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1,10-Phenanthrolinium Ionic Liquid Crystals

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The 1,10-phenanthrolinium cation is introduced as a new building block for the design of ionic liquid crystals. 1,10-Phenanthroline, 5-methyl-1,10-phenanthroline, 5-chloro-1,10-phenanthroline, and 4,7-diphenyl-1,10-phenanthroline were quaternized by reaction with 1,3-dibromopropane or 1,2-dibromoethane. The resulting cations were combined with dodecyl sulfate or dioctyl sulfosuccinate anions. The influence of both the cation and anion type on the thermal behavior was investigated. Several of the complexes exhibit mesomorphic behavior, with smectic E phases for the dodecyl sulfate salts and smectic A phases for the dioctyl sulfosuccinate salts. Structural models for the packing of the 1,10-phenanthrolinium and anionic moieties in the liquid-crystalline phases are presented. The ionic compounds show fluorescence in the solid state and in solution.

Introduction

1,10-Phenanthroline and its derivatives are well-known, versatile bidentate ligands that can form stable complexes with many metal ions in different oxidation states.[1−3] It is also possible to functionalize the 1,10-phenanthroline moiety in many ways to synthesize different types of liquid crystals. The aromatic core can be extended to form calamitic (rodlike) liquid crystals, but it can also be used to design discotic (disklike), bent-core or polycatenar liquid crystals. Polycatenar (literally “many-tailed”) liquid crystals consist of an extended, linear, usually aromatic core that is decorated with several long alkoxy chains at both ends.[4] The first 3,8-disubstituted 1,10-phenanthroline-containing calamitic liquid crystals were described by Bousquet and Bruce and showed smectic and nematic phases.[5] Related tetracatenar ligands and their corresponding rhenium(I) complexes exhibit a hexagonal columnar mesophase (Col_h).[6] In this case, ester linkages and triple bonds were used to connect the aromatic units in order to develop a long aromatic core to counterbalance the bulky metallic fragment. A rich mesomorphism, including smectic C, cubic, hexagonal, and rectangular columnar phases, depending on the alkoxy chain length, is exhibited by a rigid, extended, tetracatenar 3,8-disubstituted 1,10-phenanthroline with acetylenic linkers.[7] Other mesomorphic systems include tetrahedral copper(I) complexes derived from a nonsymmetrical phenanthroline, which were found to show an oblique columnar mesophase (Col_o).[8] The functionalization of 1,10-phenanthroline in the 5 and 6 positions by a 2-substituted imidazole ring led to imidazo-[4,5-f]-1,10-phenanthrolines, which are very versatile ligands for the design of liquid-crystalline metal complexes (metallomesogens).[9] Related mesogenic ligands are the pyrazino[2,3-f]-1,10-phenanthrolines.[10]

In this article, we present a novel approach to liquid crystals based on 1,10-phenanthroline. 1,10-Phenanthroline and some of its derivatives were quaternized by the reaction of their two nitrogen atoms with an α,ω-dibromoalkane. Exchanging the bromide ions of the resulting 1,10-phenanthrolinium bromides for dodecyl sulfate (DOS) or dioctyl sulfosuccinate (DOSS) anions resulted in a new class of ionic liquid crystals.[11,12]

Experimental Section

Defect textures of the mesophases were observed with an Olympus BX60 polarizing optical microscope equipped with a Linkam THMS600 hot stage and a Linkam TMS93 programmable temperature controller. DSC traces were recorded with a Mettler-Toledo DSC822e module (heating/cooling rate of 10 °C min^{-1}, helium atmosphere). Powder X-ray diffractograms were recorded with a Bruker AXS D8 Discover diffractometer mounted with a copper X-ray ceramic tube, working at 1.6 kW. The emitted Cu Kα radiation ($\lambda = 1.5418$ Å) was focused on the sample by a Göbel mirror. All of the samples (without a thermal history) were prepared by spreading the compounds on a thin, clean silicon wafer. Diffractograms were recorded using Bragg−Brentano reflection geometry ($\theta/2\theta$ setup) at an angular resolution (in 2θ) of 0.03° per step. The deviation between the temperature on the surface of the sample holder and the set temperature was about 3%. The scattering signal was recorded with a 1D detector (LynxEye). Absorption spectra were measured on a Varian Cary 5000 spectrophotometer on freshly prepared methanol solutions of the 1,10-phenanthrolinium salts in quartz

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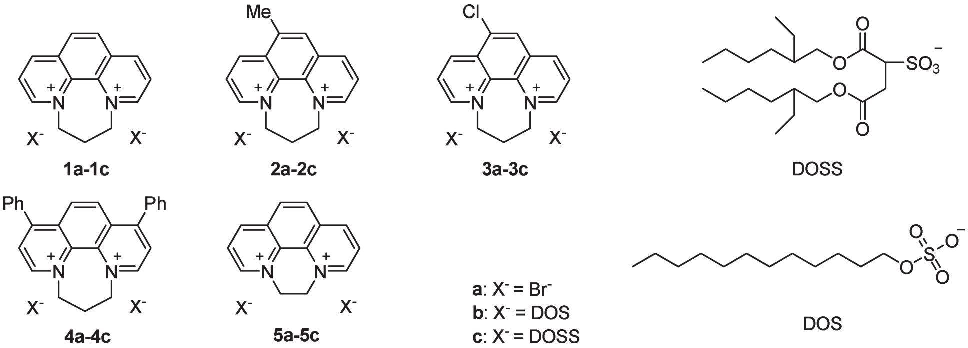
Chart 1. Overview of the 1,10-Phenanthrolinium Salts



Suprasil cells (optical path length, 1 cm). Luminescence spectra were recorded on an Edinburgh Instruments FS900 or FS920 steady-state spectrofluorimeter for solid-state samples or solutions in methanol, respectively. These instruments are equipped with a 450 W xenon arc lamp, a microsecond flash lamp (pulse length, 2 μs), and a red-sensitive (300−850 nm, Hamamatsu R928P on Edinburgh Instruments FS900) or extended red-sensitive (185−1010 nm, Hamamatsu R2658P on Edinburgh Instruments FS920) photomultiplier. The excitation wavelength was set at 308 nm for compounds **1b**, **1c**, **2b**, **2c**, **5b**, and **5c** and at 320 nm for compounds **4b** and **4c**. Quantum yields were determined by a comparative method using solutions of rhodamine 101 (Aldrich) in ethanol (Q = 100%) and quinine sulfate (Fluka) in 1 N H_2SO_4 (Q = 54.6%) as standards with an estimated error of 20%.[13] The synthesis and characterization of the ionic liquid crystals are described in the Supporting Information.

