

# Synthesis and Mesomorphic Properties of Rigid-Core Ionic Liquid Crystals

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## Supporting Information:

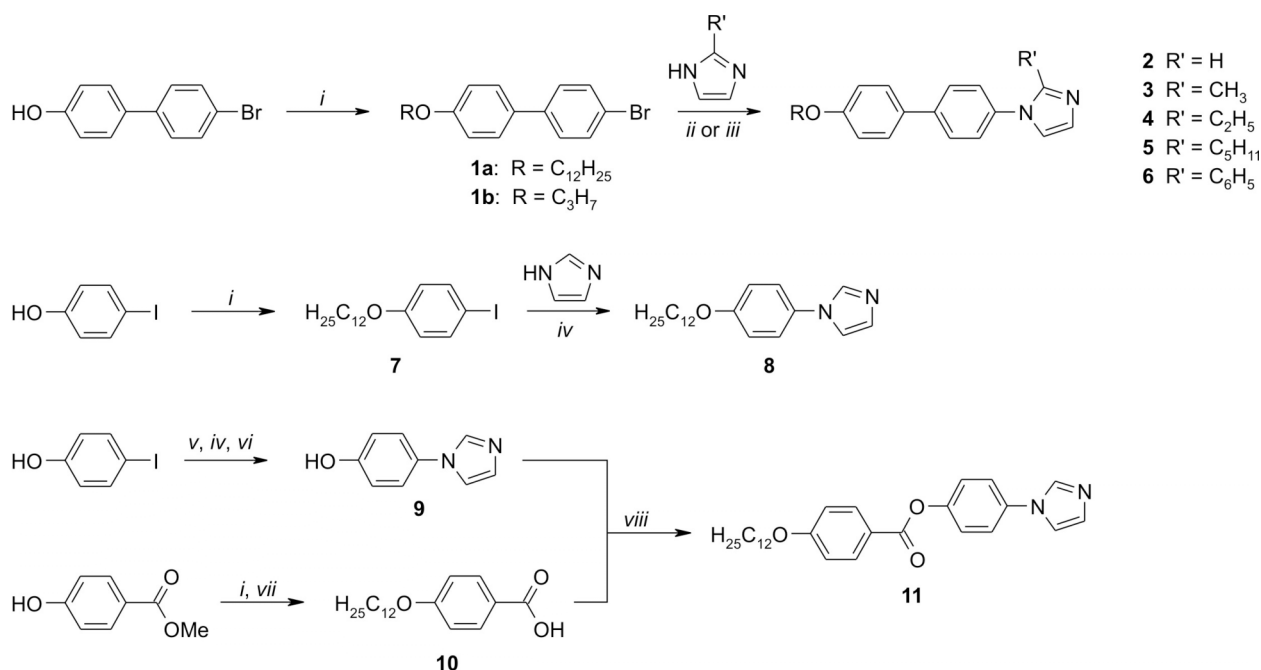
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## Synthetic procedures and characterization

**Experimental.** Synthesis and chemical characterization ( $^1\text{H}$ ,  $^{13}\text{C}$  NMR) of compounds **1–37** is described below. After purification by crystallization and/or column chromatography, the materials were dissolved in  $\text{CH}_2\text{Cl}_2$ , filtered (0.2  $\mu\text{m}$  pores) and the solvent was evaporated. Materials have been dried for 24 hrs in vacuum before analysis. Mixtures of different ILCs have been prepared by dissolving the appropriate amounts of ILC in a common solvent, which then was removed by evaporation. Mixtures were dried for 24 hrs under vacuum prior to analysis. Mixtures of ILCs with EDOT or  $\text{LiBF}_4$  were prepared by the addition of a stock solution of the salt (in THF) or the thiophene (in  $\text{CH}_2\text{Cl}_2$ ) to a weighed amount of ILC. The solutions were filtered (0.2  $\mu\text{m}$  pores) and the solvent was evaporated. Mixtures were dried for 24 hrs under vacuum prior to analysis.

**Scheme 1.** Synthesis of the ILC precursors.<sup>a</sup>



<sup>a</sup> Key: (i)  $\text{RBr}$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{KI}$ , butanone, 16 hrs reflux; (ii)  $\text{K}_2\text{CO}_3$ ,  $\text{CuI}$ ,  $N,N$ -dimethylglycine, DMSO, 24–48 hrs at 110 °C; (iii)  $\text{Ce}_2\text{CO}_3$ ,  $\text{CuI}$ , 4,7-dimethoxy-1,10-phenanthroline, PEG-600, butyronitril 4–24 hrs reflux; (iv)  $\text{K}_2\text{CO}_3$ ,  $\text{CuI}$ ,  $L$ -proline, DMSO, 16 hrs at 110 °C; (v) Tetrahydropyran,  $p$ -toluenesulphonic acid,  $\text{CH}_2\text{Cl}_2$ , 2hrs at room temperature; (vi)  $\text{MeOH}$ , 1N  $\text{HCl}$ , 2 hrs at room temperature; (vii) 1,3-Dicyclohexylcarbodiimide (DCC); 4-( $N,N$ -dimethylamino)pyridine (DMAP), THF, 40 hrs at 50 °C.

**Williamson alkylation (1a, 1b, 7 and 10) – general procedure (scheme 1).**

The appropriate aromatic alcohol (1 eq.) and alkyl bromide (1.2 eq.), together with  $K_2CO_3$  (2 eq.), KI (0.2 eq.) were stirred in DMF at 150 °C until TLC indicated full conversion (3-6 hrs). The reaction mixture was cooled and filtered, the solids washed with acetone. The amount of DMF was reduced by partial evaporation (to ~25 %) and the concentrated solution was precipitated in a 1N HCl solution. The product was extracted with  $CH_2Cl_2$  (2x) and the combined organic layers washed with 1N HCl (2x) and water (2x). Pure product was obtained after recrystallization.

**1a:** recrystallization from ethanol, yield 91% of a white solid. Results of spectroscopic analysis are in correspondence with the literature.<sup>1</sup>

**1b:** recrystallization from ethanol, yield 84% of a white solid. Results of spectroscopic analysis are in correspondence with the literature.<sup>2</sup>

**7:** recrystallization from methanol, yield 89% of a white solid. Results of spectroscopic analysis are in correspondence with the literature.<sup>3</sup>

**10:** recrystallization from methanol, yield 77% (first crop), 22% (second crop) of a white solid. Deprotection of the ester: The first crop was refluxed with a 4N KOH solution (1.2 eq. KOH) in EtOH. After 1 hr, the solution was cooled and acidified with a concentrated HCl solution until neutral. The precipitated product was filtered off and washed with aqueous methanol. After drying under vacuum 77% (as calculated from the phenol starting material) of a white solid was obtained. Results of spectroscopic analysis are in correspondence with the literature.<sup>4</sup>

**Ullmann-type amination using *N,N*-dimethylglycine/CuI (2–4) – general procedure (see scheme 1):**

The aryl bromide (1 eq.), imidazole derivative (1.2 eq.),  $K_2CO_3$  (2 eq.), CuI (0.1 eq.) and *N,N*-dimethylglycine (0.2 eq.) were stirred in dry DMSO in inert atmosphere at 110 °C. The mixture was cooled and precipitated into a large excess of 1N  $NH_4OH$ . The precipitate was filtered off, dissolved in  $CH_2Cl_2$  and washed with 1N  $NH_4OH$  (1x) and water (2x), dried ( $MgSO_4$ ) and the solvent was evaporated. Pure product was obtained by column chromatography ( $SiO_2$ ), first eluting the aryl bromide starting material with  $CH_2Cl_2$ /hexanes mixtures, then the product with EtOAc, followed by recrystallization from a  $CH_2Cl_2$ /hexanes mixture.

**2a:** Reaction time: 48 h; yield 79% of a white solid; 12% starting material was recovered.  $^1H$  NMR ( $CDCl_3$ , 500 MHz):  $\delta$  = 7.89 (s, 1H, imidazole); 7.63, 7.52, 7.42, 6.99 (4xd,  $^3J_{HH}$  = 8.5

Hz, 4×2H, CH aromatic); 7.31, 7.23 (2×br s, 2×1H, imidazole); 4.00 (t,  $^3J_{\text{HH}} = 6.5$  Hz, 2H, CH<sub>2</sub>O); 1.81, 1.50-1.22 (m, 20H, CH<sub>2</sub> aliphatic); 0.89 (t, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta = 159.83, 140.93, 136.58, 136.28, 132.64, 131.17, 128.71, 128.64, 122.43, 118.93, 115.65, 68.84, 32.64, 30.39, 30.37, 30.33, 30.31, 30.13, 30.08, 29.98, 26.77, 23.42, 14.86$ .

**2b:** Reaction time: 48 h; yield 87% of a white solid; 5% starting material was recovered. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta = 7.91$  (br s, 1H, imidazole); 7.66, 7.55, 7.45, 7.01 (4×d,  $^3J_{\text{HH}} = 8.5$  Hz, 4×2H, CH aromatic); 7.33, 7.25 (2×br s, 2×1H, imidazole); 3.99 (t,  $^3J_{\text{HH}} = 6.5$  Hz, 2H, CH<sub>2</sub>O); 1.86 (m, 2H, CH<sub>2</sub>) 1.08 (t,  $^3J_{\text{HH}} = 6.5$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta = 159.75, 141.01, 136.26, 136.05, 132.52, 130.42, 128.64, 128.57, 122.36, 119.05, 115.61, 70.29, 23.21, 11.14$ .

**3:** Reaction time: 72 h; yield: 56% of a white solid; 31% starting material was recovered. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta = 7.64, 7.54, 7.34, 7.00$  (4×d,  $^3J_{\text{HH}} = 8.5$  Hz, 4×2H, CH aromatic); 7.05, 7.04 (2×d,  $^3J_{\text{HH}} = 1.8$  Hz, 2×1H, imidazole); 4.01 (t,  $^3J_{\text{HH}} = 6.5$  Hz, 2H, CH<sub>2</sub>O); 2.41 (s, 3H, CH<sub>3</sub> imidazole); 1.84-1.78, 1.51-1.44, 1.40-1.22 (m, 20H, CH<sub>2</sub> aliphatic); 0.89 (t, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta = 159.87, 145.46, 141.53, 137.20, 132.70, 128.82, 128.46, 128.24, 126.45, 121.38, 115.65, 68.84, 32.64, 30.38, 30.36, 30.33, 30.30, 30.12, 30.07, 29.98, 26.77, 23.41, 14.85, 14.60$ .

**4:** Reaction time: 72 h; yield: 27% of a white solid; 72% starting material was recovered. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta = 7.63, 7.54, 7.31, 6.99$  (4×d,  $^3J_{\text{HH}} = 8.5$  Hz, 4×2H, CH aromatic); 7.07, 7.00 (2×d,  $^3J_{\text{HH}} = 1.8$  Hz, 2×1H, imidazole); 4.00 (t,  $^3J_{\text{HH}} = 6.5$  Hz, 2H, CH<sub>2</sub>O); 2.70 (q,  $^3J_{\text{HH}} = 7.5$  Hz, 2H, CH<sub>2</sub>Im); 1.84-1.78, 1.50-1.44, 1.39-1.22 (m, 23H, CH<sub>2</sub> aliphatic and CH<sub>3</sub>); 0.88 (t, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta = 159.88, 150.34, 141.63, 137.08, 132.67, 128.80, 128.41, 128.20, 126.76, 121.39, 115.64, 68.82, 32.64, 30.39, 30.37, 30.33, 30.31, 30.13, 30.08, 29.98, 26.77, 23.41, 21.36, 14.85, 13.09$ .

### **Ullmann-type amination using *L*-proline/CuI (8 and 9) – general procedure (scheme 1).**

The aryl bromide (1 eq.), imidazole (1.5 eq.), K<sub>2</sub>CO<sub>3</sub> (3 eq.), CuI (0.1 eq.) and *L*-proline (0.2 eq.) were stirred in dry DMSO in inert atmosphere at 130 °C. The mixture was cooled and precipitated into a large excess of 1N NH<sub>4</sub>OH. The precipitate was filtered off, dissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed with 1N NH<sub>4</sub>OH (1x) and water (2x), dried (MgSO<sub>4</sub>) and the solvent was evaporated. Pure product was obtained by column chromatography (SiO<sub>2</sub>, eluent EtOAc), followed by recrystallization from a CH<sub>2</sub>Cl<sub>2</sub>/hexanes mixture.

