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Mesophase stabilization in ionic liquid crystals through pairing equally shaped mesogenic cations and anions

Kathrin Stappert[a], Gregor Lipinski[a], Gabriel Kopiec[a,b,c], Eike T. Spielberg[a,d], Anja-Verena Mudring[a,b,c]*

[a] former affiliation: Anorganische Chemie III – Materials Engineering and Characterization, Fakultät für Chemie and Biochemie,

Ruhr-Universität Bochum, 44780, Bochum, Germany. E-mail: anja.mudring@ruhr-uni-bochum.de; Tel: +49-234-32-27408

[b]Critical Materials Institute, Ames Laboratory, 333 Spedding Hall, Ames, IA, 50011

[c]Department of Materials Science and Engineering, Iowa State University, 2220 Hoover Hall, Ames, IA, 50011, mudring@iastate.edu, Tel:+1 515 5095616

[d]Universitätsbibliothek, Universität Duisburg Essen, Universitätsstr. 9, 45141 Essen, Germany

Abstract

The synthesis and properties of a set of novel ionic liquid crystals with congruently shaped cations and anions is reported to check whether pairing mesogenic cations with mesogenic anions leads to a stabilization of a liquid crystalline phase. To that avail 1-alkyl-3-methyl-triazolium cations with an alkyl chain length of 10, 12 and 14 carbon atoms have been combined with p-alkyloxy-benzenesulfonate anions with different alkyl chain lengths (n = 10, 12, and 14). The corresponding triazolium iodides have been synthesized as reference compounds where the cation and anion have strong size and shape mismatch. The mesomorphic behavior of all compounds is studied by DSC (differential scanning calorimetry) and POM (polarizing optical microscopy). All compounds except 1-methyl-3-decyltriazolium iodide, which qualifies as an ionic liquid, are thermotropic ionic liquid crystals. All other compounds adopt smectic A phases. A comparison of the thermal phase behavior of the 1-methyl-3-decyltriazolium bromides to the corresponding p-alkoxy-benzensulfonates reveals that definitely the mesophase is stabilized by pairing the rod-shaped 1-alkyl-3-methyltriazolium cation with a rod-like anion of similar size.

Keywords. Ionic Liquids. Liquid Crystals. Ionic Liquid Crystals.

1. Introduction

Ionic liquids (ILs), salts with a melting point below 100 °C, offer unique chemical and physical properties and property combinations.[1] Properties such as negligible vapour pressure, wide liquid range, good thermal stability, considerable electric conductivity, and large electrochemical window are advantageous for a number of applications.[2] In ionic liquid crystals (ILCs) the properties of ILs (such as mobility) can be combined with those of liquid crystals (LC). It is thereby possible to endow a useful IL property such as ionic conductivity with anisotropy. Whilst lyotropic ionic liquid crystals rely on admixture of a second component, most commonly a classical molecular solvent[3] to adopt mesophases, in thermotropic liquid it is temperature that triggers mesophase formation and in a certain temperature range a liquid crystal is formed.

The thermal behavior of ionic liquid crystals is influenced by the shape of the cation as well as by the shape of the anion as well as by subtle ion-ion interactions. Generally the thermotropic mesomorphic behavior has been introduced by a rod-shaped cation as the mesogenic unit. In that respect, the most investigated cation type is the imidazolium cation. Mesomorphic behavior has been reported for 1-alkyl-3-methylimidazolium salts bearing long alkyl chains[4,5] and rod-shaped bicationic imidazolium salts.[6,7,8] Correlating the melting and clearing point with the alkylchain length of the cation has been the focus of numerous studies.[9,10,11] Similar studies, albeit less systematically and comprehensively, have been carried out for several other types of cations, like pyrrolidinium[12,13], piperidinium[14], piperazinium[14], morpholinium[14] and triazolium[15].

As counter anions spherical anions such as simple halides, as well as other high symmetry anions like tetrafluoroborate, hexafluorophopsphate or perchlorate were chosen[16,17,18]. Only few attempts have been made to synthesize ILCs with low symmetry ions, possibly because combinations of organic cations with the bis(trifluoromethanesulfonyl)amide anion - a weakly coordinating, non-spherical anion commonly used in ionic liquids - did not lead to the desired formation of mesophases. For that reason, it is believed that comparatively large and low symmetry anions rather prevent the alkyl chains of the cations to interact with each other which is a prerequisite for mesophase formation. Only recently the mesophase formation of a bis(trifluoromethanesulfonyl)amide could be confirmed[19]. It was also observed that the anion shape can substantially impact the cation conformation and the mesomorphic behavior of the salt. This has been shown for long-chain dialkyl-imidazolium[16] and dialkyl-triazolium[15] cations. The simple iodides feature the cation in an U-shaped conformation. However, for the triiodide a linear cation conformation is found. It appears that the rod-shape of the triiodide anion forces the dialkyl-cation into a linear conformation. This results in a much lower interdigitation, hence, interaction of the alkyl-chains on the cation and ultimately prevents the formation of a mesophase [15].

Beside these inorganic anions, organic anions could well be used as counter anions and potentially open up new avenues for stabilizing a mesophase. Sulfonate anions, as commonly encountered in soaps featuring typically the sodium salt[20], are well known to give lyotropic phases. The formation of thermotropic mesophases of alkylsulfonate or alkylbenzenesulfonate was observed for different organic cations[21,22,23] and rod-shaped sulfonates like 1-3-dialkylimidazolium cations are mesogenic units. It was proposed that congruently rod-shaped anions and cations would lead to mesophase stabilization due to a more efficient packing of the ions. The viability of the concept was demonstrated for guanidinium sulfonates.[24] Since both 1-alkyl-3-methyltriazolium cations and p-alkyloxy-benzenesulfonate anions with long chains are mesogenic units, the question arises, whether their combination would lead to an improvement of the ILC properties, i.e. enhance the mesophase window and lower the melting point. To this avail, a new series of salts with 1-alkyl-3-methyl-triazolium cations and p-alkyloxy-benzenesulfonate anions with alkyl groups of different lengths were synthesized (Figure 1) and their thermal behavior studied. To unravel the effect of rod-shaped, mesogenic anions the corresponding triazolium iodides where studied as well. A list of the investigated compounds is given in Table 1.

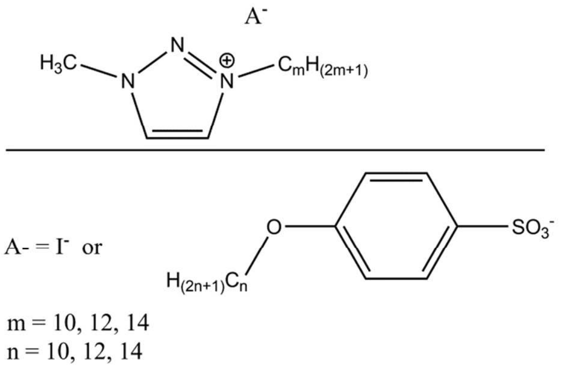


Figure 1. Structures of cations and anions which were investigated.

Table 1. Investigated compounds and compound numbering scheme.

	C_{10}I	**C_{12}I**	**C_{14}I**	**$C_{10}A_{10}$**	**$C_{10}A_{12}$**	**$C_{10}A_{14}$**	**$C_{12}A_{10}$**	**$C_{12}A_{12}$**	**$C_{12}A_{14}$**	**$C_{14}A_{10}$**	**$C_{14}A_{12}$**	**$C_{14}A_{14}$**
m	10	12	14	10	10	10	12	12	12	14	14	14
Anion	I^-	I^-	I^-	n= 10	n= 12	n= 14	n= 10	n= 12	n= 14	n= 10	n= 12	n= 14

2. Experimental Section

Synthesis

The alkyl azides were synthesized according to a common literature method[25]. All other starting materials and solvents were purchased from standard commercial sources and were used without further purification. No protective atmosphere was used during synthesis.

General procedure for the preparation of 1-alkyl-1,2,3-triazole (1a – 3a)

5g Alkyl azide (23.7 mmol) and 10 ml vinyl acetate were irradiated with microwaves (CEM Discover) in a closed glass tube for 5 hours at 120 °C. After addition of 200 ml n-hexane, the suspension was filtered and the solution cooled to -40 °C for 24 hours. The precipitated product was filtered off and dried overnight in vacuum at room temperature.

1-Decyl-1,2,3-triazole (4a).

