Synthesis of Novel Chiral Ionic Liquids and Their Phase Behavior in Mixtures with Smectic and Nematic Liquid Crystals

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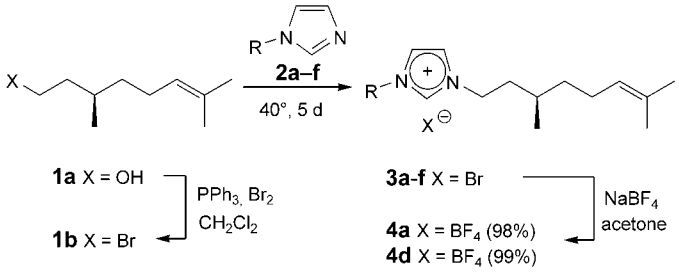
Alkylation of 1-alkyl-1*H*-imidazoles **2a**–**f** with citronellyl bromide **1b** opens access to chiral 1*H*-imidazolium bromides **3a**–**f** (*Scheme 1*). A similar strategy yielded the chiral pyridinium ionic liquid **6** (*Scheme 2*). Dialkylation of 1*H*-imidazole (**7**) gave the C_2-symmetric 1,3-dicitronellyl-1*H*-imidazolium bromide (**8**) (*Scheme 3*). Differential scanning calorimetry and optical polarizing microscopy revealed smectic mesophases for 1-citronellyl-3-tetradecy-1*H*-limidazolium bromide (**3e**) and 1-citronellylpyridinium bromide (**6**) (*Table*). In binary mixtures with smectic and nematic liquid crystals **9** and **10**, 1-citronellyl-3-methyl-1*H*-imidazolium bromide (**3a**) behaved differently. Increasing quantities of **3a** cause a decrease of the smectic-phase width for the mixture **3a**/**9** (*Fig. 3*), whereas the phase width of the nematic phase for **3a**/**10** remained nearly constant (*Fig. 4*).

Introduction. – Since the seminal work by *Seddon* and co-workers [1], *Levelut* and co-workers [2], *Haramoto* and co-workers [3], *Kresse* and co-workers [4], and others [5], it has been recognized that room temperature ionic liquids are capable of forming thermotropic mesophases. However, the issue of chiral mesogenic ionic liquids and their miscibility with common liquid crystals has been only briefly explored [7][8]. This might be due to the fact that the introduction of complex stereocenters often increases the melting point [9]. The lack of suitable chiral ionic liquids with mesogenic properties prompted us to investigate this subject in more detail. We anticipated that the combination of alkyl-1*H*-imidazolium salts with chiral moieties derived from citronellol (= 3,7-dimethyloct-6-en-1-ol) should meet the requirements of chiral mesogenic compounds and should generate suitable chiral dopants. The results towards this goal are reported below.

Results and Discussion. – The synthesis of chiral 1*H*-imidazolium salts **3** is outlined in *Scheme 1*. Following a method by *Sankaranarayanan* and *Chattopadhyay* [10], (3*R*)-citronellol (**1a**) was treated with PPh_3 and Br_2 in CH_2Cl_2 at room temperature to give the corresponding bromide **1b** in 68% yield, whereas the use of PBr_3 and pyridine [11] afforded only 25% of **1b**. Bromide **1b** was heated with 1-alkyl-1*H*-imidazoles **2a**–**f** for several days, and, after evaporation of volatile starting materials, the 1*H*-imidazolium salts **3a**–**f** were isolated as analytically pure compounds. Metathesis of 1*H*-imidazolium bromides **3a** and **3d** with sodium tetrafluoroborate in acetone yielded the corresponding salts **4a** and **4d** (*Scheme 1*).

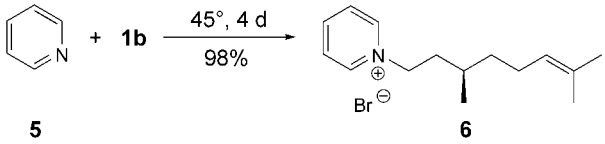
In addition, pyridinium salt **6** was prepared in 98% yield by heating pyridine (**5**) with bromide **1b** at 45° for 4 d (*Scheme 2*).

Scheme 1



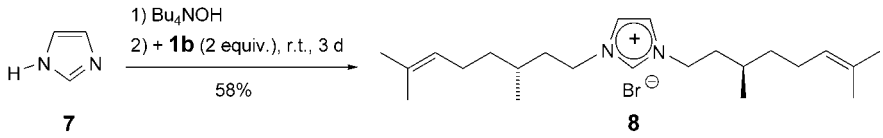
	3a	3b	3c	3d	3e	3f
R	Me	Bu	C_6H_{13}	$C_{12}H_{25}$	$C_{14}H_{29}$	$C_{18}H_{37}$
Yield [%]	78	46	84	85	94	72

Scheme 2



Dzyuba and *Bartsch* have reported surprising phase behavior of C_2-symmetric 1*H*-imidazolium salts with unbranched alkyl chains [12]. We assume that the phase behavior of a C_2-symmetric chiral 1*H*-imidazolium salt may differ from its C_1-symmetric counterparts, and thus, we prepared the 1,3-di-citronellyl-1*H*-imidazolium bromide (**8**) from 1*H*-imidazole (**7**) by deprotonation with tetrabutylammonium hydroxide and subsequent treatment with 2 equiv. of the chiral bromide **1b** to give **8** in 58% yield (*Scheme 3*).

