



Sulfur makes the difference: synthesis and mesomorphic properties of novel thioether-functionalized imidazolium ionic liquid crystals



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ABSTRACT

Novel thioether-linked imidazolium ionic liquid crystals were synthesized starting from methyl 2-mercaptoacetate. The mesomorphic properties were determined by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction. All mesogens displayed smectic A mesophase geometries with strongly interdigitated bilayer structures. Comparison of the thioether-linked imidazolium salts with the corresponding amine- and amide-linked imidazolium salts as well as simple *N*-alkyl-imidazolium salts showed that both mesophase width and stability increased with increasing softness of the linking unit, thus indicating the beneficial effect of sulfur. Additionally, an increase of the length of the linking unit decreased the interdigitation of the alkyl chains.

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1. Introduction

The introduction of sulfur atoms into organic structures generates a plethora of opportunities regarding molecular electronics applications. Archetypal examples for such sulfur compounds are thiophenes¹ and tetrathiafulvalenes.² The incorporation of such moieties in thermotropic liquid crystals is also well known.^{3,4} For example, because of the soft character of the sulfur atom due to the more delocalized *d*-orbitals, discotic hexathioalkyltriphenylenes show a decreased electronic band-gap and charge carrier mobilities, which are up to three orders of magnitude larger than those for the corresponding hexaalkoxytriphenylenes.^{5,6} The combination of properties of liquid crystals with those of ionic liquids creates the special features of ionic liquid crystals as anisotropically-ordered liquid electrolytes.⁷ Very recently, this novel class of materials has been successfully applied as anisotropic lithium ion conductors,⁸ as electrolytes in solid-state dye-sensitized solar cells (DSSCs)⁹ and in particular, iodine-free DSSCs.¹⁰ Among the various cationic head-groups employed for ionic liquid crystals, imidazolium salts are the most widely used class of compounds.^{7d,11} Although some thiophene-based ILCs are known in the literature,¹² the issue of sulfur-containing ILCs is much less explored as compared to classical thermotropic liquid crystals. Based on our recent work on glycine-derived imidazolium ILCs,¹³ we noticed that the incorporation of an amine or amide moiety in the side chain influenced mesophase widths significantly as compared to the corresponding *N*-methyl-*N*-alkylimidazolium salts. Thus, we wondered how the replacement of a hard amine by a soft sulfur would affect the mesomorphic properties of ILCs. The results are discussed below.

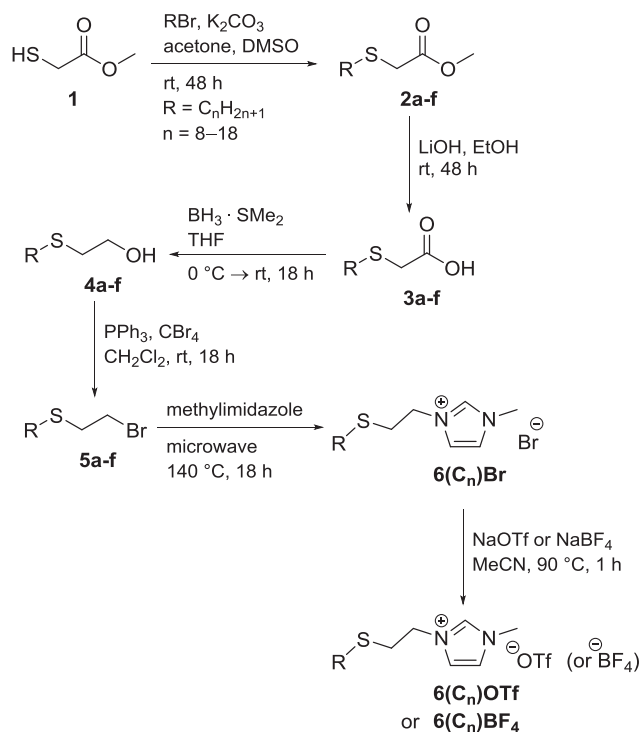
2. Results and discussion

The synthesis of thioether-containing ILCs **6(C_n)X** commenced with the *S*-alkylation of methyl 2-mercaptoacetate **1** in the presence of K₂CO₃ according to the procedure by Townsend (Scheme 1).¹⁴ Subsequent saponification of the methylester **2** with LiOH in EtOH provided the free carboxylic acid **3**, which was reduced with borane dimethylsulfide to the corresponding alcohol **4**. Compound **4** was submitted to Appel reaction following the procedure by Kukovinets¹⁵ and the resulting bromide **5** was subsequently reacted with *N*-methylimidazole under microwave conditions to give the desired imidazolium bromide **6(C_n)Br**. A final salt metathesis step yielded the ILCs **6(C_n)X** with different anions.

