Synthesis of Novel Phasmidic, Gemini-Type Bisimidazolium Salts

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Dedicated to Prof. Dieter Hoppe on the occasion of his 70th birthday

Abstract: New bisimidazolium salts based on pyrogallol with flexible ethyl and *p*-xylyl spacers and with a series of different counterions were prepared. ^{1}H NMR studies showed a good linear correlation of the chemical shift with the radius of the anion.

Key words: ionic liquid, heterocycles, substituent effects, spectroscopy, halogens

Tethered bisimidazole derivatives have recently received a good deal of attention from two different scientific communities. Such bisimidazoles with either rigid or flexible spacers have been employed as bridging ligands for metal-organic frameworks (MOFs), i.e. novel 3D coordination polymers,[2] or as precursors of N-heterocyclic carbene (NHC) complexes for applications in catalysis.[3–5] Surprisingly little work has been carried out on the synthesis of the corresponding charged species, although many groups worldwide have utilized imidazolium salts as ionic liquid crystals.[6,7] Tethered bisimidazolium salts are expected to combine the properties of liquid crystals and ionic liquids, i.e. self-assembly into mesophases, anisotropic physical properties, low volatility, low viscosity, thermal stability, adjustable melting points, and tunable polarity.[6a,8] Therefore they lend themselves to being used as electrolytes in polymer light-emitting diodes (PLEDs), ion-conductive materials, organic reaction media, or self-assembling nanostructured materials.[6] In contrast to the classical amphiphilic imidazolium-based ionic liquid crystals, which mainly form bilayer type (SmA), columnar or cubic mesophases, the introduction of a second imidazolium moiety, which is tethered via a flexible or rigid spacer to the first one, can lead to novel liquid crystalline phases. This was indeed observed by Bruce and Shreeve, who studied a series of tethered bisimidazolium salts,[9] where fluorination of the tether or side chain led to novel mesomorphic properties. For example, compound **1**, which contains a rigid spacer between the imidazolium units, shows an unusual modulated ribbon SmÃ phase with *c*2*mm* symmetry, whereas the corresponding nonfluorinated analogue shows only isotropic melting (Figure 1). Gin reported on gemini ionic liquid crystals **2** and **3** where the two imidazolium moieties are tethered via a flexible alkyl or oligoethyleneglycol spacer.[10]

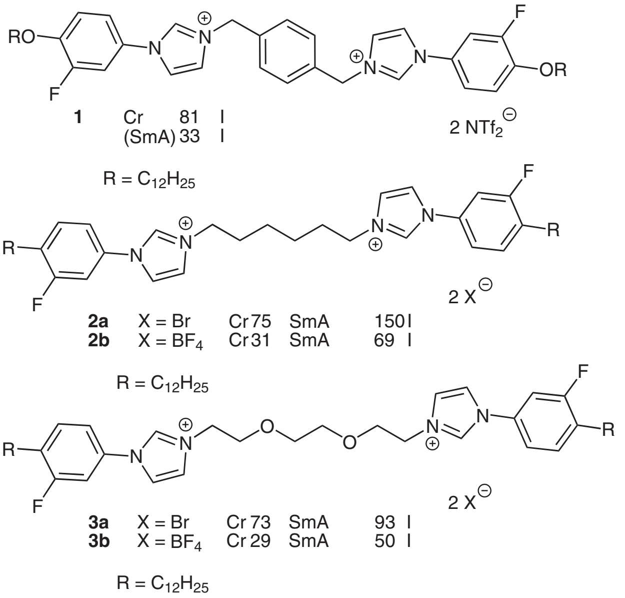
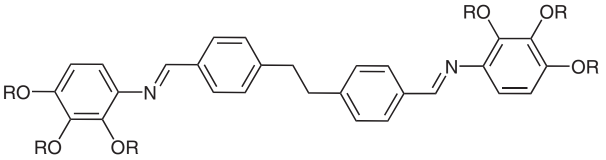


Figure 1 Examples for linked bisimidazolium ionic liquid crystals

If there are three flexible chains on each side of an elongated rigid core, then these molecules are called phasmidic compounds.[11–13] Previous work by Judeinstein et al.[14] revealed that tethered phasmidic liquid crystals such as compound **4** form nematic phases as long as they carry *o*,*m*,*p*-tris(alkyloxy)aryl side chains with a chain length of between six and ten carbon atoms (Figure 2).



