RESEARCH FRONT

CSIRO PUBLISHING

Aust. J. Chem. **2014**, *67*, 1088–1099
http://dx.doi.org/10.1071/CH14376

Full Paper

Cyanobiphenyl versus Alkoxybiphenyl: Which Mesogenic Unit Governs the Mesomorphic Properties of Guanidinium Ionic Liquid Crystals?

Johannes Christian Haenle,[A] *Manuel M. Neidhardt,*[A] *Stuart Beardsworth,*[A] *Jochen Kirres,*[A] *Angelika Baro,*[A] *and Sabine Laschat*[A,B]

[A]Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany.
[B]Corresponding author. Email: sabine.laschat@oc.uni-stuttgart.de

A series of phenylguanidinium salts **3·X**, which are linked via an alkoxy spacer either to a 4-decyloxy- or 4-cyano-substituted biphenyl mesogen, was prepared and the mesomorphism studied. A decyloxybiphenyl core and a spacer of at least C6 chain length were required for mesophase formation. Replacement of the chloride counterion by other anions like bromide or tetrafluoroborate improved the thermal stability of the mesophase. A comparison of substitution pattern (*meta v. para*) on the phenyl ring revealed decreased melting and clearing points for the bent cationic head group. All guanidinium ionic liquid crystals **3** displayed only smectic A (SmA) phases. A packing model is assumed where the molecules in a bilayer stack over each other in opposite direction with interdigitated terminal decyloxy groups and spacers.

Manuscript received: 28 March 2014.
Manuscript accepted: 11 June 2014.
Published online: 30 June 2014.

Introduction

Guanidine derivatives and guanidinium ions have attracted researchers from various fields over the last decade.[1–5] With high thermal stability, the ease of charge delocalization and coordination properties as well as the possibility to attach up to six different substituents on the guanidine moiety has driven research activities in diverse directions, resulting in their use as superbases,[6,7] ligands for coordination complexes,[8–11] organocatalysts,[12–16] stimuli-responsive materials,[17] hydrogels,[18] anion exchange polymer electrolytes for fuel cells,[19] and biologically active compounds[20–29] for drug development. Furthermore, guanidinium salts have also entered the field of ionic liquid crystals (ILCs)[30–45] as an alternative cationic head group to the imidazolium-derived ILCs, which have dominated this research area so far.[46]

ILCs provide an ideal combination of the physical properties of ionic liquids,[47–50] and thermotropic liquid crystals[51] giving access to novel materials with fluid-like viscosity, anisotropic properties such as birefringence, wide thermal and electrochemical stability as well as 1D ionic and electronic conductivity.[42–45]

The formation of stable mesophases in ILCs is caused by nanosegregation of subunits of different polarity such as lipophilic side chains and polar aryl moieties with cationic (and/or anionic) head groups.[52–54] In addition, the presence of rod-shaped (calamitic) or disk-shaped (discotic) mesogens connected to the cationic head group may further contribute to mesophase stabilization and the preference of a certain mesophase type, as was recently shown for cyanobiphenyl- and triphenylene-imidazolium ILCs.[55–58] Imidazolium salt derivatives **1a**,**b** with a calamitic *p*-alkoxybiphenyl mesogen displayed two smectic (SmE and SmA) phases regardless of spacer length (Chart 1).[59]

For the structurally related pyridinium salt **2a**, SmE and SmA phases were also observed, whereas the corresponding 4-decyloxybiphenyl derivative **2b** displayed a SmC instead of a SmA phase.[60] In contrast, cyanobiphenyl pyridinium bromide **2c** formed only a SmA phase.

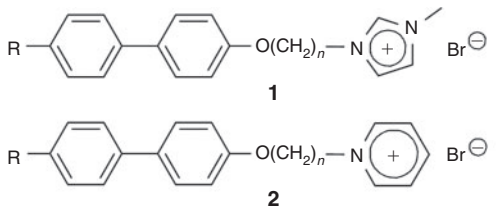
Based on these results, we envisaged a class of ILC derivatives **3**, in which the pyridinium was replaced with a guanidinium-substituted phenol under maintenance of the central 4-cyano- or 4-decyloxybiphenyl mesogen (Chart 1). Studying the mesomorphism of *m*- and *p*-**3**, we were interested to see whether the mesogenic unit, the spacer lengths, or the substitution pattern of the head group controls the mesomorphic properties with a focus on the formation of SmC mesophases. The results towards this goal are reported below.