Results and Discussion

1,10-Phenanthroline and its derivatives 5-methyl-1,10-phenanthroline, 5-chloro-1,10-phenanthroline, and 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline) have been used as starting materials. An overview of the 1,10-phenanthrolinium salts is given in Chart 1. Bromide salts **1a**−**5a** were prepared via double quaternization (Menschutkin reaction) of the respective 1,10-phenanthroline compound with 1,3-dibromopropane (**1a**−**4a**) or 1,2-dibromoethane (**5a**) in nitrobenzene.[14] DOS salts **1b**−**5b** were synthesized via a metathesis reaction between bromide salts **1a**−**5a** and silver dodecyl sulfate in ethanol. DOSS salts **1c**−**5c** were prepared via a metathesis reaction between bromide salts **1a**−**5a** and sodium dioctyl sulfosuccinate in water. Yields were in the range of 65−94% for all of the 1,10-phenanthrolinium salts. The purity of all of the compounds was verified via ^{1}H and ^{13}C NMR spectroscopy and CHN elemental analysis.

The thermal properties of all of the 1,10-phenanthrolinium compounds were examined by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC) and for some compounds by powder X-ray diffraction (PXRD) at elevated temperatures. The transition temperatures and thermodynamic data for the dodecyl sulfate and the dioctyl sulfosuccinate salts are summarized in Table 1.

With the exception of the DOSS salts (**1c**−**5c**), two or more crystalline phases were observed for the 1,10-phenanthrolinium salts, which is not unusual for ionic compounds. The absence of crystalline polymorphism for the DOSS salts (**1c**−**5c**) can be attributed to the large, bulky anions, which prevent good packing within the crystalline solid phase. It should be mentioned that all of the DOSS salts (**1c**−**5c**) were obtained as waxy solids.

Table 1. Transition Temperatures and Thermodynamic Data for the 1,10-Phenanthrolinium Compounds

compound	transition[a]	T (°C)[b]	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
1b	$Cr_1 \rightarrow Cr_2$	88	44.5	123
	$Cr_2 \rightarrow Cr_3$	133	17.8	44
	$Cr_3 \rightarrow$ SmE	143	17.2	41
	SmE → dec	> 200		
2b	$Cr_1 \rightarrow Cr_2$	87	34.6	96
	$Cr_2 \rightarrow$ SmE	149	11.5	27
	SmE → dec	> 200		
3b	$Cr_1 \rightarrow Cr_2$	40	1.5	5
	$Cr_2 \rightarrow Cr_3$	62	74.4	222
	$Cr_3 \rightarrow Cr_4$	100	0.9	2
	$Cr_4 \rightarrow$ SmE	185	3.2	7
	SmE → dec	> 200		
4b	$Cr_1 \rightarrow Cr_2$	34	1.8	6
	$Cr_2 \rightarrow$ I	190[c]	14.7	32
5b	$Cr_1 \rightarrow Cr_2$	41	0.9	3
	$Cr_2 \rightarrow Cr_3$	93	61.9	169
	$Cr_3 \rightarrow$ dec	> 200		
1c	Cr → SmA	81[c]	28.6	81
	SmA → I	171	0.1	0.2
2c	Cr → SmA	63[c]	15.2	45
	SmA → I	157[c]	2.4	5
3c	Cr → SmA	65[c]	8.7	26
	SmA → I	146	2.3	5
4c	g → I	66	0.1	0.2
5c	Cr → SmA	116	6.8	17
	SmA → I	182	2.1	5

[a] Abbreviations: Cr, Cr_1, Cr_2, Cr_3, and Cr_4, crystalline phases; g, glass; SmE, smectic E phase; SmA, smectic A phase; I, isotropic liquid; dec, decomposition. [b] Onset temperatures obtained by DSC at heating/cooling rates of 10 °C min^{-1} (helium atmosphere). [c] Peak temperature.

None of the bromide salts (**1a**−**5a**) were liquid-crystalline, which is not unexpected because these compounds do not contain any aliphatic chains. Except for the compounds containing the 4,7-diphenyl-1,10-phenanthrolinium cation (**4b** and **4c**) and DOS salt **5b**, the DOS (**1b**−**3b**) and DOSS (**1c**−**3c** and **5c**) salts were liquid-crystalline. Considering the data in Table 1 (phase behavior of **1b**, **5b**, **1c**, and **5c**), one can expect that compound **5b** is intrinsically able to form a mesophase but its melting point is so high that the material thermally decomposes before it can melt into the liquid-crystalline phase. Upon heating, the DOS salts (**1b**−**3b**) showed a smectic E phase, whereas the DOSS salts (**1c**−**3c** and **5c**) showed a smectic A phase. The identification of the mesophases was confirmed by PXRD (see below).