4 Cr 34 N 64 I
R = C$_8$H$_{17}$

Figure 2 Example of a phasmidic liquid crystal that forms a nematic phase[14]

We were curious whether or not this nematogenic motif could be transferred to gemini-type bisimidazolium salts, thus leading to ionic liquid crystals with nematic mesophases, which are quite rare in this class of compounds.[15] Here we report on first results in relation to this goal.

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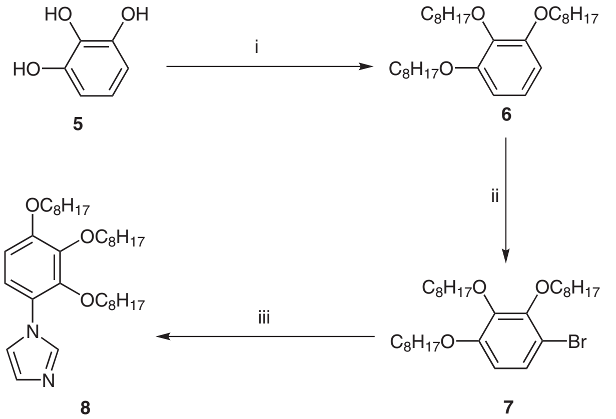
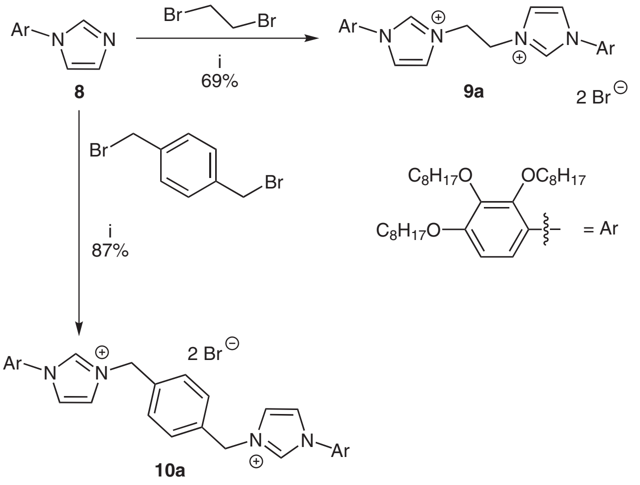
The synthesis of the desired bisimidazolium salts started with the etherification of pyrogallol **5** with bromooctane in *N*,*N*-dimethylformamide at 60 °C with 97% yield according to a procedure by Percec (Scheme 1).[16] α-Bromination of **6** was achieved with *N*-bromosuccinimide at 60 °C in dichloromethane yielding 85% of **7**. The C–N bond formation was accomplished by an Ullmann reaction of **7** with imidazole in *N*,*N*-dimethylformamide at 110 °C in the presence of copper(I) iodide and cesium carbonate in 79% yield.



