aromatic, BB' system, J = 8.79 Hz), 7.45 (m, 4H, aromatic, AA' system, J = 8.79 Hz), 7.63 (br t, 2H, ${}^{3}J =$ 1.65 Hz, C_5-H imidazolium), 7.66 (br t, 2H, ${}^{3}J$ = 1.92 Hz, C_4-H imidazolium), 9.06 (2H, s, C₂–H imidazolium). ¹³C NMR (MeOD; 75 MHz): δ_c 27.09, 30.26, 30.43, 30.63 (CH₂ aliphatic chain), 36.58 (CH₃-N), 53.73 (N-CH₂-Ph), 69.15 (CH₂-O), 116.25 (CH phenyl), 123.45 (C₅–H imidazolium), 125.13 (C₄–H imidazolium), 126.75 (C phenyl), 131.40 (CH phenyl), 137.67 $(C_2-H \text{ imidazolium})$, 161.37 (C phenyl). IR (KBr, cm⁻¹): $v_{max} =$ 2922 (m, C-H aliphatic), 2854 (m, C-H aliphatic), 1608 (s, C=C aromatic), 1517 (s, C=C aromatic), 1252 (s, methyl alkyl), 836 (m, C–H aromatic). UV–vis (MeOH): $\lambda(\epsilon) = 231(5568)$, 271(2811). Elem. anal. calcd (%) for C₃₄H₄₈Br₂N₄O₂·0.75H₂O, M = 718,10: C, 56.87; H, 6.95; N, 7.80. Found: C, 56.90; H, 6.94; N, 7.54

General procedure for compounds 2a to 2f anion metathesis of 1.

A solution of potassium cyanometallate dissolved in water (4 mL) was added to a solution of compound **1** 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 was required. *Synthesis of 3,3'-(((dodecane-1,12-diylbis(oxy))bis(4,1-phenylene))bis(methylene))bis(1-methyl-1H-imidazol-3-ium)*

dicyanoargentate(I) (2a). Prepared from compound 1 (100 mg, 0.139 mmol) and potassium dicyanoargentate(I) (57 mg, 0.284 mmol) according to the general procedure to yield 2a as a pure white solid (107 mg, 0.124 mmol, 89%). ¹H NMR (MeOD/CD₂Cl₂:1/1; 300 MHz): δ 1.38 (br s, 12H, CH₂ aliphatic chain), 1.52 (m, 4H, CH₂ aliphatic chain), 1.84 (m, 4H, J = 6.59 Hz, CH_2 - CH_2 -O), 3.97 (s, 6H, N- CH_3), 4.04 (t, 4H, ³J = 6.04 Hz, CH2-O), 5.34 (s, 4H, N-CH2-Ph), 7.03 (m, 4H, aromatic, BB' system, J = 8.78 Hz), 7.39 (4H, m, aromatic, AA' system, J = 8.78 Hz), 7.54 (br s, 4H, C_4 –H imidazolium and C_5 –H imidazolium), 8.92 (s, 2H, C₂-H imidazolium). ¹³C NMR (MeOD/CD₂Cl₂:1/1; 75 MHz): δ_c 26.72, 29.89, 30.11, 30.29, 30.90, 30.91 (CH₂ aliphatic chain), 36.57 (CH₃-N), 53.74 (N-CH₂-Ph), 69.02 (CH₂-O), 116.08 (CH phenyl), 123.15 (C₅-H imidazolium), 124.76 (C₄-H imidazolium), 125.50 (C phenyl), 131.02 (CH phenyl), 161.13 (C phenyl). IR (KBr, cm⁻¹): $v_{max} =$ 2923 (w, C-H aliphatic), 2853 (w, C-H aliphatic), 2127 (w, C=N), 1607 (s, C=C aromatic), 1516 (m, C=C aromatic), 1253 (s, methyl alkyl), 832 (w, C–H aromatic). UV–vis (MeOH): $\lambda(\epsilon)$ =

235(14432), 273(5243). Elem anal calcd (%) for $C_{38}H_{48}Ag_2N_8O_2$, M = 864,59: C, 52.79; H, 5.60; N, 12.96. Found: C, 52.79; H, 5.62; N, 12.63.