Mesomorphic properties of thioether-imidazolium ILCs **6(C_n)X** were initially studied by differential scanning calorimetry (DSC). The results in Table 1 and Fig. 1 clearly reveal the strong dependence of the mesophase stability on the chain lengths and on the hard/soft character of the counterions. While imidazolium bromide **6(C₈)Br** showed no crystallisation point or glass transition in the cooling cycles, a liquid crystalline phase was observed between 22 °C and 51 °C during the heating cycles (Fig. 1a). The corresponding homologous imidazolium bromide **6(C₁₀)Br** displayed enantiotropic mesomorphism between 35 °C and 148 °C in the heating cycle and a significant hysteresis possibly due to supercooling (Fig. 1b). However, for compounds **6(C_n)Br** with *n*=12, 14, 16 and 18 the clearing points were shifted to around 200 °C and isotropization was accompanied by decomposition (Table 1 entries 3–6) (Fig. 1c).

Further evidence for the thermal instability of the bromides was verified using thermogravimetric analysis (TGA) (see Supplementary data, Fig. S1). In prior work we were able to improve the thermal stability by replacing bromide by triflate counterions.^{13,16}

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compound	yields [%]							
n	2-5	2	3	4	5	6(C _n)Br	6(C _n)OTf	6(C _n)BF ₄
8	a	96	83	80	46	56	57	-
10	b	86	83	83	30	56	91	-
12	c	92	87	96	61	59	98	-
14	d	91	quant.	95	47	62	61	-
16	e	76	92	62	45	67	87	-
18	f	quant.	95	quant.	71	91	87	87

Scheme 1. Synthesis of thioether-imidazolium ILs **6(C_n)X**.

Table 1
Phase transition temperatures [°C] and enthalpies [kJ mol⁻¹] of thioether-imidazolium ILs **6(C_n)X** (X=Br, OTf, BF₄)^{a,b}

Entry	n	X	Phase transition		Phase	Enthalpy [kJ mol ⁻¹]	Heating cycle
(1)	8	Br	Cr	22 (24.0)	SmA	51 (0.2)	I
(2)	10	Br	Cr	35 (30.2)	SmA	148 (0.7)	I
(3)	12	Br	Cr	46	SmA	~200	I (dec)
(4)	14	Br	Cr	55	SmA	~200	I (dec)
(5)	16	Br	Cr	62	SmA	~200	I (dec)
(6)	18	Br	Cr	41	SmA	~200	I (dec)
(7)	8	OTf	Liquid				Second heat
(8)	10	OTf	Cr	4 (17.3)	I		Second heat
(9)	12	OTf	Cr	6 (11.4)	SmA	36 (0.3)	I
(10)	14	OTf	Cr	28 (16.6)	SmA	71 (0.8)	I
(11)	16	OTf	Cr	43 (22.4)	SmA	124 (0.7)	I
(12)	18	OTf	Cr	54 (24.9)	SmA	149 (0.7)	I
(13)	18	BF ₄	Cr	64 (27.9)	SmA	~200	I (dec)

^a Phase transitions were determined by DSC upon second heating. Heating/cooling rate 10 K min⁻¹.

^b The following phases were observed: crystalline (Cr), smectic A (SmA), isotropic (I).

^c In case of entries (3)–(6), (13) exothermic decomposition was observed during isotropization. Therefore, melting points were determined by polarizing optical microscopy (POM).

