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Counterion Effects on the Mesomorphic Properties of Chiral Imidazolium and Pyridinium Ionic Liquids

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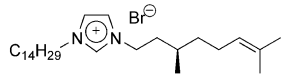
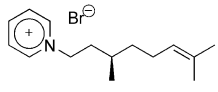
Novel calamitic *N*-methylimidazolium and pyridinium salts with modified citronellyl side-chains and various counterions **3**–**14** have been synthesised by utilising the commercially available (*R*)-citronellol (**15**) as the starting material. Differential scanning calorimetry (DSC), polarising optical microscopy (POM) and temperature-dependent X-ray diffraction studies revealed smectic A (SmA) mesophases for all the series. ^{1}H NMR studies of the *N*-methylimidazolium salts have shown that there is a correlation between the mesophase dependence on the counterion and the counterion-dependent chemical shifts of the acidic 2-H proton.

Introduction

Ionic liquids have received increasing interest over the last decade due to their promising applications, which range from green designer solvents to electrolytes for solar cells and electrodeposition.[1] Of particular interest are chiral ionic liquids, which can be used as solvents, ligands or organocatalysts in asymmetric synthesis.[2] Another useful feature of many ionic liquids is their ability to form mesophases, that is, liquid crystalline phases, a phenomenon that was first described by Seddon and Bruce and their coworkers[3] and later explored by many other groups.[4,5] In contrast, chiral ionic liquid crystals have rarely been investigated,[2a,4a,6–8] which is somewhat surprising because these systems should be highly valuable as chiral ordered reaction media for stoichiometric and catalytic processes.[9] We have recently shown that citronellyl-derived imidazolium and pyridinium ionic liquids **1** and **2**, respectively, display smectic phases (Scheme 1).[7] However, the mesophases were monotropic and covered only a small temperature range. In addition, variation of the citronellyl side-chain, and thus systematic analysis of the structure/property relationships, was not easy. Therefore we decided to study two series of chiral imidazolium and pyridinium salts **3**–**8** and **9**–**14**, respectively (Scheme 2), which can be synthesised from a common precursor derived from the commercially available (*R*)-citronellol (**15**) with easy modification of both the chain length R and the counterion X. Of particular interest are the effects of the counterion on the mesomorphic properties because from a limited literature precedence a significant influence regarding mesophase type and stability was anticipated.[5] The results are reported below.

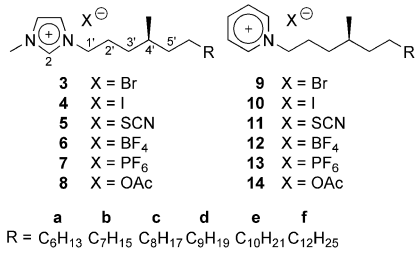


1 Cr 9 (SmA 45) I



2 g -56 (SmA 30) dec.

Scheme 1.



Scheme 2.

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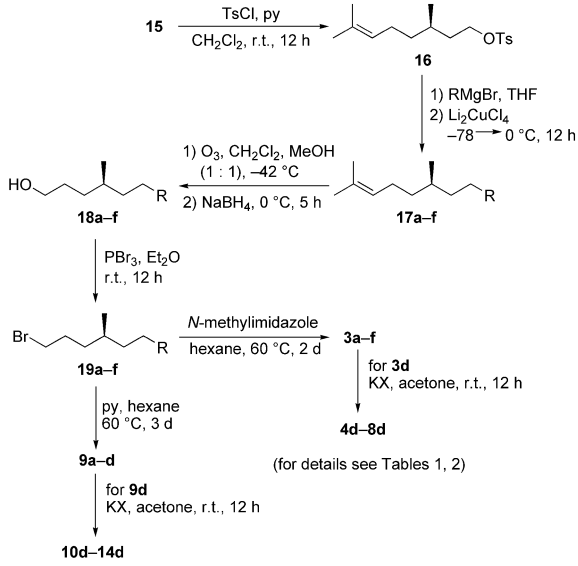
Results and Discussion

Following the procedure of Mori and co-workers,[10] (*R*)-citronellol (**15**) was converted into the corresponding tosylate **16**, which was treated with various alkylmagnesium bromides in the presence of 2 mol-% of LiCl and 1 mol-% of CuCl[11] in THF at –78 °C for 12 h to give after hydrolytic work-up the heterocoupling products **17** in 70–77% yields (Scheme 3 and Tables S1 and S2 of the Supporting Information). Compounds **17** were submitted to ozonolysis in CH_2Cl_2/MeOH at –78 °C followed by reductive work-up with $NaBH_4$[12] to give the alcohols **18** in 68–80% yields. Subsequent treatment with PBr_3 yielded the bromides **19** in 71–93% yields, which were converted into the *N*-methylimidazolium bromides **4d**–**8d** and pyridinium bromides **10d**–**14d** by heating **19** with *N*-methylimidazole or pyridine in hexane at 60 °C for 2–3 d. Whereas the *N*-methylimidazolium bromides **3a**–**f** were formed within 2 d and were isolated in good yields (77–93%), the corresponding pyridinium bromides **9a**–**d** required 3 d for complete conversion and only moderate yields (36–56%) were obtained. It was also found that the pyridinium bromides **9a**–**d** showed poorer thermal stability upon prolonged storage or repetitive DSC heating/cooling cycles. Presumably compounds **9a**–**d** are prone to *N*-dealkylation, a phenomenon that has recently been described for other pyridinium ionic liquid crystals (Figure 1).[5c]

To obtain the ionic liquids **4d**–**8d** and **10d**–**14d** with different counterions, compounds **3d** and **9d** were treated with potassium salts in acetone at room temperature to give the corresponding ionic liquids **4d**–**8d** and **10d**–**14d** in almost quantitative yields.



Scheme 3. Synthesis of *N*-methylimidazolium (**3**–**8**) and pyridinium derivatives **9**–**14** starting from (*R*)-citronellol (**15**).

The mesomorphic properties of compounds **3**, **4**, **8** and **9** were investigated by differential scanning calorimetry and polarising optical microscopy. First, the effect of chain length was studied. As shown in Table 1, *N*-methylimidazolium bromides **3a**–**f** displayed enantiotropic mesophases irrespective of the chain length. For example, upon a second heating, compound **3d** with a nonyl chain showed a melting transition at 9 °C and a clearing transition at 167 °C.

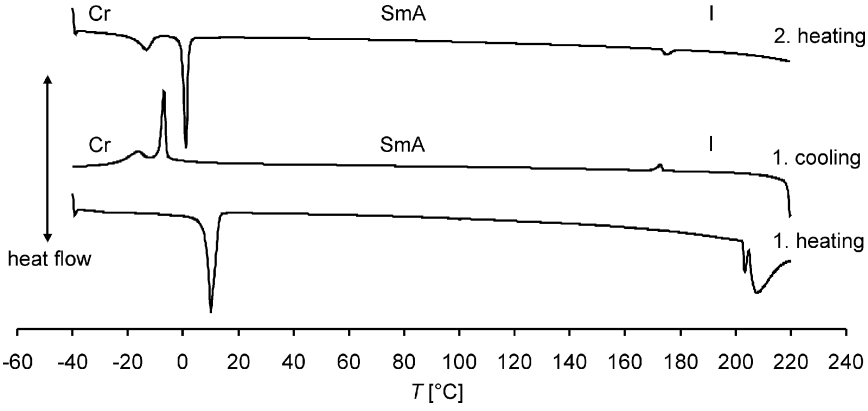


Figure 1. DSC of compound **9d** (after storage for 1 year); heating/cooling rate: 5 K min^{-1}. In the first heating cycle the broad peak after the clearing point was presumably caused by partial decomposition.