Yield: 70 %, ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.69 (s, 1H), 7.52 (s, 1H), 4.37 (t, *J* = 7.2 Hz, 2H), 2.00 – 1.78 (m, 2H), 1.25 (s, 14H), 0.87 (t, *J* = 6.3 Hz, 3H).

1-Dodecyl-1,2,3-triazole (4b).

Yield: 71 %, ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.69 (s, 1H), 7.52 (s, 1H), 4.38 (t, *J* = 7.2 Hz, 2H), 1.92 (dd, *J* = 12.4, 5.7 Hz, 2H), 1.25 (s, 18H), 0.88 (t, *J* = 6.3 Hz, 4H).

1-Tetradecyl-1,2,3-triazole (4c).

Yield: 75 %, ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.52 (s, 1H), 4.38 (t, *J* = 7.2 Hz, 2H), 1.99 – 1.83 (m, 2H), 1.25 (s, 22H), 0.88 (t, *J* = 6.4 Hz, 3H).

1-Alkyl-3-methyl-1,2,3-triazolium iodides (C_mI)

A solution of the 1-alkyl-1,2,3-triazole (**4a – c**) and two equivalents of methyl iodide was heated under reflux in acetonitrile for three days. After cooling to room temperature the solution was poured into cold ethyl acetate and kept at -40 °C for 5 hours. The white precipitate was filtered off and dried under vacuum at room temperature to give the products in good yields and purity (80 – 85 %).

1-Decyl-3-methyl-1,2,3-triazolium iodide (C_{10}I)

Yield: 85 %, ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.48 (d, *J* = 1.1 Hz, 1H), 9.38 (d, *J* = 1.2 Hz, 1H), 4.74 (t, *J* = 7.4 Hz, 2H), 4.52 (s, 3H), 2.03 (dd, *J* = 8.2, 6.1 Hz, 2H), 1.36 – 1.19 (m, 14H), 0.85 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 132.51, 131.52, 54.53, 41.19, 31.91, 29.92 – 28.73, 26.20, 22.74, 14.20. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3124, 3072, 3039, 2953, 2918, 2847, 1528, 1463, 1353, 1309, 1195, 1129, 1088, 814, 723, 427. MS (FAB): *m/z* = 224 (100%, C_{10}^+), 84 (12 %, C_{10}^+ - $C_{10}H_{21}$), 350 (10 %, C_{10}^+ - CH_3 + $C_{10}H_{21}$). Elemental analysis: calcd % for $C_{13}H_{26}IN_3$ (M = 351,2 g/mol): C 44.45, H 7.46, N 11.96, found: C 44.6, H 7.63, N 11.97.

1-Decyl-3-methyl-1,2,3-triazolium iodide (C_{12}I)

Yield: 81 %, ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.50 (d, *J* = 1.3 Hz, 1H), 9.34 (d, *J* = 1.4 Hz, 1H), 4.80 – 4.66 (m, 2H), 4.53 (s, 3H), 2.12 – 1.99 (m, 2H), 1.25 (s, 18H), 0.88 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 132.55, 131.55, 54.56, 41.20, 31.98, 29.58, 28.94 (s), 26.22 (s), 22.76, 14.19. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3124, 3073, 2953, 2916, 1528, 1462, 1353, 1311, 1205, 1193, 1129, 1088, 814, 723. MS (FAB^+): *m/z* = 84 (11 %, K^+-$C_{12}H_{24}$), 252 (100 %, K^+), 631 (6 %, 2*K^+ + I^-). Elemental analysis (%) calcd for ($C_{15}H_{30}N_3I$): C 47.5, H 7.97, N 11.08; found: C 47.61, H 7.38, N 11.16.

1-Decyl-3-methyl-1,2,3-triazolium iodide (C_{14}I)

Yield: 80 %, ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.52 (s, 1H), 9.36 (d, *J* = 1.1 Hz, 1H), 4.73 (t, *J* = 7.4 Hz, 2H), 4.53 (s, 3H), 2.05 (dd, *J* = 9.1, 6.8 Hz, 2H), 1.29 (d, *J* = 17.8 Hz, 22H), 0.87 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 132.69, 131.55, 54.60, 41.11, 32.05, 29.57, 28.97, 26.26, 22.82, 14.26. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3125, 3073, 2916, 2846, 1528, 1463, 1202, 1188, 1129, 1088, 814, 723, 428. MS (FAB): *m/z* = 280 (100%, C_{12}^+), 84 (12 %, C_{12}^+ - $C_{12}H_{25}$), 462 (47 %, C_{12}^+ - CH_3 + $C_{12}H_{25}$). Elemental analysis: calcd % for $C_{13}H_{26}IN_3$ (M = 351,2 g/mol): C 50.12, H 8.44, N 10.31, found: C 50.92, H 8.53, N 10.07.

General procedure for the preparation of 4-(alkyloxy)benzene-1-sulfonyl chlorides (2a-c)

Sodium 4-hydroxybenzenesulfonate dihydrate (1.5 g, 6.45 mmol) and well powdered potassium hydroxide (1.1 g, 9.7 mmol) were stirred in dimethyl sulfoxide (150 mL) at room temperature until completely dissolved. The corresponding alkyl bromide (9.7 mmol) was added and the suspension was stirred at room temperature overnight. The mixture was then poured into water. The precipitating white solid was filtered off and dried under vacuum. The resulting alkyloxybenzene sulfonates were used without further purification. In a second reaction, dimethylformamide (5.5 ml, 71 mmol) was cooled to 0 °C and 5.9 ml (64.5 mmol) phosphoryl chloride was added dropwise and the solution stirred for further 10 minutes. Alkyloxybenzene sulfonate (**1a-c**), dissolved in dichloromethane, was added and the mixture was allowed to reach room temperature. After stirring for another hour the suspension was poured over ice and extracted with dichloromethane. The combined organic phases were dried over sodium sulfate, filtered and the solvent was removed under reduced pressure.

4-(Decyloxy)benzene-1-sulfonylchloride (2a)

Yield: 87 %, ^{1}H NMR (200 MHz, CDCl3) δ: 7.98 – 7.78 (m, 2H), 7.11 – 6.85 (m, 2H), 4.04 (t, *J* = 6.5 Hz, 2H), 1.94 – 1.60 (m, 2H), 1.58 – 1.05 (m, 14H), 0.86 (t, *J* = 6.4 Hz, 3H).

4-(Dodecyloxy)benzene-1-sulfonyl chloride (2b)

Yield: 88 %, ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.96 (d, J = 9.1 Hz, 2H), 7.02 (d, J = 9.1 Hz, 2H), 4.06 (t, J = 6.5 Hz, 2H), 1.89-1.75 (m, 2H), 1.49-1.14 (m, 18H), 0.88 (t, J = 6.4 Hz, 3H).

4-(Tetradecyloxy)benzene-1-sulfonyl chloride (2c)

Yield: 89 %, **^{1}H NMR** (200 MHz, CDCl3) δ 7.96 – 7.70 (m, 2H), 7.07 – 6.79 (m, 2H), 3.94 (dt, J = 35.0, 11.9 Hz, 2H), 1.82 – 1.71 (m, 2H), 1.20 (s, 22H), 0.80 (d, J = 6.9 Hz, 3H)

General procedure for the synthesis of methyl 4-(alkyloxy)benzenesulfonates 3a-c

Sodium hydride (0.16 g, 6,47 mmol) was dissolved in 10 ml dry methanol and added dropwise at 0 °C to a solution of the corresponding sulfonyl chloride (**2a-c**) (4.31 mmol) in dry methanol. The reaction mixture was stirred for further 15 minutes and then quenched with water (0.15 ml, 8.26 mmol). The solvent was removed in vacuum and the residue dissolved in dichloromethane, dried over sodium sulfate and filtered. The dichloromethane was evaporated and the residue dried under vacuum to give the a white product.

Methyl 4-(decyloxy)benzenesulfonate (3a)

Yield: 72 %, ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.89 – 7.63 (m, 2H), 7.07 – 6.82 (m, 2H), 4.11 – 3.91 (m, 2H,), 3.71 (s, 3H), 1.89 – 1.58 (m, 2H), 1.53 – 1.00 (m, 14H), 0.87 (t, J = 6.4 Hz, 3H).

Methyl 4-(dodecyloxy)benzenesulfonate (3b)

Yield: 70 %, ^{1}H-NMR (200 MHz, $CDCl_3$): δ= 7.82 (d, J = 8.9 Hz, 2H), 6.99 (d, J = 8.9 Hz, 2H), 4.02 (t, J = 6.6 Hz, 2H), 3.72 (s, 3H), 1.88-1.74 (m, 2H), 1.48-1.19 (m, 18H), 0.87 (s, 3H).