Scheme 3



The phase behavior of compounds **3a**–**f**, **4a**,**d**, **6**, and **8** was studied by both differential scanning calorimetry (DSC) and optical polarizing microscopy. The results from DSC measurements are summarized in the *Table*. The 1*H*-imidazolium bromides **3a**–**c** with a methyl, butyl, or hexyl side chain display only glass transitions during repeated heating and cooling cycles. For the dodecyl-substituted compound **3d**, a glass transition as well as a crystalline-to-isotropic transition at 6° was observed. However, a crystalline-to-mesogenic-phase transition at 9° and a mesogenic-phase-to-isotropic transition at 45° were found for the tetradecyl-substituted salt **3e**. In contrast to the results of *Seddon* and co-workers [1], chiral 1*H*-imidazolium bromides with more than

Table. *Phase-Transition Temperatures and Enthalpies of Chiral 1*H*-Imidazolium and Pyridinium Ionic Liquids* **3**, **4**, **6**, *and* **8**

	R	X	T_g [°]	ΔC_p [kJ mol^{-1}]	T_m [°]	ΔH [kJ mol^{-1}]	T_c [°]	ΔH [kJ mol^{-1}]
3a	Me	Br	– 57	101	–	–	–	–
3b	C_4H_9	Br	– 52	159	–	–	–	–
3c	C_6H_{13}	Br	– 57	146	–	–	–	–
3d	$C_{12}H_{25}$	Br	– 70	539	6[a])	4.46	–	–
3e	$C_{14}H_{29}$	Br	–	–	9[b])	13.1	45[c])	1.26
3f	$C_{18}H_{37}$	Br	–	–	–	–	41[a])	42.8
4a	Me	BF_4	– 73	144	–	–	–	–
4d	$C_{12}H_{25}$	BF_4	–	–	7	28.1	–	–
6	–	Br	– 47	132	–	–	–	–
8	–	Br	– 56	200	–	–	–	–

[a]) Cr → I transition. [b]) Cr → mesogenic-phase transition. [c]) Mesogenic phase → I transition.

14 C-atoms in the side chain, such as octadecyl derivative **3f**, did not give a smectic A phase but revealed only isotropic melting.

Replacing bromide by tetrafluoroborate as counterion resulted in minor changes of the phase behavior in the case of **4a**. Tetrafluoroborate **4d** with the dodecyl side chain, however, displayed isotropic melting instead of a glass transition as observed for the corresponding bromide **3d**. For both chiral pyridinium bromide **6** and the C_2-symmetrical 1*H*-imidazolium bromide **8**, only a glass transition was detected. Under the optical polarizing micro-scope, tetradecyl derivative **3e** displayed textures of a mesophase upon cooling from the isotropic liquid (*Fig. 1*).

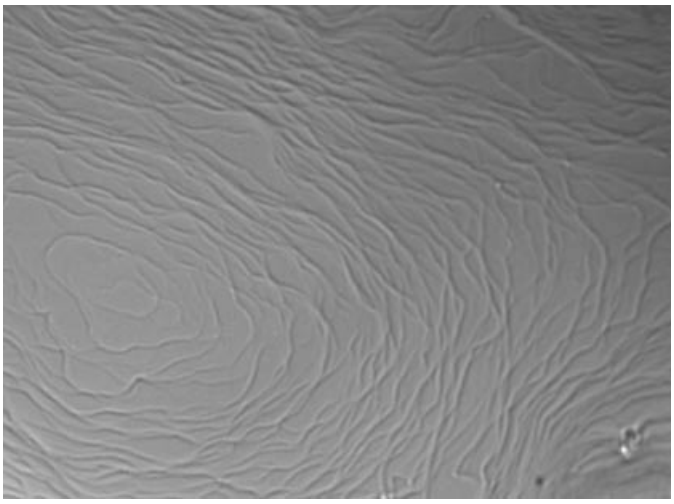


Fig. 1. *Texture of citronellyl-1*H*-imidazolium bromide* **3e** *as seen between crossed polarizers at 24° upon cooling from the isotropic liquid* (magnification 100 ×)

In contrast to the DSC curves of 1-citronellylpyridinium bromide (**6**), showing only a glass transition, a fan-shaped smectic texture was observed under the microscope (*Fig. 2*). Unfortunately, we did not obtain suitable X-ray-diffraction results from the smectic derivatives **3e** and **6** due to their extremely high viscosity.