3,3'-(((dodecane-1,12-diylbis(oxy))bis(4,1-Synthesis of phenylene))bis(methylene))bis(1-methyl-1H-imidazol-3-ium) tetracyanonickelate(II) (2b). Prepared from compound 1 (100 mg, 0.139 mmol) and potassium tetracyanonickelate(II) (35 mg, 0.142 mmol) according to the general procedure to yield **2b** as a pure white solid (89 mg, 0.124 mmol, 89%). ¹H NMR (MeOD/CD₂Cl₂:1/1; 300 MHz): δ 1.37 (br s, 12H, CH₂ aliphatic chain), 1.51 (m, 4H, CH₂ aliphatic chain), 1.83 (m, 4H, J = 6.86 Hz, CH_2 - CH_2 -O), 4.00 (s, 6H, N- CH_3), 4.04 (t, 4H, ${}^{3}J$ = 6.59 Hz, CH₂-O), 5.39 (s, 4H, N-CH₂-Ph), 7.03 (br d, 4H, aromatic, J = 8.78 Hz), 7.45 (br d, 4H, aromatic, J = 8.51 Hz), 7.54 (br s, 2H, C_4 –*H* imidazolium), 7.55 (br s, 2H, C_5 –*H* imidazolium). ¹³C NMR (CDCl_3; 75 MHz): δ_c 26.60, 29.80, 29.84, 29.86, 30.02, 30.09 (CH₂ aliphatic chain), 36.75 (CH₃-N), 53.76 (N-CH₂-Ph), 68.92 (CH₂–O), 116.06 (CH phenyl), 123.06 (C₅–H imidazolium), 124.86 (C₄-H imidazolium), 125.83 (C phenyl), 131.21 (CH phenyl), 133.69 (C2-H imidazolium), 161.02 (C phenyl). IR (KBr, cm⁻¹): v_{max} = 2923 (w, C–H aliphatic), 2854 (w, C–H aliphatic), 2119 (m, C=N), 1607 (s, C=C aromatic), 1516 (m, C=C aromatic), 1255 (s, methyl alkyl), 837 m, (C-H aromatic). UVvis (MeOH): λ(ε) = 237(12540), 267(16973). Elem anal calcd (%) for $C_{38}H_{48}NiN_8O_2 \cdot 0.5H_2O$, M = 716,56: C, 63.70; H, 6.89; N, 15.64. Found: C, 63.79; H, 6.88; N, 15.36.

3,3'-(((dodecane-1,12-diylbis(oxy))bis(4,1-Synthesis of phenylene))bis(methylene))bis(1-methyl-1H-imidazol-3-ium) tetracyanoplatinate(II) (2c). Prepared from compound 1 (100 mg, 0.139 mmol) and potassium tetracyanoplatinate(II) (66 mg, 0.142 mmol) according to the general procedure to yield 2c as a pure white solid (109 mg, 0.129 mmol, 93%). ¹H NMR (MeOD/CD₂Cl₂:1/1; 300 MHz): δ 1.37 (br s, 12H, CH₂ aliphatic chain), 1.51 (m, 4H, CH₂ aliphatic chain), 1.82 (m, 4H, J = 6.86 Hz, CH_2 - CH_2 -O), 4.00 (s, 6H, N- CH_3), 4.04 (t, 4H, ³J = 6.59 Hz, CH2-O), 5.39 (s, 4H, N-CH2-Ph), 7.02 (m, 4H, aromatic, BB' system, J = 8.78 Hz), 7.43 (m, 4H, aromatic, AA' system, J = 8.78 Hz), 7.49 (br d, 2H, J = 1.92 Hz, C₅–H imidazolium), 7.52 (br d, 2H, J = 1.92 Hz, C_4 –H imidazolium). ¹³C NMR (MeOD/CD₂Cl₂:1/1; 75 MHz): δ_c 26.54, 26.57, 29.73, 29.80, 29.96, 30.03 (CH₂ aliphatic chain), 36.78 (CH₃-N), 53.74 (N-CH₂-Ph), 68.87 (CH₂-O), 116.00 (CH phenyl), 123.03 (C₅-H imidazolium), 124.73 (C_4 –H imidazolium), 125.57 (C phenyl), 131.20 (CH phenyl), 160.91 (C phenyl). IR (KBr, cm⁻¹): $v_{max} =$ 2922 (m, C–H aliphatic), 2852 (m, C–H aliphatic), 2124 (s, C≡N), 1516 (s, C=C aromatic), 1254 (s, methyl alkyl), 835 (m, C-H aromatic). Elem anal calcd (%) for C₃₈H₄₈N₈O₂Pt' M = 843.94: C, 54.08; H, 5.73; N, 13.28. Found: C, 54.15; H, 5.75; N, 12.78.