Methyl 4-(tetradecyloxy)benzenesulfonate (3c)

Yield: 66 % ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.91 – 7.73 (m, 2H), 7.03 – 6.94 (m, 2H), 4.02 (t, J = 6.5 Hz, 2H), 3.72 (s, 3H), 1.79 (d, J = 8.3 Hz, 2H), 1.26 (s, 22H), 0.86 (d, J = 4.9 Hz, 3H).

General procedure for the preparation of 1- alkyl-3-methyl-triazolium 4-alkoxybenzenesulfonates (C_mA_n)

A solution of the 1-alkyl-1,2,3-triazole (**4a-c**) and one equivalent of the respective methyl 4-(alkyloxy)benzenesulfonate was heated under reflux in acetonitrile for three days. After cooling to room temperature the solution was poured into cold ethyl acetate and kept at -40 °C for 16 hours. The white precipitate was filtered off and dried under vacuum at room temperature to give the products in good yield and purity (80 – 85 %).

1- Decyl-3-methyl-triazolium 4-decyloxybenzenesulfonate ($C_{10}A_{10}$)

Yield: 40 %, ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.40 (s, 1H), 9.24 (s, 1H), 7.81 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 4.59 (t, J = 7.4 Hz, 2H), 4.40 (s, 3H), 3.94 (t, J = 6.6 Hz, 2H), 1.93 (s, 2H), 1.74 (d, J = 6.8 Hz, 4H), 1.25 (d, J = 6.1 Hz, 26H), 0.87 (t, J = 6.4 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 160.08, 138.61, 136.90, 131.80, 127.50, 113.83, 68,15, 65.33, 40.20, 31.91, 29.45, 26.03, 22.69, 14.13. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2916s, 2851m, 1596w, 1493w, 1468m, 1245s, 1211s, 1193s, 1120s, 1103m, 1030s, 1003m, 833s, 819m, 799m, 719m, 697m, 609s, 564s, 551m. MS (pos. ESI, MeOH): *m/z* = 224 (26%, C_{10}^{+}), 761 (100%, $2*C_{10}^{+} + 1*A_{10}^{-}$), 1298 (72%, $3*C_{10}^{+} + 2*A_{10}^{-}$), 1836 (12%, $4*C_{10}^{+} + 3*A_{10}^{-}$). MS (neg. ESI, MeOH): *m/z* = 172 (8%, $A_{10}^{-} - C_{10}H_{21}$), 313 (100%, A_{10}^{-}), 850 (8%, $2*A_{10}^{-} + 1*C_{10}^{+}$), 1387 (9%, $3*A_{10}^{-} + 2*C_{10}^{+}$), 1925 (5%, $4*A_{10}^{-} + 3*C_{10}^{+}$). Elemental analysis: calcd % for $C_{29}H_{51}N_3O_4S$ (M = 537,8 g/mol): C 64.77, H 9.56, N 7.81, S 5.96, found: C 64.15, H 9.8, N 7.41, S 5.82. Water content: 1.49 %.

1- Decyl-3-methyl-triazolium 4-dodecyloxybenzenesulfonate ($C_{10}A_{12}$)

Yield: 45 %, ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.39 (s, 1H), 9.26 (s, 1H), 7.80 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 4.59 (t, *J* = 7.4 Hz, 2H), 4.39 (s, 3H), 3.94 (t, *J* = 6.6 Hz, 2H), 1.98 (d, 4H), 1.75 (dd, *J* = 14.1, 6.7 Hz, 2H), 1.25 (d, *J* = 5.7 Hz, 30H), 0.87 (t, *J* = 6.3 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 160.27, 138.43, 132.83, 131.92, 127.64, 113.96, 68.26, 54.05, 40.30, 32.02, 29.69, 26.14, 22.80, 14.25. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2915s, 2850m, 1597w, 1493w, 1468m, 1193s, 1120s, 1030s, 1003m, 832s, 719m, 698m, 605s, 564s. MS (pos. ESI, MeOH): *m/z* = 224 (27%, C_{10}^{+}), 789 (100%, $2*C_{10}^{+} + 1*A_{12}^{-}$), 1354 (30%, $3*C_{10}^{+} + 2*A_{12}^{-}$), 1920 (5%, $4*C_{10}^{+} + 3*A_{12}^{-}$). MS (neg. ESI, MeOH): *m/z* = 172 (5%, $A_{12}^{-} - C_{12}H_{25}$), 341 (100%, A_{12}^{-}), 906 (7%, $2*A_{12}^{-} + 1*C_{10}^{+}$), 1471 (5%, $3*A_{12}^{-} + 2*C_{10}^{+}$). Elemental analysis: calcd % for $C_{31}H_{55}N_3O_4S$ (M = 565,85 g/mol): C 65.8, H 9.8, N 7.43, S 5.67, found: C 65.41, H 10.01, N 7.09, S 5.32. Water content: 2.75 %.

1- Decyl-3-methyl-triazolium 4-tetradecyloxybenzenesulfonate ($C_{10}A_{14}$)

Yield: 53 %, ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.34 (s, 1H), 9.25 (s, 1H), 7.79 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.57 (t, *J* = 7.4 Hz, 2H), 4.45 – 4.28 (m, 3H), 3.93 (t, *J* = 6.6 Hz, 2H), 1.90 (s, 2H), 1.74 (dd, *J* = 14.1, 6.8 Hz, 2H), 1.24 (d, *J* = 5.6 Hz, 36H), 0.87 (t, *J* = 6.4 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 160.27, 138.39, 132.83, 131.91, 127.65, 113.95, 68.26, 54.04, 40.29, 32.05, 29.81, 26.15, 22.82, 14.26. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2915s, 2850m, 1597w, 1494w, 1469m, 1193s, 1121s, 1031s, 1003m, 832s, 719m, 697m, 609s, 564s. MS (pos. ESI, MeOH): *m/z* = 224 (100%, C_{10}^+), 406 (53%, $1^*C_{10}^+ - CH_3 + C_{14}H_{29}$), 817 (97%, $2^*C_{10}^+ + 1^*A_{14}^-$), 999 (17%, $2^*C_{10}^+ + 1^*A_{14}^- - CH_3 + C_{14}H_{29}$), 1410 (27%, $3^*C_{10}^+ + 2^*A_{14}^-$). MS (neg. ESI, MeOH): *m/z* = 172 (5%, $A_{14}^- - C_{14}H_{29}$), 369 (100%, A_{14}^-), 962 (6%, $2^*A_{14}^- + 1^*C_{10}^+$), 1555 (3%, $3^*A_{14}^- + 2^*C_{10}^+$). Elemental analysis: calcd % for $C_{33}H_{59}N_3O_4S$ (M = 593,9 g/mol): C 66.74, H 10.01, N 7.08, S 5.4, found: C 66.9, H 10.44, N 6.44, S 4.89. Water content: 1.05 %.

1- Dodecyl-3-methyl-triazolium 4-decyloxybenzenesulfonate ($C_{12}A_{10}$)

Yield: 74 %, ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.44 (s, 1H) 9.23 (s, 1H), 7.85 (d, J = 8.9 Hz, 2H), 6.87 (d, J = 8.9 Hz, 2H), 4.63 (t, J = 7.4 Hz, 2H), 4.44 (s, 3H), 3.98 (t, J = 6.6 Hz, 2H), 1.97 (s, 2H), 1.78 (d, J = 7.3 Hz, 2H), 1.64 (s, 4H), 1.28 (d, J = 4.9 Hz, 28H), 0.91 (t, J = 6.4 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 160.16, 138.87, 132.89, 131.94, 127.60, 113.95, 68.27, 54.08, 40.31, 32.04, 29.60, 28.99, 26.16, 22.82, 14.26. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2917s, 2849m, 1596w, 1468m, 1298w, 1186s, 1120s, 1030s, 1004m, 831m, 819m, 700m, 605s, 562s. MS (pos. ESI, MeOH): *m/z* = 252 (21%, C_{12}^+), 817 (100%, $2^*C_{12}^+ + 1^*A_{10}^-$), 1382 (49%, $3^*C_{12}^+ + 2^*A_{10}^-$). MS (neg. ESI, MeOH): *m/z* = 172 (6%, $A_{10}^- - C_{10}H_{21}$), 313 (100%, A_{10}^-), 878 (10%, $2^*A_{10}^- + 1^*C_{12}^+$), 1443 (11%, $3^*A_{10}^- + 2^*C_{12}$). Elemental analysis: calcd % for $C_{31}H_{55}N_3O_4S$ (M = 565,85 g/mol): C 65.8, H 9.8, N 7.43, S 5.67, found: C 65.19, H 9.97, N 7.15, S 5.62. Water content: 2.19 %.