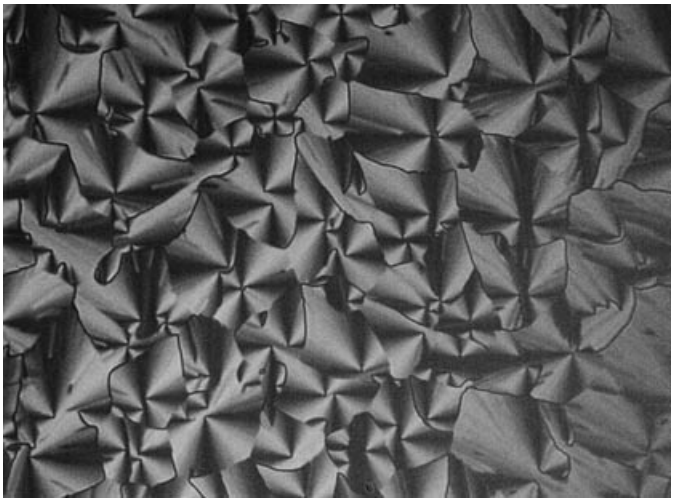
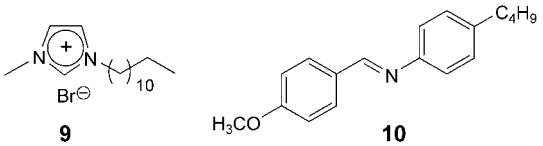


Fig. 2. *Texture of pyridinium bromide* **6** *as seen between crossed polarizers at* $-56°$ *upon cooling from the isotropic liquid* (magnification 200 ×)

Although the citronellyl moiety did not lead to the formation of chiral mesophases, we investigated the possibility of using short-chain derivative **3a** (R = Me) as a chiral dopant. Contact preparation with the known smectic mesogen **9** [1] and the nematic mesogen **10** revealed complete miscibility. Thus, binary mixtures of **3a** and **9** were studied by DSC. The resulting phase diagram is depicted in *Fig. 3*. With increasing amounts of chiral dopant **3a**, the width of the smectic A phase steadily decreased. In the case of almost equimolar quantities of **3a** and **9**, only melting was found. No additional smectic C* phase could be detected.



9 **10**

Finally, binary mixtures of 1*H*-imidazolium bromide **3a** and the nematic benzylideneaniline **10** were investigated. As can be seen from *Fig. 4*, the phase width of the nematic phase remained almost constant over an extended range (x(**3a**) = 0 – 0.7), and again no chiral mesophase was observed.

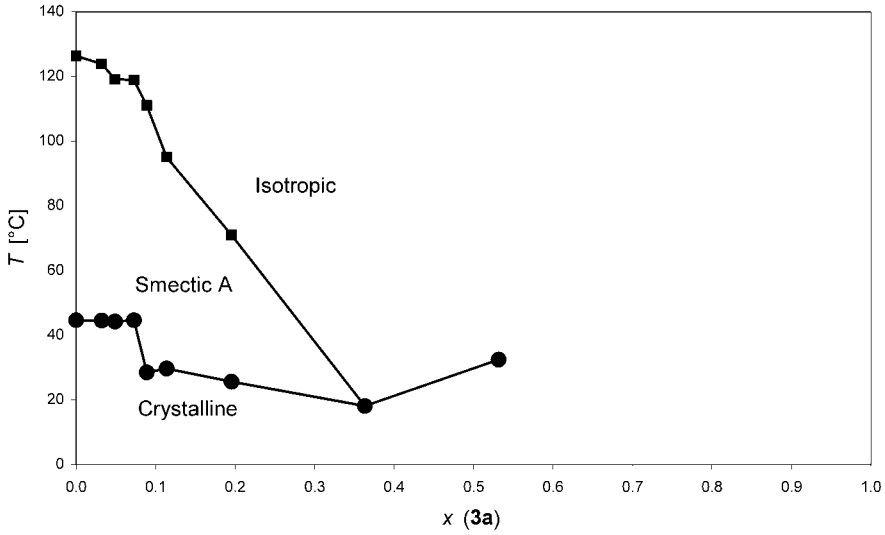


Fig. 3. *Phase diagram of a binary mixture of (*R*)-1-citronellyl-3-methyl-1*H*-imidazolium bromide* (**3a**) *and the known smectic mesogen 1-dodecyl-3-methyl-1*H*-imidazolium bromide* **9**