Synthesis of 3,3'-(((dodecane-1,12-diylbis(oxy))bis(4,1phenylene))bis(methylene))bis(1-methyl-1H-imidazol-3-ium) hexacyanocobaltate(III) (2d). Prepared from compound 1 (100 mg, 0.139 mmol) and potassium hexacyanocobaltate(III) (32 mg, 0.095 mmol) according to the general procedure to yield 2d as a pure white solid (91 mg, 0.043 mmol, 92%). ¹H NMR (MeOD/CD₂Cl₂:1/1; 300 MHz): δ 1.37 (br s, 12H, CH₂ aliphatic chain), 1.49 (m, 4H, CH₂ aliphatic chain), 1.81 (m, 4H, J = 6.31 Hz, CH_2 - CH_2 -O), 4.00 (t, 4H, ${}^{3}J$ = 6.45 Hz, CH_2 -O), 4.06 (s, 6H, N-CH₃), 5.44 (s, 4H, N-CH₂-Ph), 6.97 (m, 4H, aromatic, BB' system, J = 8.51 Hz), 7.42 (br t, 2H, ${}^{3}J = 1.92$ Hz, $C_{5}-H$ imidazolium), 7.44 (m, 4H, aromatic, AA' system, J = 8.78 Hz), 7.50 (br t, 2H, ${}^{3}J$ = 1.78 Hz, C₄–H imidazolium), 9.12 (br s, 2H, C₂-H imidazolium). ¹³C NMR (MeOD/CD₂Cl₂:1/1; 75 MHz): δ_r Published on 21 February 2017. Downloaded by University of California - San Diego on 21/02/2017 07:55:37

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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 (C₅-H imidazolium), 124.64 (C₄-H imidazolium), 126.15 (C phenyl), 131.20 (CH phenyl), 137.14 (C2-H imidazolium), 160.69 (C phenyl). IR (KBr, cm⁻¹): v_{max} = 2921 (w, C–H aliphatic), 2854 (w, C-H aliphatic), 2134 (w, C=N), 1605 (s, C=C aromatic), 1516 (C=C aromatic), 1254 (m, methyl alkyl), 833 (w, C-H aromatic). UV–vis (MeOH): $\lambda(\epsilon) = 235(10811)$, 273(5730). Elem anal calcd (%) for $C_{114}H_{144}Co_2N_{24}O_6\cdot 3.5H_2O$, M = 2127,49: C, 64.36; H, 7.15; N, 15.80. Found: C, 64.31; H, 7.18; N, 15.49. Svnthesis of 3,3'-(((dodecane-1,12-diylbis(oxy))bis(4,1phenylene))bis(methylene))bis(1-methyl-1H-imidazol-3-ium) hexacyanoferrate(III) (2e). Prepared from compound 1 (100 mg, 0.139 mmol) and potassium hexacyanoferrate (III) (32 mg, 0.095 mmol) according to the general procedure to yield 2e as a pure dark yellow solid (91 mg, 0.043 mmol, 92%). ¹H NMR (MeOD/CD₂Cl₂:1/1; 300 MHz): δ 1.37 (br s, 12H, CH₂ aliphatic chain), 1.49 (m, 4H, CH₂ aliphatic chain), 1.80 (m, 4H, J = 6.04 Hz, CH_2 - CH_2 -O), 3.59 (s, 6H, N- CH_3), 3.99 (t, 4H, ${}^{3}J$ = 6.31 Hz, CH₂-O), 5.01 (s, 4H, N-CH₂-Ph), 6.92 (br d, 4H, aromatic, J = 8.23 Hz), 7.13 (br s, 2H, C₅-H imidazolium), 7.14 (br s, 2H, C₄-H imidazolium), 7.23 (br d, 4H, aromatic, J = 8.23 Hz), 7.94 (br s, 2H, C₂–H imidazolium). ¹³C NMR (MeOD/CD₂Cl₂:1/1; 75 MHz): δ_c 26.55, 29.76, 29.89, 30.00 (CH₂ aliphatic chain), 40.04 (CH₃-N), 55.59 (N-CH₂-Ph), 68.83 (CH₂-O), 115.94 (CH phenyl), 123.45 (C_5 –H imidazolium), 125.55 (C_4 –H imidazolium), 126.06 (C phenyl), 131.67 (CH phenyl), 141.06 (C2-H imidazolium), 160.74 (*C* phenyl). IR (KBr, cm⁻¹): v_{max} = 2919 (m, C–H aliphatic), 2851 (m, C-H aliphatic), 2106 (s, C=N), 1612 (s, C=C aromatic), 1514 (s, C=C aromatic), 1250 (s, methyl alkyl), 836 (s, C-H aromatic). UV-vis (MeOH): λ(ε) = 234(11351), 273(3514), 420 (≈ 55) Elem anal calcd (%) for C₁₁₄H₁₄₄Fe₂N₂₄O₆·3.75.H₂O, M = 2125,81: C, 64.41; H, 7.18; N, 15.81. Found: C, 64.19; H, 7.19; N, 15.39.