**8:** Reaction time: 6 h; yield: 92% of a white solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  = 7.76 (s, 1H, imidazole); 7.28, 6.97 (2xd,  $^3J_{\text{HH}}$  = 8.5 Hz, 4x2H, CH aromatic); 7.20, 7.18 (2xt,  $^3J_{\text{HH}}$  = 1.8 Hz, 2x1H, imidazole); 3.98 (t,  $^3J_{\text{HH}}$  = 6.5 Hz, 2H,  $\text{CH}_2\text{O}$ ); 1.80 (p,  $^3J_{\text{HH}}$  = 6.5 Hz, 2H); 1.50-1.22 (m, 20H,  $\text{CH}_2$  aliphatic); 0.88 (t, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  = 159.21, 136.57, 131.19, 123.88, 119.48, 116.11, 69.14, 32.23, 30.37, 30.34, 30.31, 30.30, 30.09, 30.06, 29.89, 26.71, 23.40, 14.84.

**9:** Reaction time: 16 h; yield: 80% of a white solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  = 7.73 (br s, imidazole); 7.25, 7.11 (2xd,  $^3J_{\text{HH}}$  = 8.5 Hz, 2x2H, CH aromatic); 7.18, 7.15 (2xbr s, 2x1H, imidazole); 5.41 (t,  $^3J_{\text{HH}}$  = 3.5 Hz, CH THP), 3.89-3.83, 3.62-3.57, 2.05-1.93, 1.90-1.82, 1.76-1.55 (m, 8H, THP).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  = 157.02, 136.51, 132.05, 130.79, 123.69, 119.375, 118.16, 97.19, 62.73, 30.90, 25.79, 19.30.

After deprotection of the THP group with *p*-toluenesulphonic acid in methanol (quantitative).  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , 500 MHz):  $\delta$  = 9.95 (br s, 1H, OH); 8.04, 7.56, 7.04 (3xs, 3x1H, imidazole); 7.38, 6.85 (2xd,  $^3J_{\text{HH}}$  = 8.5 Hz, 2x2H, CH aromatic).

### **Ullmann-type amination using 4,7-dimethoxy-1,10-phenanthroline/CuI (2a, 5 and 6) – general procedure (scheme 1).**

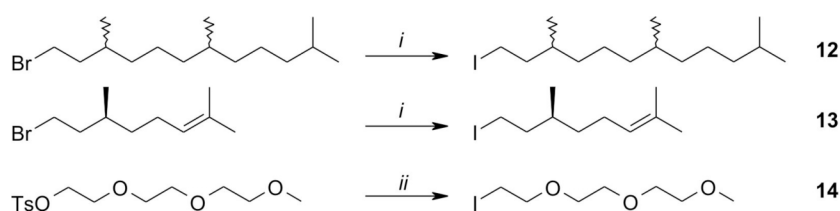
The aryl bromide (1 eq.), imidazole derivative (1.5 eq.),  $\text{Cs}_2\text{CO}_3$  (3 eq.), CuI (0.025 eq.), 4,7-dimethoxy-1,10-phenanthroline (0.075 eq.) and poly(ethyleneglycol) ( $M_w$  = 600 g/mol) were stirred in butyronitril in inert atmosphere at 130 °C. The mixture was cooled and precipitated into a large excess of 5N  $\text{NH}_4\text{OH}$ . The precipitate was filtered off, dissolved in  $\text{CH}_2\text{Cl}_2$  and washed with 1N  $\text{NH}_4\text{OH}$  (1x) and water (2x), dried ( $\text{MgSO}_4$ ) and the solvent was evaporated. Pure product was obtained by column chromatography ( $\text{SiO}_2$ , eluent EtOAc), followed by recrystallization from a  $\text{CH}_2\text{Cl}_2$ /hexanes mixture.

**2a:** Reaction time: 36 h; yield: 93% of a white solid. NMR analysis given above.

**5:** Reaction time: 40 h; yield: 65% of a white solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  = 7.59, 7.54, 7.27, 6.99 (4xd,  $^3J_{\text{HH}}$  = 8.5 Hz, 4x2H, CH aromatic); 7.48-7.44, 7.31-7.26 (2xm, 5H, Ph); 7.30, 7.21 (2xd,  $^3J_{\text{HH}}$  = 1.8 Hz, 2x1H, imidazole); 4.02 (t,  $^3J_{\text{HH}}$  = 6.5 Hz, 2H,  $\text{CH}_2\text{O}$ ); 1.83, 1.51-1.24 (m, 20H,  $\text{CH}_2$  aliphatic); 0.90 (t, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 159.93, 149.54, 141.65, 137.20, 132.74, 128.83, 128.47, 128.20, 126.88, 121.32, 115.70, 68.89, 32.66, 32.25, 30.38, 30.34, 30.15, 30.09, 30.02, 28.58, 27.87, 26.80, 23.43, 23.07, 14.86, 14.66.

**6:** Reaction time: 40 h; yield 62% of a white solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  = 7.64, 7.55, 7.32, 7.00 (4xd,  $^3J_{\text{HH}}$  = 8.5 Hz, 4x2H, CH aromatic); 7.07, 7.01 (2xd,  $^3J_{\text{HH}}$  = 1.8 Hz, 2x1H, imidazole); 4.01 (t,  $^3J_{\text{HH}}$  = 6.5 Hz, 2H,  $\text{CH}_2\text{O}$ ); 2.67 (t,  $^3J_{\text{HH}}$  = 6.5 Hz, 2H,  $\text{CH}_2\text{Im}$ ); 1.85-1.78, 1.74-1.68, 1.51-1.22 (m, 26H,  $\text{CH}_2$  aliphatic); 0.88, 0.84 (2xt, 2x3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 159.94, 147.50, 141.44, 137.81, 132.64, 131.17, 129.87, 129.39, 129.07, 128.96, 128.80, 128.20, 126.83, 123.66, 115.72, 68.92, 32.68, 30.40, 30.36, 30.16, 30.11, 30.03, 26.81, 23.45, 14.88.

**11:** Esterification of **9** and **10**. A mixture of **10** (10 mmol), DMF (5 drops) and thionyl chloride (10 mL) was refluxed in toluene (50 mL). After 2 hrs, the solvent was removed under reduced pressure, dry toluene was added which was removed under reduced pressure again to remove traces of remaining thionyl chloride. This procedure was repeated one more time. The acid chloride was dissolved in pyridine (25 mL) and this solution was added dropwise over 5 minutes to a solution of **9** (5 mmol) and 4-(*N,N*-dimethylamino)pyridine (50 mg) in pyridine (30 mL) cooled to 0 °C. The reaction was allowed to warm to room temperature and terminated after 24 hrs by precipitation of the mixture in a 1 N HCl solution. An aqueous work-up gave a crude product that was further purified by column chromatography ( $\text{SiO}_2$ , eluent EtOAc) and one recrystallization from methanol. Yield: 2.8 mmol (56%) of a white solid. NMR:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  = 8.15, 7.43, 7.32, 6.99 (4xd,  $^3J_{\text{HH}}$  = 8.5 Hz, 4x2H, CH aromatic); 7.84, 7.27, 7.22 (3xs, 3x1H, imidazole); 4.04 (t,  $^3J_{\text{HH}}$  = 6.5 Hz, 2H,  $\text{CH}_2\text{O}$ ); 2.70 (q,  $^3J_{\text{HH}}$  = 7.5 Hz, 2H,  $\text{CH}_2\text{Im}$ ); 1.84-1.78, 1.51-1.44, 1.39-1.22 (m, 20H,  $\text{CH}_2$  aliphatic); 0.88 (t,  $^3J_{\text{HH}}$  = 6.5 Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  = 165.47, 164.49, 150.83, 136.44, 135.60, 133.08, 131.23, 128.06, 123.41, 121.63, 119.19, 115.09, 69.08, 32.62, 30.37, 30.34, 30.30, 30.27, 30.07, 30.06, 29.79, 26.68, 23.40, 14.85.

**Scheme 2.** Synthesis of alkyl iodides.<sup>a</sup>

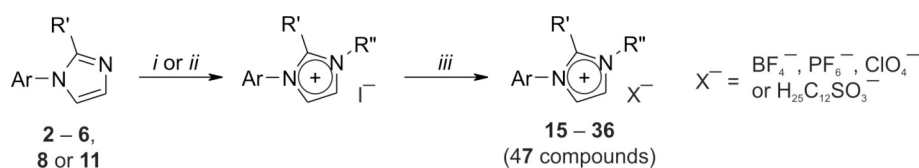
<sup>a</sup> Key: (i) NaI, acetone, 16 hrs at room temperature; (ii) KI, butanone, 16 hrs reflux

**Finkelstein reactions: alkyl bromide to alkyl iodide (12 and 13) – general procedure****(scheme 2):**

A mixture of the alkylbromide (40 mmol) and NaI (100 mmol) was stirred in acetone (50 mL) in the dark at room temperature overnight. Then the solution was filtered and the solvent was removed under reduced pressure. The residue was dissolved in hexanes and the solution was washed with dilute Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (1x) and water (3x), dried (MgSO<sub>4</sub>) and the solvent was evaporated. Additional purification was not required. Yields: 92 % (for **12**) and 94 % (for **13**) of a colorless liquid. Characterization is in correspondence with literature<sup>5,6</sup>

**Finkelstein reactions: alkyl tosylate to alkyl iodide 14 (scheme 2):**

A mixture of 3,6,9-trioxo-1-decyl tosylate (20 mmol) and NaI (50 mmol) was refluxed in butanone (50 mL) in the dark overnight. After cooling to room temperature, the solution was filtered and the solvent was removed under reduced pressure. The residue was dissolved in hexanes and the solution was washed with dilute Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (1x) and water (3x), dried (MgSO<sub>4</sub>) and the solvent was evaporated. Additional purification was not required. Yield: 76 % of a colorless liquid. Characterization is in accordance with literature.<sup>7</sup>

**Scheme 3.** Synthesis of the ILCs.<sup>a</sup>

<sup>a</sup> Key: (i) Propyl or dodecyl iodide, neat, 4–24 hrs at 100 °C; (ii) **12**, **13** or **14**, toluene, 16–40 hrs at 100 °C; (iii) Ion exchange:  $\text{BF}_4^-$  and  $\text{PF}_6^-$  by multiple washes with concentrated aqueous  $\text{NaBF}_4$  or  $\text{NH}_4\text{PF}_6$  solutions, respectively;  $\text{ClO}_4^-$  through a  $\text{AgClO}_4$  solution;  $\text{H}_{25}\text{C}_{12}\text{SO}_3^-$  (dodecyl sulphonate) through pre-functionalized beads.

**Alkylation reactions propyl iodide (15,20,23,26,28,30,33) – general procedure:**

About 200 mg of the imidazole derivative was heated in *n*-propyl iodide (ca. 3 mL) at 80 °C until TLC indicated complete conversion of the starting material (commonly 8-16 hrs). The mixture was cooled, hexanes were added and the precipitate was separated by centrifugation. The solids were dissolved in  $\text{CH}_2\text{Cl}_2$ , washed with dilute  $\text{Na}_2\text{S}_2\text{O}_5$ , water (2x) and concentrated  $\text{NaI}$  (1x), dried ( $\text{MgSO}_4$ ) and the solvent was evaporated. The crude product was dissolved in  $\text{CH}_2\text{Cl}_2$  (<1 mL) and precipitated with hexanes and centrifuged to separate off the product. This procedure was repeated 3x. After the final precipitation, the product was dissolved in  $\text{CH}_2\text{Cl}_2$  and filtered over a 0.2  $\mu\text{m}$  filter and the solvent was evaporated. About 100 mg of the product was used to prepare the tetrafluoroborate salt. The iodide was dissolved in  $\text{CH}_2\text{Cl}_2$  (25 mL) and the solution was washed with a concentrated aqueous  $\text{NaBF}_4$  solution (25 mL, 3x) and water (2x). The solution was dried ( $\text{MgSO}_4$ ) and the solvent evaporated. The sample was crystallized at least four times (as described above) and filtered over a 0.2  $\mu\text{m}$  filter. NMR data of the iodides and the  $\text{BF}_4$  salts are shown in Tables S1 ( $^1\text{H}$  NMR) and S2 ( $^{13}\text{C}$  NMR). Yields are given in Tables 2 and 3 in the paper.

**15c.** A solution of **15a** (115 mg, 0.2 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was washed with a concentrated aqueous  $\text{NH}_4\text{PF}_6$  solution (5 mL, 3x) and water (2x). The solution was dried ( $\text{MgSO}_4$ ) and the solvent evaporated. The sample was crystallized at least four times (as described above) and filtered over a 0.2  $\mu\text{m}$  filter. The NMR results are shown in Table S1 and S2. Yield: 98 % of a white solid.

**15d.** A solution of **15a** (115 mg, 0.2 mmol) in THF (20 mL) was stirred with  $\text{AgClO}_4$  (0.3 mmol) in the dark at room temperature. After 16 hrs, the dark mixture was filtered through a plug of celite. The solvent was replaced with  $\text{CH}_2\text{Cl}_2$  and the solution was washed with water (1x), dilute  $\text{Na}_2\text{S}_2\text{O}_5$  and water (2x), dried ( $\text{MgSO}_4$ ) and the solvent was evaporated. The



sample was crystallized at least four times (as described above) and filtered over a 0.2  $\mu\text{m}$  filter. The NMR results are shown in Table S1 and S2. Yield: 88 % of a white solid.