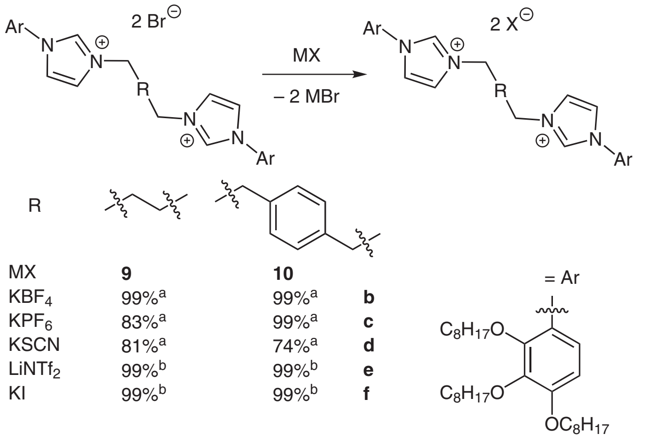
Scheme 1 Synthesis of the N-arylated wing group **8**. *Reagents and conditions*: (i) BrC_8H_{17}, K_2CO_3, DMF, 60 °C, 4 h, 97%; (ii) NBS, CH_2Cl_2, 60 °C, 12 h, 85%; (iii) imidazole, DMF, CuI, Cs_2CO_3, 110 °C, 5 d, 79%.

The tethered bisimidazolium salts were obtained by reaction of the N-arylated compound **8** with the desired dibromo central unit at 110 °C with 69% yield for **9** and 87% yield for **10**, respectively (Scheme 2).



Scheme 2 Coupling of the wing group **8** with the central unit. *Reagents and conditions*: (i) MeCN, 110 °C, 5 d.

Anion exchange of the phasmidic dibromo compounds were performed either in acetonitrile at 90 °C or with a *tert*-butyl methyl ether–water mixture at room temperature with the desired potassium or lithium salt in good yields (Scheme 3).



MX	9	10	
KBF_4	99%[a]	99%[a]	**b**
KPF_6	83%[a]	99%[a]	**c**
KSCN	81%[a]	74%[a]	**d**
$LiNTf_2$	99%[b]	99%[b]	**e**
KI	99%[b]	99%[b]	**f**

Scheme 3 Anion exchange of compounds **9** and **10**. *Reagents and conditions*: [a] Method A: MeCN, 90 °C, 4 h; [b] Method B: MTBE–H_2O, r.t.

In agreement with previous publications[17] we also observed significant proton resonance upfield shifts in the ^1H NMR spectra upon replacement of bromide by bigger anions. In contrast to similar NMR studies in our group[18] we observed not only a shift of the CH of the imidazolium group but also a shift of the N–CH_2 protons adjacent to the imidazolium unit. Typical spectra of **9** are shown in Figure 3. The following tendency of $\delta_{(CH)}$ and $\delta_{(CH2)}$ is preserved for **9**·X and **10**·X (X = Br, BF_4, PF_6, SCN, NTf_2, I): Br > I > SCN > BF_4 > NTf_2 > PF_6. Details of the anion-dependent ^1H NMR shifts of compound **10**·X are described in the Supporting Information.

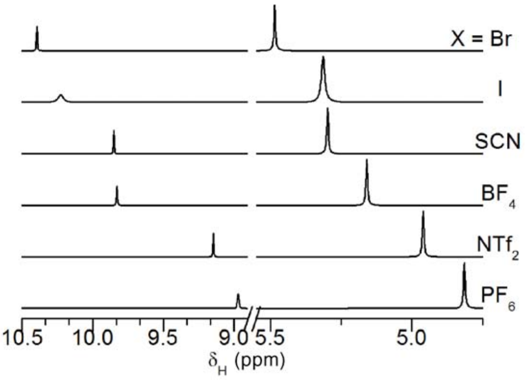


Figure 3 Lowfield section of the ^1H NMR spectra (500 MHz, $CDCl_3$, r.t.) of the phasmidic salts **9**·X with different anions X. In the lower field, the C–H resonances of the imidazole proton could be observed, whereas in the higher field the adjacent CH_2 groups resonate. For reasons of clarity, only the signals for $\delta_{(CH)}$ and $\delta_{(CH2)}$ are shown.