Table 1. Phase transition temperatures and enthalpies (ΔH) of *N*-methylimidazolium bromides **3a**–**f**.[a]

3	R	Cr	*T* [°C]	ΔH [kJ mol^{-1}]	SmA	*T* [°C]	ΔH [kJ mol^{-1}]	I
a	C_6H_{13}		7	6.40	+	102	0.63	+
b	C_7H_{15}	+	17	18.3	+	153	1.21	+
c	C_8H_{17}	+	1	10.5	+	144	1.23	+
d	C_9H_{19}	+	9	12.0	+	167	0.92	+
e	$C_{10}H_{21}$	+	20	13.7	+	159	0.52	+
f	$C_{12}H_{25}$	+	30	17.5	+	177	0.92	+

[a] The following phases were observed during the second heating: crystalline, smectic A, isotropic; heating rate: 10 K min^{-1}.

An odd/even effect was observed for the clearing points of the series **3a**–**e**. POM revealed textures that are not characteristic of the expected smectic phase[13] (see Figure S1 of the Supporting Information) and thus X-ray diffraction (XRD) experiments were undertaken.

X-ray diffraction (XRD) studies of an aligned sample of compound **3d** revealed a diffraction pattern (Figure 2) typical of smectic mesophases with a strong fundamental diffraction peak (001), a small second-order peak (002) and diffuse scattering from the alkyl chains. On the basis of the diffraction patterns of **3d**, a SmA mesophase was proposed because the first-order peak is parallel to the magnetic field and the wide-angle scattering is perpendicular to the (001) reflection.

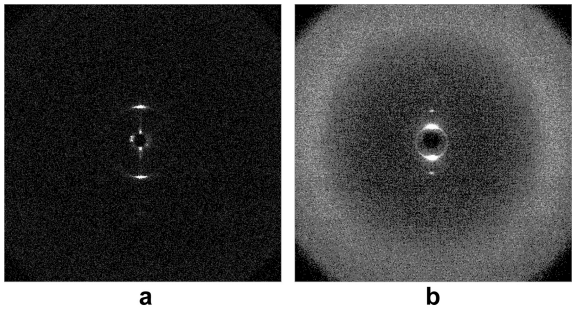


Figure 2. X-ray diffraction pattern of **3d** at 80 °C in the SmA phase; left side: SAXS; right side: WAXS section.

The two-dimensional diffraction pattern of the WAXS section of compound **3d** is shown in Figure 3. The (001) peak was fitted with a Gaussian distribution to obtain the exact layer spacing (d_{001}) of the SmA phase of **3d**, which is 32.5 Å at 80 °C, whereas the calculated molecular length of **3d** is about 23.6 Å, determined for the stretched molecule by molecular modelling using Chem3D Ultra®.

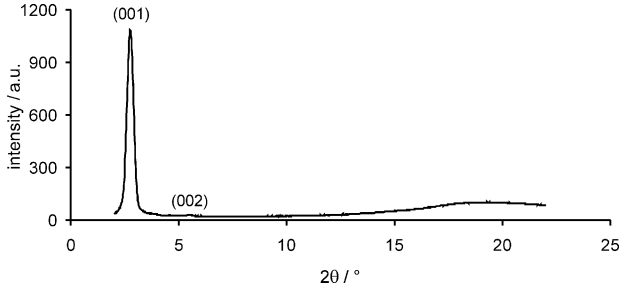


Figure 3. 2D diffraction pattern (WAXS) of compound **3d** at 80 °C.

Similar trends were found for the corresponding pyridinium bromides **9a**–**d** (Table 2). Enantiotropic mesomorphism was found for all the derivatives **9a**–**d** with melting points between –27 (for **9a** with a C_6 chain) and –1 °C (for **9d** with a C_9 chain) and clearing points between 127 and 184 °C for **9a** and **9d**, respectively. Thus, the mesophase widths increased significantly for a certain chain length whenS and SAXS data for **9d** (Figure 4) confirmed a SmA phase with a layer spacing of 32.7 Å at 55 °C, whereas the molecular length of **9d** is about 22.8 Å, as calculated for the stretched molecule by molecular modelling (Chem3D Ultra®). This means that the layer dimensions are only slightly influenced by the different head groups. The two-dimensional diffraction pattern of the WAXS section of compound **9d** is shown in Figure 5.

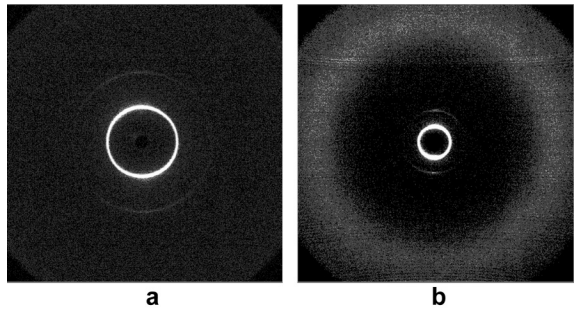


Figure 4. X-ray diffraction pattern of **9d** at 70 °C in the SmA phase; left side: SAXS; right side: WAXS section.

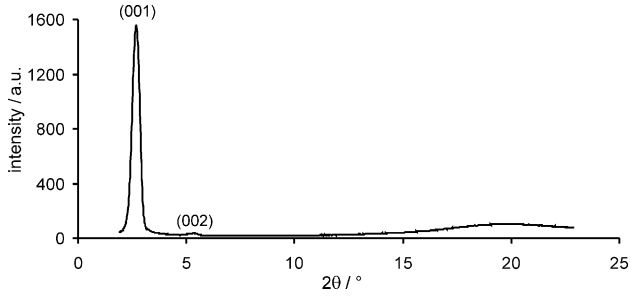


Figure 5. 2D diffraction pattern (WAXS) of compound **9d** at 70 °C.

Next, the counterion effects were studied. For easier comparison, *N*-methylimidazolium salts **3d**–**8d** and pyridinium salts **9d**–**14d** with a C_9 chain were submitted to DSC and POM. With the exception of the crystalline derivative

Table 2. Phase transition temperatures and enthalpies (ΔH) for pyridinium bromides **9a**–**d**.[a,b]

9	R	Cr	T [°C]	ΔH [kJ mol^{-1}]	SmA	T [°C]	ΔH [kJ mol^{-1}]	I
a	C_6H_{13}	+	–27	1.36	+	127	0.66	+
b	C_7H_{15}	+	–8	6.06	+	184	0.84	+
c	C_8H_{17}	+	–1	7.43	+	184	0.88	+
d	C_9H_{19}	+	–1	9.00	+	173	0.68	+

[a] The following phases were observed during the second heating: crystalline, smectic A, isotropic; heating rate: 10 K min^{-1}. [b] Phase sequence for **9d**: Cr_1 –18 (3.21) Cr_2 –1 (9.00) SmA 173 (0.68) I; heating rate: 5 K min^{-1}.

13d, all the examined compounds showed mesomorphic behaviour. As a typical example the enantiotropic DSC traces of derivative **7d** are shown in Figure 6.

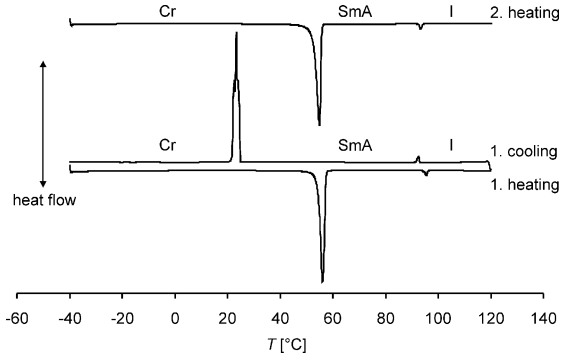


Figure 6. DSC investigation of **7d**; heating/cooling rate: 5 K min^{-1}.

Upon cooling from the isotropic melts to the smectic mesophases, focal conical textures, which are typical of SmA phases,[13] were observed for the derivatives **7d** and **11d** (Figure 7). The other derivatives, for which no focal conical textures could be observed, presumably display spontaneous homeotropic alignment during cooling from the isotropic melts to the smectic mesophases, resulting in homeotropic textures. This is also a characteristic of SmA mesophases.