The smectic A phases of the DOSS salts (**1c**−**3c** and **5c**) were identified by polarizing optical microscopy via the formation of bâtonnets on cooling from the isotropic liquid (Figure 1). On further cooling, these bâtonnets coalesced into fans so that a fan texture with homeotropic domains was formed (Figure 1). The smectic E phases of the DOS salts showed an oily streak texture

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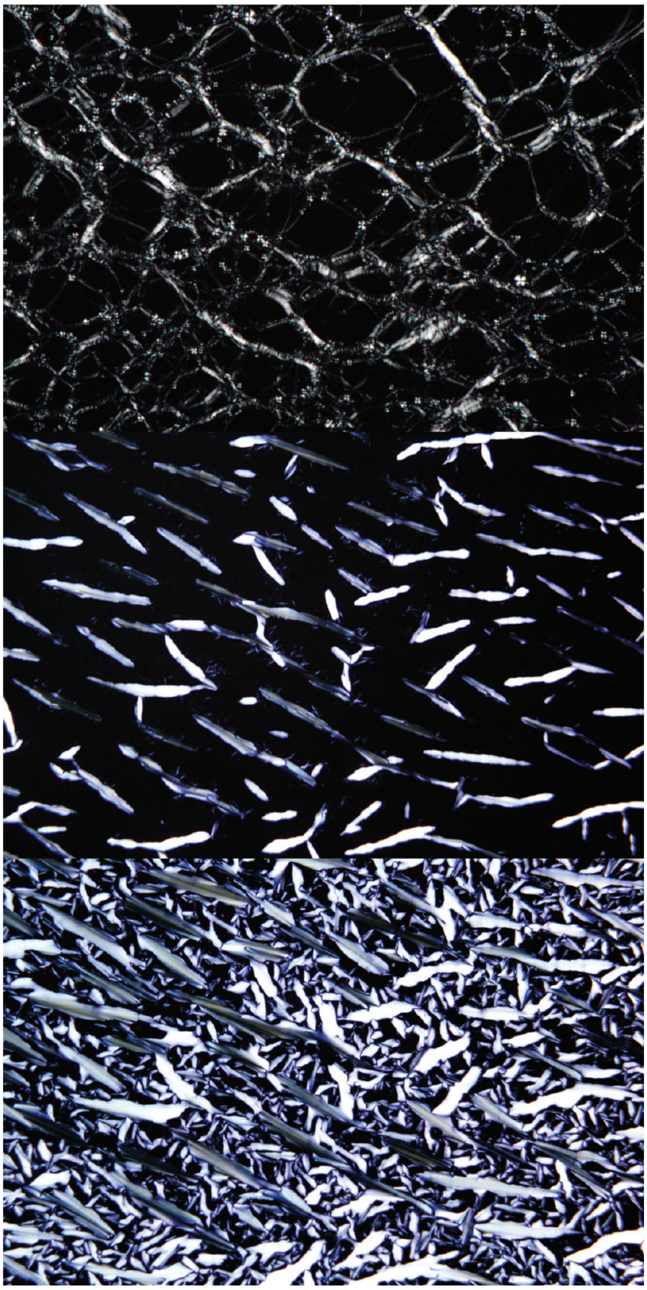

Figure 1. Mesophase defect textures observed by polarizing optical microscopy (POM). (Top) Oily streak texture of the smectic E phase of **1b** at 150 °C (200× magnification). (Middle) Appearance of bâtonnets during the formation of the smectic A phase of **2c** at 155 °C on cooling from the isotropic liquid phase (100× magnification). (Bottom) Fan texture with homeotropic domains of the smectic A phase of **2c** at 150 °C (100× magnification).

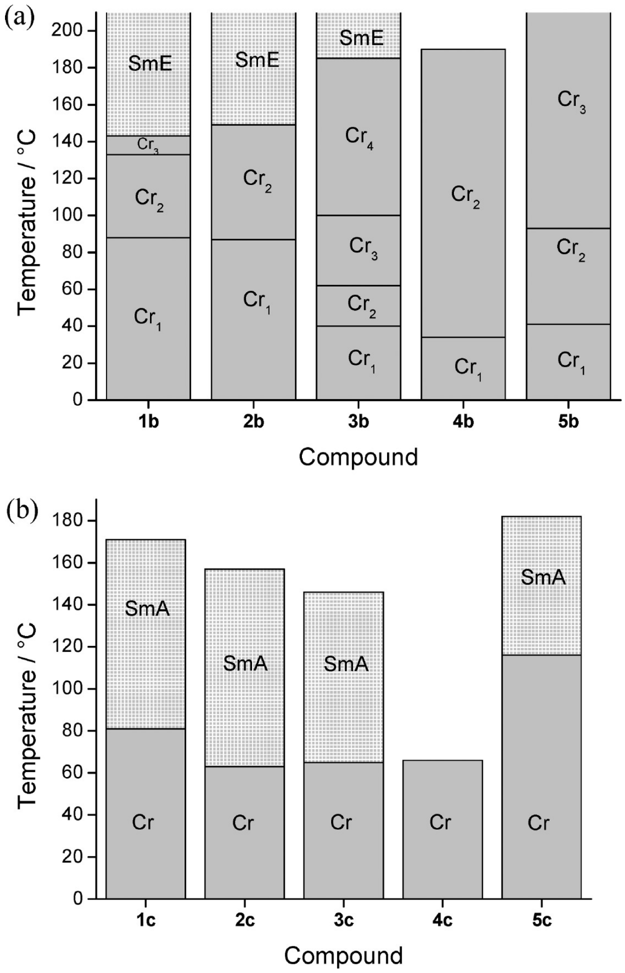

Figure 2. (a) Thermal behavior of 1,10-phenanthrolinium dodecyl sulfate (DOS) salts **1b**−**5b**. Abbreviations: Cr_1, Cr_2, Cr_3, and Cr_4, crystalline phase; SmE, smectic E phase. (b) Thermal behavior of 1,10-phenanthrolinium dioctyl sulfosuccinate (DOSS) salts **1c**−**5c**. Abbreviations: Cr, crystalline phase; SmA, smectic A phase.

with pseudohomeotropic domains (Figure 1), a texture that is usually not observed for smectic E phases.[15,16]

In Figure 2, an overview of the thermal behavior of the DOS (**1b**−**5b**) and DOSS (**1c**−**5c**) salts is given. For the DOS salts (**1b**−**5b**), the lowest melting point was observed for the unsubstituted 1,10-phenanthrolinium cation (**1b**). However, for the DOSS salts (**1c**−**5c**), the lowest melting point was observed for the 5-methyl-1,10-phenanthrolinium cation (**2c**). The DSC traces of compound **2c** (second heating/cooling cycle) are given in Figure 3. The mesophase temperature range was about 95 °C for DOSS salts **1c**−**3c**, but the mesophase temperature range for DOSS salt **5c** was smaller (66 °C). Mesomorphic DOS salts **1b**−**3b** decomposed in the liquid-crystalline phase before the clearing point was reached. DOSS salts **1c**−**5c** had lower melting points than DOS analogues **1b**−**5b**.