Functionalized polystyrene beads (IRA-67, Aldrich) were prefunctionalised with dodecylsulphonate anions by stirring 1 gram of dry beads with a concentrated solution of sodium dodecylsulphonate in 50 mL THF/methanol (1:1). After 24 hrs, the beads were filtered from the solution and washed with water. This procedure was repeated once more.

**15e.** A mixture of **15a** (115 mg, 0.2 mmol) and the pretreated beads (200 mg dry beads) in THF (10 mL) was stirred at room temperature. After 24 hrs, the beads were filtered off, washed with THF and fresh, pretreated beads (200 mg) were added to the solution. After stirring for another 24 hrs, the beads were removed by filtration and the solvent was replaced by  $\text{CH}_2\text{Cl}_2$ . The solution was washed with water (2x), dried ( $\text{MgSO}_4$ ) and the solvent was evaporated. The sample was crystallized at least four times (as described above) and filtered over a 0.2  $\mu\text{m}$  filter. The NMR results are shown in Table S1 and S2. Yield: 71 % of a white solid.

**33e.** For the preparation of the dodecylsulphonate salt of **33a** the procedure described above was followed. The NMR results are shown in Tables S1 and S2. Yield: 71 % of a white solid.

#### **Alkylation reactions *dodecyl iodide* (16,21,24,27,29,31,32,34):**

The general procedure described for the propyl-substituted ILCs was used, but now the imidazole derivatives were stirred in 1-iodododecane (ca. 5 mL) at 80 °C. Reaction times generally increased somewhat (16-40 hrs) compared to the propyl iodide reactions. Work-up, as described above, consisted of an initial precipitation, aqueous washing of the product and multiple crystallizations from  $\text{CH}_2\text{Cl}_2$ /hexane. After the final precipitation, the product was dissolved in  $\text{CH}_2\text{Cl}_2$  and filtered over a 0.2  $\mu\text{m}$  filter and the solvent was evaporated.

About 100 mg of the product was used to prepare the tetrafluoroborate salt. The iodide was dissolved in  $\text{CH}_2\text{Cl}_2$  (25 mL) and the solution was washed with a concentrated aqueous  $\text{NaBF}_4$  solution (25 mL, 3x) and water (2x). The solution was dried ( $\text{MgSO}_4$ ) and the solvent evaporated. The sample was crystallized at least four times (as described above) and filtered over a 0.2  $\mu\text{m}$  filter. NMR data of the iodides and the  $\text{BF}_4$  salts are shown in Tables S3 ( $^1\text{H}$  NMR) and S4 ( $^{13}\text{C}$  NMR). Yields are given in Tables 2 and 3 in the paper.

**34e.** For the preparation of the dodecylsulphonate salt from **34a** the procedure described for **15e** was followed. The NMR results are shown in Tables S3 and S4. Yield: 62 % of a white solid.

**Alkylation reactions 3,7,11-trimethyldodecyl iodide (17,22,25,35):**

A solution of the imidazole derivative (200 mg) and 1-iodo-3,7,11-trimethyldodecane (0.5 mL) in toluene (3 mL) was heated to 100 °C until TLC indicated complete conversion of the starting material (24-40 hrs). The mixture was cooled, hexanes were added and the precipitate was separated by centrifugation. The solids were dissolved in CH<sub>2</sub>Cl<sub>2</sub>, washed with dilute Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, water (2x) and concentrated NaI (1x), dried (MgSO<sub>4</sub>) and the solvent was evaporated. The crude product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (<1 mL) and precipitated with hexanes and centrifuged to separate off the product. This procedure was repeated 3x. After the final precipitation, the product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered over a 0.2 µm filter and the solvent was evaporated.

About 100 mg of the product was used to prepare the tetrafluoroborate salt. The iodide was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (25 mL) and the solution was washed with a concentrated aqueous NaBF<sub>4</sub> solution (25 mL, 3x) and water (2x). The solution was dried (MgSO<sub>4</sub>) and the solvent evaporated. The sample was crystallized at least four times (as described above) and filtered over a 0.2 µm filter. NMR data of the iodides and the BF<sub>4</sub> salts are shown in Tables S5 (<sup>1</sup>H NMR) and S6 (<sup>13</sup>C NMR). Yields are given in Tables 2 and 3 in the paper.

**Alkylation reactions citronellyl iodide (18):**

The procedure described for the trimethyldodecyl-substituted ILCs was followed (see above). The NMR results of the iodide and the BF<sub>4</sub> salt are shown in Tables S7 (<sup>1</sup>H NMR) and S8 (<sup>13</sup>C NMR). Yields are given in Tables 2 and 3 in the paper.

**Alkylation reactions 3,6,9-trioxadecyl iodide (19,36):**

The procedure described for the trimethyldodecyl-substituted ILCs was followed (see above). Reactions with this particular iodide, however, proceeded much faster (4-16 hrs, dependent on the concentration).

Work-up of the glycol was hampered a little due to the fact that they poorly crystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexanes mixtures (or impurities precipitated just as well). Therefore, both **19a** and **36a** were purified by column chromatography (SiO<sub>2</sub>, eluent gradient CH<sub>2</sub>Cl<sub>2</sub>/MeOH (49:1) to CH<sub>2</sub>Cl<sub>2</sub>/MeOH (9:1), after which the iodides crystallized better. In a second run (multi-gram scale reaction), **19a** could be precipitated readily from the crude reaction mixture and chromatography was omitted. Iodides were converted to the BF<sub>4</sub> salt according to the procedures described above. The NMR results of the iodide and the BF<sub>4</sub> salt are shown in Tables S9 (<sup>1</sup>H NMR) and S10 (<sup>13</sup>C NMR). Yields are given in Tables 2 and 3 in the paper.

**Table S1:** <sup>1</sup>H NMR data of propyl-substituted ILCs. The coupling constants and integrations are as shown for compound **15a**, unless noted otherwise.

ILC	O-tail (R)	aromatic (Ar)	imidazole	2-imidazole substituents (R')	Propyl (R'')
<b>15a</b>	3.96 (t, <sup>3</sup> J <sub>HH</sub> = 6.5 Hz, 2H) 1.78 (p, <sup>3</sup> J <sub>HH</sub> = 6.5 Hz, 2H) 1.48-1.21 (m, 20H) 0.86 (t, <sup>3</sup> J <sub>HH</sub> = 6.5 Hz, 3H)	7.82 (d, <sup>3</sup> J <sub>HH</sub> = 8.5 Hz, 2H) 7.67 (d, <sup>3</sup> J <sub>HH</sub> = 8.5 Hz, 2H) 7.46 (d, <sup>3</sup> J <sub>HH</sub> = 8.5 Hz, 2H) 6.95 (d, <sup>3</sup> J <sub>HH</sub> = 8.5 Hz, 2H)	10.45 (s, 1H) 7.80 (dd, <sup>3</sup> J <sub>HH</sub> = 1.8 Hz, 1H) 7.76 (dd, <sup>3</sup> J <sub>HH</sub> = 1.8 Hz, 1H)	–	4.50 (t, <sup>3</sup> J <sub>HH</sub> = 7.0 Hz, 2H) 2.02 (m, 2H) 1.01 (t, <sup>3</sup> J <sub>HH</sub> = 7.0 Hz, 3H)
<b>15b</b>	3.98, 1.78, 1.48-1.22, 0.89	7.65, 7.62, 7.45, 6.95	9.24, 7.66, 7.56	–	4.31, 1.95, 0.98
<b>15c</b>	3.97, 1.78, 1.48-1.22, 0.89	7.63, 7.54, 7.44, 6.94	8.85, 7.56, 7.47	–	4.23, 1.92, 0.95
<b>15d</b>	3.97, 1.79, 1.48-1.22, 0.88	7.63, 7.60, 7.44, 6.94	9.26, 7.65, 7.55	–	4.31, 1.95, 0.97
<b>15e<sup>a</sup></b>	3.98, 1.80, 1.48-1.22, 0.88	7.80, 7.68, 7.47, 6.95	10.53, 7.71, 7.50	–	4.62, 1.97, 1.00
<b>20a</b>	4.02, 1.80, 1.49-1.21, 0.86	8.07, 7.92, 7.36, 6.95	10.42, 7.85, 7.70	–	4.48, 2.02, 1.00
<b>20b</b>	4.00, 1.80, 1.50-1.22, 0.86	8.05, 7.66, 7.32, 6.94	9.12, 9.65, 9.52	–	4.25, 1.93, 0.94
<b>23a</b>	3.93, 1.75, 1.45-1.20, 0.84	7.66, 6.97	10.36, 7.74, 7.67	–	4.49, 2.01, 0.99
<b>26a</b>	3.99, 1.80, 1.48-1.22, 0.87	7.69, 7.68, 7.50, 6.98	7.72, 7.38 (2xd, <sup>3</sup> J <sub>HH</sub> = 1.8 Hz)	2.79 (s, 3H)	4.30, 2.01, 1.07
<b>26b</b>	3.99, 1.81, 1.50-1.22, 0.88	7.68, 7.51, 7.50, 6.98	7.48, 7.28 (2xd, <sup>3</sup> J <sub>HH</sub> = 1.8 Hz)	2.59 (s, 3H)	4.16, 1.92, 1.03
<b>28a</b>	3.98, 1.79, 1.48-1.21, 0.85	7.70, 7.65, 7.51, 6.98	7.82, 7.37 (2xd, <sup>3</sup> J <sub>HH</sub> = 1.8 Hz)	3.13 (q, <sup>3</sup> J <sub>HH</sub> = 7.0 Hz, 2H), 1.16 (t, <sup>3</sup> J <sub>HH</sub> = 7.0 Hz, 3H)	4.32, 2.04, 1.08
<b>28b</b>	4.00, 1.81, 1.50-1.22, 0.88	7.70, 7.51, 7.50, 6.99	7.53, 7.28 (2xd, <sup>3</sup> J <sub>HH</sub> = 1.8 Hz)	3.01 (q, <sup>3</sup> J <sub>HH</sub> = 7.0 Hz, 2H), 1.14 (t, <sup>3</sup> J <sub>HH</sub> = 7.0 Hz, 3H)	4.18, 1.98, 1.06
<b>30a<sup>c</sup></b>	3.99, 1.80, 1.48-1.20, 0.89	7.71, 7.69, 7.52, 7.00	7.80, 7.37	3.09 (t, <sup>3</sup> J <sub>HH</sub> = 7.0 Hz, 2H), 1.52-1.20 (m, 6H, superposed with C <sub>12</sub> -tail), 0.86 (t, <sup>3</sup> J <sub>HH</sub> = 7.0 Hz, 2H)	4.29, 2.05, 1.09
<b>30b<sup>c</sup></b>	3.99, 1.80, 1.55-1.10, 0.87	7.67, 7.51, 7.27, 6.98	7.53, 7.49	2.96, (t, <sup>3</sup> J <sub>HH</sub> = 7.0 Hz, 2H), 1.55-1.10 (m, 6H, superposed with C <sub>12</sub> -tail), 0.76 (t, <sup>3</sup> J <sub>HH</sub> = 7.0 Hz, 2H)	4.15, 1.97, 1.05
<b>33a</b>	3.91 (t), 1.78 (m), 1.01 (t)	7.81, 7.64, 7.43, 6.93	10.54, 7.83, 7.79	–	4.50, 2.02, 0.99
<b>33e<sup>b</sup></b>	3.93 (t), 1.81 (m), 1.04 (t)	7.78, 7.65, 7.45, 6.94	10.42, 7.79, 7.59	–	4.42, 1.94, 0.96

<sup>a</sup> Additional signals from the anion: 2.88 (m, 2H), 1.87 (m, 2H), 1.42-1.22 (m, 18H overlapping with the 18H of the C<sub>12</sub> tail), 0.87 (t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 3H).<sup>b</sup> Additional signals from the anion: 2.86 (m, 2H), 1.86 (m, 2H), 1.40-1.20 (m, 18H), 0.85 (t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 3H).<sup>c</sup> Collected on a 300 MHz spectrometer.**Table S2:** <sup>13</sup>C NMR data of propyl-substituted ILCs.