A fairly good relation between the degree of upfield shift and the anion radius could be observed (Figure 4, SCN and NTf_2 are not included because of the anisotropic shape of the molecules).[19] This suggests that the position of the anion is close to the CH of the imidazoles and the bridging atoms next to them.[18a]

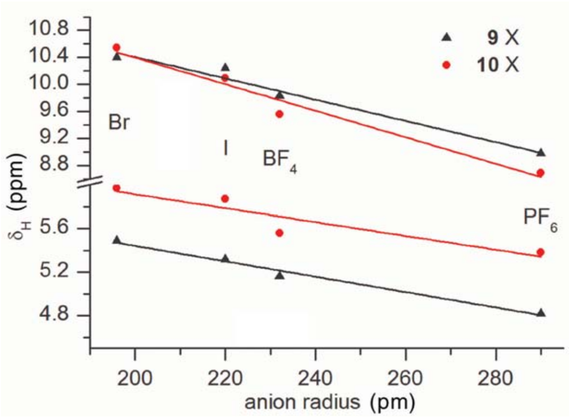


Figure 4 Correlation of the CH (lowfield section) and CH$_2$ (highfield section) chemical shifts for **9**·X and **10**·X (δ, CDCl$_3$, r.t.) with the anionic radii.

All compounds **9**·X and **10**·X were investigated with regard to their mesomorphic properties by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM), whereas no mesophases could be observed. The rationale for not forming mesophases may be two fold. Firstly, the C8 chain could be too short to induce mesomorphic properties, which is somewhat surprising as Judeinstein reported a decrease and disappearance of mesophases for derivatives with longer alkyl chain lengths. Secondly, the flexibility, or rather rigidity, of the spacer may not be optimal, meaning mesophases may not form.

In conclusion, phasmidic compounds with different spacers are easily accessible by the described route and the anion exchange is possible with good yields. The most promising strategy to generate derivatives with mesomorphic properties seems to be the introduction of longer alkyl chains and/or different spacers.

Melting points were measured on a Stuart SMP10 apparatus and are uncorrected. IR spectra were recorded with a Bruker Vector 22 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance 500 spectrometer with TMS as an internal standard. Mass spectra were recorded with a Bruker Daltonics microTOF-Q (ESI) spectrometer with N$_2$ as carrier gas. Flash chromatography was performed using Kieselgel 60 silica powder, 40–63 mm (Fluka). All solvents were dried, and reactions were performed in dried glassware using standard Schlenk techniques unless stated otherwise. The following compounds were prepared according to literature procedures: **6**.[16]

General experimental procedure for compounds **7**, **8**, **9a**,**b**,**e**, and **10a** are provided here; experimental data for the other salts of **9** and **10** are provided in the Supporting Information.

1-Bromo-2,3,4-tris(octyloxy)benzene (7)

A soln of 1,2,3-tris(octyloxy)benzene (**6**, 9.25 g, 20 mmol) and NBS (3.92 g, 22 mmol) in CH$_2$Cl$_2$ (40 mL) was heated at reflux for 12 h. After cooling to r.t. the resulting soln was filtered and the solvent was evaporated. The crude product was purified by column chromatography (silica gel, cyclohexane) yielding **7** (9.02 g, 17.0 mmol, 85%) as a viscous, pale yellow oil; R_f = 0.05 (cyclohexane).

IR (ATR): 2923, 2854, 1967, 1573, 1463, 1443, 1378, 1295, 1267, 1210, 1125, 1087, 1011, 960, 911, 868, 788, 723, 639 cm^{-1}.

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.15 (d, ^3J = 8.9 Hz, 1 H, H6), 6.54 (d, ^3J = 9.0 Hz, 1 H, H5), 4.03 (t, ^3J = 6.7 Hz, 2 H, OCH$_2$), 3.97 (t, ^3J = 6.6 Hz, 2 H, OCH$_2$), 3.93 (t, ^3J = 6.5 Hz, 2 H, OCH$_2$), 1.80 (m, 6 H, 3 β-CH$_2$), 1.47 (m, 6 H, 3 γ-CH$_2$), 1.38–1.22 (m, 24 H, CH$_2$), 0.89 (t, ^3J = 6.9 Hz, 9 H, CH$_3$).