To obtain more information about the molecular arrangement of the 1,10-phenanthrolinium compounds in the smectic phases, the liquid-crystalline compounds were further investigated by PXRD. Unfortunately, no well-resolved peaks could be observed for DOS salt **3b** because of partial thermal decomposition above the rather high melting point (185 °C). Because of POM textures similar to those of **1b** and **2b**, the mesophase of **3b** was assumed to be the same as that of compounds **1b** and **2b** (see below). Table 2 gives an overview of the Bragg reflections collected from the X-ray diffractograms of DOS salts **1b** and **2b** and DOSS salts **1c**, **2c**, **3c**, and **5c**. The diffractograms of DOS salts **1b** and **2b** showed several strong equidistant reflections in the small-angle region. These reflections are related to the thickness *d* of the smectic layers. In the wide-angle region, two sharp peaks were visible. These reflections indicate a 2D ordering of the molecules within the smectic layers and were indexed as the (110) and (200)

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reflections of a 2D centered rectangular lattice. No other (*hkl*) signals (mixing of (00*l*) and (*hk*0), with *h* and/or $k \neq 0$, $l \neq 0$), which could have pointed to substantial interlayer coupling, were found. Only a diffuse signal centered at about 4.4 Å was additionally observed in the wide-angle region. This signal is related to the lateral short-range order of the molten aliphatic chains. The diffractograms of DOSS salts **1c**, **2c**, **3c**, and **5c** showed up to three sharp, equidistant reflections in the small-angle region, corresponding to the layer thickness *d* of the smectic A layers. In the wide-angle region, a diffuse signal was observed at about 4.5 Å corresponding to the lateral short-range order of the molten aliphatic chains.

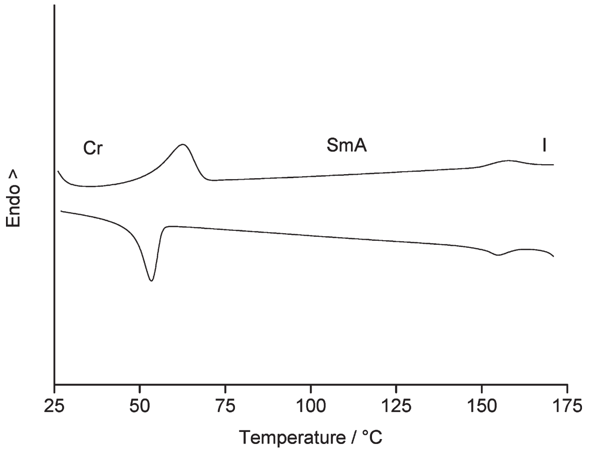

Figure 3. DSC trace of **2c**: second heating (upper curve) and cooling (lower curve) runs at a heating/cooling rate of 10 °C min^{-1} in a He atmosphere. Abbreviations: Cr, crystalline phase; SmA, smectic A phase; I, isotropic liquid.

From the diffractograms obtained for the smectic E phases shown by DOS salts **1b** and **2b**, parameters A_M, *a*, and *b* could be calculated (Table 2). A_M corresponds to the area occupied by the ionic clusters (a head-to-head arrangement of two 1,10-phenanthrolinium dications and four DOS anions) within the smectic layers. It was estimated using the relation $A_M = 2V_M/d$, where V_M is the molecular volume (estimated as $V_M = (M/0.6022)f$, *M* is the molecular mass (g mol^{-1}), and *f* is a temperature correction factor ($f = 0.9813 + 7.474 \times 10^{-4}T$, with *T* in °C)), and *d* is the smectic layer thickness.[17] At 161 °C, this calculation yields a value of $A_M \approx 90$ Å^2 for both **1b** and **2b**. Parameters *a* and *b* are the dimensions of the 2D rectangular lattice unit cell in the smectic E phase (for a 2D rectangular lattice, $1/d_{hk}^2 = h^2/a^2 + k^2/b^2$). For **1b** and **2b**, similar values were found for *a* and *b*: about 7.7 and about 5.4 Å, respectively. Consequently, the area of the rectangular lattice unit cell equals about 42 Å^2. Considering these values, it can be concluded that the four alkyl chains of an ionic cluster are almost fully interdigitated (the cross-sectional area of one fully stretched aliphatic chain equals about 23.4 Å^2 at 161 °C).[18] In Figure 4, a model of the molecular arrangement in the smectic E phases is proposed. In the model, the smectic layers are composed of ionic sublayers on one hand and aliphatic sublayers on the other hand. This is due to electrostatic interactions between the positively and negatively charged ionic headgroups and van der Waals interactions between the relatively long aliphatic chains, which both lead to microphase separation. Each ionic sublayer is in fact a bilayer of 1,10-phenanthrolinium dications. Such a bilayer arrangement has been observed for other ionic liquid crystals.[19,20] The planes of the dications are oriented perpendicular to the smectic layers, thus exposing their positive charges most effectively to the sulfate anions. Inside each ionic bilayer, the 1,10-phenanthrolinium moieties are arranged in such a way that a herringbone molecular packing is achieved, which is typical

