Experimental Section

**General Methods.** N-(Trimethylsilyl)imidazole, NaBF$_4$, NaClO$_4$, NH$_4$PF$_6$, lithium trifluoromethanesulfonate and lithium bis(trifluoromethanesulfonyl) amide were purchased from ACROS and used without further purification. 1-Chlorodecane, 1-chlorotetradecane, 1-chlorohexadecane, and 1-chlorooctadecane were purchased from Fluka and used as received. 1,3-didodecylimidazolium chloride, 1,3-didodecylimidazolium tetrafluoroborate, [C$_{12}$C$_{12}$IM][BF$_4$], was synthesized according to our previously reported method.¹
$^1$H NMR spectra were recorded on JEOL 400 MHz and 270 MHz instruments, operating at respective frequencies of 399.782 MHz and 269.714 MHz with a probe temperature of 23 °C. $^{13}$C NMR spectra were recorded on JEOL 400 MHz and 270 MHz instruments operating at respective frequencies of 100.525 MHz and 67.82 MHz with a probe temperature of 23 °C. Chemical shifts were reported relative to the peak for SiMe$_4$ using $^1$H (residual) chemical shifts of the solvent as a secondary standard and are reported in ppm. Elemental analysis results for C, H, and N were obtained from the Analytical Laboratories at the Friedrich-Alexander-University Erlangen-Nürnberg (Erlangen, Germany).

**Preparation of [C$_{12}$C$_{12}$IM][PF$_6$].** To a solution (10 mL) of 1,3-didodecylimidazolium chloride (0.974 g, 2.21 mmol) in acetonitrile was added NH$_4$PF$_6$ (1.1 g, 6.64 mmol). The mixture was stirred for 2 h, followed by removal of the solvent. Dichloromethane (10 mL) was then added to the solids and the resulting mixture was filtered. The filtrate was evaporated to dryness to give 1,3-didodecylimidazolium hexafluorophosphate. Yield: 1.168 g (96 %). $^1$H NMR (270 MHz, DMSO-$d_6$): $\delta$ 9.15 (s, 1H, imidazole C(2)H), 7.75 (d, $J = 1.2$ Hz, 2H, imidazole CH=CH), 4.11 (t, $J = 7.0$ Hz, 4H, NCH$_4$), 1.74 (quintet, $J = 6.8$ Hz, NCH$_2$CH$_2$), 1.19 (m, 36H, (CH$_2$)$_n$), 0.81 (t, $J = 6.5$ Hz, CH$_3$). $^{13}$C{$^1$H} NMR (67.5 MHz, DMSO-$d_6$): $\delta$ 136.46, 123.01, 49.37, 31.84, 29.74, 29.57, 29.46, 29.40, 29.26, 28.85, 25.97, 22.63, 14.44.

Anal. Calcd for C$_{27}$H$_{53}$N$_2$PF$_6$: C, 58.89; H, 9.70; N, 5.09. Found: C, 59.18; H, 10.08; N, 5.08.

**Preparation of [C$_{12}$C$_{12}$IM][CF$_3$SO$_3$].** Lithium trifluoromethanesulfonate (467 mg, 2.99 mmol) was added to a solution of 1,3-didodecylimidazolium chloride (1.2 g, 2.72 mmol) in 10 mL dichloromethane and stirred for 2 days. The suspension was filtered to remove precipitated lithium chloride salt and the organic phase was washed with small amounts of water (ca. 30 mL) until no precipitation of AgCl was observed in the aqueous phase on addition of a concentrated AgNO$_3$ solution. The organic phase was then washed with water to ensure complete removal of the lithium chloride salt. The solvent
was removed in vacuo and the resulting ionic liquid was dried at 70 °C in vacuo for 24 h.
Yield: 1.22 g (81%). \(^1\)H NMR (270 MHz, DMSO-\(d_6\)): \(\delta\) 9.18 (s, 1H, imidazole C(2)H), 7.79 (s, 2H, imidazole CH=CH), 4.14 (t, \(J = 7.0\) Hz, 4H, NCH\(_2\)) 1.74 (quintet, \(J = 6.2\) Hz, NCH\(_2\)CH\(_2\)), 1.22 (m, 36H, (CH\(_2\))\(_n\) ), 0.84 (t, \(J = 6.2\) Hz, CH\(_3\)). \(^{13}\)C\{\(^1\)H\} NMR (67.5 MHz, DMSO-\(d_6\)): \(\delta\) 135.90, 122.48, 48.83, 31.28, 29.18, 29.00, 28.90, 28.84, 28.70, 28.29, 25.41, 22.08, 13.93.