^{13}C NMR (125 MHz, CDCl$_3$): δ = 153.26 (C4), 150.79 (C2), 143.29 (C3), 126.66 (C6), 109.56 (C5), 108.76 (C1), 74.16, 74.04 (C2-O*C*H$_2$, C3-O*C*H$_2$), 69.08 (C4-O*C*H$_2$), 32.02, 32.01, 31.96, 30.43, 30.39, 29.64, 29.59, 29.50, 29.45, 29.44, 29.41, 26.24, 26.23, 26.20, 22.83, 22.82, 22.81 (CH$_2$), 14.24 (CH$_3$).

HRMS (ESI): *m/z* [M + NH$_4^+$] calcd for C$_{30}$H$_{57}$BrNO$_3$: 558.3516; found: 558.3526.

Anal. Calcd for C$_{30}$H$_{53}$BrO$_3$: C, 66.52; H, 9.86. Found: C, 66.23; H, 9.63.

1-[2,3,4-Tris(octyloxy)phenyl]-1*H*-imidazole (8)

A suspension of **7** (5.42 g, 10 mmol), imidazole (0.95 g, 14 mmol), CuI (0.38 g, 2.0 mmol) and Cs$_2$CO$_3$ (3.25 g, 10 mmol) in degassed DMF (30 mL) was stirred for 5 d at 110 °C under an N$_2$ atmosphere. After cooling to r.t., MTBE (50 mL) were added and the suspension was washed with NH$_4$OH soln (3 × 20 mL) and H$_2$O (2 × 50 mL). The organic layers were dried (MgSO$_4$) and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, CH$_2$Cl$_2$–MTBE, 15:1) yielding **8** (4.15 g, 7.85 mmol, 79%) as a brown oil; R_f = 0.10–0.25 (CH$_2$Cl$_2$–MTBE, 15:1).

IR (ATR): 2923, 2854, 1966, 1599, 1505, 1456, 1370, 1281, 1243, 1198, 1138, 1091, 1064, 977, 902, 797, 725, 659 cm^{-1}.

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.78 (br s, 1 H, H8), 7.26 (br s, 2 H, H10, H11), 6.93 (d, ^3J = 8.8 Hz, 1 H, H6), 6.67 (d, ^3J = 8.8 Hz, 1 H, H5), 4.03 (t, ^3J = 6.6 Hz, 2 H, C3-OCH$_2$), 3.99 (t, ^3J = 6.5 Hz, 2 H, C4-OCH$_2$), 3.79 (t, ^3J = 6.6 Hz, 2 H, C2-OCH$_2$), 1.81 (m, 4 H, C3-OCH$_2$C*H*$_2$, C4-OCH$_2$C*H*$_2$), 1.49 (m, 6 H, γ-CH$_2$), 1.42–1.11 (m, 26 H, C2-OCH$_2$C*H*$_2$, CH$_2$), 0.88 (m, 9 H, CH$_3$).

^{13}C NMR (125 MHz, CDCl$_3$): δ = 153.42 (C4), 147.50 (C2), 142.84 (C3), 125.26 (C1), 119.74 (C6), 107.99 (C5), 74.45 (C2-O*C*H$_2$), 74.05 (C3-O*C*H$_2$), 69.12 (C4-O*C*H$_2$), 32.01, 31.95, 31.94, 30.48, 30.11, 29.64, 29.48, 29.41, 29.32, 26.23, 25.85, 22.81, 22.79, 22.77 (CH$_2$), 14.22 (CH$_3$).

HRMS (ESI): *m/z* [M + H$^+$] calcd for C$_{33}$H$_{57}$N$_2$O$_3$: 529.4364; found: 529.4367.

Anal. Calcd for C$_{33}$H$_{56}$N$_2$O$_3$: C, 74.95; H, 10.67; N, 5.30. Found: C, 74.74; H, 10.52; N, 5.23.