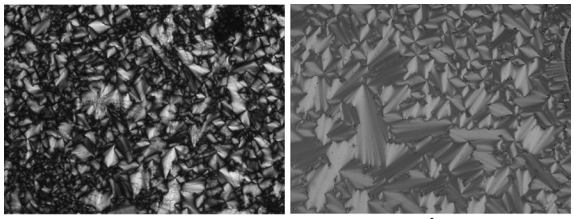


Figure 7. Focal conical textures of the imidazole derivative **7d** (left) and the pyridinium derivative **11d** (right) under crossed polarisers at 60 and 80 °C, respectively, upon cooling from the isotropic phase (cooling rate: 1 K min^{-1}, magnification 200×).

As shown in Table 3, mesophase stability was observed to decrease in the order $Br^- > OAc^- > I^- > BF_4^- > SCN^- > PF_6^-$ for the *N*-methylimidazolium salts **3d**–**8d**. A similar trend was observed for the pyridinium salts **9d**–**12d** and **14d** except for the iodide and tetrafluoroborate salts **10d** and **12d**, respectively, which are in reverse order compared with the *N*-methylimidazolium salts **4d** and **6d**: $Br^- > OAc^- > BF_4^- > I^- > SCN^-$.

Again the clearing temperatures for the pyridinium salts were higher than those of the *N*-methylimidazolium salts, but also the melting points were higher. For *N*-methylimidazolium iodide **4d** WAXS and SAXS measurements revealed a layer distance of 33.1 Å at 20 °C (the calculated molecular length of 23.6 Å for **4d** is of course similar to that for **3d**). Thus, the exchange of bromide by iodide resulted in only a small increase in the layer distance, which indicates that the anions are well buried among the cationic head groups that form the double sheet.

From the X-ray diffraction data a packing model can be proposed (Figure 8) with interdigitating double layers. For compounds **3d**, **4d** and **9d** the ratio of the smectic layer distance obtained from the X-ray diffraction study and the calculated molecular length (L_{XRD}/L_{calc}) is 1.4 irrespective of the counterion or head group. This result is in good agreement with previous work on ionic liquid crystals.[14] Note also that no experimental evidence for chiral nematic (N*) or chiral smectic C (SmC*) phases were found for compounds **3**–**14**. Thus, the stereogenic centre seems to have no influence on the phase behaviour, except for operating as a "stopper" for layer interdigitation.

With regard to the ^{1}H NMR spectra of the *N*-methylimidazolium salts **3d**–**8d** it was found that the anion has a remarkable influence on the chemical shift of the most acidic proton 2-H (Figure 9). In comparison with the bromide **3d** (δ = 10.49 ppm), upfield shifts were observed for all the other counterions (up to δ = 8.52 ppm for **7d**). Thus, the chemical shifts of the nonyl-substituted derivatives **3d**–**8d** were observed to decrease in the following order: $Br^- > OAc^- > I^- > BF_4^- > SCN^- > PF_6^-$

Table 3. Phase transition temperatures and enthalpies (ΔH) of the *N*-methylimidazolium (**3d**–**8d**) and pyridinium salts **9d**–**14d**.[a]

Salt	Anion	Cr_1	T [°C]	ΔH [kJ mol^{-1}]	Cr_2	T [°C]	ΔH [kJ mol^{-1}]	SmA	T [°C]	ΔH [kJ mol^{-1}]	I
3d	Br	–	–	–	+	9	12.0	+	167	0.92	+
4d	I	–	–	–	+	6	12.9	+	147	0.97	+
5d	SCN	–	–	–	+	8	13.0	+	116	0.83	+
6d	BF_4	–	–	–	+	5	11.8	+	127	0.75	+
7d	PF_6[b]	–	–	–	+	53	30.6	+	93	0.72	+
8d	OAc	–	–	–	+	4	14.4	+	153	1.12	+
9d	Br[b]	–	–18	3.21	+	–1	9.0	+	173	0.68	+
10d	I	+	–6	3.28	+	41	22.8	+	171	1.46	+
11d	SCN	+	2	1.81	+	21	15.3	+	135	0.82	+
12d	BF_4	+	–19	1.18	+	1	11.3	+	140	0.88	+
13d	PF_6[c]	+	63	3.67	+	80	16.1	–	126	9.76	+
14d	OAc	–	–	–	+	0	16.2	+	162	2.97	+

[a] +: the corresponding phase was observed; –: the corresponding phase was not observed during the second heating: Cr_1: crystalline 1, Cr_2: crystalline 2, SmA: smectic A, I: isotropic; heating rate: 10 K min^{-1}. [b] Heating rate: 5 K min^{-1}. [c] Compound **13d** displayed no mesomorphic properties; Cr_1 63 Cr_2 80 Cr_3 126 I.

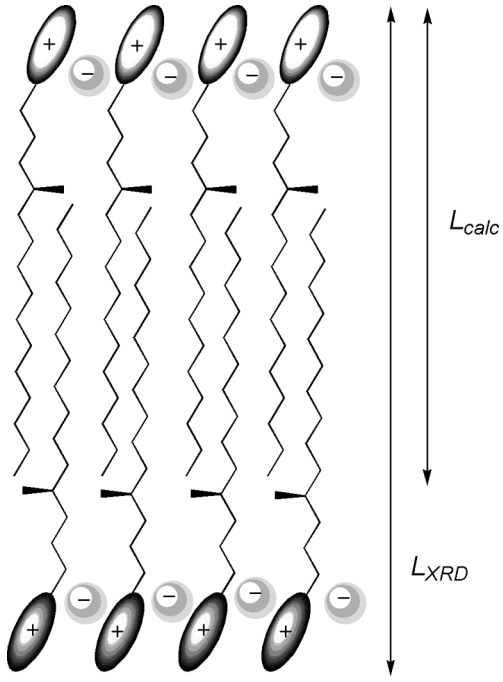


Figure 8. Proposed model of the SmA phase of compounds **3d** and **9d** with a partially interdigitated double layer. L_{XRD} is the smectic layer distance obtained from X-ray diffraction experiments and L_{calc} is the molecular length calculated from molecular modelling using Chem3D Ultra®.

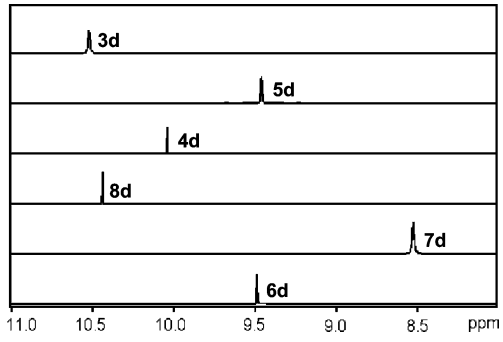


Figure 9. ^{1}H NMR chemical shifts of 2-H of various *N*-methylimidazolium salts **3d**–**8d**.

Owing to the delocalised positive charge the *N*-methylimidazolium ion can be considered to be a large soft cation. With increasing transfer of electron density from the anion to the cation, the bond strengths of the acidic C2–H bond is weakened to a lesser extent and thus the signals are shifted upfield. Note that Shah and Maginn carried out Monte Carlo simulations on *N*-butyl-*N*-methylimidazolium hexafluorophosphate, which clearly revealed a preferred interaction of the anion with 2-H.[15]

When mixtures of *N*-methylimidazolium salts **3d**–**8d** with the same cation, that is, the same alkyl chain length but different anions, were studied by ^{1}H NMR spectroscopy, only a single set of signals was observed particularly with respect to 2-H. Presumably on the NMR timescale rapid anion exchange results in an average value for the chemical shift of 2-H.

In addition, when mixtures of the bromide salt **3d** with increasing ratios of the hexafluorophosphate **8d** were investigated by ^{1}H NMR spectroscopy, the chemical shift of 2-H showed a linear dependence on the hexafluorophosphate concentration (Figure 10). Thus, the chemical shift of 2-H in the *N*-methylimidazolium salts serves as a sensitive probe for the anions and mixtures thereof.