Anal. Calcd for C\(_{28}\)H\(_{53}\)N\(_2\)F\(_3\)O\(_3\)S: C, 60.62; H, 9.63; N, 5.05. Found: C, 60.93; H, 9.77; N, 5.06.

**Preparation of [C\(_{12}\)C\(_{12}\)IM][(CF\(_3\)SO\(_2\))\(_2\)N].** This compound was synthesized analogously to [C\(_{12}\)C\(_{12}\)IM][CF\(_3\)SO\(_3\)] described above: reaction of 1,3-didodecylimidazolium chloride (533 mg, 1.21 mmol) and lithium bis(trifluoromethanesulfonyl) amide (382 mg, 1.33 mmol) generates [C\(_{12}\)C\(_{12}\)IM] [(CF\(_3\)SO\(_2\))\(_2\)N]. Yield 647 mg (78 %). \(^1\)H NMR (270 MHz, DMSO-\(d_6\)): \(\delta\) 9.18 (s, 1H, imidazole C(2)H), 7.78 (s, 2H, imidazole CH=CH), 4.14 (t, \(J = 6.8\) Hz, 4H, NCH\(_2\)) 1.77 (quintet, \(J = 6.8\) Hz, NCH\(_2\)CH\(_2\)), 1.22 (m, 36H, (CH\(_2\))\(_n\) ), 0.84 (t, \(J = 6.2\) Hz, CH\(_3\)). \(^{13}\)C\{\(^1\)H\} NMR (67.5 MHz, DMSO-\(d_6\)): \(\delta\) 136.44, 122.99, 49.36, 31.82, 29.72, 29.56, 29.43, 29.37, 29.24, 28.82, 25.94, 22.61, 14.41.


**Preparation of [C\(_{10}\)C\(_{10}\)IM][BF\(_4\)].** To a solution of 1,3-decylimidazolium chloride (1.2 g, 3.12 mmol) in acetone (10 mL) was added NaBF\(_4\) (0.41 g, 3.74 mmol). The mixture was stirred for 2 days, followed by complete removal of the solvent in vacuo. Dicloromethane (10 mL) was added to the solids followed by filtration of the suspension. The filtrate was evaporated to dryness to give 1,3-didecylimidazolium tetrafluoroborate. Yield: 1.27 g (93 %). \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 9.17 (s, 1H, imidazole C(2)H), 7.79 (s, 2H, imidazole CH=CH), 4.16 (t, \(J = 7.0\) Hz, 4H, NCH\(_2\)) 1.78 (quintet, \(J = 7.1\) Hz, NCH\(_2\)CH\(_2\)), 1.23 (m, 28H, (CH\(_2\))\(_n\) ), 0.85 (t, \(J = 6.8\) Hz, CH\(_3\)). \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, DMSO-\(d_6\)): \(\delta\) 136.48, 123.03, 49.43, 31.87, 29.82, 29.46, 29.44, 29.26, 28.91, 26.02, 22.67, 14.47.
Anal. Calcd for C\textsubscript{23}H\textsubscript{45}N\textsubscript{2}BF\textsubscript{4}: C, 63.30; H, 10.39; N, 6.42. Found: C, 63.54; H, 10.60; N, 6.44.

**Preparation of [C\textsubscript{10}C\textsubscript{10}IM][ClO\textsubscript{4}].** NaClO\textsubscript{4} (0.52 g, 4.24 mmol) was added to a solution of 1,3-didecylimidazolium chloride (1.09 g, 2.83 mmol) in 10 mL dichloromethane and stirred for 2 days. The suspension was filtered to remove the precipitated sodium chloride salt and the organic phase was washed with small volumes of water (ca. 30 mL) until no precipitation of AgCl occurred in the aqueous phase on addition of a concentrated AgNO\textsubscript{3} solution. The organic phase was then washed with water to ensure complete removal of the chloride salt. The solvent was removed *in vacuo* and the resulting ionic liquid was dried at 100 °C *in vacuo* for 24 h. Yield: 1.12 g (88 %). \textsuperscript{1}H NMR (400 MHz, DMSO-\textsubscript{d}\textsubscript{6}): \(\delta\) 9.20 (s, 1H, imidazole C(2)H), 7.79 (d, \(J = 1.2\) Hz, 2H, imidazole CH=CH), 4.16 (t, \(J = 7.2\) Hz, 4H, NCH\textsubscript{2}), 1.78 (quintet, \(J = 7.2\) Hz, NCH\textsubscript{2}CH\textsubscript{2}), 1.23 (m, 28H, (C\textsubscript{2}H\textsubscript{2})\textsubscript{n}), 0.85 (t, \(J = 6.8\) Hz, CH\textsubscript{3}). \textsuperscript{13}C{\textsuperscript{1}H} NMR (100 MHz, DMSO-\textsubscript{d}\textsubscript{6}): \(\delta\) 136.51, 123.05, 49.44, 31.86, 29.80, 29.45, 29.42, 29.25, 28.89, 26.02, 22.66, 14.49.