Table 2. Bragg Reflections Collected from the X-ray Diffractograms of the Enantiotropic Mesophases

compound	d_{meas}/Å[a]	*I*[b]	*hkl*[c]	d_{calc}/Å[a]	parameters of the liquid-crystalline phase at temperature *T*[d,e,f]
1b	30.64	VS	001	30.89	SmE: $T = 161$ °C
	15.40	M	002	15.45	$V_M = 1378$ Å^3
	10.41	S	003	10.30	$A_M = 89.2$ Å^2
	7.73	M	004	7.72	$a = 7.74$ Å
	4.42	M	110	4.42	$b = 5.38$ Å
	4.40	br	h_{CH}		
	3.86	M	200	3.87	
2b	30.64	VS	001	30.67	SmE: $T = 161$ °C
	15.24	M	002	15.34	$V_M = 1403$ Å^3
	10.33	S	003	10.22	$A_M = 91.5$ Å^2
	7.65	S	004	7.67	$a = 7.70$ Å
	5.08	W	006	5.11	$b = 5.31$ Å
	4.48	br	h_{CH}		
	4.37	M	110	4.37	
	3.85	W	200	3.85	
1c	23.09	VS	001	23.09	SmA: $T = 100$ °C
	11.55	W	002	11.54	$V_M = 1868$ Å^3
	7.69	VW	003	7.70	$A_M = 161.8$ Å^2
	4.45	br	h_{CH}		
2c	22.75	VS	001	22.75	SmA: $T = 120$ °C
	4.46	br	h_{CH}		$V_M = 1921$ Å^3
					$A_M = 168.9$ Å^2
3c	22.92	VS	001	22.92	SmA: $T = 120$ °C
	4.46	br	h_{CH}		$V_M = 1957$ Å^3
					$A_M = 170.8$ Å^2
5c	25.04	VS	001	25.04	SmA: $T = 120$ °C
	4.55	br	h_{CH}		$V_M = 1871$ Å^3
					$A_M = 149.4$ Å^2

[a] d_{meas} and d_{calc} are the measured and calculated diffraction spacings, respectively. [b] *I* is the intensity of the reflections: VS, very strong; S, strong; M, medium; W, weak; VW, very weak; br, broad reflection. [c] *hkl* are the Miller indices of the reflections, and h_{CH} is the periodicity corresponding to the liquid-like order of the molten aliphatic chains. [d] *T* is the temperature at which the X-ray diffractogram was recorded. [e] V_M is the molecular volume, and A_M the molecular area. *a* and *b* are the lattice parameters of the smectic E phase. [f] Abbreviations: SmE, smectic E phase; SmA, smectic A phase.