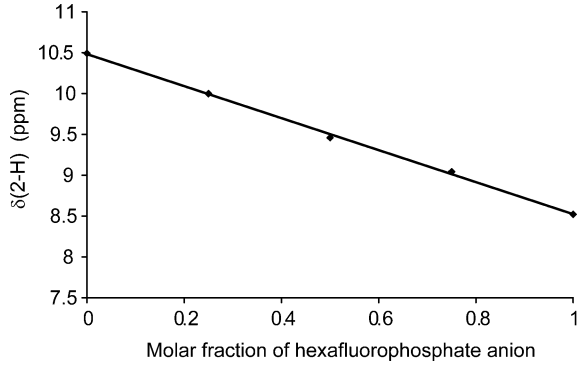


Figure 10. ^{1}H NMR chemical shifts of 2-H of mixtures of *N*-methylimidazolium salts **3d** and **8d** as a function of molar fraction.

Conclusions

Two series of chiral *N*-methylimidazolium and pyridinium salts have been prepared that display smectic A mesophases, the phase stabilities of which are strongly influenced by the counterion rather than the chain lengths of the salts. The mesophase dependence on the counterion correlates well with the counterion-dependent chemical shifts of the acidic proton 2-H of the *N*-methylimidazolium salts. These experimental results may be regarded as a hint of the importance of contact ion-pairs on the self-assembly and physical properties of ionic liquid crystals. Note that chiral *N*-methylimidazolium salt **3d** can be used as a dopant to induce chiral nematic phases in a nematic host phase of 4′-pentyl-4-cyanobiphenyl, however, a more detailed investigation is required, which is currently in progress in our laboratory.

Experimental Section

General: Melting points were determined with a Büchi SMP 20 apparatus and are uncorrected. NMR spectra were recorded with a Bruker Avance 300 or Avance 500 (^{1}H: 300 or 500 MHz; ^{13}C: 75 or 125 MHz) spectrometer with TMS as the internal standard. Signal assignments are based on DEPT and COSY experiments. IR spectra were recorded with a Bruker Vector 22 FTIR spectrometer with a MKII Golden Gate Single Reflection Diamant ATR system. Mass spectra were obtained with a Varian MAT 711 spectrometer using EI at 70 eV and with a Bruker Daltonics micrOTOF-Q spectrometer using ESI. Chromatography was performed on silica gel 60 (230–400 mesh, Macherey–Nagel). Differential scanning calorimetry was performed with a Mettler-Toledo DSC822e instrument (heating rates were 2, 5 or 10 K min^{-1}). Polarising optical microscopy was carried out with an Olympus BX50 polarising microscope combined with a Linkam TP93 central processor. X-ray ex-

periments were performed with a Bruker AXS Nanostar C diffractometer employing Ni-filtered Cu-K_α radiation (λ = 1.5418 Å). Commercial reagents were used without further purification. All reactions were carried out using standard Schlenk techniques unless otherwise noted.

(*R*)-3′,7′-Dimethyloct-6′-enyl *p*-toluenesulfonate (**16**) was prepared according to a literature procedure.[10b] The following derivatives are known: **17a**–**19a**,[12] **17c**,[16] **17e**,[17] **17f**,[18] **18c**,**e**[19] and **18f**.[20]

General Procedure for the Reaction of Tosylate 16 with Cuprates: 1-Bromoalkene (47.0 mmol) in THF (80 mL) was added dropwise to a suspension of Mg turnings (1.42 g, 58.3 mmol) in THF (10 mL) so that a steady reflux of the mixture was maintained. Then the mixture was heated at reflux for a further 30 min, cooled to room temp. and then added dropwise to a cooled solution of tosylate **16** (4.10 g, 13.2 mmol) in THF (30 mL) at –78 °C. Then a solution of LiCl (33.4 g, 0.79 mmol) and $CuCl_2$ (56.6 g, 0.42 mmol) in THF (10 mL) was added dropwise and the resulting mixture was stirred for 5 h at –78 °C, warmed to room temp. overnight and hydrolysed with satd. NH_4Cl (100 mL). The layers were separated, the aqueous layer was extracted with hexanes (2 × 200 mL) and the combined organic layers were washed with H_2O (2 × 100 mL) and brine (100 mL) and concentrated. The crude products were purified by distillation under reduced pressure (for **17a**–**c**) or by column chromatography on SiO_2 (hexanes) (for **17d**–**f**).

(6*S*)-2,6-Dimethyl-2-heptadecene (17d): From **16** (35.0 g, 113 mmol) a colourless oil (21.0 g, 78.9 mmol, 70%) was obtained. $[a]_D^{22}$ = –4.1 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (d, *J* = 6.5 Hz, 3 H, 6-CH_3), 0.88 (t, *J* = 6.7 Hz, 3 H, 17-H) 1.02–1.46 (m, 23 H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H), 1.59–1.61 (m, 3 H, 1-H), 1.67–1.69 (m, 3 H, 2-CH_3), 1.88–2.05 (m, 2 H, 4-H), 5.06–5.13 (m, 1 H, 3-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (C-17), 17.6 (2-CH_3), 19.6 (6-CH_3), 22.7 (C-16), 25.6–32.5 (C-1, C-4, C-6, C-8, C-9, C-10, C-11, C-12, C-13, C-14, C-15), 37.0–37.2 (C-5, C-7), 125.1 (C-3), 130.9 (C-2) ppm. FTIR (ATR): $\tilde{\nu}$ = 2957 (s), 2921 (s), 2853 (s), 1459 (m), 1377 (m), 984 (w), 828 (w), 721 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 266.3 (29) $[M]^+$, 126.1 (40), 111.2 (56), 97.1 (40), 83.1 (32), 69.1 (100). HMRS (EI): calcd. for $C_{19}H_{38}$ 266.2974; found 266.2969 $[M]^+$.

General Procedure for the Ozonolysis of Alkenes 17: Ozone was bubbled through a cooled solution of alkene **17** (4.46 mmol) in CH_2Cl_2 (10 mL) and MeOH (10 mL) at –42 °C until the blue colour remained. Excess of ozone was removed by bubbling N_2 through the solution. Then $NaBH_4$ (228 mg, 6.03 mmol) was added in small portions, the mixture was warmed to 0 °C and stirring was continued for 5 h. After hydrolysis with satd. NH_4Cl (25 mL), the solvent was evaporated and the colourless precipitate was removed by filtration. The aqueous layer was extracted with Et_2O (2 × 25 mL) and the combined organic layers were washed with H_2O (50 mL) and brine (50 mL) and dried with $MgSO_4$ and concentrated. The crude product was purified by column chromatography on SiO_2 (hexanes/EtOAc = 10:1) to yield the product **18** and the starting material **17**, which was resubmitted to ozonolysis. For each compound **18** three subsequent ozonolysis cycles were carried out.

(4*S*)-4-Methyl-1-pentadecanol (18d): From **17d** (7.50 g, 28.1 mmol) a colourless oil (5.11 g, 21.1 mmol, 75%) was obtained. $[a]_D^{22}$ = –1.8 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (d, *J* = 6.5 Hz, 3 H, 4-CH_3), 0.88 (t, *J* = 6.8 Hz, 3 H, 15-H) 1.06–1.48 (m, 23 H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H), 1.54–1.69 (m, 2 H, 2-H), 3.62 (t, *J* = 6.7 Hz, 2 H, 1-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (C-15), 19.7 (4-CH_3), 22.7 (C-14), 27.0–33.0 (C-2, C-3, C-4, C-6, C-7, C-8, C-9, C-10, C-11, C-12, C-13), 37.0 (C-5), 63.4 (C-1) ppm. FTIR (ATR): $\tilde{\nu}$ = 3326 (br), 2954 (s), 2921 (s), 2852 (s), 1464 (m), 1377 (m), 1057 (br), 898 (w), 721 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 242.1 (2) $[M]^+$, 224.2 (46), 196.2 (100), 181.2 (18), 126.1 (20), 111.1 (22), 97.1 (42), 84.1 (42), 69.1 (96). HMRS (EI): calcd. for $C_{16}H_{34}O$ 242.2610; found 242.2574 $[M]^+$.