1- Dodecyl-3-methyl-triazolium 4-dodecyloxybenzenesulfonate ($C_{12}A_{12}$)

Yield: 50 %, ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.41 (s, 1H) 9.23 (s, 1H), 7.81 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 4.60 (t, J = 7.4 Hz, 2H), 4.41 (s, 3H), 3.94 (t, J = 6.6 Hz, 2H), 1.94 (s, 2H), 1.74 (d, J = 6.2 Hz, 4H), 1.25 (d, J = 3.9 Hz, 34H), 0.88 (t, J = 6.4 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 160.18, 138.71, 132.81, 131.93, 127.59, 113.93, 68.25, 54.08, 40.33, 32.04, 29.74, 26.23, 22.81, 14.25. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2915s, 2850m, 1597w, 1493w, 1469m, 1194s, 1121s, 1030s, 1003m, 833s, 719m, 698m, 610s, 565s. MS (pos. ESI, MeOH): *m/z* = 252 (38%, C_{12}^{+}), 845 (100%, 2*C_{12}^{+} + 1*A_{12}^{-}), 1438 (35%, 3*C_{12}^{+} + 2*A_{12}^{-}). MS (neg. ESI, MeOH): *m/z* = 172 (5%, A_{12}^{-} - $C_{12}H_{25}$), 341 (100%, A_{12}^{-}), 934 (8%, 2*A_{12}^{-} + 1*C_{12}^{+}), 1527 (7%, 3*A_{12}^{-} + 2*C_{12}^{+}). Elemental analysis: calcd % for $C_{33}H_{59}N_3O_4S$ (M = 593,9 g/mol): C 66.74, H 10.01, N 7.08, S 5.4, found: C 66.36, H 10.38, N 6.79, S 5.16. Water content: 1.22 %.

1- Dodecyl-3-methyl-triazolium 4-tetradecyloxybenzenesulfonate ($C_{12}A_{14}$)

Yield: 49 %, ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.13 (s, 1H), 8.97 (s, 1H), 7.77 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.56 – 4.47 (m, 2H), 4.34 (s, 3H), 3.93 (t, *J* = 6.5 Hz, 2H), 2.04 (s, 8H), 1.25 (s, 36H), 0.87 (t, *J* = 6.2 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 160.22, 138.47, 132.75, 131.88, 127.60, 113.92, 68.24, 53.98, 40.25, 32.03, 29.79, 26.14, 22.80, 14.23. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2915s, 2850m, 1597w, 1494w, 1469m, 1194s, 1121s, 1030s, 1003m, 832s, 719m, 698m, 609s, 564s. MS (pos. ESI, MeOH): *m/z* = 252 (82%, C_{12}^{+}), 434 (36%, 1*C_{12}^{+} - CH_3 + $C_{14}H_{29}$), 873 (100%, 2*C_{12}^{+} + 1*A_{14}^{-}), 1055 (11%, 2*C_{12}^{+} + 1*A_{14}^{-} - CH_3 + $C_{14}H_{29}$), 1495 (21%, 3*C_{12}^{+} + 2*A_{14}^{-}). MS (neg. ESI, MeOH): *m/z* = 172 (6%, A_{14}^{-} - $C_{14}H_{29}$), 369 (100%, A_{14}^{-}), 990 (7%, 2*A_{14}^{-} + 1*C_{12}^{+}), 1611 (3%, 3*A_{14}^{-} + 2*C_{12}^{+}). Elemental analysis: calcd % for $C_{35}H_{63}N_3O_4S$ (M = 621,96 g/mol): C 67.59, H 10.21, N 6.76, S 5.16, found: C 66.87, H 10.61, N 6.08, S 4.75. Water content: 1.75 %.

1- Tetradecyl-3-methyl-triazolium 4-decyloxybenzenesulfonate ($C_{14}A_{10)}$

^{1}H NMR (250 MHz, $CDCl_3$) δ: 9.42 (s, 1H), 9.32 (s, 1H), 7.80 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.60 (t, *J* = 7.4 Hz, 2H), 4.40 (s, 3H), 3.94 (t, *J* = 6.6 Hz, 2H), 1.93 (s, 2H), 1.83 – 1.69 (m, 2H), 1.43 – 1.18 (m, 36H), 0.88 (t, *J* = 6.3 Hz, 6H). ^{13}C NMR (63 MHz, $CDCl_3$) δ: 160.25, 132.83, 131.96, 127.64, 113.98, 68.30, 54.06, 40.30, 32.04, 30.02 – 29.16 (m), 29.00, 26.20, 22.81, 14.23. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3137, 3124, 2954, 2913, 2871, 2848, 1598, 1580, 1496, 1471, 1456, 1296, 1239, 1198, 1173, 1121, 1101, 1053, 1031, 1005, 824, 717, 699, 606, 561. MS (pos. ESI, MeOH): m/z = 280 (28%, C_{14}^{+}), 462 (6%, C_{14} -CH_3 + $C_{14}H_{25}$), 873 (100%, 2*C_{14}^{+} + 1*A_{14}^{-}), 1466 (46%, 3*C_{14}^{+} + 2*A_{10}^{-}). MS (neg. ESI, MeOH): m/z = 172 (8%, A_{10}^{-} - $C_{10}H_{21}$), 313 (100%, A_{10}^{-}), 906 (16%, 2*A_{10}^{-} + 1*C_{14}^{+}), 1499 (23%, 3*A_{10}^{-} + 2*C_{14}^{+}). Elemental analysis:

calcd % for $C_{33}H_{59}N_3O_4S$ (M = 593.9 g/mol): C 66.74, H 10.01, N 7.08, S 5.40, found: C 66.96, H 9.62, N 6.97, S 5.56. Water content: 0.93 %.

1- Tetradecyl-3-methyl-triazolium 4-dodecyloxybenzenesulfonate ($C_{14}A_{12}$)

^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.36 (s, 1H), 9.28 (d, *J* = 1.3 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.58 (t, *J* = 7.4 Hz, 2H), 4.38 (s, 3H), 3.93 (t, *J* = 6.6 Hz, 2H), 1.90 (s, 2H), 1.83 – 1.68 (m, 2H), 1.25 (d, *J* = 2.6 Hz, 40H), 0.87 (t, *J* = 6.4 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 160.29, 138.35, 132.82, 131.90, 127.65, 113.96, 68.27, 54.04, 40.29, 32.05, 30.17 – 28.80, 26.20, 22.82, 14.25. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2955, 2916, 2849, 1597, 1579, 1496, 1469, 1301, 1245, 1216, 1186, 1122, 1102, 1030, 1004, 830, 821, 720, 701, 607, 562. MS (pos. ESI, MeOH): m/z = 280 (91%, C_{14}^+), 901 (100%, 2*C_{14}^+ + 1*A_{12}^-), 1522 (8%, 3*C_{14}^+ + 2*A_{12}^-). MS (neg. ESI, MeOH): m/z = 172 (5%, A_{12}^- - $C_{12}H_{29}$), 341 (100%, A_{12}^-), 962 (8%, 2*A_{12}^- + 1*C_{14}^+), 1583 (8%, 3*A_{12}^- + 2*C_{14}^+). Elemental analysis: calcd % for $C_{35}H_{63}N_3O_4S$ (M = 621.9 g/mol): C 67.59, H 10.21, N 6.76, S 5.16, found: C 67.44, H 10.76, N 6.47, S 4.82. Water content: 1.72 %.