3,3′-(Ethane-1,2-diyl)bis{1-[2,3,4-tris(octyloxy)phenyl]-1*H*-imidazolium} Bromide (9a); Typical Procedure

A soln of **8** (1.058 g, 2.0 mmol) and 1,2-dibromoethane (188 mg, 1.0 mmol) in MeCN (7 mL) was stirred for 5 d at 110 °C. The solvent was removed and the crude product was dissolved in Et$_2$O (5 mL). The product was precipitated from Et$_2$O by addition of MeCN and cooling to –20 °C yielding **9a** (861 mg, 0.69 mmol, 69%) as a colorless solid; mp 207 °C.

IR (ATR): 2924, 2855, 2364, 2189, 1965, 1549, 1494, 1465, 1379, 1343, 1303, 1235, 1183, 1119, 1084, 966, 921, 908, 799, 725, 641 cm^{-1}.

^{1}H NMR (500 MHz, CDCl$_3$): δ = 10.39 (s, 2 H, H8), 9.05 (s, 2 H, H10), 7.42 (s, 2 H, H11), 7.20 (d, ^3J = 8.9 Hz, 2 H, H6), 6.74 (d, ^3J = 9.1 Hz, 2 H, H5), 5.49 (s, 4 H, H12), 4.08 (t, ^3J = 6.9 Hz, 4 H, C2-OCH$_2$), 4.02 (t, ^3J = 6.6 Hz, 8 H, C3-OCH$_2$, C4-OCH$_2$), 1.86 (m, 4 H, C4-OCH$_2$C*H*$_2$), 1.78 (m, 4 H, C3-OCH$_2$C*H*$_2$), 1.53 (m, 4 H, g-CH$_2$), 1.49 (m, 8 H, g-CH$_2$), 1.42–1.20 (m, 52 H, C2-OCH$_2$C*H*$_2$, CH$_2$), 0.90 (m, 18 H, CH$_3$).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.68 (C4), 146.68 (C2), 142.36 (C3), 136.80 (C8), 124.15 (C10), 123.23 (C11), 120.91 (C1), 119.72 (C6), 108.07 (C5), 74.94 (C2-O*C*H$_2$), 74.20 (C3-O*C*H$_2$), 69.22 (C3-O*C*H$_2$), 48.09 (C12), 31.90, 31.85, 31.82, 30.31, 30.12, 29.51, 29.37, 29.35, 29.30, 29.26, 29.17, 26.09, 25.70, 22.72, 22.70, 22.66 (CH_2), 14.14 (CH_3).

MS (ESI): *m*/*z* = 1166 [M – Br$^-$], 543 [M – 2 Br$^-$].

HRMS (ESI): *m*/*z* [M – Br$^-$] calcd for $C_{68}H_{116}N_4O_6Br$: 1163.8073; found: 1163.8091.

Anal. Calcd for $C_{68}H_{116}Br_2N_4O_6$: C, 65.58; H, 9.39; N, 4.50. Found: C, 65.05; H, 9.34; N, 4.34.

3,3′-[1,4-Phenylenebis(methylene)]bis{1-[2,3,4-tris(octyloxy)phenyl]-1*H*-imidazolium} Bromide (10a)

Following the typical procedure for **9a** using **8** (1.058 g, 2.0 mmol) and 1,4-bis(bromomethyl)benzene (0.264 g, 1.0 mmol) gave **10a** (1.145 g, 0.87 mmol, 87%) as a colorless solid; mp 194 °C.