General Procedure for the Bromination of Alcohols 18: PBr_3 (90 μL, 0.96 mmol) was added dropwise to a solution of alcohol **18** (1.75 mmol) in Et_2O (15 mL) at room temp. After stirring for 12 h the mixture was hydrolysed with ice-cooled H_2O (15 mL), the layers were separated and the organic layer was washed with satd. $NaHCO_3$ (50 mL), brine (50 mL) and H_2O (2 × 50 mL), dried with $MgSO_4$ and the solvents evaporated. The crude product was purified by column chromatography on SiO_2 (hexanes/EtOAc = 20:1).

(4*S*)-4-Methyl-1-pentadecyl Bromide (19d): From **18d** (3.00 g, 13.1 mmol) a colourless oil (3.26 g, 13.4 mmol, 88%) was obtained. $[a]_D^{22}$ = –4.4 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (d, *J* = 6.5 Hz, 3 H, 4-CH_3), 0.88 (t, *J* = 6.8 Hz, 3 H, 15-H) 1.05–1.50 (m, 23 H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H), 1.72–1.95 (m, 2 H, 2-H), 3.39 (t, *J* = 6.9 Hz, 2 H, 1-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (C-15), 19.6 (4-CH_3), 22.7 (C-14), 26.9–34.3 (C-1, C-2, C-3, C-4, C-6, C-7, C-8, C-9, C-10, C-11, C-12, C-13), 35.5 (C-3), 36.9 (C-5) ppm. FTIR (ATR): $\tilde{\nu}$ = 2956 (s), 2921 (s), 2852 (s), 1462 (m), 1377 (m), 1256 (w), 1206 (w), 721 (m), 644 (w) cm^{-1}. MS (EI): *m*/*z* (%) = 306.2 (4), 304.2 (5) $[M]^+$, 151.0 (98), 149.0 (100) $[C_5H_{10}Br]^+$, 113.1 (5), 99.1 (10), 85.1 (28), 71.1 (50.0), 69.1 (76). HMRS (EI): calcd. for $C_{16}H_{33}Br$ 304.1766, 306.1745; found 304.1763, 306.1760 $[M]^+$.

General Procedure for the Preparation of *N*-Methylimidazolium Bromides 3: A solution of bromide **19** (0.71 mmol) and 1-methylimidazole (58.0 mg, 0.71 mmol) in hexanes (2 mL) was heated at reflux for 48 h. After cooling to room temp., the solvent was removed in vacuo and the crude product was washed with Et_2O (2 × 1 mL) under sonification, diluted in MeCN (2 mL), washed with *n*-hexane (2 × 2 mL) and dried in vacuo for 2 d at 90 °C.

(4′*S*)-1′-Methyl-3′-(4′-methylpentadecyl)imidazolium Bromide (3d): From **19d** (2.97 g, 9.73 mmol) a colourless waxy solid (3.47 g, 8.94 mmol, 92%) was obtained. $[a]_D^{22}$ = –1.3 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (d, *J* = 6.7 Hz, 3 H, 4′-CH_3), 0.88 (t, *J* = 6.9 Hz, 3 H, 15′-H), 1.01–1.50 (m, 23 H, 3′-H, 4′-H, 5′-H, 6′-H, 7′-H, 8′-H, 9′-H, 10′-H, 11′-H, 12′-H, 13′-H, 14′-H), 1.79–2.04 (m, 2 H, 2′-H), 4.15 (s, 3 H, N-CH_3), 4.31 (t, *J* = 7.4 Hz, 2 H, 1′-H), 7.35 (t, *J* = 1.7 Hz, 1 H, 4-H), 7.53 (t, *J* = 1.7 Hz, 1 H, 5-H), 10.49 (br. s, 2-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (C-15′), 19.3 (4′-CH_3), 22.6 (C-14′), 27.0–33.4 (C-3′, C-4′, C-6′, C-7′, C-8′, C-9′, C-10′, C-11′, C-12′, C-13′), 36.8–37.1 (C-5′, N-CH_3), 50.4 (C-1′), 121.8 (C-4), 123.8 (C-5), 137.2 (C-2) ppm. FTIR (ATR): $\tilde{\nu}$ = 3139 (w), 3069 (w), 2955 (s), 2921 (s), 2852 (s), 1630 (w), 1572 (s), 1464 (s), 1378 (m), 1168 (vs), 842 (w), 751 (m), 648 (w), 620 (s) cm^{-1}. $C_{20}H_{39}BrN_2$ (387.44): calcd. C 62.00, H 10.15, N 7.23, Br 20.62; found C 61.97, H 10.16, N 7.23, Br 20.67. MS (ESI, +ve): *m*/*z* = 307.3 $[M]^+$, 151.0, 123.1, 109.1, 95.1, 83.1. MS (ESI, –ve): *m*/*z* = 467.1 $[MBr_2]^-$. HRMS (ESI): calcd. for $[C_{20}H_{39}N_2]^+$ 307.3108; found 307.3110 $[M]^+$.

General Procedure for the Preparation of Pyridinium Bromides 9: A solution of bromide **19** (0.65 mmol) and pyridine (56.6 mg, 0.71 mmol) in hexanes (2 mL) was heated at reflux for 3 d. After cooling to room temp. the solvent was removed in vacuo and the crude product was washed with Et_2O (2 × 2 mL) under sonification, diluted in MeCN (2 mL), washed with *n*-hexane (2 × 2 mL) and dried in vacuo for 3 d at 120 °C.

(4′*S*)-(4′-Methylpentadecyl)pyridinium Bromide (9d): From **19d** (3.00 g, 9.82 mmol) a colourless waxy solid (2.10 g, 5.47 mmol, 56%) was obtained. $[\alpha]_D^{22}$ = +18.8 (*c* = 1.00, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.85 (d, *J* = 6.6 Hz, 3 H, 4′-CH_3), 0.88 (t, *J* = 6.8 Hz, 3 H, 15′-H), 1.05–1.49 (m, 23 H, 3′-H, 4′-H, 5′-H, 6′-H, 7′-H, 8′-H, 9′-H, 10′-H, 11′-H, 12′-H, 13′-H, 14′-H), 1.99–2.27 (m, 2 H, 2′-H), 5.07 (t, *J* = 7.3 Hz, 2 H, 1′-H), 8.11–8.15 (m, 2 H, 3-H, 5-H), 8.49–8.51 (m, 1 H, 4-H), 9.44–9.46 (m, 2 H, 2-H, 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (C-15'), 19.3 (4′-CH_3), 22.7 (C-14′), 27.0–33.2 (C-3′, C-4′, C-6′, C-7′, C-8′, C-9′, C-10′, C-11′, C-12′, C-13′), 36.8 (C-5′), 62.5 (C-1′), 128.4 (C-3, C-5), 144.9 (C-4), 145.2 (C-2, C-6) ppm. FTIR (ATR): $\tilde{\nu}$ = 3081 (w), 2956 (s), 2922 (s), 2853 (s), 2361 (w), 1572 (s), 1465 (s), 1378 (m), 1170 (vs), 847 (w), 747 (m), 624 (s) cm^{-1}. $C_{21}H_{38}BrN$ (384.44): calcd. C 65.61, H 9.96, N 3.64, Br 20.78; found C 65.64, H 9.93, N 3.64, Br 20.77. MS (ESI, +): *m*/*z* = 304.3 $[M]^+$, 148.1, 132.1, 120.1, 106.1, 80.0. HMRS (ESI, +ve): calcd. for $C_{21}H_{38}N^+$ 304.2999; found 304.2999 $[M]^+$. HRMS (ESI, –ve): calcd. for Br^- 78.9183, 80.9163; found 78.9178, 80.9155 $[Br^-]$.