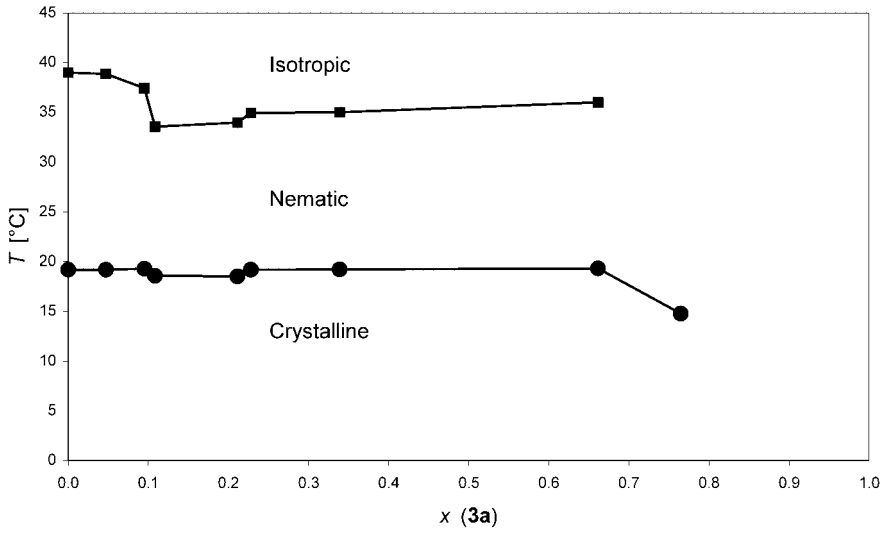


Fig. 4. *Phase diagram of a binary mixture of (*R*)-1-citronellyl-3-methyl-1*H*-imidazolium bromide* (**3a**) *and the nematic mesogen 4-butyl-*N*-[(1*E*)-(4-methoxyphenyl)methylene]benzenamine* (**10**)

Conclusions. – Chiral citronellyl-derived ionic liquids **3** with potential mesomorphic properties are conveniently available. However, the relationship between molecular structure (chain length, counterion, symmetry) and mesomorphic properties is not easily deduced as compared to the unbranched analogues. Thus, further investigations

are necessary to design chiral mesomorphic ionic liquids suitable for applications in liquid-crystal chemistry.

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Experimental Part

General. FT-IR Spectra: $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker AC-250 F* and *Bruker ARX-500*; δ in ppm and *J* in Hz. FAB-MS: *m/z* (rel. %).

*1-Butyl-1*H-*imidazole* (**2b**). To a soln. of **7** (27.2 g, 0.39 mol) in MeOH (56 ml), aq. 10N NaOH (52 ml) was added. The stirred mixture was heated to 70°, and 1-bromobutane (54.8 ml, 0.52 mol) was added dropwise over 3 h. After 2 h at r.t., the mixture was evaporated, the residue taken up in $CHCl_3$ (60 ml) and separated from precipitated NaBr, the org. soln. dried (Na_2SO_4) and evaporated, and the residue distilled under vacuum through a *Vigreux* column (20 cm): **2b** (29.0 g, 60%). B.p. 94°/8 Torr. ^{1}H-NMR (250 MHz, $CDCl_3$): 0.94 (*t*, *J* = 7.3, Me(4′)); 1.31(*m*, CH_2(3′)); 1.76 (*m*, CH_2(2′)); 3.93 (*t*, *J* = 7.1, CH_2(1′)); 6.90 (*s*, H–C(5)), 7.05 (*s*, H–C(4)), 7.46 (*s*, H–C(2)). ^{13}C-NMR (63 MHz, $CDCl_3$): 13.5 (Me(4′)); 19.7 (C(3′)); 33.1 (C(2′)); 46.7 (C(1′)); 118.8 (C(4)); 129.3 (C(5)); 137.1 (C(2)).

Preparation of **2c**–**f**: *General Procedure.* A soln. of **7** (10 mmol) in abs. THF (8 ml) was added to a stirred soln. of NaH (1.5 equiv. of a 55% suspension in oil) and abs. THF (4 ml). After stirring at r.t. for 1 h, a soln. of the 1-bromoalkane (1.0 equiv.) in abs. THF (6 ml) was added followed by Bu_4NI (*ca*. 0.03 equiv.). The mixture was stirred under N_2 at r.t. for the given times, and filtered. The filtrate was evaporated and the residue fractionally distilled under vacuum through a *Vigreux* column (20 cm).

*1-Hexyl-1*H-*imidazole* (**2c**): Reaction time 16 h, yield 2.60 g (10%). Colorless liquid. B.p. 94°/4 Torr. ^{1}H-NMR (250 MHz, $CDCl_3$): 0.87 (*t*, *J* = 6.1, Me(6′)); 1.24–1.32 (*m*, CH_2(3′), CH_2(4′), CH_2(5′)); 1.70–1.80 (*m*, CH_2(2′)); 3.91 (*t*, *J* = 7.2, CH_2(1′)); 6.89 (*s*, H–C(5)); 7.04 (*s*, H–C(4)); 7.44 (*s*, H–C(2)).

*1-Dodecyl-1*H-*imidazole* (**2d**): Reaction time 22 h, yield 6.0 g (62%). Colorless liquid. B.p. 125°/0.08 Torr. ^{1}H-NMR (250 MHz, $CDCl_3$): 0.87 (*t*, *J* = 6.1, Me(12′)), 1.25 (*m*, CH_2(3′) to CH_2(11′)); 1.77 (*m*, CH_2(2′)); 3.92 (*t*, *J* = 7.1, CH_2(1′)); 6.90 (*s*, H–C(5)); 7.04 (*s*, H–C(4)); 7.44 (*s*, H–C(2)). ^{13}C-NMR (63 MHz, $CDCl_3$): 14.1 (Me(12′)); 20.8 (C(11′)); 22.7–31.9 (C(2′) to C(10′)); 47.1 (C(1′)); 118.8 (C(4)); 129.4 (C(5)); 137.1 (C(2)).