1- Tetradecyl-3-methyl-triazolium 4-tetradecyloxybenzenesulfonate ($C_{14}A_{14}$)

^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.38 (s, 1H), 9.14 (s, 1H), 7.80 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.60 (t, *J* = 7.5 Hz, 2H), 4.42 (s, 3H), 3.94 (t, *J* = 6.6 Hz, 2H), 2.03 – 1.88 (m, 2H), 1.82 – 1.69 (m, 2H), 1.26 (s, 44H), 0.87 (t, *J* = 6.4 Hz, 6H). ^{13}C NMR (63 MHz, $CDCl_3$) δ: 138.34, 132.78, 131.90, 127.65, 113.97, 68.29, 54.02, 40.27, 32.03, 29.99 – 29.15 (m), 28.99, 26.19, 22.80, 14.21. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2915, 2850, 1597, 1578.1, 1494, 1469, 1297, 1194, 1121, 1031, 1004, 832, 699, 610, 564. MS (pos. ESI, MeOH): m/z = 280 (100%, C_{14}^+), 462 (31%, C_{14} - CH_3 + $C_{14}H_{25}$), 929 (69%, 2*C_{14}^+ + 1*A_{14}^-), 1578 (8%, 3*C_{14}^+ + 2*A_{14}^-). MS (neg. ESI, MeOH): m/z = 172 (4%, A_{14}^- - $C_{14}H_{29}$), 369 (100%, A_{14}^-), 1018 (6%, 2*A_{14}^- + 1*C_{14}^+), 1667 (5%, 3*A_{14}^- + 2*C_{14}^+). Elemental analysis: calcd % for $C_{37}H_{67}N_3O_4S$ (M = 650 g/mol): C 68.37, H 10.39, N 6.46, S 4.93, found: C 68.48, H 11.29, N 6.16, S 4.41. Water content: 2.16 %.

Instrumentation

Differential scanning calorimetry (DSC) was performed with a computer-controlled Phoenix DSC 204 F1 thermal analyzer (Netzsch, Selb, Germany). Measurements were carried out at a heating rate of 5 °C/min in a cold-sealed aluminum crucible with an argon flow rate of 20 mL/min. Given temperatures correspond to the onset of the respective thermal process.

Temperature dependent polarized optical microscopy (POM) analyses were carried out with an Axio Imager A1 microscope (Carl Zeiss MicroImaging GmbH,Göttingen, D) equipped with a hot stage, THMS600 (Linkam Scientific Instruments Ltd, Surrey, UK), and Linkam TMS 94 temperature controller (Linkam Scientific Instruments Ltd, Surrey, UK). Images were recorded at a magnification of 100× as a video with a digital camera during heating and cooling the sample which was placed between two cover slips. Heating and cooling rates were 5 °C/min^{-1}.

Thermogravimetric analysis (TG) were performed with a TG 449 F3 Jupiter (Netzsch, Selb, Germany). Measurements were carried out in aluminum oxide crucibles with a heating rate of 5 °C/min and nitrogen as purge gas.

Infrared spectroscopy (IR) was conducted with a Bruker Alpha-P ATR-spectrometer (Karlsruhe, Germany) in attenuated total reflection configuration. The data evaluation was carried out with the program OPUS.

Nuclear magnetic resonance spectra (^{1}H-NMR and ^{13}C-NMR) were recorded with a Bruker Advance DPX 200 spectrometer (Karlsruhe, Germany) at frequencies of 200 MHz and 50 MHz, respectively. Deuterated chloroform (Deutero GmbH) was used as solvent. The chemical shift δ is given in ppm. The peak multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

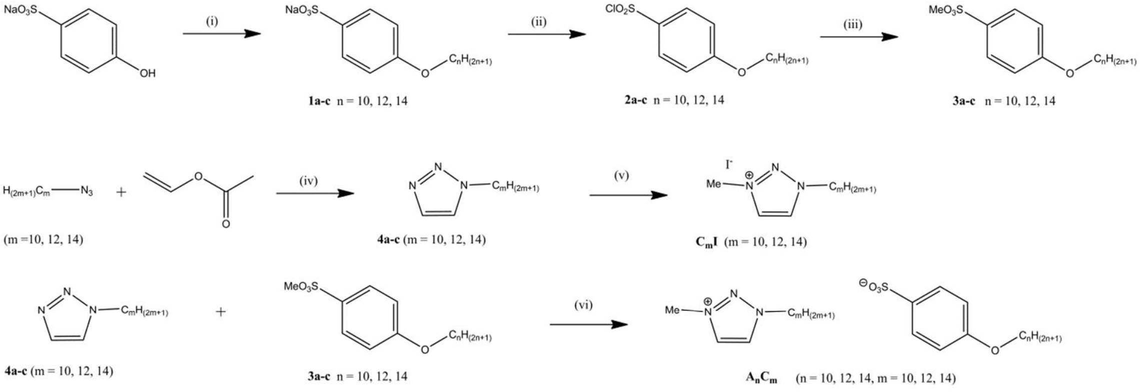
Mass spectrometric analysis was carried out on a VG Autospec mass spectrometer with EBEE geometry (VG instruments, Kent, USA). Fast atom bombardment (FAB) was used to ionize the samples.

Elemental analysis was conducted with a Vario EL C, H, N, S analyzer (Elmentar, Hanau, Germany).

3. Results and Discussion

Synthesis

To obtain the triazolium salts, the respective alkylazide was reacted with an excess of vinyl acetate to give the 1-alky-1,2,3-triazole (Scheme 1). These (**4a-4c**) were alkylated at the N-3 position with methyl iodide to obtain the desired triazolium iodides (**C_{10}I, C_{12}I, C_{14}I**). The methyl sulfonates (**3a-c**) were obtained from alkylated sodium 4-hydroxybenzenesulfonate (**1a-c**) via chlorination with phosphoryl chloride in dimethylformamide (DMF) and dichloromethane (DCM). In the last step the methyl sulfonates (**3a-c**) were used as methylation reagents to generate the triazolium cations and the benzenesulfonate anions (**A_nC_m**). After recrystallization from ethyl acetate all compounds were obtained as white solids.



Scheme 1. Synthesis of triazolium iodides (C_mI) and triazolium sulfonate ion pairs (A_nC_m). i) $C_nH_{(2n+1)}$Br, KOH , DMSO, RT, 24 h; ii) $POCl_3$, DMF, DCM, 1 h; iii) NaOMe, MeOH, RT, 15 min; iv) mw-irradiation, 120 °C, 5 h; v) acetonitrile, reflux, 3d; vi) acetonitrile, reflux, 3d.

Crystal Structural Analysis

Although it was not possible to grow anhydrous single crystals of sufficient quality for structure analysis from solution, colorless single crystals of partially hydrated $C_{12}A_{14}$ could be obtained from acetonitrile solution. 1-Dodecyl-3-methyl-triazolium 4-tetradecyloxybenzene sulfonate hydrate (**$C_{12}A_{14}$·0.35 H_2O**) crystallizes with the triclinic space group $P\bar{1}$ (No. 2) with two formula units in the unit cell. The elongated ions form a bilayer structure (Figure 2). The two crystallographically distinct triazolium cations deviate in the conformation of the alkyl chain. In one triazolium cation the bond from the second to the third carbon atoms of the chain is *gauche* and in the other triazolium cation the bond between the seventh and the eighth carbon atom (counted from the triazolium head group) is *gauche*. All other bonds in the alkyl chains are in *trans* conformation. The conformation of the alkyl chains of the two distinct sulfonate anions is *all trans,* except the bond between the first and the second carbon after the oxygen atom which is *gauche*. Alternating cations and anions are arranged parallel to each other forming layers (Figure 3, left). Their orientation reverses between two layers. In consequence, a clear segregation of charged, polar domains formed by triazolium and sulfonate head groups and apolar, hydrophobic alkyl tails of cation and anion are seen in the structure. The solvent water molecule is situated close to the polar head groups of the ions. The crystal structure of 1-methyl-3-dodecyl triazolium iodide has been published before.[26] $C_{12}I$ crystalizes in the triclinic space group $P\bar{1}$ (No. 2) with two formula units in the unit cell. The rod-shaped cations form an interdigitated bilayer-structure with the triazolium cations not facing each other directly but alternating with the iodide anions (Figure 3, right).

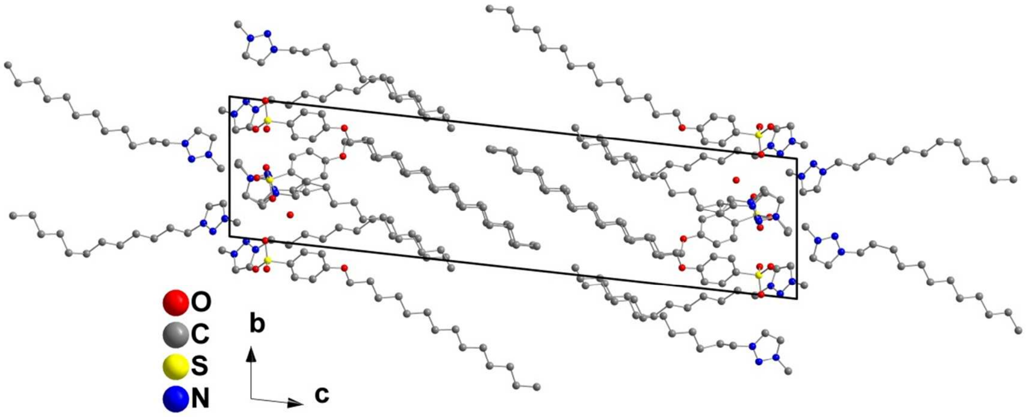


Figure 2. Crystal packing of 1-dodecyl-3-methyl-triazolium 4-tetradecyloxybenzenesulfonate ($C_{12}A_{14}$.x0.35H_2O).