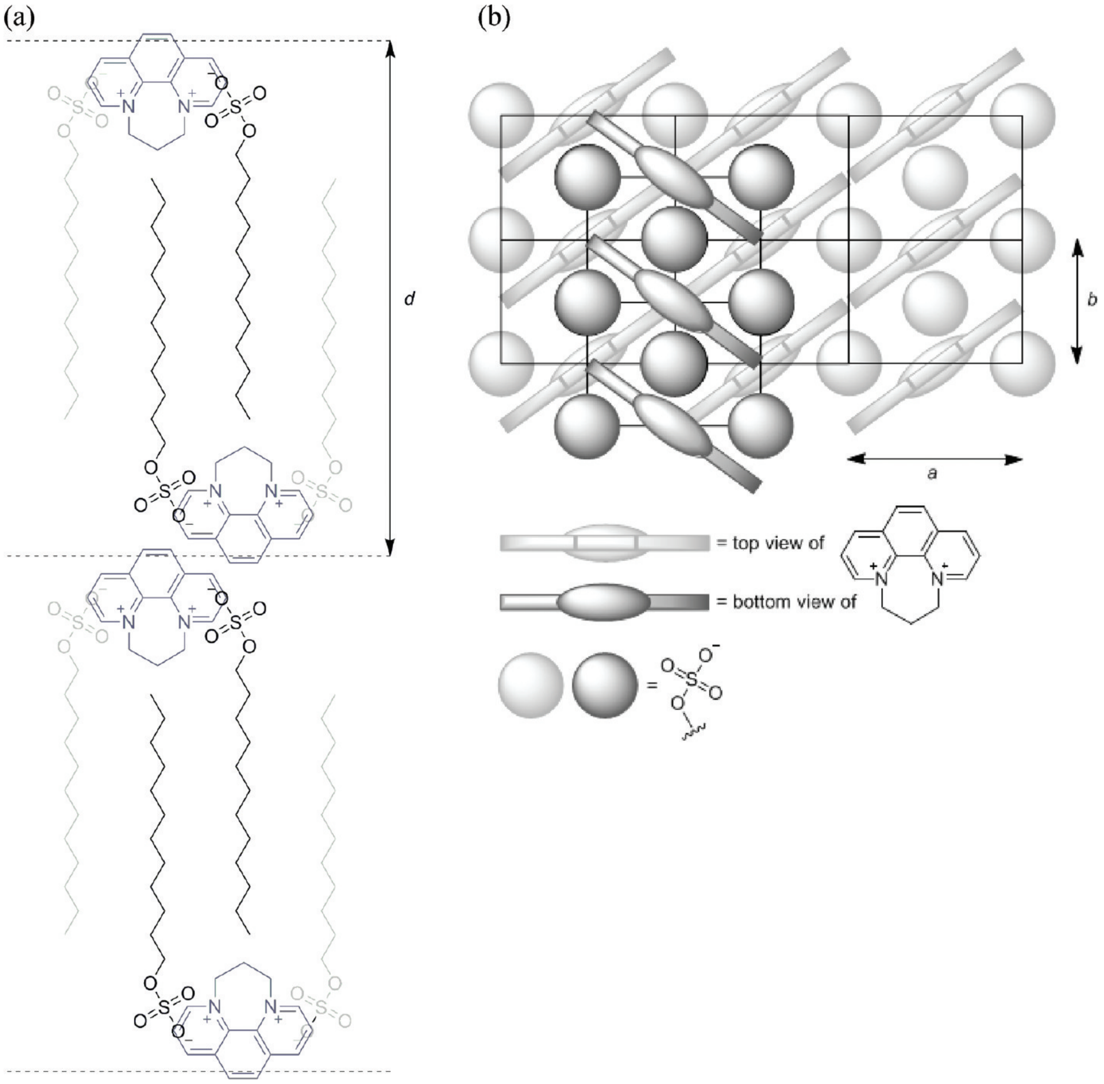

Figure 4. Structural model (idealized) for the smectic E phase exhibited by compound **1b**. (a) Side view. The smectic layer thickness is indicated by d (at 161 °C, d = 30.89 Å and $A_M \approx 89$ Å^2 (Table 2)). In reality, the phenanthroline moieties are tilted out of the plane of the paper. (b) Top view of the 2D rectangular lattice. The lower half of an ionic bilayer is depicted in pale gray, and the upper half of this bilayer is depicted in dark gray. The aliphatic chains (which point toward and away from the reader) are omitted for clarity. The dimensions of a unit cell of the 2D rectangular lattice are indicated by a and b (at 161 °C, a = 7.74 Å and b = 5.38 Å (Table 2)).

for E phases.[15,21] From Figure 4b, it becomes clear that the polyaromatic moieties can nicely fit on top of each other. (Pay attention to the topography of the 1,10-phenanthrolinium parts.) The 2D rectangular lattice unit cells are also filled with the sulfate headgroups. The slightly rotated orientation of the 1,10-phenanthrolinium planes with respect to the long side of the rectangular lattice unit cells allows for an efficient electrostatic interaction between one 1,10-phenanthrolinium dication and two sulfate headgroups. The alkyl chains attached to the sulfate anions point away from the ionic sublayer, and alkyl chains attached to sulfate groups belonging to different ionic sublayers are nearly fully interdigitated to form the aliphatic sublayers. The E-phase structure proposed in Figure 4 differs somewhat from previously reported E phases shown by ionic liquid crystals[19,22,23] because of the fact that the phenanthrolinium moieties are dipositive rather than having a single charge (like pyridinium or pyrrolidinium cations). A consideration of the dimensions of the rectangular lattice unit cell and a glance at Figure 4b (which is drawn to scale) show that the 1,10-phenanthrolinium cations are not free to rotate around the axis normal to the smectic layer planes.

A structural model for the SmA phases of DOSS salts **1c**, **2c**, and **3c** is proposed in Figure 5. The molecules segregate into ionic and aliphatic sublayers but without additional ordering or correlations within the ionic bilayers. In contrast to the dodecyl sulfate anions, the dioctyl sulfosuccinate anions each contain two branched alkyl chains. This explains the much higher A_M values that were found for the DOSS salts ($A_M \approx 162-171$ Å^2) in

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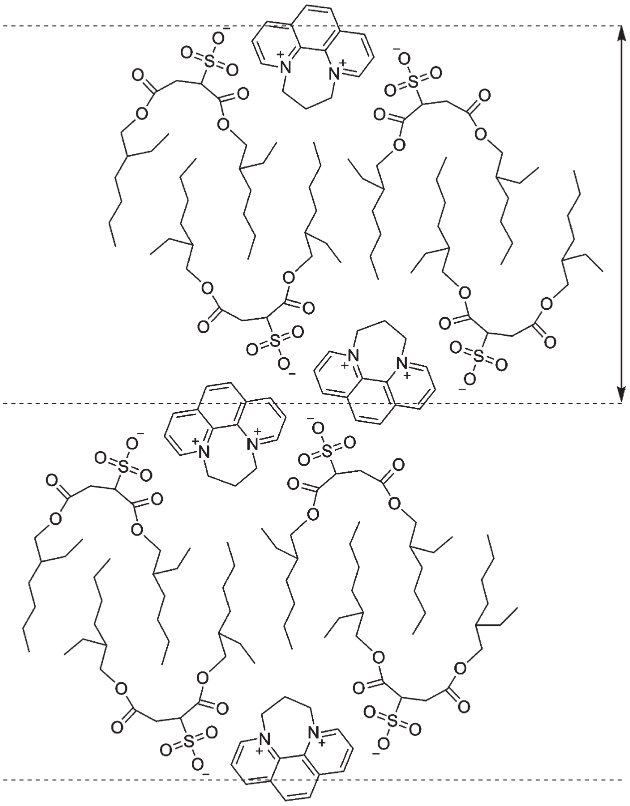

Figure 5. Structural model (idealized) for the smectic A phase exhibited by compound **1c**. The smectic layer thickness is indicated by d (at 100 °C, d = 23.09 Å and $A_M \approx 162$ Å^2 (Table 2)).

comparison to those for the DOS salts. The larger cross-sectional area occupied by the branched DOSS anions in comparison to the DOS anions does not allow strict 2D intralayer ordering as in the case of an E phase.

Many unsuccessful attempts have been made to obtain single crystals suitable for structure determination by X-ray diffraction. Nevertheless, the literature data on single crystals of 1,10-phenanthrolinium compounds show that a propylene bridge connecting the two nitrogen atoms causes a much larger deformation of the 1,10-phenanthroline ring system from a planar structure than an ethylene bridge.[24-26]