*1-Tetradecyl-1*H-*imidazole* (**2e**): Reaction time 23 h, yield 6.47 g (66%). Colorless liquid. B.p. 142°/0.001 Torr. ^{1}H-NMR (250 MHz, $CDCl_3$): 0.96 (*t*, *J* = 7.2, Me(14′)); 1.31 (*m*, CH_2(3′) to CH_2(13′)); 1.77 (*m*, CH_2(2′)); 3.91 (*t*, *J* = 7.0, CH_2(1′)); 6.90 (*s*, H–C(5)); 7.05 (*s*, H–C(4)); 7.46 (*s*, H–C(2)).

*1-Octadecyl-1*H-*imidazole* (**2f**): Reaction time 24 h, yield 3.28 g (55%). Pale yellow solid, 110°/0.01 Torr. ^{1}H-NMR (250, $CDCl_3$): 0.88 (*t*, *J* = 6.6, Me(18′)), 1.25(*m*, CH_2(3′) to CH_2(17′)); 1.77 (*m*, CH_2(2′)); 3.92 (*t*, *J* = 7.1, CH_2(1′)); 6.90 (*s*, H–C(5)); 7.05 (*s*, H–C(4)); 7.47 (*s*, H–C(2)). ^{13}C-NMR (63 MHz, $CDCl_3$): 14.1 (Me(18′)); 22.7 (C(17′)); 26.6–31.9 (C(2′) to C(16′)); 47.1 (C(1′)); 118.8 (C(4)); 129.3 (C(5)); 137.1 (C(2)).

Preparation of **3a**–**f**: *General Procedure*. A soln. of **1b** (0.22 g, 1.0 mmol) and the respective 1-alkyl-1*H*-imidazole **2** (1.0 mmol) was heated at 40° for 5 d. Removal of volatile unreacted starting materials at 40°/0.1–0.001 Torr for 2 d gave products **3**.

*1-[(3*R*)-3,7-Dimethyloct-6-enyl]-3-methyl-1*H-*imidazolium Bromide* (**3a**): Yield 1.31 g (78%). Pale yellow viscous oil. $[\alpha]_D^{22} = -1.4$ (*c* = 1.00, $CHCl_3$). FT-IR: 3129*m* and 3052*m* (C–H, arom.), 2960*s*, 2916*s* and 2853*s* (C–H, aliph.), 1568*m*, 1452*m*, 1378*m*, 1168*vs*, 1117*w*, 1019*w*, 985*w*, 828*m*, 752*m*, 654*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.90 (*d*, *J* = 6.7, Me(3′)); 1.19–1.79 (*m*, CH_2(2′), CH_2(4′)); 1.59 (*s*, Me(8′)); 1.67 (*s*, Me(7′)); 1.91–2.03 (*m*, H–C(3′); CH_2(5′)); 4.15 (*s*, NMe); 4.29–4.39 (*m*, CH_2(1′)); 5.05 (*t*, *J* = 6.9, H–C(6′)); 7.46 (*s*, H–C(5)); 7.70 (*s*, H–C(4)); 10.40 (*s*, H–C(2)). ^{13}C-NMR (125 MHz, $CDCl_3$): 17.8 (*Me*–C(7′)); 19.1 (*Me*–C(3′)); 25.2 (C(5′)); 25.7 (C(8′)); 29.9 (C(3′)); 36.7 (C(2′)); 36.8 (MeN); 37.4 (C(4′)); 48.4 (C(1′)); 121.9 (C(5)); 123.9 (C(4));124.0 (C(6′)); 131.8, (C(7′)); 137.0 (C(2)). FAB-MS: 521 (5, $C_{28}H_{50}BrN_4^+$), 221 (100, M^+), 83 (7, $C_4H_7N_2^+$), 69 (2, $C_3H_5N_2^+$), 41 (2, $C_2H_3N^+$). Anal. calc. for $C_{14}H_{25}BrN_2$ (301.27): C 55.81, H 8.36, Br 26.52, N 9.30; found: C 55.68, H 8.31, Br 26.52, N 9.18.

*1-Butyl-3-[(3*R*)-3,7-dimethyloct-6-enyl]-1*H-*imidazolium Bromide* (**3b**): Yield 1.20 g (46%). Pale yellow viscous oil. $[\alpha]_D^{22} = -2.2$ (*c* = 1.00, $CHCl_3$). FT-IR: 3129*m* and 3050*m* (C–H, arom.), 2956*s*, 2924*s* and 2856*s* (C–H, aliph.), 1562*s*, 1455*s*, 1378*s*, 1163vs, 1118*w*, 1023*w*, 985*w*, 829*m*, 775*m*, 645*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.97 (*t*, *J* = 7.4, Me(4″)); 0.99 (*d*, *J* = 6.6, Me–C(3′)); 1.19–1.80 (*m*, CH_2(2′), CH_2(4′), CH_2(3″)); 1.59 (*s*, Me(8′)); 1.67 (*s*, Me–C(7′)); 1.90–2.05 (*m*, H–C(3′), CH_2(5′), CH_2(2″)); 4.32–4.43 (*m*, CH_2(1′), CH_2(1″)); 5.05 (*dt*, *J* = 1.1, 6.4, H–C(6′)); 7.52 (*t*, *J* = 1.7, H–C(5)); 7.64 (*t*, *J* = 1.5, H–C(4)); 10.54 (*s*, H–C(2)). ^{13}C-NMR