General Procedure for the Anion Exchange of (4′*S*)-1-Methyl-3-(4′-methylpentadecyl)imidazolium Bromide (3d): KX (0.30 mmol, X = I, SCN, BF_4, PF_6, OAc) was added to a solution of (4′*S*)-1-methyl-3-(4′-methylpentadecyl)imidazolium bromide (**3d**; 117 mg, 0.30 mmol) in acetone (2 mL) and the mixture was stirred overnight at room temp. The colourless precipitate was removed by filtration and the filtrate was concentrated in vacuo. The solid residue was diluted in $CHCl_3$ (2 mL) and the remaining precipitate was removed by filtration. After concentration of the filtrate in vacuo, the resulting solid was dried in vacuo for 2 d at 80 °C.

(4′*S*)-1′-Methyl-3′-(4′-methylpentadecyl)imidazolium Iodide (4d): From **3d** (117 mg, 0.30 mmol) an orange waxy solid (130 mg, 0.30 mmol, 98%) was obtained. $[\alpha]_D^{22}$ = +7.1 (*c* = 1.00, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.87 (d, *J* = 6.6 Hz, 3 H, 4′-CH_3), 0.88 (t, *J* = 6.8 Hz, 3 H, 15′-H) 1.02–1.46 (m, 23 H, 3′-H, 4′-H, 5′-H, 6′-H, 7′-H, 8′-H, 9′-H, 10′-H, 11′-H, 12′-H, 13′-H, 14′-H), 1.81–1.99 (m, 2 H, 2′-H), 4.15 (s, 3 H, N-CH_3), 4.31 (t, *J* = 7.47 Hz, 2 H, 1′-H), 7.47 (t, *J* = 1.7 Hz, 1 H, 4-H), 7.65 (t, *J* = 1.7 Hz, 1 H, 5-H), 10.04 (br. s, 1 H, 2-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1 (C-15′), 19.4 (4′-CH_3), 22.6 (C-14′), 27.0–33.4 (C-3′, C-4′, C-6′, C-7′, C-8′, C-9′, C-10′, C-11′, C-12′, C-13′), 36.8–37.1 (C-5′, N-CH_3), 50.5 (C-1′), 122.1 (C-4), 123.9 (C-5), 136.8 (C-2) ppm. FTIR (ATR): $\tilde{\nu}$ = 3102 (w) 2955 (s), 2922 (s), 2852 (s), 1464 (m), 1378 (m), 1047 (br), 831 (w), 741 (m), 621 (s) cm^{-1}. $C_{20}H_{39}IN_2$ (434.44): calcd. C 55.29, H 9.05, N 6.45; found C 55.32, H 9.06, N 6.53. MS (ESI, +ve): *m*/*z* = 307.3 $[M]^+$, 151.1, 123.1, 109.1, 95.1, 83.1. MS (ESI, –ve): *m*/*z* = 561.0 $[MI_2]^-$, 126.9 $[I]^-$. HMRS (ESI): calcd. for $[C_{20}H_{39}N_2]^+$ 307.3108; found 307.3115 $[M]^+$.

(4′*S*)-1′-Methyl-3′-(4′-methylpentadecyl)imidazolium Thiocyanate (5d): From **3d** (114 mg, 0.29 mmol) a yellow waxy solid (106 mg, 0.27 mmol, 97%) was obtained. $[\alpha]_D^{22}$ = –15.8 (*c* = 1.00, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.86 (d, *J* = 6.7 Hz, 3 H, 4′-CH_3), 0.88 (t, *J* = 6.9 Hz, 3 H, 15′-H) 1.02–1.46 (m, 23 H, 3′-H, 4′-H, 5′-H, 6′-H, 7′-H, 8′-H, 9′-H, 10′-H, 11′-H, 12′-H, 13′-H, 14′-H), 1.78–1.96 (m, 2 H, 2′-H), 4.12 (s, 3 H, N-CH_3), 4.29 (t, *J* = 7.4 Hz, 2 H, 1′-H), 7.37 (t, *J* = 1.7 Hz, 1 H, 4-H), 7.63 (t, *J* = 1.7 Hz, 1 H, 5-H), 9.46 (br. s, 1 H, 2-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1 (C-15′), 19.3 (4′-CH_3), 22.7 (C-14′), 27.0–33.4 (C-3′, C-4′, C-6′, C-7′, C-8′, C-9′, C-10′, C-11′, C-12′, C-13′), 36.8–36.9 (C-5′, N-CH_3), 50.8 (C-1′), 122.0 (C-4), 123.7 (C-5), 137.2 (C-2) ppm. FTIR (ATR): $\tilde{\nu}$ = 3149 (w), 3102 (w), 2956 (s), 2922 (s), 2852 (s), 2050 (s), 1636 (w), 1573 (m), 1465 (s), 1378 (m), 1169 (vs), 842 (w), 721 (w), 623 (s) cm^{-1}. $C_{21}H_{39}N_3S$ (365.62): calcd. C 51.21, H 7.98, N 8.53, S 6.51; found C 51.28, H 8.00, N 8.49, S 6.50. MS (ESI, +ve): *m*/*z* = 307.3 $[M]^+$, 151.1, 123.1, 109.1, 95.1, 83.1 83.1. MS (ESI, –ve): *m*/*z* = 423.2 $[M(SCN)_2]^-$. HMRS (ESI): calcd. for $[C_{20}H_{39}N_2]^+$ 307.3108; found 307.3111 $[M]^+$.

(4′*S*)-1′-Methyl-3′-(4′-methylpentadecyl)imidazolium Tetrafluoroborate (6d): From **3d** (130 mg, 0.34 mmol) a red waxy solid (131 mg, 0.33 mmol, 98%) was obtained. $[\alpha]_D^{22}$ = +12.9 (*c* = 1.00, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.86 (d, *J* = 6.6 Hz, 3 H, 4′-CH_3), 0.88 (t, *J* = 7.1 Hz, 3 H, 15′-H) 1.02–1.46 (m, 23 H, 3′-H, 4′-H, 5′-H, 6′-H, 7′-H, 8′-H, 9′-H, 10′-H, 11′-H, 12′-H, 13′-H, 14′-H), 1.78–1.96 (m, 2 H, 2′-H), 4.01 (s, 3 H, N-CH_3), 4.23 (t, *J* = 7.1 Hz, 2 H, 1′-H), 7.39 (t, *J* = 1.7 Hz, 1 H, 4-H), 7.52 (t, *J* = 1.7 Hz, 1 H, 5-H), 9.49 (br. s, 1 H, 2-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1 (C-15′), 19.3 (4′-CH_3), 22.7 (C-14′), 27.0–33.4 (C-3′, C-4′, C-6′, C-7′, C-8′, C-9′, C-10′, C-11′, C-12′, C-13′), 36.5–36.8 (C-5′, N-CH_3), 50.4 (C-1′), 122.0 (C-4), 123.8 (C-5), 136.8 (C-2) ppm. FTIR (ATR): $\tilde{\nu}$ = 3158 (w), 3117 (w), 2956 (s), 2921 (s), 2852 (s), 1627 (w), 1574 (s), 1465 (s), 1378 (m), 1169 (vs), 1055 (vs), 847 (w), 751 (m), 648 (w), 623 (s) cm^{-1}. $C_{20}H_{39}BF_4N_2$ (394.34): calcd. C 60.92, H 9.97, N 7.10; found C 60.95, H 10.03, N 7.04. MS (ESI, +ve): *m*/*z* = 307.3 $[M]^+$, 151.1, 123.1, 109.1, 95.1, 83.1. MS (ESI, –ve): *m*/*z* = 481.3 $[M(BF_4)_2]^-$, 87.0 $[BF_4]^-$. HMRS (ESI): calcd. for $[C_{20}H_{39}N_2]^+$ 307.3108; found 307.3114 $[M]^+$.