As shown in **Table 1**, this strategy was successful for the derivatives with the chain lengths C₁₂–C₁₈. Whereas imidazolium triflates **6(C₈)OTf** and **6(C₁₀)OTf** displayed only isotropic melting (entries 7, 8), all other derivatives **6(C_n)OTf** where n=12–18 showed enantiotropic mesomorphism with almost no hysteresis (entries 9–12) (**Fig. 1d**). The TGA experiments further revealed that the clearing

point, which is hardly visible in the DSC curve, was significantly shifted below the decomposition temperature. Replacement of the triflate counterion by tetrafluoroborate for the C₁₈ derivative **6(C₁₈)BF₄** showed again a pronounced tendency for decomposition during the clearing process (entry 13).

Investigations by polarizing optical microscopy (POM) yielded homeotropic textures typical for SmA phases. Characteristic examples of the obtained POM textures are shown in **Fig. 2**.

Upon comparison with the simple *N*-alkyl-*N*-methyl-imidazolium salts **7(C_n)X**¹⁷ and previously-prepared amine and amide derivatives **8(C_n)X** and **9(C_{n-1})X**, respectively (**Scheme 2**, **Fig. 3**), it is clearly visible that sulfur does indeed have a beneficial effect on both the mesophase width and stability as long as triflates are concerned. Thus clearing points are increased while melting points are in the range from ambient temperature up to 55 °C. Furthermore, the clearing points of the triflates are still far below their decomposition temperatures (see Supplementary data, **Fig. S1**).

Small- and wide-angle X-ray diffraction measurements (SAXS and WAXS, respectively) confirmed the proposed SmA phase geometry. A representative WAXS pattern of **6(C₁₈)OTf** is shown in **Fig. 4** with a strong fundamental diffraction peak (001) in the small-angle region and a diffuse halo in the wide-angle region from the molten alkyl chains.

Layer spacings *d*₀₀₁ were obtained at different temperatures using a Gaussian distribution on the corresponding diffraction signal (001). All thioether-linked triflates **6(C_n)OTf** showed, as seen with the previous published amines and amides,¹³ a linear temperature-dependency of the layer spacing (**Fig. 5**), whereby the layer spacing decreased with increasing temperature. These values indicate a bilayer structure of the molecules with strongly interdigitated alkyl chains and *d*₀₀₁ values of *L*_{calcd} < *d*₀₀₁ < 2*L*_{calcd}, where *L*_{calcd} is the length of the fully extended molecule with an all-*trans* configuration of the alkyl moiety. Layer spacings *d*_{red} at a reduced temperature (*d*₀₀₁ at 0.95 *T*_{iso})¹⁹ were determined for better comparison of the imidazolium salts bearing different groups (**Table 2**). For example, the calculated molecular length of **6(C₁₆)OTf** is 2770 pm,¹⁸ whereas *d*_{red} is 3498 pm. This concludes that the mesogens are organized in a bilayer structure (**Fig. 6**). The calculated layer spacing *d*_{calcd} is 3480 pm¹⁸ (fully interdigitated alkyl chains of the cations 2060 pm plus two times the methyl-imidazolium core with 710 pm each), which is close to the *d*_{red} value of 3480 pm (**Table 2**). Overall, the layer spacings *d*₀₀₁ increase with increasing alkyl chain length.

A comparison of the smectic layer distances *d*_{red} of thioethers **6(C_n)OTf** with the distances for amines **8(C_n)OTf** and amides **9(C_{n-1})OTf**, respectively, showed that the interdigitation of thioethers **6(C_n)X** lies in between smaller *d*_{red} values for amines **8(C_n)X** and larger *d*_{red} values for amides **9(C_{n-1})X** (**Fig. 5**).

3. Conclusion

We have presented the synthesis of novel imidazolium ionic liquid crystals bearing a thioether unit. Simple reaction conditions were used with good to quantitative yields throughout. The sulfur-linked bromides displayed decreased mesophase ranges compared to the corresponding alkylated species. After an anion exchange from Br to OTf the thioether compounds showed the widest mesophases compared to previously described amines and amides. The following trend was observed: The softer the anion, the wider was the mesophase range. All mesogens displayed smectic A mesophase geometries and with increasing alkyl chain lengths an increase of the mesophase width was observed.

XRD experiments showed an almost linear dependency of the layer spacings *d*₀₀₁ with increasing temperature and a bilayer alignment of the mesogens. A maximum degree of interdigitation up to the heteroatom group is assumed for the analyzed thioethers.

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