IR (ATR): 3039, 2922, 2853, 1966, 1597, 1553, 1496, 1466, 1379, 1345, 1302, 1281, 1233, 1191, 1123, 1082, 955, 814, 749, 724, 636 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.53 (s, 2 H, H8), 7.97 (s, 2 H, H10), 7.73 (s, 4 H, H14, H14¢), 7.51 (s, 2 H, H11), 7.38 (d, ^3J = 9.0 Hz, 2 H, H6), 6.75 (d, ^3J = 9.1 Hz, 2 H, H5), 5.97 (s, 4 H, H12), 4.04 (t, ^3J = 6.9 Hz, 4 H, C2-OCH$_2$), 4.00 (t, ^3J = 6.6 Hz, 8 H, C3-OCH$_2$, C4-OCH$_2$), 1.84 (m, 4 H, C4-OCH$_2$C*H*$_2$), 1.77 (m, 4 H, C3-OCH$_2$C*H*$_2$), 1.56 (m, 4 H, g-CH$_2$), 1.47 (m, 8 H, g-CH$_2$), 1.40–1.20 (m, 52 H, C2-OCH$_2$C*H*$_2$, CH$_2$), 0.88 (m, 18 H, CH$_3$).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.32 (C4), 146.42 (C2), 142.23 (C3), 136.77 (C8), 134.74 (C14, C14′), 130.17 (C13), 123.58 (C11), 122.34 (C10), 121.10 (C1), 120.09 (C6), 108.29 (C5), 74.83 (C2-O*C*H$_2$), 74.11 (C3-O*C*H$_2$), 69.14 (C3-O*C*H$_2$), 52.38 (C12), 31.90, 31.85, 31.83, 30.32, 30.08, 29.53, 29.37, 29.29, 29.20, 26.11, 26.10, 25.73, 22.71, 22.70, 22.68 (CH_2), 14.16, 14.13 (CH_3).

MS (ESI): *m*/*z* = 1241 [M – Br$^-$], 581 [M – 2 Br$^-$].

HRMS (ESI): *m*/*z* [M – Br$^-$] calcd for $C_{74}H_{120}N_4O_6Br$: 1239.8386; found: 1239.8367.

Anal. Calcd for $C_{74}H_{120}Br_2N_4O_6$: C, 67.25; H, 9.15; N, 4.24. Found: C, 67.37; H, 9.07, N; 4.25.

Anion Exchange

Method A: Bromide of the phasmidic compound **9a** or **10a** (0.1 mmol) was dissolved in MeCN (10 mL) and the respective salt (2 mmol) was added. The soln was stirred for 4 h at 90 °C. The hot soln was filtered and the solvent was removed under reduced pressure. $CHCl_3$ (10 mL) was added, the suspension was filtered and the solvent was removed under vacuum.

3,3′-(Ethane-1,2-diyl)bis{1-[2,3,4-tris(octyloxy)phenyl]-1*H*-imidazolium} Tetrafluoroborate (9b)

Colorless solid; yield: 124 mg (0.099 mmol, 99%); mp 200 °C.

IR (ATR): 3422, 2923, 2854, 1594, 1555, 1495, 1466, 1381, 1348, 1304, 1281, 1232, 1190, 1123, 1084, 814, 733, 640 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.89 (s, 2 H, H8), 8.68 (s, 2 H, H10), 7.44 (s, 2 H, H11), 7.17 (d, ^3J = 9.0 Hz, 2 H, H6), 6.74 (d, ^3J = 9.1 Hz, 2 H, H5), 5.22 (s, 4 H, H12), 4.07 (t, ^3J = 6.9 Hz, 4 H, C2-OCH$_2$), 4.02 (t, ^3J = 6.6 Hz, 8 H, C3-OCH$_2$, C4-OCH$_2$), 1.85 (m, 4 H, C4-OCH$_2$C*H*$_2$), 1.78 (m, 4 H, C3-OCH$_2$C*H*$_2$), 1.56 (m, 4 H, g-CH$_2$), 1.48 (m, 8 H, g-CH$_2$), 1.40–1.20 (m, 52 H, C2-OCH$_2$C*H*$_2$, CH$_2$), 0.87 (m, 18 H, CH$_3$).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.71 (C4), 146.59 (C2), 142.30 (C3), 136.66 (C8), 123.86 (C10), 123.64 (C11), 120.74 (C1), 119.60 (C6), 108.05 (C5), 74.89 (C2-O*C*H$_2$), 74.17 (C3-O*C*H$_2$), 69.18 (C3-O*C*H$_2$), 48.04 (C12), 31.86, 31.81, 31.77, 30.27, 30.04, 29.47, 29.33, 29.31, 29.26, 29.24, 29.22, 29.13, 26.05, 25.66, 22.68, 22.66, 22.61 (CH_2), 14.10, 14.09 (CH_3).