(4′*S*)-1′-Methyl-3′-(4′-methylpentadecyl)imidazolium Hexafluorophosphate (7d): From **3d** (79.6 mg, 0.20 mmol) a grey waxy solid (91.8 mg, 0.20 mmol, 99%) was obtained. $[\alpha]_D^{22}$ = –22.1 (*c* = 1.00, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.86 (d, *J* = 6.6 Hz, 3 H, 4′-CH_3), 0.88 (t, *J* = 6.8 Hz, 3 H, 15'-H) 1.02–1.46 (m, 23 H, 3′-H, 4′-H, 5′-H, 6′-H, 7′-H, 8′-H, 9′-H, 10′-H, 11′-H, 12′-H, 13′-H, 14′-H), 1.78–1.96 (m, 2 H, 2′-H), 3.91 (s, 3 H, N-CH_3), 4.12 (t, *J* = 7.1 Hz, 2 H, 1′-H), 7.25 (br. s, 1 H, 4-H), 7.29 (br. s, 1 H, 5-H), 8.52 (br. s, 1 H, 2-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1 (C-15′), 19.2 (4′-CH_3), 22.6 (C-14′), 27.0–33.4 (C-3′, C-4′, C-6′, C-7′, C-8′, C-9′, C-10′, C-11′, C-12′, C-13′), 36.2–36.8 (C-5′, N-CH_3), 50.5 (C-1′), 122.0 (C-4), 123.7 (C-5), 136.0 (C-2) ppm. FTIR (ATR): $\tilde{\nu}$ = 3180 (w), 3132 (w), 2957, 2916 (s), 2849 (s), 1573 (s), 1468 (m), 1321 (w), 1171 (vs), 817 (vs), 755 (m), 661 (s), 624 (vs), 554 (vs) cm^{-1}. $C_{20}H_{39}F_6N_2P$ (452.50): calcd. C 53.09, H 8.69, N 6.19; found C 53.04, H 8.70, N 6.25. MS (ESI, +ve): *m*/*z* = 307.3 $[M]^+$, 151.1, 123.1, 109.1, 95.1, 83.1. MS (ESI, –ve): *m*/*z* = 597.2 $[M(PF_6)_2]^-$, 144.9 $[PF_6]^-$. HMRS (ESI): calcd. for $[C_{20}H_{39}N_2]^+$ 307.3108; found 307.3106 $[M]^+$.

(4′*S*)-1′-Methyl-3′-(4′-methylpentadecyl)imidazolium Acetate (8d): From **3d** (93.4 mg, 0.24 mmol) a colourless waxy solid (87.5 mg, 0.23 mmol, 97%) was obtained. $[\alpha]_D^{22}$ = –21.8 (*c* = 1.00, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.86 (d, *J* = 6.7 Hz, 3 H, 4′-CH_3), 0.88 (t, *J* = 6.9 Hz, 3 H, 15'-H) 1.02–1.46 (m, 23 H, 3′-H, 4′-H, 5′-H, 6′-H, 7′-H, 8′-H, 9′-H, 10′-H, 11′-H, 12′-H, 13′-H, 14′-H), 1.78–1.96 (m, 2 H, 2′-H), 4.14 (s, 3 H, N-CH_3), 4.30 (t, *J* = 7.4 Hz, 2 H, 1′-H), 7.42 (t, *J* = 1.65 Hz, 1 H, 4-H), 7.63 (t, *J* = 1.7 Hz, 1 H, 5-H), 10.44 (br. s, 1 H, 2-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1 (C-15′), 19.4 (4′-CH_3), 22.7 (C-14′), 27.0–33.4 (C-3′, C-4′, C-6′, C-7′, C-8′, C-9′, C-10′, C-11′, C-12′, C-13′), 36.7–36.8 (C-5′, N-CH_3), 50.4 (C-1′), 121.8 (C-4), 123.7 (C-5), 137.6 (C-2) ppm. FTIR (ATR): $\tilde{\nu}$ = 3150 (w), 3090 (w), 2956 (s), 2921 (s), 2852 (s), 1573 (s), 1464 (s), 1377 (m), 1168 (vs), 1046 (br), 849 (w), 746 (m), 621 (s) cm^{-1}. $C_{22}H_{42}N_2O$ (350.58): calcd. C 75.37, H 12.08, N 7.99; found C 75.33, H 12.20, N 8.02. MS (ESI, +ve): *m*/*z* = 307.3 $[M]^+$, 151.1, 123.1, 109.1, 95.1, 83.1. HMRS (ESI): calcd. for $[C_{20}H_{39}N_2]^+$ 307.3108; found 307.3119 $[M]^+$.

General Procedure for the Anion Exchange of (4′*S*)-(4′-Methylpentadecyl)pyridinium Bromide (9d): KX (0.55 mmol, X = I, SCN, BF_4,

PF_6, OAc) was added to a solution of (4′*S*)-(4′-methylpentadecyl)-pyridinium bromide (**9d**; 211 mg, 0.55 mmol) in acetone (2 mL) and the mixture was stirred overnight at room temp. The colourless precipitate was removed by filtration and the filtrate was concentrated in vacuo. The solid residue was diluted in $CHCl_3$ (2 mL) and the remaining precipitate was removed by filtration. After concentration of the filtrate in vacuo, the resulting solid was dried in vacuo for 2 d at 80 °C.

(4′*S*)-(4′-Methylpentadecyl)pyridinium Iodide (10d): From **9d** (211 mg, 0.55 mmol) a yellow waxy solid (230 mg, 0.53 mmol, 97%) was obtained. $[\alpha]_D^{22}$ = +10.9 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (d, *J* = 6.5 Hz, 3 H, 4′-CH_3), 0.88 (t, *J* = 6.8 Hz, 3 H, 15'-H), 1.01–1.50 (m, 23 H, 3′-H, 4′-H, 5′-H, 6′-H, 7′-H, 8′-H, 9′-H, 10′-H, 11′-H, 12′-H, 13′-H, 14′-H), 1.92–2.24 (m, 2 H, 2′-H), 4.95 (t, *J* = 7.6 Hz, 2 H, 1′-H), 8.16–8.21 (m, 2 H, 3-H, 5-H), 8.55–8.61 (m, 1 H, 4-H), 9.39–9.41 (m, 2 H, 2-H, 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (C-15'), 19.4 (4′-CH_3), 22.7 (C-14′), 27.0–33.1 (C-3′, C-4′, C-6′, C-7′, C-8′, C-9′, C-10′, C-11′, C-12′, C-13′), 36.8 (C-5′), 62.5 (C-1′), 128.6 (C-3, C-5), 144.9 (C-4), 145.4 (C-2, C-6) ppm. FTIR (ATR): $\tilde{\nu}$ = 3107 (w), 2955 (s), 2921 (s), 2852 (s), 1570 (s), 1464 (vs), 1378 (m), 1165 (vs), 838 (s), 745 (s), 621 (s) cm^{-1}. MS (ESI, +ve): *m*/*z* = 304.3 $[M]^+$, 148.1, 120.1, 106.1, 80.0. $C_{21}H_{38}IN$ (431.44): calcd. C 58.46, H 8.88, N 3.25; found C 58.51, H 8.89, N 3.19. MS (ESI, –ve): *m*/*z* = 126.9 $[I]^-$. HMRS (ESI): calcd. for $[C_{21}H_{38}N]^+$ 304.2999; found 304.3002 $[M]^+$.

(4′*S*)-(4′-Methylpentadecyl)pyridinium Thiocyanate (11d): From **9d** (175 mg, 0.45 mmol) a colourless waxy solid (160 mg, 0.44 mmol, 98%) was obtained. $[\alpha]_D^{22}$ = –5.2 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (d, *J* = 6.6 Hz, 3 H, 4′-CH_3), 0.88 (t, *J* = 6.8 Hz, 3 H, 15'-H) 1.03–1.47 (m, 23 H, 3′-H, 4′-H, 5′-H, 6′-H, 7′-H, 8′-H, 9′-H, 10′-H, 11′-H, 12′-H, 13′-H, 14′-H), 1.99–2.27 (m, 2 H, 2′-H), 4.82 (t, *J* = 7.6 Hz, 2 H, 1′-H), 8.16–8.20 (m, 2 H, 3-H, 5-H), 8.54–8.56 (m, 1 H, 4-H), 9.05–9.08 (m, 2 H, 2-H, 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (C-15'), 19.3 (4′-CH_3), 22.7 (C-14′), 27.0–33.3 (C-3′, C-4′, C-6′, C-7′, C-8′, C-9′, C-10′, C-11′, C-12′, C-13′), 36.8 (C-5′), 63.0 (C-1′), 128.7 (C-3, C-5), 144.7 (C-4), 145.4 (C-2, C-6) ppm. FTIR (ATR): $\tilde{\nu}$ = 3384 (w), 3093 (w), 2956 (s), 2922 (s), 2852 (s), 2190 (br), 2048 (s), 1573 (s), 1465 (s), 1378 (w), 1168 (vs), 844 (w), 621 (s) cm^{-1}. $C_{22}H_{38}N_2S$ (362.62): calcd. C 72.87, H 10.56, N 7.73, S 8.84; found C 72.90, H 10.57, N 7.68, S 8.83. MS (ESI, +ve): *m*/*z* = 304.3 $[M]^+$, 148.1, 132.1, 120.2, 106.1, 93.1, 80.1. HMRS (ESI): calcd. for $[C_{21}H_{38}N]^+$ 304.2999; found 304.3002 $[M]^+$.