Anal. Calcd for C\textsubscript{23}H\textsubscript{45}N\textsubscript{2}ClO\textsubscript{4}: C, 61.52; H, 10.10; N, 6.24. Found: C, 61.78; H, 10.08; N, 6.54.

**Preparation of [C\textsubscript{14}C\textsubscript{14}IM][BF\textsubscript{4}].** Procedure analogous to the preparation of [C\textsubscript{10}C\textsubscript{10}IM][BF\textsubscript{4}]. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 8.86 (s, 1H, imidazole C(2)H), 7.35 (d, \(J = 1.6\) Hz, 2H, imidazole CH=CH), 4.18 (t, \(J = 7.4\) Hz, 4H, NCH\textsubscript{2}), 1.86 (quintet, \(J = 6.8\) Hz, NCH\textsubscript{2}CH\textsubscript{2}), 1.23 (m, 44H, (CH\textsubscript{2})\textsubscript{n}), 0.86 (t, \(J = 6.8\) Hz, CH\textsubscript{3}). \textsuperscript{13}C{\textsuperscript{1}H} NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 135.87, 122.34, 50.22, 31.99, 30.19, 29.77, 29.74, 29.73, 29.70, 29.61, 29.48, 29.43, 29.04, 26.29, 22.75, 14.17.

Anal. Calcd for C\textsubscript{31}H\textsubscript{61}N\textsubscript{2}BF\textsubscript{4}: C, 67.87; H, 11.21; N, 5.11. Found: C, 68.17; H, 11.24; N, 5.16.

**Preparation of [C\textsubscript{14}C\textsubscript{14}IM][ClO\textsubscript{4}].** Procedure analogous to the preparation of [C\textsubscript{10}C\textsubscript{10}IM][ClO\textsubscript{4}]. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 8.99 (s, 1H, imidazole C(2)H), 7.32
(d, J = 3.6 Hz, 2H, imidazole CH=CH), 4.21 (t, J = 7.4 Hz, 4H, NCH₂), 1.88 (quintet, J = 6.8 Hz, NCH₂CH₂), 1.24 (m, 44H, (CH₂)₅), 0.87 (t, J = 6.8 Hz, CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 136.22, 122.15, 50.40, 32.00, 30.18, 29.77, 29.73, 29.70, 29.60, 29.47, 29.44, 29.04, 26.32, 22.76, 14.19.


**Preparation of [C₁₆C₁₆IM][BF₄].** Procedure analogous to the preparation of [C₁₀C₁₀IM][BF₄]. ¹H NMR (400 MHz, CDCl₃): δ 8.93 (s, 1H, imidazole C(2)H), 7.31 (d, J = 3.6 Hz, 2H, imidazole CH=CH), 4.19 (t, J = 7.4 Hz, 4H, NCH₂), 1.87 (quintet, J = 6.6 Hz, NCH₂CH₂), 1.24 (m, 52H, (CH₂)₅), 0.87 (t, J = 6.8 Hz, CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 136.09, 122.20, 50.26, 32.00, 30.18, 29.78, 29.75, 29.74, 29.71, 29.61, 29.48, 29.44, 29.04, 26.30, 22.76, 14.18.