ILC	O-tail	aromatic	imidazole	Im-substituents	propyl
<b>15a</b>	68.87, 32.61, 30.37, 30.33, 30.31, 30.29, 30.12, 30.05, 29.95, 26.74, 23.39, 14.84	160.23, 143.55, 133.31, 131.56, 129.01, 128.81, 122.95, 115.75	135.57, 124.11, 121.57	–	52.64, 24.51, 11.47
<b>15b</b>	68.87, 32.63, 30.39, 30.36, 30.33, 30.32, 30.14, 30.07, 29.97, 26.74, 23.41, 14.85	160.27, 143.70, 133.39, 131.55, 129.05, 128.83, 122.88, 115.75	135.14, 123.76, 121.78	–	52.68, 24.26, 11.33
<b>15c</b>	68.86, 32.67, 30.40, 30.37, 30.35, 30.33, 30.16, 30.08, 29.98, 26.77, 23.41, 14.85	160.27, 143.68, 133.36, 131.47, 128.96, 128.80, 122.99, 115.73	134.27, 123.89, 122.07	–	52.64, 24.09, 11.25
<b>15d</b>	68.86, 32.64, 30.40, 30.36, 30.34, 30.32, 30.16, 30.08, 29.98, 26.77, 23.41, 14.85	160.25, 143.55, 133.41, 131.50, 128.97, 128.80, 122.94, 115.73	134.93, 124.01, 121.98	–	52.73, 24.26, 11.40
<b>15e<sup>a</sup></b>	68.85, 32.64, 30.39, 30.37, 30.36, 30.33, 30.31, 30.26, 30.22, 30.14, 30.07, 29.97, 29.80, 26.76, 26.23, 23.40, 14.84 (some from anion)	160.20, 143.31, 133.55, 131.70, 129.00, 128.78, 122.60, 115.71	137.28, 123.38, 121.09	–	52.97, 24.44, 11.47
<b>20a</b>	69.12, 32.60, 30.35, 30.33, 30.29, 30.26, 30.07,	165.17, 164.65, 152.86, 133.14, 132.29,	135.74, 124.11, 121.88	–	52.69, 24.43, 11.49

Supporting Information: Kouwer and Swager, Ionic Liquid Crystals

	30.05, 29.77, 26.67, 23.39, 14.84	124.74, 124.19, 121.11, 115.17			
<b>20b</b>	69.15, 32.64, 30.39, 30.36, 30.32, 30.29, 30.11, 30.08, 29.83, 26.71, 23.41, 14.85	165.17, 164.66, 152.93, 133.13, 132.52, 124.71, 124.06, 122.19, 115.19	135.08, 122.17, 121.23	–	52.655, 24.16, 11.31
<b>23a</b>	69.33, 32.59, 30.34, 30.31, 30.28, 30.25, 30.06, 30.03, 29.74, 26.65, 23.37, 14.82	161.09, 127.79, 124.20, 166.66	135.45, 123.97, 121.86	–	52.50, 24.54, 11.46
<b>26a</b>	68.86, 32.62, 30.37, 30.34, 30.32, 30.29, 30.11, 30.06, 29.94, 26.75, 23.57, 14.85	160.31, 144.34, 133.38, 131.76, 128.98, 128.87, 127.35, 115.77	145.16, 123.10, 122.79	13.31	51.97, 23.40, 11.46
<b>26b</b>	68.87, 32.63, 30.39, 30.36, 30.33, 30.31, 30.14, 30.07, 29.97, 26.77, 23.47, 14.85	160.28, 144.16, 133.55, 131.79, 128.96, 128.86, 127.02, 115.75	145.07, 122.90, 122.55	11.62	51.17, 23.41, 11.08
<b>28a</b>	68.87, 32.61, 30.37, 30.33, 30.31, 30.28, 30.10, 30.05, 29.94, 26.74, 23.39, 14.84	160.33, 144.51, 133.32, 131.67, 128.99, 128.93, 127.36, 115.77	149.19, 123.62, 122.88	19.54, 13.07	51.60, 24.13, 11.89
<b>28b</b>	68.87, 32.63, 30.38, 30.35, 30.33, 30.31, 30.13, 30.07, 29.96, 26.76, 23.41, 14.85	160.32, 144.38, 133.48, 131.73, 128.98, 128.92, 127.18, 115.76	149.03, 123.47, 122.54	17.98, 12.52	50.92, 23.99, 11.66
<b>30a<sup>c</sup></b>	68.88, 32.62, 30.37, 30.34, 30.31, 30.29, 30.11, 30.06, 29.93, 26.74, 23.40, 14.85	160.35, 144.46, 133.48, 131.69, 128.98, 128.86, 127.44, 115.79	148.56, 123.57, 122.72	31.78, 27.93, 25.76, 22.49, 14.30	51.63, 23.98, 11.09
<b>30b<sup>c</sup></b>	68.15, 31.87, 29.58, 29.55, 29.36, 29.30, 29.20, 26.00, 23.14, 22.63, 14.06	159.61, 143.57, 132.89, 131.00, 128.22, 128.11, 126.45, 115.06	147.51, 122.77, 121.81	30.97, 26.79, 24.86, 21.69, 13.49	50.21, 23.38, 10.92
<b>33a</b>	70.32, 23.23, 11.22	160.19, 143.45, 133.32, 131.57, 128.97, 128.79, 122.90, 115.74	135.47, 124.25, 121.65	–	52.54, 24.53, 11.46
<b>33e<sup>b</sup></b>	70.30, 23.26, 11.22	160.16, 143.15, 133.56, 131.68, 128.91, 128.74, 122.52, 115.70	136.84, 123.72, 121.32	–	52.43, 24.43, 11.43

<sup>a</sup> Additional signals from the anion: 52.56 and more in aliphatic area overlapping with the C12-tail of the mesogen.

<sup>b</sup> Additional signals from the anion: 53.00, 32.61, 30.38, 30.36, 30.35, 30.26, 30.22, 30.06, 29.80, 26.25, 23.39, 14.84.

<sup>c</sup> Collected on a 300 MHz spectrometer.

**Table S3:**  $^1\text{H}$  NMR data of dodecyl-substituted ILCs. The coupling constants and integrations are as shown for compound **16a**, unless noted otherwise.

ILC	O-tail	aromatic	imidazole	Im-substituents	dodecyl
<b>16a</b>	3.98 (t, $^3J_{\text{HH}} = 6.5$ Hz, 2H) 1.80 (p, $^3J_{\text{HH}} = 6.5$ Hz, 2H) 1.49-1.42, 1.40-1.20 (m, 18H) 0.88/0.86 (t, $^3J_{\text{HH}} = 6.5$ Hz, 3H)	7.84 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H) 7.68 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H) 7.47 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H) 6.96 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H)	10.56 (s, 1H) 7.79 (dd, $^3J_{\text{HH}} = 1.8$ Hz, 1H) 7.67 (dd, $^3J_{\text{HH}} = 1.8$ Hz, 1H)	–	4.54 (t, $^3J_{\text{HH}} = 6.5$ Hz, 2H) 1.96 (p, $^3J_{\text{HH}} = 6.5$ Hz, 2H) 1.40-1.20 (m, 18H) 0.88 /0.86 (t, $^3J_{\text{HH}} = 6.5$ Hz, 3H)
<b>16b</b>	4.00, 1.80, 1.49-1.20, 0.86/0.85	7.65, 7.62, 7.46, 6.95	9.28, 7.64, 7.60	–	4.37, 1.91, 1.40-1.20, 0.86/0.85
<b>21a</b>	4.02, 1.80, 1.49-1.20, 0.86/0.85	8.07, 7.93, 7.35, 6.94	10.37, 7.88, 7.60	–	4.48, 1.96, 1.40-1.20, 0.86/0.85
<b>21b</b> <sup>a</sup>	4.02, 1.81, 1.53-1.15, 0.87/0.85	8.06, 7.66, 7.32, 7.94	9.11, 7.68, 7.50	–	4.28, 1.89, 1.40-1.15, 0.87/0.85
<b>24a</b>	3.96, 1.78, 1.48-1.20, 0.86/0.85	7.69, 7.02	10.45, 7.57, 7.53	–	4.53, 1.97, 1.40-1.20, 0.87/0.86
<b>24b</b> <sup>a</sup>	3.94, 1.77, 1.50-1.18, 0.86/0.85	7.50, 6.98	9.08, 7.58, 7.52	–	4.29, 1.89, 1.38-1.18, 0.86/0.85
<b>27a</b>	4.00, 1.81, 1.51-1.20, 0.88/0.87	7.71, 7.70, 7.51, 6.99	7.66, 7.40	2.80 (s, 3H)	4.31, 1.95, 1.40-1.20, 0.88/0.87
<b>27b</b>	3.99, 1.81, 1.48-1.20, 0.89/0.87	7.67, 7.51, 7.50, 6.98	7.43, 7.28	2.58 (s, 3H)	4.15, 1.87, 1.40-1.20, 0.89/0.87
<b>29a</b>	4.00, 1.81, 1.50-1.21, 0.87	7.72, 7.70, 7.52, 6.99	7.69, 7.35	3.14 (q, $^3J_{\text{HH}} = 7.0$ Hz, 2H) 1.18 (t, $^3J_{\text{HH}} = 7.0$ Hz, 3H)	4.33, 1.98, 1.41-1.21, 0.87
<b>29b</b>	4.00, 1.81, 1.50-1.21, 0.88	7.70, 7.52, 7.51, 6.98	7.48, 7.29	3.02 (q, $^3J_{\text{HH}} = 7.0$ Hz, 2H) 1.15 (t, $^3J_{\text{HH}} = 7.0$ Hz, 3H)	4.20, 1.92, 1.41-1.21, 0.88
<b>31a</b>	4.01, 1.81, 1.48-1.20, 0.86	7.71, 7.70, 7.54, 7.00	7.63, 7.32	3.10 (br t, 2H), 1.48-1.20 (m, 6H), 0.86 (m, 3H)	4.30, 1.85, 1.40-1.10, 0.86
<b>31b</b> <sup>a</sup>	4.00, 1.82, 1.48-1.20, 0.86-0.84	7.70, 7.69, 7.50, 6.96	7.50, 7.30	2.95 (t, 2H); 1.48-1.20 (m, 6H), 0.86-0.84 (m, 3H)	4.17, 1.89, 1.48-1.20, 0.86-0.84
<b>32a</b>	3.94, 1.76, 1.46-1.10, 0.85/0.84	7.70, 7.46, 7.38, 6.90	8.04, 7.69	7.56-7.43 (m, 5H)	4.21, 1.85, 1.46-1.10, 0.85/0.84
<b>32b</b>	3.93, 1.78, 1.48-1.10, 0.86/0.85	7.69, 7.44, 7.32, 6.88	7.92, 7.63	7.56-7.40 (m, 5H)	4.21, 1.87, 1.48-1.10, 0.86/0.85
<b>33a</b>	3.94, 1.82 (m, 2H), 1.04 (t, 3H)	7.82, 7.67, 7.46, 6.95	10.55, 7.77, 7.64	–	4.52, 1.96, 1.40-1.16, 0.85
<b>33b</b> <sup>a</sup>	3.94, 1.82 (m, 2H), 1.05 (t, 3H)	7.62, 7.59, 7.43, 6.94	9.18, 7.65, 7.50	–	4.29, 1.90, 1.38-1.18, 0.86
<b>33e</b> <sup>a,b</sup>	3.97, 1.84 (m, 4H), 1.06 (t, 3H)	7.80, 7.72, 7.50, 7.98	10.57, 7.59, 7.37	–	4.53, 1.95, 1.45-1.18, 0.87

<sup>a</sup> Collected on a 300 MHz spectrometer.<sup>b</sup> Additional signals from the anion: 2.88 (m, 2H), ~1.85 (m, 2H), 1.45-1.18 (m, 18H overlapping with the 18H of the C<sub>12</sub> tail), 0.87 (t,  $^3J_{\text{HH}} = 7.0$  Hz, 3H).