(4′*S*)-(4′-Methylpentadecyl)pyridinium Tetrafluoroborate (12d): From **9d** (157 mg, 0.41 mmol) a pale-brown waxy solid (159 mg, 0.40 mmol, 99%) was obtained. $[\alpha]_D^{22}$ = –12.0 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (d, *J* = 6.5 Hz, 3 H, 4′-CH_3), 0.88 (t, *J* = 6.8 Hz, 3 H, 15'-H) 1.00–1.48 (m, 23 H, 3′-H, 4′-H, 5′-H, 6′-H, 7′-H, 8′-H, 9′-H, 10′-H, 11′-H, 12′-H, 13′-H, 14′-H), 1.92–2.19 (m, 2 H, 2′-H), 4.75 (t, *J* = 7.5 Hz, 2 H, 1′-H), 8.01–8.11 (m, 2 H, 3-H, 5-H), 8.47–8.52 (m, 1 H, 4-H), 9.02–9.04 (m, 2 H, 2-H, 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (C-15'), 19.3 (4′-CH_3), 22.7 (C-14′), 27.0–33.2 (C-3′, C-4′, C-6′, C-7′, C-8′, C-9′, C-10′, C-11′, C-12′, C-13′), 36.7 (C-5′), 62.8 (C-1′), 128.5 (C-3, C-5), 144.7 (C-4), 145.4 (C-2, C-6) ppm. FTIR (ATR): $\tilde{\nu}$ = 3119 (w), 2956 (s), 2922 (s), 2852 (s), 2178 (br), 1966 (br), 1573 (s), 1465 (s), 1381 (w), 1170 (vs), 1054 (vs), 847 (w), 752 (s), 650 (w), 624 (s), 622 (s) cm^{-1}. $C_{21}H_{38}BF_4N$ (391.34): calcd. C 64.95, H 9.79, N 3.58; found C 64.88, H 9.83, N 3.60. MS (ESI, +ve): *m*/*z* = 304.3 $[M]^+$, 148.1, 132.1, 120.1, 106.1, 93.1, 80.0. MS (ESI, –ve): *m*/*z* = 87.0 $[BF_4]^-$. HMRS (ESI): calcd. for $[C_{21}H_{38}N]^+$ 304.2999; found 304.3002 $[M]^+$.

(4′*S*)-(4′-Methylpentadecyl)pyridinium Hexafluorophosphate (13d): From **9d** (209 mg, 0.52 mmol) a grey waxy solid (233 mg, 0.52 mmol, 96%) was obtained. $[\alpha]_D^{22}$ = –56.4 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (d, *J* = 6.6 Hz, 3 H, 4′-CH_3), 0.88 (t, *J* = 6.7 Hz, 3 H, 15'-H) 1.05–1.49 (m, 23 H, 3′-H, 4′-H, 5′-H, 6′-H, 7′-H, 8′-H, 9′-H, 10′-H, 11′-H, 12′-H, 13′-H, 14′-H), 1.99–2.27 (m, 2 H, 2′-H), 4.60 (t, *J* = 7.6 Hz, 2 H, 1′-H), 8.04–8.06 (m, 2 H, 3-H, 5-H), 8.46–8.49 (m, 1 H, 4-H), 8.70–8.73 (m, 2 H, 2-H, 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (C-15'), 19.2 (4′-CH_3), 22.7 (C-14′), 27.0–33.3 (C-3′, C-4′, C-6′, C-7′, C-8′, C-9′, C-10′, C-11′, C-12′, C-13′), 36.8 (C-5′), 62.9 (C-1′), 128.6 (C-3, C-5), 144.1 (C-4), 145.5 (C-2, C-6) ppm. FTIR (ATR): $\tilde{\nu}$ = 3179 (w), 2957 (s), 2916 (s), 2849 (s), 2181 (br), 1978 (br), 1573 (s), 1468 (vs), 1381 (w), 1167 (vs), 843 (s), 818 (vs), 755 (s), 661 (s), 624 (s), 555 (vs) cm^{-1}. $C_{21}H_{38}F_6NP$ (449.50): calcd. C 56.11, H 8.52, N 3.12; found C 56.24, H 8.52, N 3.07. MS (ESI, +ve): *m*/*z* = 304.3 $[M]^+$, 148.1, 132.1, 120.1, 80.0. MS (ESI, –ve): *m*/*z* = 145.9 $[PF_6]^-$. HMRS (ESI): calcd. for $[C_{21}H_{38}N]^+$ 304.2999; found 304.3006 $[M]^+$.

(4′*S*)-(4′-Methylpentadecyl)pyridinium Acetate (14d): From **9d** (151 mg, 0.40 mmol) a pale-yellow waxy solid (138 mg, 0.38 mmol, 95%) was obtained. $[\alpha]_D^{22}$ = +4.4 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (d, *J* = 6.6 Hz, 3 H, 4′-CH_3), 0.88 (t, *J* = 6.8 Hz, 3 H, 15'-H) 1.05–1.49 (m, 23 H, 3′-H, 4′-H, 5′-H, 6′-H, 7′-H, 8′-H, 9′-H, 10′-H, 11′-H, 12′-H, 13′-H, 14′-H), 1.99–2.27 (m, 2 H, 2′-H), 4.98 (t, *J* = 7.3 Hz, 2 H, 1′-H), 8.12–8.15 (m, 2 H, 3-H, 5-H), 8.49–8.52 (m, 1 H, 4-H), 9.43–9.46 (m, 2 H, 2-H, 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (C-15'), 19.3 (4′-CH_3), 22.7 (C-14′), 27.0–33.2 (C-3′, C-4′, C-6′, C-7′, C-8′, C-9′, C-10′, C-11′, C-12′, C-13′), 36.8 (C-5′), 63.0 (C-1′), 128.4 (C-3, C-5), 145.0 (C-4), 145.1 (C-2, C-6) ppm. FTIR (ATR): $\tilde{\nu}$ = 3080 (w), 2956 (s), 2922 (s), 2852 (s), 1572 (s), 1463 (s), 1377 (m), 1167 (vs), 930 (w), 833 (br), 746 (br), 648 (s), 620 (vs), 555 (s) cm^{-1}. $C_{23}H_{41}NO$ (347.58): calcd. C 79.48, H 11.89, N 4.03; found C 79.47, H 11.94, N 4.06. MS (ESI, +ve): *m*/*z* = 304.3 $[M]^+$, 148.1, 132.1, 120.1, 106.1, 80.0. HMRS (ESI): calcd. for $[C_{21}H_{38}N]^+$ 304.2999; found 304.3008 $[M]^+$.

Supporting Information (see also the footnote on the first page of this article): Yields of compounds **3**, **4**–**14** and **17**–**19**, POM texture of **3d**, spectroscopic and analytical data for compounds **17a**–**c**,**e**,**f**, **18a**–**c**,**e**,**f**, **19a**–**c**,**e**,**f**, **3a**–**c**,**e**,**f** and **9a**–**c** and X-ray diffraction patterns of compounds **3d**, **4d**, **7d**, **9d** and **10d**.

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