3,3'-(((dodecane-1,12-diylbis(oxy))bis(4,1-Synthesis of phenylene))bis(methylene))bis(1-methyl-1H-imidazol-3-ium) hexacyanoferrate (II) (2f). Prepared from compound 1 (100 mg, 0.139 mmol) and potassium hexacyanoferrate (II) (30 mg, 0.071 mmol) according to the general procedure to yield 2f as a pure yellow solid (83 mg, 0.062 mmol, 89%). ¹H NMR (MeOD/CD₂Cl₂:1/1; 300 MHz): δ 1.37 (br s, 12H, CH₂ aliphatic chain), 1.49 (m, 4H, CH₂ aliphatic chain), 1.81 (m, 4H, J = 6.59 Hz, CH₂- CH₂-O), 3.99 (m, 10H, CH₂-O and N-CH₃), 5.40 (s, 4H, N-CH₂-Ph), 6.94 (m, 4H, aromatic, BB' system, J = 8.51 Hz), 7.29 (br d, 2H, J = 1.92 Hz, C_5-H imidazolium), 7.39 (m, 4H, aromatic, AA' system and C_4-H imidazolium). ¹³C NMR (MeOD/CD₂Cl₂:1/1; 75 MHz): δ_c 25.66, 28.88, 29.00, 29.11 (CH₂ aliphatic chain), 37.13 (CH₃-N), 53.21 (N-CH₂-Ph), 67.96 (CH₂-O), 114.98 (CH phenyl), 121.69 (C₅-H imidazolium), 123.86 (C₄-H imidazolium), 125.43 (C phenyl), 130.46 (CH phenyl), 159.95 (C phenyl). IR (KBr, cm⁻¹): v_{max} = 2922 (w, C–H aliphatic), 2854 (w, C-H aliphatic), 2044 (m, C=N), 1607 (s, C=C aromatic), 1517 (m, C=C aromatic), 1256 (s, methyl alkyl), 835 (m, C-H aromatic). UV–vis (MeOH): λ(ε) = 235(9189), 273(3730) 425 (≈ 85). Elem anal calcd (%) for C₇₄H₉₆FeN₁₄O₄·2H₂O, M = 1337.55: C, 66.45; H, 7.54; N, 14.66. Found: C, 66.32; H, 7.50; N, 15.45.

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Table of contents entry

Rare examples of bolaform ionic materials containing cyanometallates and their lamellar mesormorphic supramolecular architectures are characterized.

Bolaform Ionic liquid crystal