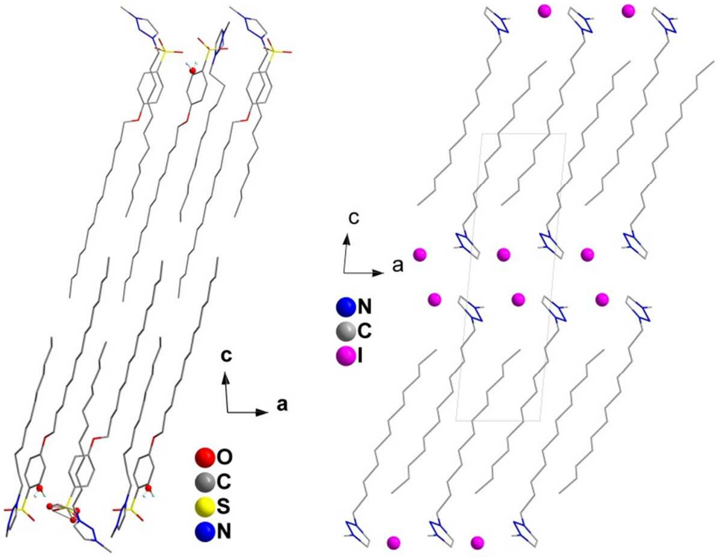


Figure 3. Crystal structure of 1-dodecyl-3-methyl-triazolium 4-tetradecyloxybenzenesulfonate (left) and 1-dodecyl-3-methyl-triazolium iodide (right).

In comparison with the respective triazolium iodide (Figure 3, right) the alkyl chains are less interdigitated in the sulfonate and the distance between the polar domains is much larger (35 Å between the sulfonate vs. 27 Å between the iodide anions). In **C$_{12}$I** all alkyl chains of the cations are parallel to each other and the triazolium head groups alternate with the iodides. In contrast to that, in **C$_{12}$A$_{14}$.x0.35H$_2$O** the alkyl chains of the cations are not parallel, but are tilted at different positions (Figure 2). Only the second halves of the alkyl chains run parallel together with the alkyl chains of the anions. The charged head groups to not alternate regularly like in the iodide compound. The two triazolium rings and the two benzene rings of the sulfonates in the unit cell are perpendicular to each other, due to several hydrogen bonds (Figure 4).

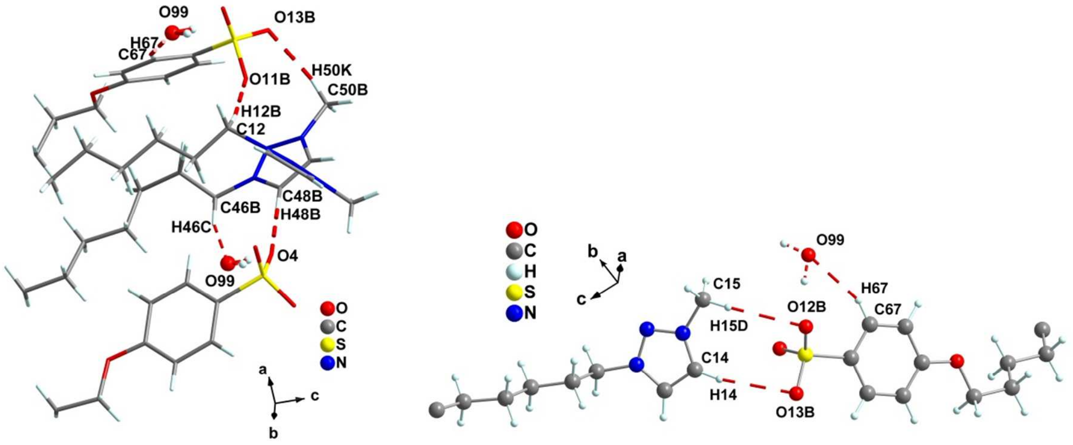


Figure 4. Hydrogen bonding interactions in $C_{12}A_{14}.0.35H_2O$.

Table 2. H-bond details for $C_{12}A_{14}.0.35H_2O$.

$C_{12}A_{14}$	H···A (Å)	H···A (deg)
C12-H12B···O11B	2.319(2)	170.46(1)
C50B-H50K···O13B	2.374(3)	154.44(5)
C67-H67···O99	2.496(3)	156.10(1)
C46B-H46C···O99	1.493(3)	159.24(2)
C48-H48B···O4	1.937(5)	136.86(4)
C14-H14···O13B	2.807(4)	169.91(1)
C15-H15D···O12B	2.825(3)	167.12(2)

Several hydrogen bonds can be found in the structure (Table 2). Within the layers C-H•••O hydrogen bonds are formed from the single methyl group of the triazolium cation, from the first carbon of the long alkyl chain and from one CH-group of the triazolium ring to the oxygen atoms of the sulfonate anions (Figure 4, left). The second triazolium cation features a C-H•••O hydrogen bond from the first carbon of the long alkyl chain to a water molecule. This is the reason for the different conformations of the triazolium cations. Beside these interactions within the layers, there are also hydrogen bonds that interconnect the layers: C-H•••O hydrogen bonds are formed between the oxygen atoms of the sulfonate group (the one that is connected to two other cations and the water molecule) and one of the two CH-groups of the triazolium ring (which has the gauche conformation at the end of the alkyl tail) and to the single methyl group of this cation (Figure 4, right).

Table 3. Crystallographic and refinement details for $C_{12}I$ and $C_{12}A_{14}\cdot0.35H_2O$.

	$C_{12}I$	**$C12A14\cdot0.35H_2O$**
Empirical formula	$C_{15}H_{30}N_3I$	$C_{35}H_{63}N_3O_4S$
Formular weight (g/mol)	379.38	621.94
Temperature (K)	170	170
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	*a* = 5.6056(6) Å *b* = 8.9070(10) Å *c* = 19.523(3) Å α = 79.80(2) ° β = 83.50(2) ° γ = 81.78(2) °	*a* = 8.5428(1) Å *b* = 10.3685(2) Å *c* = 41.7163(6) Å α = 95.789(1) ° β = 93.071(1) ° γ = 98.116(1) °
Volume	945.6(2)	3630.76(7)
Z	2	2
Calculated density (g/cm^3)	1.17	1.15
Absorption coefficient (mm^{-1})	2.168	1.098
Θ-range for data collection	2.34 to 25.00 °	3.2 to 68.0 °
Reflections collected/ unique	8211 / 3342	65716 / 13196
Refinement method	Full-matrix least-squares on F^2	
Data / parameters	3342 / 173	13196 / 840
Goodness-of-fit on F^2	0.989	1.054
Final R indices (I>2sigma(I))	R_1 = 0.045 wR_2 = 0.071	R_1 = 0.037 wR_2 = 0.098
R indices (all data)	R_1 = 0.077 wR_2 = 0.082	R_1 = 0.041 wR_2 = 0.101

Thermal Investigations

The thermal properties of all compounds were examined by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The transition temperatures, enthalpies and phase transition assignments are listed in Table 4 together with the thermal decomposition temperatures which were determined via thermogravimetric analysis. The benzenesulfonates decompose between 272 and 292 °C depending on the chain length, whereas the iodides decompose around 200 °C (Table 4). Thus, the introduction of the rod-like benzenesulfonate anion leads to increased thermal stability. All investigated compounds, with exception of C10I, which melts directly to the isotropic liquid, are thermotropic liquid crystals with quite similar LC behavior. The representative DSC traces of $C_{12}A_{12}$ are shown in Figure 5. (The detailed DSC traces of the other compounds can be seen in supporting information. The phase transition temperatures will be discussed below in combination with the results from polarizing optical microscopy, which allows for phase assignment.) $C_{12}A_{12}$ shows two endothermal events upon heating. Temperature dependent POM identifies the first transition to be the flow point (S→LC) while the second belongs to the clearing point (LC→LISO). Both transitions are reversible and reappear upon cooling, albeit at slightly lower temperatures, as is commonly observed in ILs and ILCs[27].