(125 MHz, $CDCl_3$): 13.5 (Me(4″)); 17.7 (*Me*–C(7′)); 19.1 (*Me*–C(3′)); 19.5 (C(3″)); 25.3 (C(5′)); 25.7 (C(8′)); 30.0 (C(3′)); 32.2 (C(2″)); 36.7 (C(2′)); 37.4 (C(4′)); 48.4 (C(1′)); 49.8 (C(1″)); 122.0 (C(5)); 122.4 (C(4)); 124.1 (C(6′)); 131.7 (C(7′)); 137.0 (C(2)). FAB-MS: 605 (2, $C_{34}H_{62}BrN_4^+$), 263 (100, M^+), 69 (5, $C_3H_5N_2^+$), 41 (2, $C_2H_3N^+$). Anal. calc. for $C_{17}H_{31}BrN_2$ (343.27): C 59.47, H 9.10, Br 23.27, N 8.16; found: C 58.99, H 9.08, Br 23.26, N 8.12.

*3-[(3*R*)-3,7-Dimethyloct-6-enyl]-3-hexyl-1*H*-imidazolium Bromide* (**3c**): Yield 1.58 g (84%). Pale yellow viscous oil. $[\alpha]_D^{22} = -1.1$ ($c = 1.00$, $CHCl_3$). FT-IR: 3128*m* and 3050*m* (C–H, arom.), 2958*s*, 2926*s* and 2871*s* (C–H, aliph.), 1562*s*, 1456*s*, 1377*s*, 1164*vs*, 1116*w*, 1022*w*, 985*w*, 948*w*, 827*m*, 752*m*, 633*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.87 (*t*, $J = 7.0$, Me(6″)); 0.99 (*d*, $J = 6.7$, Me–(3′)); 1.19–1.80 (*m*, CH_2(2′), CH_2(4′), CH_2(3″), CH_2(4″), CH_2(5″)); 1.59 (*s*, Me(8′)); 1.67 (*s*, Me–(7′)); 1.91–2.03 (*m*, H–C(3′), CH_2(5′), CH_2(2″)); 4.32–4.43 (*m*, CH_2(1′), CH_2(1″)); 5.05 (*dt*, $J = 1.1$, 6.4, H–C(6′)); 7.53 (*t*, $J = 1.7$, H–C(5)); 7.61 (*t*, $J = 1.7$ Hz, H–C(4)); 10.56 (*s*, H–C(2)). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.3 (Me(6″)); 18.1 (*Me*–C(7′)); 19.4 (*Me*–C(3′)); 22.7 (C(5″)); 25.6 (C(5′)); 26.0 (C(8′)); 26.2 (C(3″)); 30.3 (C(3′)); 30.6 (C(4″)); 31.4 (C(2″)); 37.0 (C(2′)); 37.7 (C(4′)); 48.5 (C(1′)); 50.4 (C(1″)); 122.4 (C(5)); 122.7 (C(4)); 124.4 (C(6′)); 132.0 (C(7′)); 137.4 (C(2)). FAB-MS: 661 (4, $C_{38}H_{70}BrN_4^+$), 291 (100, M^+), 221 (2, $C_{14}H_{25}N_2^+$), 69 (4, $C_3H_5N_2^+$), 41 (2, $C_2H_3N^+$). Anal. calcd. for $C_{19}H_{35}BrN_2$ (371.40): C 61.44, H 9.50, Br 21.51, N 7.54; found: C 61.21, H 9.69, Br 21.41, N 7.32.

*1-[(3*R*)-3,7-Dimethyloct-6-enyl]-3-dodecyl-1*H*-imidazolium Bromide* (**3d**): Yield 1.94 g (85%). Pale yellow viscous oil. $[\alpha]_D^{22} = -1.0$ ($c = 1.00$, $CHCl_3$). ^{1}H-NMR (250 MHz, $CDCl_3$): 0.88 (*t*, $J = 6.6$, Me(12″)); 0.99 (*d*, $J = 6.5$, Me–C(3′)); 1.18–1.40 (*m*, CH_2(2′), CH_2(4′), CH_2(3″) to CH_2(11″)); 1.59 (*s*, Me(8′)); 1.67 (*s*, Me–C(7′)); 1.92–2.00 (*m*, H–C(3′), CH_2(5′), CH_2(2″)); 4.34–4.41 (*m*, CH_2(1′), CH_2(1″)); 5.05 (*t*, $J = 1.3$, H–C(6′)); 7.44 (*t*, $J = 1.8$, H–C(5)); 7.48 (*t*, $J = 1.8$, H–C(4)); 10.55 (*s*, H–C(2)). ^{13}C-NMR (63 MHz, $CDCl_3$): 14.1 (Me(12″)); 17.7 (*Me*–C(7′)); 19.1 (*Me*–C(3′)); 22.7 (C(11″)); 25.3 (C(5′)); 25.7 (C(8′)); 26.3 (C(3″)); 29.0–30.4 (C(4″) to C(10″)); 31.9 (C(2″)); 36.7 (C(2′)); 37.4 (C(4′)); 48.4 (C(1′)); 50.2 (C(1″)); 121.6 (C(5)); 122.1 (C(4)); 124.1 (C(6′)); 131.8 (C(7′)); 137.3 (C(2)). FAB-MS: 375 (100, M^+), 69 (7, $C_3H_5N_2^+$), 41 (3, $C_2H_3N^+$). Anal. calc. for $C_{25}H_{37}BrN_2$ (455.56): C 65.91, H 10.40, Br 17.54, N 6.15; found: C 66.49, H 10.60, Br 15.48, N 5.98.