**Table S4:**  $^{13}\text{C}$  NMR data of dodecyl-substituted ILCs.

ILC	O-tail	aromatic	imidazole	Im-substituents	dodecyl substituent
<b>16a</b>	68.86, further aliphatic unresolved – peak listing at dodecyl group	160.25, 143.56, 133.30, 131.53, 129.00, 128.81, 122.94, 115.75	135.64, 123.86, 121.51	–	51.37, 32.61, 32.60, 31.07, 30.37, 30.34, 30.32, 30.30, 30.23, 30.13, 30.11, 30.06, 30.04, 29.95, 29.77, 26.97, 26.75, 23.39, 23.38, 14.84
<b>16b</b>	68.86, further aliphatic unresolved – peak listing at dodecyl group	160.27, 143.71, 133.39, 131.56, 129.04, 128.80, 122.87, 115.76	135.21, 123.61, 121.71	–	51.27, 32.63, 32.62, 30.75, 30.37, 30.35, 30.32, 30.30, 30.24, 30.14, 30.12, 30.06, 30.04, 29.96, 29.83, 26.98, 26.76, 23.40, 14.85
<b>21a</b>	69.12, further aliphatic unresolved – peak listing at dodecyl group	165.21, 164.66, 152.83, 133.14, 132.27, 124.73, 124.15, 121.11, 115.16	135.67, 123.92, 121.87	–	51.39, 32.61, 32.60, 30.36, 30.33, 30.32, 30.30, 30.29, 30.26, 30.23, 30.11, 30.07, 30.05, 30.04, 29.78, 29.75, 26.97, 26.67, 23.38, 14.84
<b>21b<sup>a</sup></b>	69.15, further aliphatic unresolved – peak listing at dodecyl group	165.18, 164.67, 152.88, 133.13, 132.52, 124.68, 123.99, 122.17, 115.18	134.97, 123.97, 121.22	–	51.29, 32.64, 30.81, 30.35, 30.12, 30.08, 29.83, 29.74, 26.99, 26.72, 23.41, 14.84
<b>24a</b>	69.36, further aliphatic unresolved – peak listing at dodecyl group	161.19, 127.76, 124.24, 11.72	135.87, 123.35, 121.55	–	51.35, 32.62, 32.60, 31.07, 30.37, 30.34, 30.31, 30.30, 30.28, 30.22, 30.10, 30.08, 30.06, 30.04, 29.77, 29.76, 26.97, 26.66, 23.39, 14.84
<b>24b<sup>a</sup></b>	69.34, further aliphatic unresolved – peak listing at dodecyl group	161.16, 127.96, 124.12, 116.67	134.76, 123.78, 122.28	–	51.18, 32.63, 30.93, 30.34, 30.13, 30.07, 29.82, 29.74, 26.97, 26.71, 23.40, 14.83
<b>27a</b>	68.86, further aliphatic unresolved – peak listing at dodecyl group	160.31, 144.31, 133.40, 131.75, 128.97, 128.85, 127.37, 115.76	145.13, 123.15, 122.62	13.36	50.61, 32.62, 32.60, 30.37, 30.34, 30.32, 30.29, 30.24, 30.15, 30.11, 30.08, 30.06, 30.04, 29.94, 29.83, 27.29, 26.75, 23.40, 14.84
<b>27b</b>	69.85, further aliphatic unresolved – peak listing at dodecyl group	160.27, 144.09, 133.57, 131.77, 128.94, 128.81, 127.01, 115.74	144.96, 122.95, 122.43	11.08	49.74, 32.63, 32.62, 30.39, 30.36, 30.33, 30.32, 30.27, 30.17, 30.14, 30.07, 30.06, 29.97, 29.82, 27.21, 26.77, 23.41, 23.40, 14.85
<b>29a</b>	68.88, further aliphatic unresolved – peak listing at dodecyl group	160.36, 149.58, 133.37, 131.69, 129.00, 128.93, 127.43, 115.79	149.33, 123.56, 122.56	19.71, 13.00	50.36, 32.62, 32.61, 30.59, 30.38, 30.35, 30.32, 30.29, 30.23, 30.14, 30.11, 30.06, 30.04, 29.94, 29.84, 27.33, 26.75, 23.40, 14.85
<b>29b</b>	68.87, further aliphatic unresolved – peak listing at dodecyl group	160.27, 149.04, 133.47, 131.72, 128.98, 128.83, 127.21, 115.77	149.04, 123.48, 122.37	18.03, 12.52	49.57, 32.63, 32.62, 30.67, 30.38, 30.36, 30.33, 30.31, 30.25, 30.15, 30.13, 30.07, 30.06, 29.96, 29.83, 27.28, 26.76, 23.40, 14.85
<b>31a<sup>a</sup></b>	68.90, further aliphatic unresolved – peak listing at dodecyl group	160.36, 144.45, 133.52, 131.71, 128.96, 128.83, 127.45, 115.81	148.55, 123.64, 122.61	31.80, 27.30, 23.38, 22.49, 14.27	50.30, 32.60, 30.50, 30.30, 30.23, 30.12, 30.10, 30.03, 29.94, 29.82, 27.89, 26.74, 25.84, 14.81
<b>31b<sup>a</sup></b>	68.86, further aliphatic unresolved – peak listing at dodecyl group	160.30, 144.21, 133.63, 131.71, 128.92, 128.79, 127.17, 115.76	148.11, 123.57, 122.46	31.72, 27.23, 23.37, 22.43, 14.24	49.51, 32.60, 30.55, 30.31, 30.24, 30.13, 30.11, 30.03, 29.95, 29.79, 27.50, 26.74, 24.12, 14.80
<b>32a<sup>a</sup></b>	68.84, further aliphatic unresolved – peak listing at dodecyl group	160.20, 145.06, 133.74, 131.67, 128.82, 128.35, 127.16, 115.68	143.50, 123.77, 121.91	133.09, 132.00, 130.24, 124.41	50.93, 32.58, 30.40, 30.27, 30.23, 30.12, 30.07, 30.01, 29.90, 29.82, 27.90, 26.70, 14.79

<b>32b</b>	68.65, further aliphatic unresolved – peak listing at dodecyl group	160.01, 144.88, 133.64, 131.66, 128.84, 128.74, 127.02, 115.64	143.15, 123.62, 121.78	133.02, 131.88, 130.21, 124.44	50.43, 32.59, 30.43, 30.30, 30.24, 30.14, 30.08, 30.02, 29.90, 29.82, 27.62, 26.72, 14.80
<b>33a</b>	70.33, 23.25, 11.23	160.25, 143.59, 133.30, 131.57, 129.05, 128.83, 122.94, 115.76	135.73, 123.72, 121.41	–	51.40, 32.60, 31.06, 30.31, 30.30, 30.22, 30.11, 30.03, 29.77, 26.97, 23.38, 14.84
<b>33b<sup>a</sup></b>	70.38, 23.32, 11.25	160.29, 143.56, 133.47, 131.59, 128.98, 128.83, 122.84, 115.80	134.88, 123.89, 121.92	–	51.31, 32.65, 30.90, 30.36, 30.28, 30.15, 30.08, 29.75, 27.00, 23.42, 14.85
<b>33e<sup>a,b</sup></b>	70.42, 23.34, 11.88	160.28, 143.61, 133.44, 131.87, 129.18, 129.91, 122.85, 115.82	137.79, 122.97, 120.91	–	51.45, 32.68, 32.01, 31.15, 30.44, 30.38, 30.34, 30.30, 30.17, 30.13, 29.96, 29.86, 27.10, 26.25, 23.45, 14.88

<sup>a</sup> Collected on a 75 MHz spectrometer.<sup>b</sup> Additional signals from the anion: 52.98 and more in aliphatic area overlapping with the C12-tail of the mesogen.**Table S5:** <sup>1</sup>H NMR data of 3,7,11-trimethyldodecyl-substituted ILCs. The coupling constants and integrations are as shown for compound **17a**, unless noted otherwise.

ILC	O-tail	aromatic	Imidazole	trimethyldodecyl substituent
<b>17a</b>	3.95 (t, <sup>3</sup> J <sub>HH</sub> = 6.5 Hz, 2H) 1.82 (p, <sup>3</sup> J <sub>HH</sub> = 6.5 Hz, 2H) 1.50-1.20 (m, 20H) 0.86 (t, <sup>3</sup> J <sub>HH</sub> = 6.5 Hz, 3H)	7.84 (d, <sup>3</sup> J <sub>HH</sub> = 8.5 Hz, 2H) 7.64 (d, <sup>3</sup> J <sub>HH</sub> = 8.5 Hz, 2H) 7.43 (d, <sup>3</sup> J <sub>HH</sub> = 8.5 Hz, 2H) 6.93 (d, <sup>3</sup> J <sub>HH</sub> = 8.5 Hz, 2H)	10.54 (s, 1H) 7.88 (dd, <sup>3</sup> J <sub>HH</sub> = 1.8 Hz, 1H) 7.69 (dd, <sup>3</sup> J <sub>HH</sub> = 1.8 Hz, 1H)	4.59-4.46 (m, 2H) 2.03-1.94, 1.83-1.76 (m, 2H) 1.60-0.96 (m, 14H) 0.97 (d, <sup>3</sup> J <sub>HH</sub> = 6.0 Hz, 3H) 0.83-0.79 (3xd, <sup>3</sup> J <sub>HH</sub> = 6.5 Hz, 9H)
<b>17b<sup>a</sup></b>	3.96, 1.90-0.78 (m)	7.61, 7.60, 7.43, 6.93	9.18, 7.66, 7.49	4.38-4.22, 2.00-0.78 (m)
<b>22a</b>	4.03, 1.81, 1.50-1.20, 0.85	8.08, 7.95, 7.36, 6.95	10.38, 7.89, 7.52	4.53-4.46, 2.03-1.94, 1.83-1.76, 1.60-0.96, 0.98, 0.83-0.79.
<b>22b</b>	4.03, 1.82, 1.50-1.20, 0.85	8.09, 7.68, 7.35, 6.96	9.13, 7.64, 7.44	4.39-4.26, 1.98-1.88, 1.77-1.68, 1.60-0.99, 0.96, 0.90-0.80.
<b>25a</b>	3.96, 1.77, 1.50-1.20, 0.85	7.69, 7.01	10.42, 7.58, 7.50	4.61-4.48, 2.02-1.94, 1.84-1.76, 1.58-0.98, 0.99, 0.89-0.80
<b>25b<sup>a</sup></b>	3.94, 1.90-0.78 (m)	7.50, 6.97	9.10, 7.59, 7.51	4.42-4.20, 2.00-0.78 (m)
<b>35a</b>	3.92, 1.80 (m, 2H), 1.03 (t, 3H)	7.83, 7.64, 7.43, 6.93	10.55, 7.84, 7.65	4.58-4.47, 2.02-1.94, 1.81-1.73, 1.56-0.95, 0.98, 0.83-0.78
<b>35b<sup>a</sup></b>	3.93, 1.82 (m, 2H), 1.04 (t, 3H)	7.60, 7.59, 7.41, 6.92	9.19, 7.70, 7.52	4.40-4.18, 2.02-0.78 (m)

<sup>a</sup> Collected on a 300 MHz spectrometer.

**Table S6:**  $^{13}\text{C}$  NMR data of 3,7,11-trimethyldodecyl -substituted ILCs.

ILC	O-tail	aromatic	Imidazole	trimethyldodecyl substituent <sup>a</sup>
<b>17a</b>	68.87, 32.60, 30.35, 30.32, 30.30, 30.28, 30.11, 30.04, 29.94, 26.74, 23.37, 14.83	160.21, 143.41, 133.31, 131.53, 128.92, 128.77, 122.90, 115.71	135.49, 123.93, 121.81	49.67, 40.00, 38.22, 38.05, 37.95, 37.93, 37.91, 37.80, 37.79, 33.46, 33.44, 31.18, 28.63, 25.49, 25.46, 24.99, 24.97, 23.42, 23.31, 20.39, 20.30, 20.02, 19.96
<b>17b</b> <sup>b</sup>	68.92, 32.68, 30.20, 30.11, 30.04, 26.82, 23.37, 14.87	160.30, 143.51, 133.48, 131.56, 128.95, 128.82, 122.84, 115.79	134.84, 123.83, 121.99,	49.66, 40.09, 38.13, 38.07, 38.01, 37.81, 33.53, 31.25, 30.39, 28.71, 25.55, 25.02, 25.00, 23.46, 20.40, 20.32, 19.69, 19.63
<b>22a</b>	69.12, 32.63, 30.37, 30.35, 30.31, 30.27, 30.08, 30.06, 29.79, 26.69, 23.40, 14.85	165.29, 164.69, 152.89, 133.17, 132.23, 124.80, 124.16, 121.10, 115.18	135.84, 123.58, 121.70	49.81, 40.04, 38.16, 38.08, 38.07, 37.98, 37.96, 37.94, 37.93, 37.79, 37.77, 33.49, 33.48, 31.19, 28.67, 25.52, 25.50, 25.02, 25.00, 23.45, 23.34, 20.41, 20.32, 20.02, 19.95
<b>22b</b>	69.12, 32.62, 30.38, 30.35, 30.31, 30.28, 30.09, 30.06, 29.80, 26.69, 23.40, 14.85	165.23, 164.66, 152.93, 133.14, 123.41, 124.77, 123.99, 121.14, 115.16	135.09, 123.73, 122.01	49.67, 40.04, 38.79, 38.15, 38.06, 37.98, 37.96, 37.75, 37.74, 33.49, 33.48, 31.19, 28.67, 25.52, 25.50, 25.00, 24.97, 23.44, 23.34, 20.37, 20.29, 19.69, 19.62
<b>25a</b>	69.35, 32.62, 30.37, 30.34, 30.31, 30.27, 30.08, 30.06, 29.76, 26.67, 23.44, 14.84	161.17, 127.77, 124.26, 116.71	135.90, 123.24, 121.65	49.73, 40.03, 38.22, 38.14, 38.06, 37.95, 37.94, 37.80, 37.79, 33.48, 33.47, 31.18, 28.67, 25.51, 25.49, 24.99, 24.98, 23.46, 23.33, 20.41, 20.32, 20.05, 19.99
<b>25b</b> <sup>b</sup>	69.32, 30.35, 30.12, 30.07, 29.82, 26.71, 23.41, 14.83	161.15, 127.98, 124.13, 116.66	134.76, 123.70, 122.36	49.53, 40.06, 38.11, 37.99, 37.79, 33.50, 32.64, 31.21, 28.68, 25.51, 24.99, 24.97, 23.43, 23.34, 20.38, 20.30, 19.67, 19.61
<b>35a</b>	70.31, 23.24, 11.22	160.21, 143.47, 133.31, 131.56, 128.97, 128.80, 122.92, 115.74	135.56, 123.83, 121.73	49.71, 40.01, 38.22, 38.12, 38.05, 37.96, 37.94, 37.80, 37.79, 33.46, 33.45, 31.19, 28.64, 25.50, 25.47, 25.00, 24.97, 23.43, 23.32, 20.40, 20.31, 20.03, 19.97
<b>35b</b> <sup>b</sup>	70.32, 23.28, 11.22	160.22, 143.39, 133.46, 131.55, 128.88, 128.76, 122.74, 115.74	134.65, 123.91, 122.04	49.59, 40.04, 38.08, 38.05, 37.97, 37.77, 33.48, 31.22, 28.66, 25.50, 24.99, 24.96, 23.43, 23.32, 20.36, 20.28, 19.63, 19.57

<sup>a</sup> Note that due to a the mixture of stereo isomers, a large number of signals from aliphatic carbon atoms is observed.