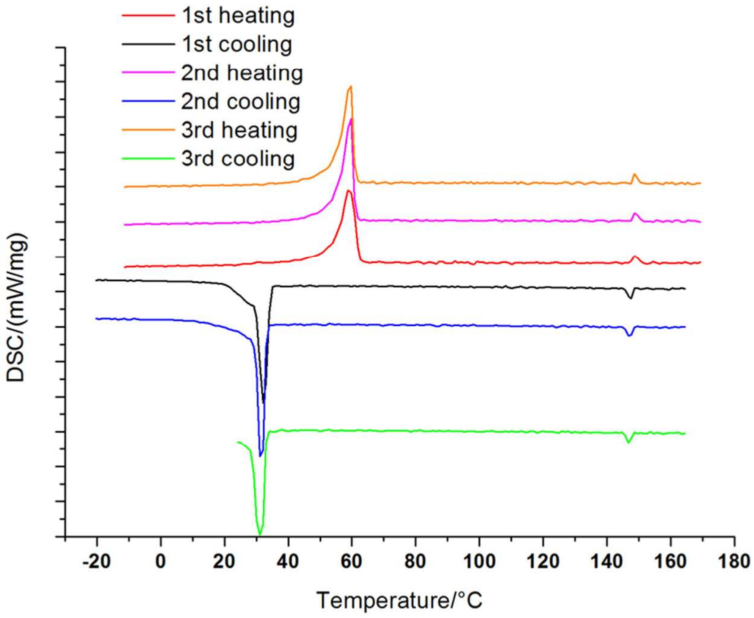


Figure 5. DSC traces of $C_{12}A_{12}$.

Table 4. Phase transition and thermal decomposition temperatures.

	T^a/°C (Δ H /kJ mol^{-1})					T_d^c [°C]
No.	Cr→Cr' ^{b}	Cr' → Cr^b	Cr→SmA^b	SmA →L$_{ISO}$^{b}	Cr →L$_{ISO}$^{b}	
C$_{10}$I	-	-	-	-	74.6 (31.87)	213.7
C$_{12}$I	-	-	83.1 (98.82)	132.3 (2.54)	-	198.3
C$_{14}$I	-	-	89.44 (39.12)	158.1 (1.01)	-	214.9
C$_{10}$A$_{10}$	-	-	40.5 (31.33)	146 (1.79)	-	280.4
C$_{10}$A$_{12}$	-	-	48.8 (43.04)	141.9 (1.78)	-	286.7
C$_{10}$A$_{14}$	-	-	49.9 (45.95)	113.8 (0.88)	-	280.4
C$_{12}$A$_{10}$	-	39.0 (13.7)	54.8 (10.27)	157.7 (1.7)	-	281
C$_{12}$A$_{12}$	-	-	55.6 (48.14)	147.9 (1.87)	-	280.7
C$_{12}$A$_{14}$	-	35.7 (22.07)	53.9 (29.66)	121.5 (0.81)	-	292.6
C$_{14}$A$_{10}$	-	64.0 (3.78)	73.9 (15.37)	151.4 (1.22)	-	278.1
C$_{14}$A$_{12}$	-	-	70.6 (33.96)	148.9 (0.66)	-	272.3
C$_{14}$A$_{14}$	47.1 (25.24)	54.8 (11.77)	64.1 (18.18)	126 (1.79)	-	283.6

[a] Phase transition temperatures (°C) and enthalpies (kJ/mol, in parenthesis) are measured during heating and cooling at 5 K/min. [b]The phase transitions were identified by POM and SAXS measurements. [c]Thermal decomposition temperature

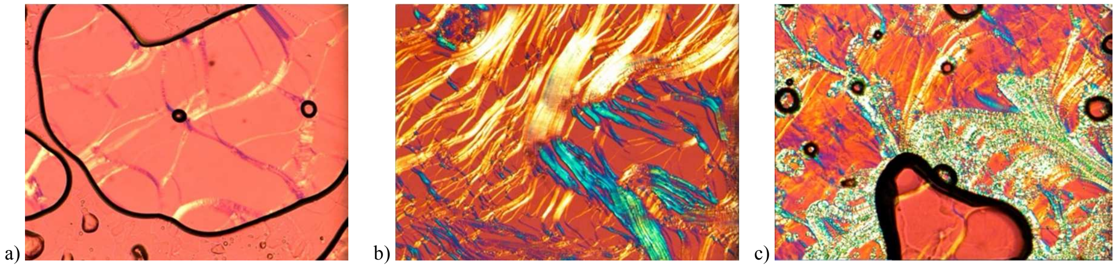


Figure 6. Representative textures as seen between crossed polarizers: oily streak texture characteristic of a smectic A phase for (a) C$_{12}$I at 97.4 °C; (b) C$_{10}$A$_{10}$ at 70.2 °C; (c) C$_{12}$A$_{10}$ at 83.5 °C.

For all compounds except 1-methyl-3-decyl-triazolium iodide (**C$_{10}$I**), an oily streak texture was observed under polarized light. This indicates the formation of a smectic A phase. Three representative POM textures are shown in Figure 6. The iodides **C$_{12}$I** and **C$_{14}$I** exhibit a smectic A phase at temperatures slightly above 80 °C, whereas the triazolium iodide with the shortest chain length (**C$_{10}$I**) melts directly to an isotropic liquid at 75 °C. Also for 1-alkyl-3-methylimidazolium halides it has been found that a chain length of twelve carbon atoms is mandatory for the formation of a mesophase[5,10]. Reducing the alkyl chain length from 14 to 12 carbon atoms for the triazolium iodides lowers both the flow and the clearing point temperature. However, the flow point is less affected leading to a larger mesophasic window for **C$_{14}$I** compared to **C$_{12}$I**. In comparison with the 1-methyl-3-dodecyl-triazolium bromide, the iodide **$C_{12}I$** has lower flow and clearing point temperatures and similar mesophasic temperature windows. For the triazolium sulfonates the phase transitions to the smectic A phase occur at lower temperatures between 40 and 65 °C depeding on the size both of the anion and the cation. (Note, that some compounds (**$C_{12}A_{10}$**, **$C_{12}A_{14}$**, **$C_{14}A_{10}$**, **$C_{14}A_{14}$**) show an additional thermal event at lower temperatures, which will not be discussed in detail but can be assigned to a solid-solid phase transition.)

Influence of the Anion

The dependence of the phase transition temperatures on the anion is shown in Figure 7 for each cation. In case of the decyltriazolium compounds the mesomorphic behavior is obviously induced by the sulfonate counter anion (the decyltriazolium iodide melts directly to the liquid phase without formation of a LC). With increasing anion length the flow point increases. The opposite trend can be observed for the clearing points. The compound with the longest anion chain length (**$C_{10}A_{14}$**) and highest size mismatch between cation and anion has thus the narrowest mesophase temperature window. The effect of the anion alkyl chain length on the flow point is similar for the other two cations, C_{12} and C_{14}, with increasing anion length it decreases. However, for the C_{12} salts the flow points seem to be largely unaffected by the anion size, whereas for the C_{14} cation larger anions lead to lower flow points. Generally for the same cation, a larger anion does only weakly affect the flow point but more clearly lowers the clearing point temperature. The mesophase stabilization by pairing the rod-shaped cation with a rod-shaped anion becomes obvious, when comparing to the iodides: for **$C_{10}I$** no mesophase is observed, for C_{12} and C_{14} the flow points for the sulfonates are observed at lower temperatures than for the iodide. In addition, the mesophase window is generally wider.