*1-[(3*R*)-3,7-Dimethyloct-6-enyl]-3-tetradecyl-1*H*-imidazolium Bromide* (**3e**): Yield 2.28 g (94%). Pale yellow viscous oil. $[\alpha]_D^{22} = -0.9$ ($c = 1.00$, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.88 (*t*, $J = 6.9$, Me(14″)); 0.99 (*d*, $J = 6.7$, Me–C(3′)); 1.20–1.42 (*m*, CH_2(2′), CH_2(4′), CH_2(3″) to CH_2(13″)); 1.59 (*s*, Me(8′)); 1.67 (*s*, Me–C(7′)); 1.91–2.02 (*m*, H–C(3′), CH_2(5′), CH_2(2″)); 4.32–4.42 (*m*, CH_2(1′), CH_2(1″)); 5.05 (*t*, $J = 7.0$, H–C(6′)); 7.48 (*s*, H–C(5)); 7.52 (*s*, H–C(4)); 10.53 (*s*, H–C(2)). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.4 (Me(14″)); 18.0 (*Me*–C(7′)); 19.5 (*Me*–C(3′)); 23.0 (C(13″)); 25.6 (C(5′)); 26.0 (C(8′)); 26.6 (C(3″)); 29.3–30.7 (C(4″) to C(12″)); 32.2 (C(2″)); 37.0 (C(2′)); 37.7 (C(4′)); 48.7 (C(1′)); 50.5 (C(1″)); 122.3 (C(5)); 122.5 (C(4)); 124.4 (C(6′)); 132.0 (C(7′)); 137.6 (C(2)). FAB-MS: 403 (100, M^+), 69 (8, $C_3H_5N_2^+$), 41 (3, $C_2H_3N^+$). Anal. calc. for $C_{27}H_{51}BrN_2$ (483.61): C 67.06, H 10.63, Br 16.52, N 5.79; found: C 66.30, H 10.81, Br 15.41, N 5.40.

*1-[(3*R*)-3,7-Dimethyloct-6-enyl]-3-octadecyl-1*H*-imidazolium Bromide* (**3f**): Yield 1.94 g (72%). Pale yellow viscous oil. $[\alpha]_D^{22} = -0.4$ ($c = 1.00$, $CHCl_3$). ^{1}H-NMR (250 MHz, $CDCl_3$): 0.88 (*t*, $J = 6.5$, Me(18″)); 0.99 (*d*, $J = 6.5$, Me–(3′)); 1.25–1.48 (*m*, CH_2(2′), CH_2(4′), CH_2(3″) to CH_2(17″)); 1.59 (*s*, Me(8′)); 1.67 (*s*, Me–C(7′)); 1.90–2.03 (*m*, H–C(3′), CH_2(5′), CH_2(2″)); 4.34–4.40 (*m*, CH_2(1′), CH_2(1″)); 5.05 (*t*, $J = 7.1$, H–C(6′)); 7.39 (*t*, $J = 1.7$, H–C(5)); 7.42 (*t*, $J = 1.7$, H–C(4)); 10.64 (*s*, H–C(2)). ^{13}C-NMR (63 MHz, $CDCl_3$): 14.1 (Me(18″)); 17.8 (*Me*–C(7′)); 19.1 (*Me*–C(3′)); 22.7 (C(17″)); 25.3 (C(5′)); 25.7 (C(8′)); 26.3 (C(3″)); 29.0–31.9 (C(4″) to C(16″)); 32.1 (C(2″)); 36.7 (C(2′)); 37.4 (C(4′)); 48.5 (C(1′)); 50.2 (C(1″)); 121.7 (C(5)); 121.9 (C(4)); 124.0 (C(6′)); 131.8 (C(7′)); 137.5 (C(2)). Anal. calc. for $C_{31}H_{59}BrN_2$ (539.72): C 68.99, H 11.02, Br 14.80, N 5.19; found: C 67.18, H 11.11, Br 14.43, N 4.94.

Preparation of **4a**,**d**: *General Procedure.* $NaBF_4$ (0.19 g, 1.73 mmol) was added to a soln. of **3a** or **3d** (1.73 mmol) in acetone (25–50 ml), and the mixture was stirred at r.t. for 2 h. Precipitated NaBr was filtered off, and the filtrate was evaporated. The residue was taken up in CH_2Cl_2 and the soln. washed with H_2O (2 × 25 ml) and evaporated. The residue was dried at r.t. 0.1–0.001 Torr for **4a**. For **4d** Et_2O was added to the residue and the mixture stored at −18° for 16 h. Et_2O was decanted and the precipitated waxy solid was dried at r.t./0.1–0.001 Torr.