**Preparation of [C₁₆C₁₆IM][ClO₄].** Procedure analogous to the preparation of [C₁₀C₁₀IM][ClO₄]. ¹H NMR (400 MHz, CDCl₃): δ 9.09 (s, 1H, imidazole C(2)H), 7.28 (d, J = 1.6 Hz, 2H, imidazole CH=CH), 4.22 (t, J = 7.6 Hz, 4H, NCH₂), 1.89 (quintet, J = 7.0 Hz, NCH₂CH₂), 1.24 (m, 52H, (CH₂)₅), 0.87 (t, J = 6.8 Hz, CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 136.43, 122.04, 50.43, 32.01, 30.19, 29.80, 29.79, 29.79, 29.75, 29.71, 29.60, 29.48, 29.45, 29.04, 26.33, 22.77, 14.20.

Anal. Calcd for C₃₅H₆₉N₂ClO₄: C, 68.09; H, 11.26; N, 4.54. Found: C, 68.30; H, 11.43; N, 4.82.

**Preparation of [C₁₈C₁₈IM][BF₄].** Procedure analogous to the preparation of [C₁₀C₁₀IM][BF₄]. ¹H NMR (400 MHz, CDCl₃): δ 9.28 (s, 1H, imidazole C(2)H), 7.27 (d, J = 1.6 Hz, 2H, imidazole CH=CH), 4.22 (t, J = 7.4 Hz, 4H, NCH₂), 1.88 (quintet, J = 7.2 Hz, NCH₂CH₂), 1.24 (m, 60H, (CH₂)₅), 0.87 (t, J = 6.8 Hz, CH₃). ¹³C{¹H} NMR (100
Preparation of \([\text{C}_{18}\text{C}_{18}\text{IM}]\text{[ClO}_4]\). Procedure analogous to the preparation of \([\text{C}_{10}\text{C}_{10}\text{IM}]\text{[ClO}_4]\). \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 9.13 (s, 1H, imidazole C(2)H), 7.28 (d, \(J = 7.6\) Hz, 2H, imidazole \(CH\textasciitilde CH\)), 4.22 (t, \(J = 7.4\) Hz, 4H, NCH\textsubscript{2}), 1.89 (quintet, \(J = 6.8\) Hz, NCH\textsubscript{2}CH\textsubscript{2}), 1.24 (m, 60H, (CH\textsubscript{2})\textsubscript{n}), 0.87 (t, \(J = 6.8\) Hz, CH\textsubscript{3}). \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 136.49, 122.00, 50.43, 32.00, 30.17, 29.78, 29.74(4), 29.73(5), 29.70, 29.60, 29.47, 29.43, 29.03, 26.33, 22.76, 14.17.

Anal. Calcd for C\textsubscript{39}H\textsubscript{77}N\textsubscript{2}ClO\textsubscript{4}: C, 69.55; H, 11.52; N, 4.16. Found: C, 69.82; H, 11.82; N, 4.06.

Characterization of Physical-Chemical Properties. Differential scanning calorimetry (DSC) measurements were performed on a Netzsch DSC 204 instrument with a heating rate of 5 K min\textsuperscript{-1} in the temperature range of 273 K and 423 K. Polarized optical microscopy (POM) was carried out using a Nikon Eclipse 50i microscope equipped with a Nikon DsFi 1 digital camera and a Linkam PE95-LinkPad heating table.
Figure S1. DSC for a) $[\text{C}_{16}\text{C}_{16}\text{IM}][\text{BF}_4]$ and b) $[\text{C}_{16}\text{C}_{16}\text{IM}][\text{ClO}_4]$. 2nd heating cycle (bottom), 2nd cooling cycle (top).
Figure S2. POM images for a) $[\text{C}_{10}\text{C}_{10}\text{IM}][\text{BF}_4]$ at 7.3 °C (200 x magnification) and b) $[\text{C}_{10}\text{C}_{10}\text{IM}][\text{ClO}_4]$ at 6.3 °C (200 x magnification).
Figure S3. POM image of \( [C_{10}C_{10}IM][BF_4] \) at 17.7 °C (200 x magnification). Liquid crystalline phase re-establishes after several minutes when cooling to 17.7 °C.

Figure S4. POM image for \( [C_{14}C_{14}IM][BF_4] \) at 70 °C (200 x magnification).
Figure S5. POM image for a) $[C_{18}C_{18}IM][BF_4]$ at 120 °C (200 x magnification) and b) $[C_{18}C_{18}IM][ClO_4]$ at 120 °C.
Figure S6. POM image for the mixture of [C\textsubscript{10}C\textsubscript{10}IM][BF\textsubscript{4}] and [C\textsubscript{12}C\textsubscript{12}IM][BF\textsubscript{4}] with the molar ratio 1:3 at 40 °C.

References