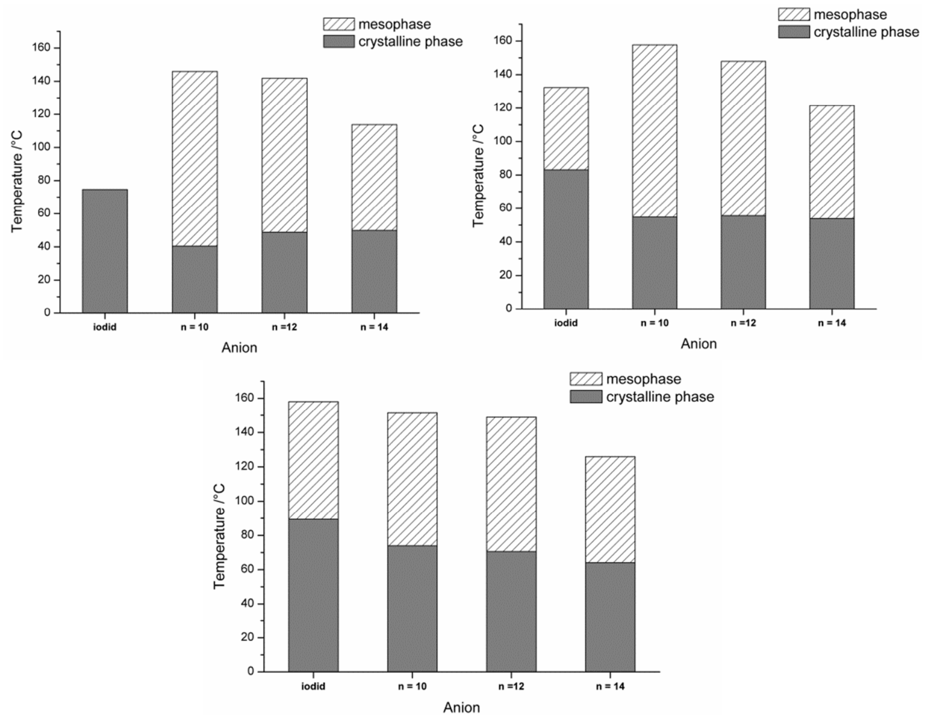


Figure 7. Phase transition temperatures of the different cations (top, left: C_{10}, top, right: C_{12}, bottom: C_{14}) in dependence of the anion.

Influence of the cation

To visualize the effect of the cation chain length on the mesophase formation, a comparison of all relevant transition temperatures is displayed in Figure 8. As mentioned above the iodide with the shortest chain, **$C_{10}I$**, does not form a liquid crystalline phase. In the other two iodides the temperatures of flow point and clearing point increase with increasing chain length. For all three sulfonate anions the flow point temperature increases with increasing cation chain length, ranging from 40.5 °C (**$C_{10}A_{10}$**) to 73.9 °C (**$C_{14}A_{10}$**). For A_{12} and A_{14} a similar effect on the clearing point is observed: The larger the cation, the higher the clearing point. For C_{10} an irregularity is observed. **$C_{10}A_{12}$** has a higher clearing point than **$C_{10}A_{10}$** and **$C_{10}A_{14}$**. This might be due to the interplay of van der Waals interactions between the alkyl chains and hydrogen bonding and ionic interactions in the polar regions of the structure. In the crystal structure of **$C_{12}A_{14}\cdot 0.35H_2O$** the alkyl chains of the cations are not part of the interdigitation, but are the “counterpart” for the alkyl chains of the sulfonate anion (Figure 2). If the anion is kept at the same length and the cation length is extended, there is less interdigitation of the alkyl chains of the anions and thus the crystalline phase is stabilized (Figure 8).

In summary, the dependence of clearing point temperatures on the cation chain length is seen to follow the inverse trend compared to the anion chain length (Figure 8 and Figure 7), i.e. increasing with increasing chain length (Fig. 8). This trend was also observed for guanidinium sulfonate ion pairs[24]. The lowest clearing point is measured for the compound with the shortest cation chain length and the longest anion chain length $\mathbf{C_{10}A_{14}}$ (113.8 °C). Here the difference in lengths between the cation and anion is the largest (Table 5). The highest overall clearing point of 157.7 °C was achieved with $\mathbf{C_{12}A_{10}}$ where the cation and the anion have a very small size difference (Table 5). The liquid crystalline temperature window is smallest for the ion pair with the longest alkyl chains, $\mathbf{C_{14}A_{14}}$ (62 °C) and largest for the compound with the shortest alkyl chains $\mathbf{C_{10}A_{10}}$ (105.5 °C). In general the mesophase temperature window is larger for ions with shorter alkyl chains.

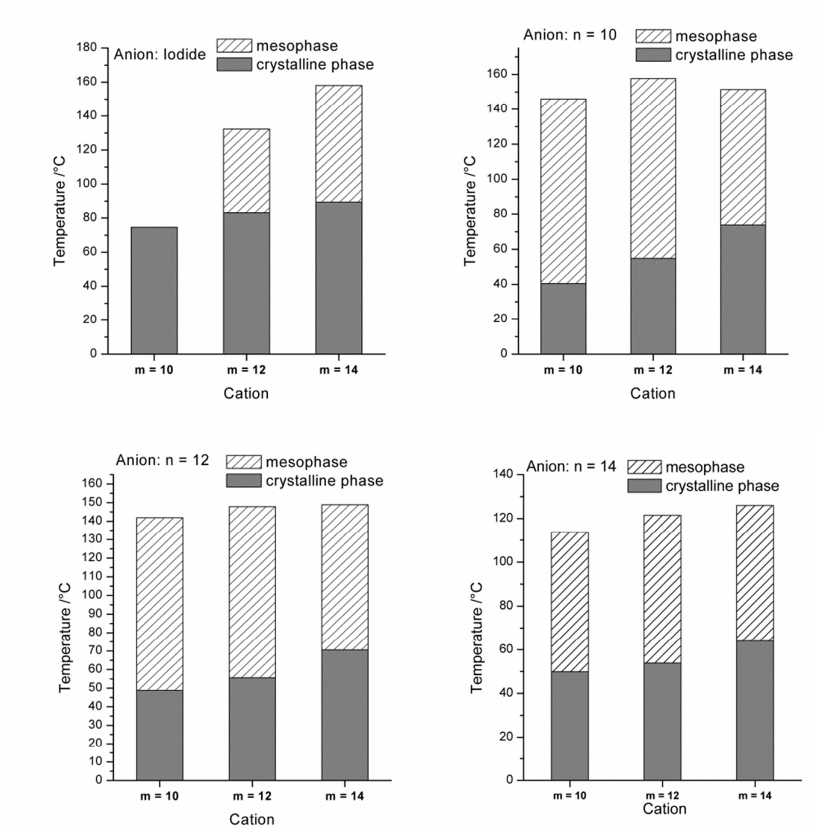


Figure 8. Phase transition temperatures of the different anions in dependence of the cation chain length.

Table 5. Length of cation and anion in Å (the length of C_{12} and A_{14} were measured in the crystal structure and the others were estimated by adding or subtracting 2.5 Å for each -CH_2CH_2- group).

	$C_{10}A_{10}$	$C_{10}A_{12}$	$C_{10}A_{14}$	$C_{12}A_{10}$	$C_{12}A_{12}$	$C_{12}A_{14}$	$C_{14}A_{10}$	$C_{14}A_{12}$	$C_{14}A_{14}$
cation	14	14	14	16.5	16.5	16.5	19	19	19
anion	18	20.5	23	18	20.5	23	18	20.5	23
difference	4	6.5	7	1.5	4	6.5	1	1.5	4

4. Conclusions

A series of nine triazolium sulfonate ionic liquid crystals with rod-like cations and anions was synthesized and characterized. The corresponding triazolium iodides where synthesized as reference materials featuring spherical counter anions. 1-Decyl-3-methyl-triazolium iodide was the only compound which does not exhibit a liquid crystalline phase, but melts at 75 °C to an isotropic liquid. Therefore, it qualifies as an ionic liquid. All other compounds, the iodides as well as the sulfonates, exhibit a smectic A phase, as established by optical microscopy. In any case, pairing the rod-shaped triazolium cations with long chain sulfonate anion stabilizes the mesophase. A mesophase temperature window of up to 105 °C for **$C_{10}A_{10}$** could be achieved. Generally, the melting and clearing temperatures increase with increasing chain length of the cation. In contrast, with increasing anion alkyl chain length the clearing point temperatures decrease. In summary, the mesophase stability is increased through pairing congruently shaped mesogenic ions, whereby the melting and the clearing point highly depend on the relative alkyl chain length of the cation and anion.

ACKNOWLEDGEMENT

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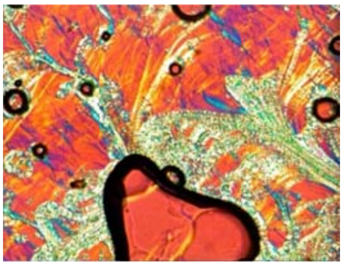

In ionic liquid crystals the mesophase stability can be increased through pairing congruently shaped mesogenic ions.