*1-[(3*R*)-3,7-Dimethyloct-6-enyl]-3-methyl-1*H*-imidazolium Tetrafluoroborate* (**4a**): Yield 0.51 g (98%). $[\alpha]_D^{22} = -1.2$ ($c = 1.00$, $CHCl_3$). Anal. calc. for $C_{14}H_{25}BF_4N_2$ (308.17): C 54.56, H 8.18, N 9.09; found: C 54.57, H 8.12, N 8.96.

*1-[(3*R*)-3,7-Dimethyloct-6-enyl]-3-dodecyl-1*H*-imidazolium Tetrafluoroborate* (**4d**). Yield 0.54 g (99%). $[\alpha]_D^{22} = -1.0$ ($c = 1.00$, $CHCl_3$). Anal. calc. for $C_{25}H_{47}BF_4N_2$ (462.46): C 64.93, H 10.24, N 6.06; found: C 64.81, H 10.27, N 6.05.

1-[(3R)-3,7-Dimethyloct-6-enyl]pyridinium Bromide (**6**). A soln. of **1b** (1.10 g, 5.02 mmol) and pyridine (**5**, 0.40 g, 5.02 mmol) was heated at 45° for 4 d. Removal of volatile unreacted starting materials at 40°/0.1–0.001 Torr for 2 d gave **6** (1.47 g, 98%). Yellow viscous oil. $[\alpha]_D^{22} = -4.7$ ($c = 1.00$, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.91 (*d*, $J = 6.7$, Me–(3′)); 1.20–1.48 (*m*, CH_2(2′), CH_2(4′)); 1.59 (*s*, Me(8′)); 1.67 (*s*, Me–C(7′)); 1.89–2.11 (*m*, H–C(3′), CH_2(5′)); 4.95 (*m*, H–C(6′)); 5.05 (*m*, CH_2(1′)); 8.24 (*m*, H–C(3), H–C(5)); 8.61 (*m*, H–C(4)); 9.55 (*m*, H–C(2), H–C(6)). ^{13}C-NMR (125 MHz, $CDCl_3$): 17.8 (*Me*–C(7′)); 19.3 (*Me*–C(3′)); 25.2 (C(5′)); 25.7 (C(8′)); 30.0 (C(3′)); 36.7 (C(2′)); 39.2 (C(4′)); 60.6 (C(1′)); 124.0 (C(6′));128.7 (C(3), C(5)), 131.8 (C(4)); 145.2, 145.3 (C(2), C(6)). FAB-MS: 218 (100, M^+), 80 (3, $C_5H_6N^+$).

1,3-Bis[(3R)-3,7-dimethyloct-6-enyl]-1H-imidazolium Bromide (**8**). A soln. of **1b** (2.20 g, 10.04 mmol), **7** (0.34 g, 5.02 mmol), and 40% Bu_4NOH soln. (0.20 g) was stirred at r.t. for 3 d. The mixture was then evaporated and washed with Et_2O (3 × 15 ml; removal of all starting materials). The viscous light yellow liquid was dried at 40°/0.1–0.001 Torr for 2 d: **8** (1.25 g, 58%). Pale yellow oil. ^{1}H-NMR (250 MHz, $CDCl_3$): 0.98 (*d*, $J = 6.6$, 6 H, Me(3′)); 1.15–1.56 (*m*, 8 H, CH_2(2′), CH_2(4′)); 1.59 (*s*, 6 H, Me(8′)); 1.67 (*s*, 6 H, Me–C(7′)); 1.75–2.04 (*m*, 6 H, H–C(3′), CH_2(5′)); 4.32–4.42 (*m*, 4 H, CH_2(1′)); 5.05 (*t*, $J = 7.1$, 2 H, H–C(6′)); 7.51 (2*s*, H–C(5), H–C(4)); 10.50 (*s*, H–C(2)). ^{13}C-NMR (63 MHz, $CDCl_3$): 17.7 (*Me*–C(7′)); 19.1 (*Me*–C(3′)); 25.2 (C(5′)); 25.7 (C(8′)); 29.7, 29.9 (C(3′)); 36.7 (C(2′)); 37.4 (C(4′)); 48.4 (C(1′)); 122.0 (C(5)); 124.0 (C(6′)); 124.1 (C(4)); 131.7 (C(7′)); 137.0 (C(2)). FAB-MS: 345 (100, M^+), 207 (4, $C_{13}H_{23}N_2^+$), 69 (12, $C_3H_5N_2^+$), 41 (4, $C_2H_3N^+$). Anal. calcd. for $C_{23}H_{41}BrN_2$ (325.49): C 64.92, H 9.71, Br 18.78, N 6.58; found: C 61.50, H 9.30, Br 16.56, N 7.41[1]).

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[1]) Due to the high viscosity of **8**, trace amounts of solvent could not be completely removed, resulting in poor elemental analysis. However, the ^{1}H-NMR revealed a purity of $\geq 98\%$.