<sup>b</sup> Collected on a 75 MHz spectrometer.

**Table S7:**  $^1\text{H}$  NMR data of (*S*)-citronellyl-substituted ILCs. The coupling constants and integrations are as shown for compound **17a**, unless noted otherwise.

ILC	O-tail	aromatic	imidazole	citronellyl substituent
<b>18a</b>	3.97 (t, $^3J_{\text{HH}} = 6.5$ Hz, 2H) 1.82-1.74, 1.40-1.20 (m, 22H – incl. 2 protons from the citronellyl group) 0.86 (t, $^3J_{\text{HH}} = 6.5$ Hz, 3H)	7.83 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H) 7.66 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H) 7.45 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H) 6.95 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H)	10.56 (s, 1H) 7.85 (dd, $^3J_{\text{HH}} = 1.8$ Hz, 1H) 7.67 (dd, $^3J_{\text{HH}} = 1.8$ Hz, 1H)	5.03 (t, $^3J_{\text{HH}} = 7.0$ Hz, 1H, C=CH) 4.60-4.47 (m, 2H), 2.04-1.76 (m, 4H) 1.63 (s, 3H), 1.56 (s, 3H), 1.00 (d, $^3J_{\text{HH}} = 7.0$ Hz, 3H)
<b>18b</b> <sup>a</sup>	3.96, 1.82-1.74, 1.40-1.20, 0.86	7.61, 7.60, 7.42, 7.92	9.18, 7.67, 7.51	5.02, 4.40-4.20, 2.05-1.75, 1.62, 1.55, 0.94

<sup>a</sup> Collected on a 300 MHz spectrometer.



**Table S8:**  $^{13}\text{C}$  NMR data of (*S*)-citronellyl-substituted ILCs.

ILC	O-tail	aromatic	imidazole	citronellyl substituent
<b>18a</b>	68.85, 32.60, 30.36, 30.33, 30.31, 30.29, 30.12, 30.05, 29.95, 26.75, 23.39, 14.84	160.22, 143.48, 133.32, 131.55, 128.97, 128.80, 122.93, 115.73	135.58, 123.89, 121.71	132.39, 124.79, 49.64, 38.05, 37.37, 30.65, 26.42, 25.95, 19.93, 18.48
<b>18b</b> <sup>a</sup>	68.91, 32.67, 30.38, 30.20, 30.11, 30.03, 26.82, 23.44, 14.87	160.29, 143.50, 133.50, 131.58, 128.95, 128.82, 122.83, 115.78	134.79, 123.92, 122.02	132.40, 124.87, 49.59, 37.87, 37.36, 30.72, 26.42, 25.96, 19.61, 18.42

<sup>a</sup> Collected on a 75 MHz spectrometer.**Table S9:**  $^1\text{H}$  NMR data of 3,6,9-trioxadecyl-substituted ILCs. The coupling constants and integrations are as shown for compound **19a**, unless noted otherwise.

ILC	O-tail	aromatic	imidazole	glycol substituent
<b>19a</b>	3.99 (t, $^3J_{\text{HH}} = 6.5$ Hz, 2H) 1.82-1.74, 1.40-1.20 (m, 20H) 0.87 (t, $^3J_{\text{HH}} = 6.5$ Hz, 3H)	7.79 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H) 7.70 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H) 7.48 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H) 6.96 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H)	10.30 (s, 1H) 8.03 (dd, $^3J_{\text{HH}} = 1.8$ Hz, 1H) 7.68 (dd, $^3J_{\text{HH}} = 1.8$ Hz, 1H)	4.81 (t, $^3J_{\text{HH}} = 7.0$ Hz, 2H) 4.02-4.00, 3.72-3.70, 3.64-3.60, 3.50-3.48 (4xm, 10H) 3.30 (s, 3H)
<b>19b</b>	4.02, 1.86-1.80, 1.52-1.24, 0.90	7.74, 7.65, 7.53, 7.01	9.36, 7.86, 7.52	4.61, 3.97-3.95, 3.72-3.70, 3.67-3.63, 3.53-3.51, 3.33
<b>36a</b>	3.97, 1.86-1.79 (m, 2H), 1.05 (t, 3H)	7.77, 7.71, 7.47, 6.97	10.40, 7.97, 7.61	4.81, 4.01-3.98, 3.72-3.69, 3.65-3.59, 3.51-3.48, 3.30
<b>36b</b> <sup>a</sup>	3.95, 1.90-1.78 (m, 2H), 1.05 (t, 3H)	7.68, 7.61, 4.47, 6.96	9.24, 7.79, 7.57	4.53, 3.93-3.89, 3.69-3.57, 3.51-3.45, 3.28

**Table S10:**  $^{13}\text{C}$  NMR data of 3,6,9-trimethyldodecyl-substituted ILCs.

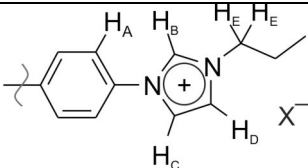
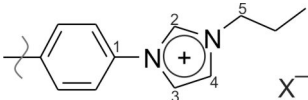
ILC	O-tail	aromatic	imidazole	glycol substituent
<b>19a</b>	68.85, 32.60, 30.35, 30.33, 30.30, 30.28, 30.10, 30.04, 29.93, 26.73, 23.38, 14.83	160.23, 143.57, 133.47, 131.61, 129.00, 128.83, 123.15, 115.74	135.81, 125.48, 121.01	72.35, 70.92, 70.87, 70.77, 69.49, 59.70, 50.91
<b>19b</b>	68.88, 32.65, 30.40, 30.37, 30.35, 30.33, 30.16, 30.09, 29.99, 26.79, 23.42, 14.86	160.25, 143.53, 133.66, 131.66, 128.96, 128.84, 125.31, 115.75	135.40, 123.09, 121.39	72.45, 70.98, 70.88, 70.77, 69.28, 59.57, 50.79
<b>36a</b>	70.35, 23.26, 11.24	160.25, 143.72, 133.48, 131.66, 129.10, 128.88, 123.12, 115.77	136.01, 125.49, 120.79	72.48, 71.00, 70.89, 70.88, 69.46, 59.66, 50.93
<b>36b</b> <sup>a</sup>	70.40, 23.31, 11.26	160.29, 143.69, 133.67, 131.73, 129.05, 128.89, 123.15, 115.82	135.56, 125.37, 121.35	72.49, 70.99, 70.90, 70.81, 69.35, 59.59, 50.87

<sup>a</sup> Collected on a 300 MHz spectrometer.

**$^1\text{H}$  and  $^{13}\text{C}$  NMR dependencies on the counter ion in 15a – 15e.**

Proton and carbon NMR analysis of the salts in deuterated chloroform showed a strong dependence of the imidazole chemical shifts on the counter ion. The results are summarized in Table S11. The largest differences in chemical shift are observed for the imidazolium proton  $\text{H}_\text{B}$  with chemical shift ranges between 8.85 and 10.53 ppm for different counter ions. The counter ion effect is also noticeable in the proton shift of the adjacent groups  $\text{H}_\text{A}$  and  $\text{H}_\text{E}$ . Carbon spectra show much smaller counter ion dependences. Only carbon atom  $\text{C}_2$  shows a significant difference in this series.

**Table S11.** Dependence of the  $^1\text{H}$  and  $^{13}\text{C}$  chemical shift on the counter ion.

LC	Anion $\text{X}^-$	 $^1\text{H}$ chemical shift $\delta$ / ppm				 $^{13}\text{C}$ chemical shift $\delta$ / ppm			
		$\text{H}_\text{A}$	$\text{H}_\text{B}$	$\text{H}_\text{C}, \text{H}_\text{D}^a$	$\text{H}_\text{E}$	$\text{C}_1$	$\text{C}_2$	$\text{C}_3, \text{C}_4^a$	$\text{C}_5$
<b>15a</b>	$\text{I}^-$	7.81	10.45	7.80, 7.76	4.50	143.55	137.57	124.11, 121.57	52.64
<b>15b</b>	$\text{BF}_4^-$	7.66	9.24	7.66, 7.56	4.31	143.70	135.14	123.76, 121.78	52.68
<b>15c</b>	$\text{PF}_6^-$	7.63	8.85	7.56, 7.47	4.23	143.68	134.27	123.89, 122.07	52.64
<b>15d</b>	$\text{ClO}_4^-$	7.64	9.26	7.65, 7.55	4.31	143.55	134.93	124.01, 121.98	52.73
<b>15e</b>	$\text{H}_{25}\text{C}_{12}\text{SO}_3^-$	7.80	10.53	7.71, 7.50	4.46	143.99	137.28	123.38, 121.09	52.97

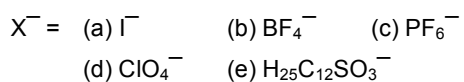
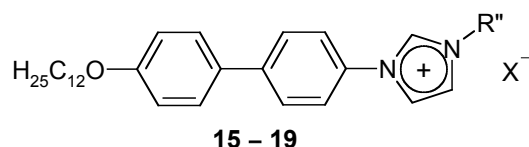
<sup>a</sup> No attempt was made to distinguish between protons  $\text{H}_\text{C}$  and  $\text{H}_\text{D}$  or carbons  $\text{C}_3$  and  $\text{C}_4$ .

## Instrumental

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian VXR-500 (500 MHz) and a Bruker AC-300 (300 MHz) spectrometer. Spectra were recorded in  $\text{CDCl}_3$  unless mentioned otherwise. Chemical shifts are reported in ppm referenced against TMS, which was added as an internal reference. Most spectra have been recorded on a Varian 500 MHz spectrometer. The spectra recorded on the Bruker 300 MHz (indicated in the tables) have substantially lower resolution. This is best noted in the aliphatic areas of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra where, in some cases, the peaks could not be deconvoluted.

Optical microscopy was carried out using standard glass microscope slides on an Olympus BX60 microscope equipped with a Mettler FP82HT hot stage and digital camera. DSC experiments were performed on a TA Instruments DSC Q100.

Variable temperature X-ray data were collected using an Inel CPS 120 position sensitive detector using an XRG 2000 generator ( $\text{Cu K}\alpha$ ) and a Minco CT 137 temperature controller. Crushed powder samples were loaded into 1.0 mm thin walled glass capillary tubes and sealed. XRD data is shown as the intensity as a function of the length of the scattering wave vector  $q$ , defined as  $q = |\mathbf{q}| = 4\pi \sin\theta / n\lambda$ , where  $\theta$  is the scattering angle,  $n$  is an integer and  $\lambda$  is the wavelength ( $\lambda_{\text{Cu},\alpha\text{K}} = 1.54 \text{ \AA}$ ). The layer spacing at a particular temperature is determined as the maximum of a fit of a Gaussian distribution to the fundamental reflection in inverse space  $q$ . Then, the (layer) spacing  $d$  was calculated by  $d_{001} = 2\pi / q_{\text{FIT}}$ , where  $q_{\text{FIT}}$  is the peak position of the fitted curve.. Temperature scans were performed as cooling runs. Because of severe hysteresis, transition temperatures observed in XRD may be lower than those recorded by DSC.