Because of the ability of 1,10-phenanthroline to form complexes with transition-metal ions, photophysical studies concerning 1,10-phenanthroline have mainly focused on these complexes. However, 1,10-phenanthroline itself is fluorescent. The photophysical properties of 1,10-phenanthroline were first studied by Badger and Walker.[27] The fluorescence spectra of the 1,10-phenanthrolinium salts were recorded in the solid state and as a solution in methanol (concentration, 10^{-5} mol L^{-1}), all at room temperature. The absorption and fluorescence spectra of the methanolic solutions are given in the Supporting Information. In Table 3, a summary of the spectroscopic properties can be found. The absorption spectra of the 1,10-phenanthrolinium DOS and DOSS salts show three main bands due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. Whereas the absorption spectrum of 1,10-phenanthroline displays two absorption bands centered at 229 and 264 nm, quaternization of the nitrogen atoms induces a significant bathochromic shift and an additional absorption band appears in the visible region between 440 and 460 nm.[2,27,28] For the 1,10-phenanthrolinium salts studied, neither the nature of the anion nor the length of the bridging alkyl chain between the nitrogen atoms has a pronounced influence on the position of the absorption bands. Substitution of the 1,10-phenanthroline group at the 5-position by an electron-donating methyl group, when going from compound **1b** to **2b** and from **1c** to **2c**, resulted in the expected small bathochromic shifts of the absorption bands. A stronger effect is observed upon phenyl substitution, as derived from the shifts of 11 and 17 nm for pairs of compounds **1b**−**4b** and **1c**−**4c**. For all the 1,10-phenanthrolinium salts dissolved in methanol, excitation at 308−320 nm resulted in broad-band green fluorescence whereas excitation in the absorption band at about 450 nm did not give any detectable fluorescence signal. Again, a significant red shift of the emission bands can be mentioned in comparison with those of 1,10-phenanthroline, which displays broad-band fluorescence centered at 355 nm. Substitution at the 5-position of 1,10-phenanthroline with a methyl and at the 4- and 7-positions with phenyl groups led to a bathochromic shift of the emission band, whereas shortening of the alkyl bridge between nitrogen atoms when going from **1** to **5** resulted in the appearance of the second band at 642 nm and a hypsochromic shift of the first band to 532−540 nm. This latter is in line with a smaller deviation from planarity of the 1,10-phenanthroline ring system with an ethylene bridge than with a propylene bridge and such a deviation causes a blue shift. As in the case of the absorption spectra, the nature of the anion has a negligible effect on the fluorescence spectra and on the quantum yields for compounds **1**, **2**, and **5**; however, the results for compound **4** were unexpected. 1,10-Phenanthrolinium DOSS salt

Table 3. Main Absorption and Emission Bands, Stokes Shifts and Quantum Yields of 1,10-Phenanthrolinium DOS and DOSS Salts in Methanol Solution (c = 10^{-5} M)[a]

compound	λ_{abs}/nm	ε/M^{-1} cm^{-1}	λ_{em}/nm	Q/%	Stokes shift/cm$^{-1\,b}$
1b	216	28 690			
	305	31 960			
	447	1662	546	0.21	4056
2b	219	29 660			
	309	31 570			
	453	1536	550	0.14	3893
4b	227 sh	22 390			
	321	24 080			
	460	1758	552 sh, 646, 702	0.08	3623
5b	217	28 970			
	306	30 900			
	452	1320	540, 642	0.02	3605
1c	216	33 540			
	305	34 601			
	448	1899	544	0.20	3939
2c	219	38 240			
	309	37 270			
	446	2218	548	0.11	4173
4c	227 sh	27 170			
	322	30 090			
	460	2183	556	0.35	3754
5c	217	35 660			
	306	36 720			
	452	1613	532, 642	0.02	3327

[a] The excitation wavelength was set at 308 nm for compounds **1b**, **1c**, **2b**, **2c**, **5b**, and **5c** and at 320 nm for compounds **4b** and **4c**. [b] Calculated to be $10^7 \times \{(1/\lambda_{abs}) - (1/\lambda_{em})\}$. Abbreviation: sh, shoulder.

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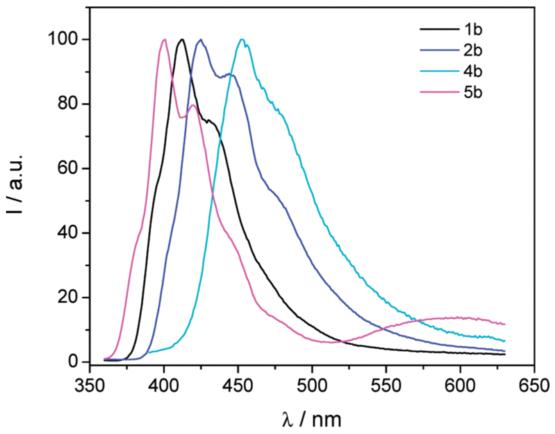

Figure 6. Normalized fluorescence spectra of the dodecyl sulfate (DOS) salts in the solid state at room temperature. The excitation wavelengths for the different spectra are **1b**, 340 nm; **2b**, 330 nm; **4b**, 350 nm; and **5b**, 330 nm.

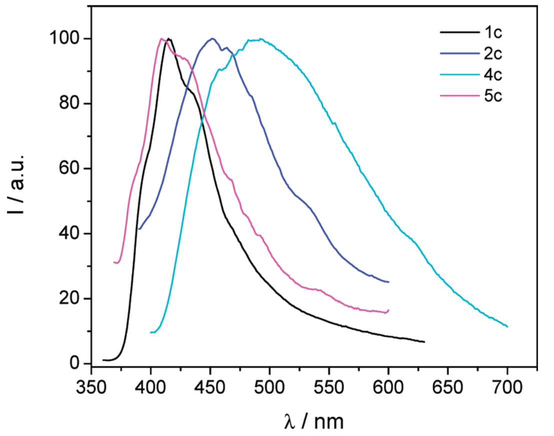

Figure 7. Normalized fluorescence spectra of the dioctyl sulfosuccinate (DOSS) salts in the solid state at room temperature. The excitation wavelengths for the different spectra are **1c**, 340 nm; **2c**, 360 nm; **4c**, 360 nm; and **5c**, 360 nm.