MS (ESI): *m*/*z* = 1172 [M – BF_4^-], 581, 542 [M – 2 BF_4^-].

HRMS (ESI): *m*/*z* [M – BF_4^-] calcd for $C_{68}H_{116}BF_4N_4O_6$: 1171.8930; found: 1171.8911.

Anal. Calcd for: $C_{68}H_{116}B_2F_8N_4O_6$: C, 64.86; H, 9.28; N, 4.45. Found: C, 64.78; H, 9.35; N, 4.34.

Method B: Phasmidic compound **9a** or **10a** (0.1 mmol) was dissolved in MTBE (10 mL) and was shaken for 1 min in a separatory funnel with a soln of the respective salt [2 mL, salt (2 g) in H_2O (10 mL)]. The procedure was repeated four times and the organic layer was washed with H_2O (3 × 10 mL). Subsequently, the organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure.

3,3′-(Ethane-1,2-diyl)bis{1-[2,3,4-tris(octyloxy)phenyl]-1*H*-imidazolium} Bis(triflatimide) (9e)

Pale-yellow oil; yield: 164 mg (0.099 mmol, 99%).

IR (ATR): 3147, 2953, 2856, 2360, 1556, 1495, 1467, 1347, 1229, 1186, 1134, 1086, 1057, 968, 906, 790, 737, 651, 616, 600, 570, 500 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.15 (s, 2 H, H8), 8.04 (s, 2 H, H10), 7.55 (s, 2 H, H11), 7.15 (d, ^3J = 8.9 Hz, 2 H, H6), 6.76 (d, ^3J = 9.1 Hz, 2 H, H5), 4.96 (s, 4 H, H12), 4.08 (t, ^3J = 6.9 Hz, 4 H, C2-OCH$_2$), 4.03 (t, ^3J = 6.6 Hz, 8 H, C3-OCH$_2$, C4-OCH$_2$), 1.86 (m, 4 H, C4-OCH$_2$C*H*$_2$), 1.78 (m, 4 H, C3-OCH$_2$C*H*$_2$), 1.55 (m, 4 H, g-CH$_2$), 1.49 (m, 8 H, g-CH$_2$), 1.42–1.20 (m, 52 H, C2-OCH$_2$C*H*$_2$, CH$_2$), 0.88 (m, 18 H, CH$_3$).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.93 (C4), 146.46 (C2), 142.22 (C3), 136. 92 (C8), 124.59 (C10), 122.91 (C11), 120.40 (C1), 119.64 (q, $^1J_{C,F}$ = 321.62 Hz, CF_3), 119.44 (C6), 107.95 (C5), 74.86 (C2-O*C*H$_2$), 74.16 (C3-O*C*H$_2$), 69.19 (C3-O*C*H$_2$), 47.84 (C12), 31.86, 31.81, 31.73, 30.24, 29.94, 29.46, 29.33, 29.26, 29.20, 29.17, 29.14, 26.07, 26.04, 25.61, 22.68, 22.67, 22.58 (CH_2), 14.10, 14.03 (CH_3).

MS (ESI): *m*/*z* 1365 [M – NTf_2^-], 543 [M – 2 NTf_2^-].

HRMS (ESI): *m*/*z* [M – NTf_2^-] calcd for $C_{70}H_{116}F_6N_5O_{10}S_2$: 1364.8062; found: 1364.8060.

Anal. Calcd for $C_{74}H_{120}F_{12}N_6O_{14}S_2$: C, 52.54; H, 7.10; N, 5.11. Found: C, 52.72; H 7.11; N 5.24.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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