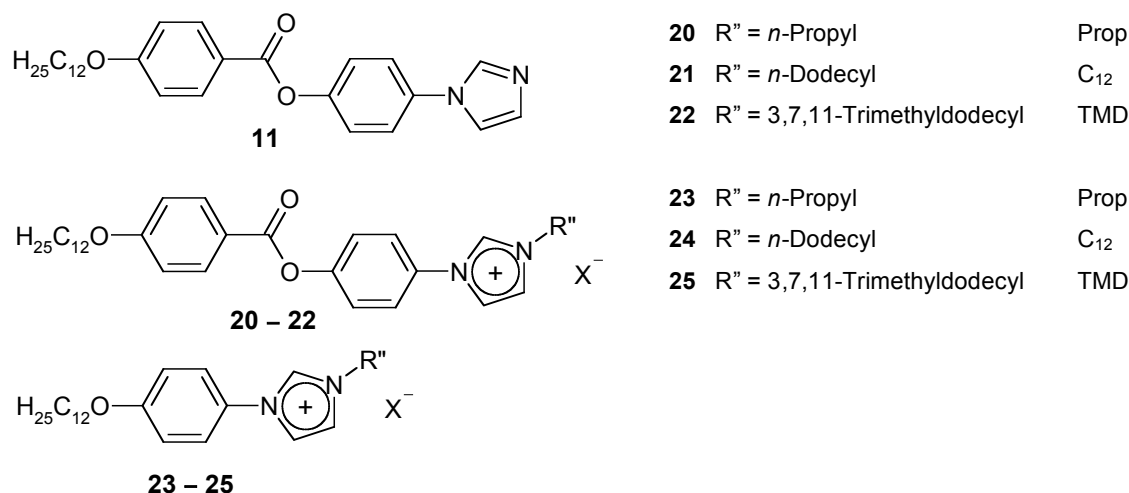
**Mesomorphic properties ionic liquid crystals 15 – 37**

<b>15</b>	$R'' = n$ -Propyl	Prop
<b>16</b>	$R'' = n$ -Dodecyl	$C_{12}$
<b>17</b>	$R'' = 3,7,11$ -Trimethyldodecyl	TMD
<b>18</b>	$R'' = (S)$ -Citronellyl	Citron
<b>19</b>	$R'' = 3,6,9$ -Trioxadecyl	EG <sub>3</sub> Me

**Chart S1:** ILC structures **15-19**.**Table S12:** Yield and mesomorphic properties of ILCs **15-19** (for structures, see Chart S1)

Mesogen	$X^-$	$y / \%$	$M$	Phase behavior: $T / ^\circ C$ and $(\Delta H / kJ mol^{-1})$					$T_{cr-cr} / ^\circ C$ ( $\Delta H / kJ mol^{-1}$ )
<b>15a</b>	$I^-$	92	574.6	Cr	93 (38.8)	SmA	220 (0.6)	I/d	30 (0.6) <sup>b</sup> 64 (22.1) <sup>c</sup> ; br $T_{cl}$
<b>16a</b>	$I^-$	86	700.9	Cr	128	SmA	> 270	d	
<b>17a</b>	$I^-$	84	742.9	CrX	151 (18.9)	SmA	235 (3.8)	I	
<b>18a</b>	$I^-$	91	670.8	CrX	152 (18.7)	SmA	222 (3.8)	I	
<b>19a</b>	$I^-$	70	678.7	G <sub>SmA</sub>	−1	SmA	70 (1.7)	I	
<b>15b</b>	$BF_4^-$	97	534.5	G <sub>SmA</sub>	8	SmA	183 (0.6)	I	67 (15.0) <sup>c</sup> ; 77 (27.0) <sup>c</sup> −14.2 <sup>d</sup>
<b>16b</b>	$BF_4^-$	98	660.7	CrX	94 (13.1)	SmA	203 (3.4)	I	
<b>17b</b>	$BF_4^-$	98	702.8	CrX	94 (14.3)	SmA	203 (3.7)	I	
<b>18b</b>	$BF_4^-$	96	630.7	CrX	94 (14.4)	SmA	168 (2.5)	I	
<b>19b</b>	$BF_4^-$	92	638.6	CrX	8 (10.4)	SmA	75 (0.16)	I	
<b>15c</b>	$PF_6^-$	98	592.7	Cr	100 (31.0)	SmA	140 (0.6)	I	84 (40.6) <sup>c</sup>
<b>15d</b>	$ClO_4^-$	88	547.2	G <sub>SmA</sub>	5	SmA	171 (0.5)	I	
<b>15e</b>	DS <sup>−a</sup>	71	697.1	Cr	105 (50.6)	SmA	181 (3.0)	I	

<sup>a</sup> DS<sup>−</sup> =  $H_{25}C_{12}SO_3^-$ ; <sup>b</sup> reversible crystal-crystal transition  $T / ^\circ C$  ( $\Delta H / kJ mol^{-1}$ ); <sup>c</sup> irreversible crystal-crystal transition (observed at 1<sup>st</sup> heating only)  $T / ^\circ C$  ( $\Delta H / kJ mol^{-1}$ ); <sup>d</sup> glass transition  $T_g / ^\circ C$ .

**Chart S2:** ILC structures **20-25** and LC precursor **11**.**Table S13:** Yield and mesomorphic properties of **11** and ILCs **20-22** (structures in Chart S2)

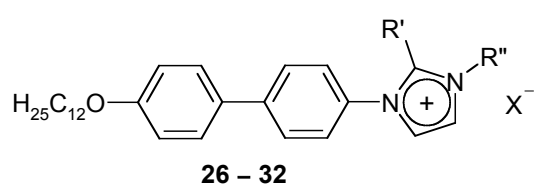
Mesogen	X <sup>−</sup>	y / %	<i>M</i>	Phase behavior: <i>T</i> / °C and (Δ <i>H</i> / kJ mol <sup>−1</sup> )					Other transitions
<b>11</b>	–	–	478.7	Cr	102 (42.8)	SmA	130 (4.2)	I	
<b>20a</b>	I <sup>−</sup>	89	618.6	CrY	140 (0.5)	SmA	214 (0.6)	I	116 (11.9) <sup>a</sup>
<b>21a</b>	I <sup>−</sup>	92	744.9	CrY	160 (43.4)	SmA	233 (4.4)	I	19 (14.8) <sup>a</sup>
<b>22a</b>	I <sup>−</sup>	90	786.9	CrZ	170 (38.0)	SmA	208 (3.4)	I	28 (4.3) <sup>a</sup> ; 47 (1.8) <sup>a</sup>
<b>20b</b>	BF <sub>4</sub> <sup>−</sup>	95	578.5	G <sub>SmA</sub>	8	SmA	175 (0.58)	I	119 (34.7) <sup>b</sup>
<b>21b</b>	BF <sub>4</sub> <sup>−</sup>	94	704.8	CrY	130 (40.3)	SmA	201 (3.8)	I	16 (14.6) <sup>a</sup>
<b>22b</b>	BF <sub>4</sub> <sup>−</sup>	96	746.8	CrY	123 (29.9)	SmA	179 (3.1)	I	26 (2.4) <sup>a</sup> ; −5.8 <sup>c</sup>

<sup>a</sup> reversible crystal-crystal transition *T* / °C ( $\Delta H$  / kJ mol<sup>−1</sup>); <sup>b</sup> irreversible crystal-crystal transition (observed at 1<sup>st</sup> heating only) *T* / °C ( $\Delta H$  / kJ mol<sup>−1</sup>); <sup>c</sup> glass transition *T<sub>g</sub>* / °C.

**Table S14:** Yield and mesomorphic properties of ILCs **23-25** (for structures, see Chart S2)

Mesogen	X <sup>−</sup>	y / %	M	Phase behavior: T / °C and (ΔH / kJ mol <sup>−1</sup> )					Other transitions
<b>23a</b>	I <sup>−</sup>	65	498.5	G <sub>SmA</sub>	1	SmA	57 (1.3)	I	79 (30.0) <sup>b</sup>
<b>24a</b>	I <sup>−</sup>	78	624.8	CrY	85 (8.5)	SmA	184 (4.0)	I	70 (29.0) <sup>a</sup>
<b>25a</b>	I <sup>−</sup>	75	666.8	CrX	83 (8.0)	SmA	153 (3.3)	I	
<b>24b</b>	BF <sub>4</sub> <sup>−</sup>	87	584.6	CrX	62 (7.5)	SmA	141 (3.0)	I	75 (69.5) <sup>b</sup>
<b>25b</b>	BF <sub>4</sub> <sup>−</sup>	90	626.7	CrX	69 (8.6)	SmA	126 (2.8)	I	

<sup>a</sup> reversible crystal-crystal transition *T* / °C ( $\Delta H$  / kJ mol<sup>−1</sup>); <sup>b</sup> irreversible crystal-crystal transition (observed at 1<sup>st</sup> heating only) *T* / °C ( $\Delta H$  / kJ mol<sup>−1</sup>).



<b>26</b>	R' = CH <sub>3</sub>	R'' = <i>n</i> -Propyl	Prop
<b>27</b>	R' = CH <sub>3</sub>	R'' = <i>n</i> -Dodecyl	C <sub>12</sub>
<b>28</b>	R' = C <sub>2</sub> H <sub>5</sub>	R'' = <i>n</i> -Propyl	Prop
<b>29</b>	R' = C <sub>2</sub> H <sub>5</sub>	R'' = <i>n</i> -Dodecyl	C <sub>12</sub>
<b>30</b>	R' = <i>n</i> -C <sub>5</sub> H <sub>11</sub>	R'' = <i>n</i> -Propyl	Prop
<b>31</b>	R' = <i>n</i> -C <sub>5</sub> H <sub>11</sub>	R'' = <i>n</i> -Dodecyl	C <sub>12</sub>
<b>32</b>	R' = C <sub>6</sub> H <sub>5</sub>	R'' = <i>n</i> -Dodecyl	C <sub>12</sub>

**Chart S3:** ILC structures **26-32****Table S15:** Yield and mesomorphic properties ILCs **26** and **27** (for structures, see Chart S3)

Mesogen	X <sup>−</sup>	y / %	M	Phase behavior: T / °C and (ΔH / kJ mol <sup>−1</sup> )					Other transitions
<b>26a</b>	I <sup>−</sup>	92	588.6	SmX?	46 (0.7)	SmA	206 (1.0)	I	11 (T <sub>g</sub> ) <sup>a</sup>
<b>27a</b>	I <sup>−</sup>	90	714.9	CrX	107 (25.3)	SmA	262 (3.6)	I/d	
<b>26b</b>	BF <sub>4</sub> <sup>−</sup>	92	548.5	SmX?	41 (0.4)	SmA	145 (0.4)	I	1 (T <sub>g</sub> ) <sup>a</sup> ; 64 (29.7) <sup>b</sup>
<b>27b</b>	BF <sub>4</sub> <sup>−</sup>	93	674.7	CrX	80 (41.8)	SmA	219 (3.2)	I/d	

<sup>a</sup> glass transition *T<sub>g</sub>* / °C; <sup>b</sup> irreversible crystal-crystal transition (observed at 1<sup>st</sup> heating only) *T* / °C ( $\Delta H$  / kJ mol<sup>-1</sup>).

**Table S16:** Yield and mesomorphic properties ILCs **28** and **29** (for structures, see Chart S3)

Mesogen	X <sup>−</sup>	y / %	M	Phase behavior: T / °C and (ΔH / kJ mol <sup>−1</sup> )					Other transitions
<b>28a</b>	I <sup>−</sup>	87	602.6	G <sub>SmA</sub>	18	SmA	148 (0.3)	I	108 (38.2) <sup>a</sup>
<b>29a</b>	I <sup>−</sup>	82	728.9	Cr	131 (34.7)	SmA	197 (2.4)	I	−10 (broad) <sup>b</sup>
<b>28b</b>	BF <sub>4</sub> <sup>−</sup>	97	562.5	G <sub>SmA</sub>	−2	SmA	123 (0.3)	I	63 (26.8) <sup>a</sup>
<b>29b</b>	BF <sub>4</sub> <sup>−</sup>	97	688.7	X?	61 (0.7)	SmA	149 (1.6)	I	−3 (T <sub>g</sub> ) <sup>c</sup>

<sup>a</sup> irreversible crystal-crystal transition (observed at 1<sup>st</sup> heating only) *T* / °C ( $\Delta H$  / kJ mol<sup>-1</sup>); <sup>b</sup> reversible crystal-crystal transition *T* / °C ( $\Delta H$  / kJ mol<sup>-1</sup>); <sup>c</sup> glass transition *T<sub>g</sub>* / °C.