4c displays the largest quantum yield among the compounds, 0.35%; however, the quantum yield of **4b** is only 0.08%, and the two bands at 646 and 702 nm become dominating in the fluorescence spectrum. If the quantum yields of other compounds are considered, it can be observed that methyl substitution leads to a lowering of the quantum yields by a factor of 1.5 to 1.8. A decrease in the length of the alkyl bridge between the nitrogen atoms has a detrimental effect on the fluorescence properties, resulting in a decrease in the quantum yield by a factor of 10 when the propylene bridge is replaced by an ethylene bridge. It should be noticed that the quantum yields of all 1,10-phenanthrolinium salts are quite low. It is known that the quantum yield of 1,10-phenanthroline is rather low because of nonemissive relaxation from the $n-\pi^*$ excited singlet states, which are close to the $\pi-\pi^*$ excited singlet states.[27]

The fluorescence spectra of the DOS salts in the solid state are shown in Figure 6, and those of the DOSS salts are shown in Figure 7. The compounds fluoresce in the violet or blue region. A visual observation of the samples makes it clear that the fluorescence intensity of the compounds in the solid state is appreciably greater than in methanol solution, although the intensity is still not very high. However, no reliable quantum yields could be measured on the thin solid films of these compounds. The spectra are red-shifted when the aromatic system becomes less planar. As mentioned above, a propylene bridge causes a stronger deformation of the aromatic system from planarity than an ethylene bridge, so the compounds with the propylene bridge fluoresce at a longer wavelength than those with an ethylene bridge. The most intense luminescence is observed for 4,7-diphenyl-1,10-phenanthrolinium (bathophenanthrolinium) salts **4b** and **4c**. These salts show a whitish blue emission with emission maxima at 453 nm for **4b** and at 492 nm for **4c**. Because of the broadness of the emission band, the fluorescence color is bluish white.

Compared to most other ionic liquid crystals, the molecular structure of the 1,10-phenanthrolinium salts is unusual. A general approach toward ionic liquid crystals is to extend the length of the alkyl chains linked to the cation of an ionic liquid. For instance, the well-studied 1-alkyl-3-methylimidazolium salts become liquid-crystalline when the alkyl chain contains about 12 carbon atoms, depending on the counterion.[29−32] The same strategy has been successfully used to obtain liquid-crystalline analogues of quaternary ammonium,[33] phosphonium,[34,35] pyridinium,[36] pyrrolidinium,[17,37] piperidinium,[23] and morpholinium[23] ionic liquids. Typically, these ionic liquid crystals have monocationic cores but ionic liquid crystals with dicationic cores, e.g. piperazinium[23] and 4,4′-bipyridinium compounds,[38,39] have also been described. Provided that an anion with a long alkyl chain is used, it is possible to obtain liquid crystallinity for a compound with a short alkyl chain on the cation. For instance, 1,3-dimethylimidazolium dodecyl sulfonate exhibits a smectic A phase.[40] The 1,10-phenanthrolinium salts are conceptually related to the latter class of ionic liquid crystals because in our compounds no long chains are linked to the cation. It should be mentioned that the dodecyl sulfate salts of imidazolium, pyridinium and ammonium cations with short chains are true ionic liquids.[41] One could assume that the relatively high melting points of the 1,10-phenanthrolinium ionic liquid crystals are due to the dicationic character of the compounds and to the resulting high lattice energies. However, one should realize that the dipositive charge is delocalized so that the charge density is not very high. The relatively elevated transition temperatures are attributed to the strong $\pi-\pi$ interactions between the 1,10-phenanthroline rings. Also, other 1,10-phenanthroline-based liquid crystals have high transition temperatures.[5−7] The thermal behavior of 4,4′-bipyridinium compounds, which are also dicationic, shows that dipositive charges on extended cationic cores do not necessarily lead to high melting points.[38,39]

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It should be noted that no ionic liquids based on 1,10-phenanthroline have been reported so far. 1,10-Phenanthrolinium DOSS salts **1c**−**4c** can be considered to be genuine ionic liquids by the definition of ionic liquids being organic salts with a melting point below 100 °C. Although the melting points of the DOS salts are much higher than those of the DOSS salts, an interesting feature of the DOS salts is the presence of the highly ordered smectic E phase (E phase).[42] This phase has also been observed in the past for ionic liquid crystals, for instance, for pyrrolidinium,[17,22] piperidinium,[23] pyridinium,[43] and imidazolium salts.[44]

Conclusions

1,10-Phenanthrolinium, 5-methyl-1,10-phenanthrolinium, 5-chloro-1,10-phenanthrolinium, and 4,7-diphenyl-1,10-phenanthrolinium (bathophenanthrolinium) cations have been combined with dodecyl sulfate (DOS) or dioctyl sulfosuccinate (DOSS) anions to design a new class of ionic liquid crystals. Except for the compounds containing a 4,7-diphenyl-1,10-phenanthrolinium cation and DOS salt **5b**, all of the DOS and DOSS salts were found to be liquid-crystalline. The DOS salts showed a highly ordered smectic E phase, whereas the DOSS salts showed a disordered smectic A phase. Although the compounds exhibit a greenish or whitish fluorescence in the solid state and dissolve in methanol, the fluorescence intensities are weak at room temperature. The differences in the positions of the emission bands and quantum yields can be related to the nature of the substituents on the 1,10-phenanthroline ring and to the planarity of the heterocyclic ring system. Given the high temperatures at which most mesophases occur, no measurable fluorescence is expected for the compounds in the mesophase.

The combination of an organic cation (with or without alkyl chains) with a dialkyl sulfosuccinate anion is proposed as a facile general approach toward ionic liquid crystals. We realize that the quaternization of the nitrogen atoms in 1,10-phenanthroline, as demonstrated in this article, is not the only method for the easy functionalization of 1,10-phenanthroline and other nitrogen-containing molecules. For instance, noncovalent interactions such as H-bond formation between a nitrogen atom and the proton of a carboxylic acid and halogen bonding are alternative methods of functionalization.[45−52] This could lead to other types of 1,10-phenanthroline-derived liquid crystals.

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Supporting Information Available: Synthesis procedures and characterization of all of the compounds. Absorption and fluorescence spectra of the compounds dissolved in methanol. X-ray diffractogram of the smectic E phase. DSC traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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