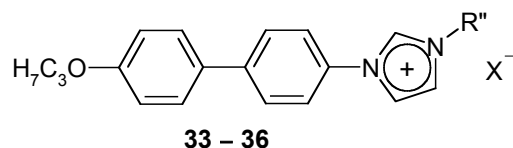
**Table S17:** Yield and properties of **30** and **31** (for structures, see Chart S3)

Mesogen	X <sup>−</sup>	y / %	<i>M</i>	Phase behavior: <i>T</i> / °C and (Δ <i>H</i> / kJ mol <sup>−1</sup> )			Other transitions
<b>30a</b>	I <sup>−</sup>	83	644.8	Cr	90 (27.5)	I	57 (6.9) <sup>a</sup> ; 101 (13.0) <sup>a</sup>
<b>31a</b>	I <sup>−</sup>	76	771.0	Cr	123 (25.6)	I	
<b>30b</b>	BF <sub>4</sub> <sup>−</sup>	98	604.6	Cr	76 (32.8)	I	
<b>31b</b>	BF <sub>4</sub> <sup>−</sup>	93	730.9	Cr	85 (25.2)	I	

<sup>a</sup> reversible crystal-crystal transition *T* / °C ( $\Delta H$  / kJ mol<sup>-1</sup>).

**Table S18:** Yield and properties of **32** (for structures, see Chart S3)

Mesogen	X <sup>-</sup>	y / %	M	Phase behavior: <i>T</i> / °C and ( $\Delta H$ / kJ mol <sup>-1</sup> )	<i>T</i> <sub>cr-cr</sub> / °C ( $\Delta H$ / kJ mol <sup>-1</sup> )
<b>32a</b>	I <sup>-</sup>	67	777.0	Cr 87 (39.0) I	
<b>32b</b>	BF <sub>4</sub> <sup>-</sup>	72	736.8	Cr 82 (27.4) I	



**33** R = *n*-Propyl Prop  
**34** R = *n*-Dodecyl C<sub>12</sub>  
**35** R = 3,7,11-Trimethyldodecyl TMD  
**36** R = 3,6,9-Trioxadecyl EG<sub>3</sub>Me

**Chart S4:** ILC structures **33-36**.**Table S19:** Yield and properties of **32** and **33** (for structures, see Chart S3)

Mesogen	X <sup>-</sup>	y / %	M	Phase behavior: <i>T</i> / °C and ( $\Delta H$ / kJ mol <sup>-1</sup> )	<i>T</i> <sub>cr-cr</sub> / °C ( $\Delta H$ / kJ mol <sup>-1</sup> )
<b>33a</b>	I <sup>-</sup>	80	448.4	G <sub>Iso</sub> 36 – I	147 (34.0) <sup>a</sup>
<b>34a</b>	I <sup>-</sup>	90	574.6	CrX 120 (14.3) SmA 199 (4.2) I	
<b>35a</b>	I <sup>-</sup>	92	616.7	CrX 143 (15.8) SmA 189 (4.2) I	12 ( <i>T</i> <sub>g</sub> ) <sup>b</sup>
<b>36a</b>	I <sup>-</sup>	59	552.5	G <sub>Iso</sub> -24 I	147 (8.3) <sup>a</sup>
<b>34b</b>	BF <sub>4</sub> <sup>-</sup>	96	534.5	G <sub>SmA</sub> -8 SmA 121 (2.1) I	
<b>35b</b>	BF <sub>4</sub> <sup>-</sup>	93	576.6	CrX 68 (4.4) SmA 132 (3.3) I	74 (10.3) <sup>c</sup>
<b>36b</b>	BF <sub>4</sub> <sup>-</sup>	67	512.4	G <sub>Iso</sub> -30 I	
<b>33e</b>	DS <sup>-</sup>	71	570.9	Cr 104 (54.4) I	
<b>34e</b>	DS <sup>-</sup>	62	697.1	Cr 135 (37.4) I	

<sup>a</sup> irreversible crystal-crystal transition (observed at 1<sup>st</sup> heating only) *T* / °C ( $\Delta H$  / kJ mol<sup>-1</sup>); <sup>b</sup> glass transition *T*<sub>g</sub> / °C; <sup>c</sup> reversible crystal-crystal transition *T* / °C ( $\Delta H$  / kJ mol<sup>-1</sup>).

## X-ray diffraction results of selected mesogens

**Table S20:** Phase behavior and XRD results: Effect of the alkyl substituent

Mesogen	$X^-$	$T_{\text{Iso}} / \text{K}$	$L_{\text{calc}} / \text{\AA}$	@ $T = 0.95 \cdot T_{\text{Iso}}$			@ $T = 0.90 \cdot T_{\text{Iso}}$			$\frac{L_{0.90} / L_c}{L_{0.95} / L_c}$
				$T / \text{K}$	$l_{\text{XRD}} / \text{\AA}$	$L / L_c$	$T / \text{K}$	$l_{\text{XRD}} / \text{\AA}$	$L / L_c$	
<b>15b</b>	Prop	456	30.5	433	44.5	0.73	410	46.9	0.77	0.039
<b>16b</b>	C <sub>12</sub>	476	41.5	452	31.7	0.76	428	32.3	0.78	0.014
<b>17b</b>	TMD	476	41.2	452	30.9	0.75	428	31.4	0.76	0.012
<b>18b</b>	Citron	441	36.7	419	29.5	0.80	397	29.8	0.81	0.007
<b>19b</b>	EG <sub>3</sub> Me	348	38.0	331	48.4	0.64	313	53.3	0.70	0.065
<b>19b</b> + 0.5 eq. LiBF <sub>4</sub>		428	38.0	407	45.5	0.60	385	47.2	0.62	0.022
<b>19b</b> + 1 eq. LiBF <sub>4</sub>		468	38.0	445	45.2	0.59	421	46.8	0.62	0.021

**Table S20:** Phase behavior and XRD results: Effect of the counter ion

Mesogen	$X^-$	$T_{\text{Iso}} / \text{K}$	$L_{\text{calc}} / \text{\AA}$	@ $T = 0.95 \cdot T_{\text{Iso}}$			@ $T = 0.90 \cdot T_{\text{Iso}}$			$\frac{L_{0.90} / L_c}{L_{0.95} / L_c}$
				$T / \text{K}$	$l_{\text{XRD}} / \text{\AA}$	$L / L_c$	$T / \text{K}$	$l_{\text{XRD}} / \text{\AA}$	$L / L_c$	
<b>15a</b>	I <sup>-</sup>	493	30.5	468	41	0.67	444	44.7	0.73	0.061
<b>15b</b>	BF <sub>4</sub> <sup>-</sup>	456	30.5	433	44.5	0.73	410	46.9	0.77	0.039
<b>15c</b>	PF <sub>6</sub> <sup>-</sup>	413	30.5	392	45.5	0.75	372	47.5	0.78	0.033
<b>15d</b>	ClO <sub>4</sub> <sup>-</sup>	444	30.5	422	43.5	0.71	400	46.3	0.76	0.046
<b>15e</b>	DS <sup>-</sup>	454	44.2	431	32	0.72	409	33.0	0.75	0.023

**Table S21:** Phase behavior and XRD results: Effect of the core size (R = C<sub>12</sub>H<sub>25</sub>)

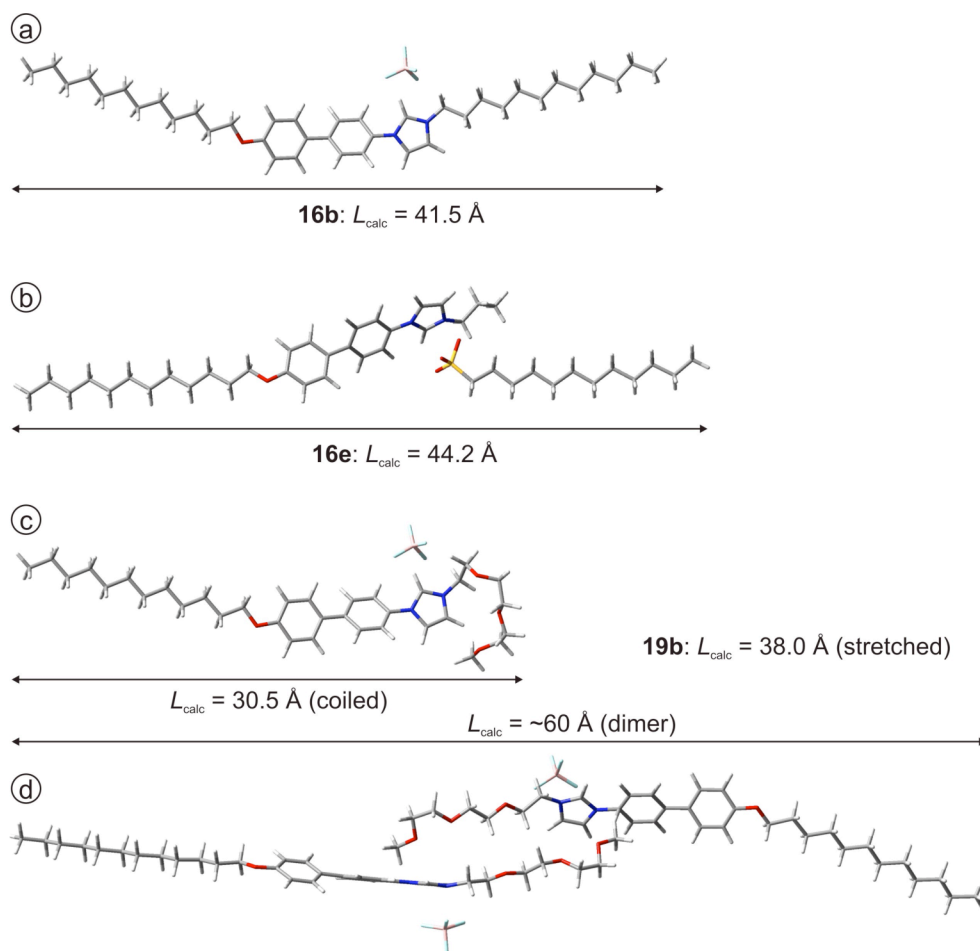
Mesogen	core	$T_{\text{Iso}} / \text{K}$	$L_{\text{calc}} / \text{\AA}$	@ $T = 0.95 \cdot T_{\text{Iso}}$			@ $T = 0.90 \cdot T_{\text{Iso}}$			$\frac{L_{0.90} / L_c}{L_{0.95} / L_c}$
				$T / \text{K}$	$l_{\text{XRD}} / \text{\AA}$	$L / L_c$	$T / \text{K}$	$l_{\text{XRD}} / \text{\AA}$	$L / L_c$	
<b>16b</b>	PhPhIm	476	41.5	452	31.7	0.76	428	32.3	0.78	0.014
<b>21b</b>	PhCO <sub>2</sub> PhIm	474	44	450	32.9	0.75	427	33.7	0.77	0.019
<b>24b</b>	PhIm	457	37.5	434	26.4	0.70	411	27.0	0.72	0.015
<b>27b</b>	PhPhMeIm	492	41.5	467	30.5	0.73	443	30.7	0.74	0.005
<b>29b</b>	PhPhEtIm	422	41.5	401	30.9	0.74	380	31.2	0.75	0.008



## Molecular modeling

All structures were first subjected to structural minimization by molecular mechanics,<sup>23a</sup> which yielded extended all-trans conformations (Figure S1a). When the dodecylsulphonate group was used as anion (Figure S1b) we also obtained fully extended structures and reliable values for the molecular length. The structures of three selected mesogens did not change significantly after subjecting them to more advanced semi-empirical or *ab initio* methods (AM1, PM3 and Hartree-Fock STO, 6-31G\* force fields).<sup>23b</sup> Since the main purpose of this study was to define the molecular dimensions of the extended geometry of the mesogens (to be compared with the XRD results), further theoretical analysis of the structures was not pursued.

Interesting behavior was observed for the glycol material **19b**. Calculations by multiple methods (all single molecule in the gas phase) showed that the oligoethyleneglycol tail was not extended, but rather folded over in order to interact with the imidazolium cation with the oxygen atoms pointing towards the charged ring (Figure S1c). This tail-imidazolium interaction is likely the cause for the unusual mesomorphic properties that this particular material displays. Molecular dynamics studies of two mesogenic groups also give strongly interdigitated dimers wherein, the glycol tail of one mesogen interacts with the imidazolium group of the other and *vice versa*. Such structures could be considered more favorable since the glycol tails are more extended and are the structures are also consistent with the large degree of interdigitation observed in x-ray diffraction experiments. The “dimer” shown in Figure S1d is energy minimized. However, to obtain a more reliable picture, one would need to minimize a sufficiently large ensemble of these molecules, which lies far beyond our own capabilities.



**Figure S1.** Minimized structures of (a) **16b**; (b) **15e**; and (c) **15d**. The dimeric structure in (d) represents the strongly interdigitated bilayered structure with glycol-imidazolium interactions, discussed in the text.

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(b) Gaussian 03W Version 6.0.