Results and Discussion

Synthesis of Guanidinium ILCs

The synthesis commenced with a Williamson etherification of acetamide **4** with 1,10-dibromodecane to yield bromide *m*-**5** in 58 % yield (Scheme 1). Subsequent Williamson etherification of bromides *m*-**5** and *p*-**5**[61] with 4′-decyloxy- (**6a**) or 4′-cyano-1-hydroxybiphenyl (**6b**) provided the tethered compounds **7a**,**b** without any problems in 59–87 % yield. However, with exception of *m*-**7a**, attempted hydrolysis of the acetamide turned out to be problematic. Under various conditions either no conversion or decomposition was observed (see Supplementary Material for details).

Therefore, *N*-Boc-protected hydroxyanilines **8** were used instead (Scheme 2). In a similar fashion compounds **8** were submitted to two sequential Williamson etherifications via



Compd	R	n	phase					
1a	OC_3H_7	8	g 29	SmE	138	SmA	156	I
1b	OC_3H_7	12	g 38	SmE	154	SmA	180	I
2a	OC_3H_7	10		SmE	150	SmA	183	I
2b	$OC_{10}H_{21}$	10		Cr	136	SmC	165	I
2c	CN	6		g	17	SmA	65	I

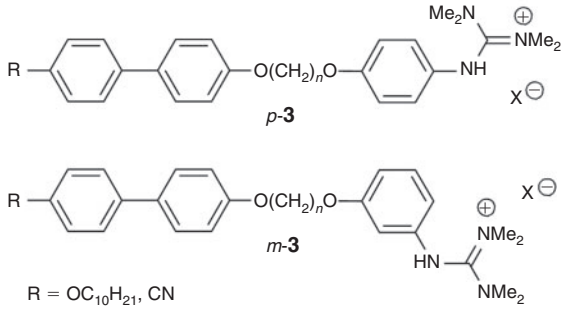
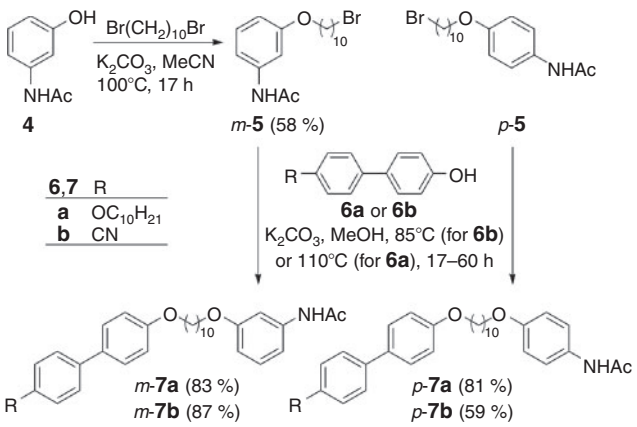


Chart 1.



Scheme 1.

bromides **9** giving the tethered compounds *p*-**10a**,**b** and *m*-**10b**–**e** in 78–88 % yield. *N*-Boc-deprotection to derivatives *p*-**11a**,**b** and *m*-**11b**–**e** was achieved very cleanly with methane sulfonic acid in $CHCl_3$. Derivative *m*-**11a** was obtained in 94 % yield by acidic hydrolysis[62] of acetamide *m*-**7a**. The aniline derivatives **11** were finally treated with chloro-*N*,*N*,*N*′,*N*′-tetramethylformamidinium chloride[63] and either NEt_3 or $NaHCO_3$. Workup strictly required an inert gas atmosphere to provide the neat target guanidinium salts **3·Cl** in 70–98 % yield. To further study the anion effect, decyloxybiphenyl guanidinium chloride *m*-**3a·Cl** was submitted to salt metathesis with NaBr, KI, NaOTf, $NaBF_4$, KPF_6, KOAc, and KSCN yielding the corresponding guanidinium ILCs *m*-**3a·X** (Scheme 2).

Anion Effect in Guanidinium ILCs

Comparison of the ^{1}H NMR spectra of phenylguanidinium salts *m*-**3a·X** revealed a significant downfield shift of the N–H signal from ~7.5 to 12.0 ppm in the following order: $PF_6 < BF_4 <$ OTf < I < SCN < Br ≈ Cl (Fig. 1).

This correlation between the anion and the N–H proton shift indicates the presence of contact between the ion pairs that also led to small chemical shifts of the aromatic protons of the phenylguanidinium moiety (Fig. 1, grey). To estimate the effect of concentration on the N–H signal, ^{1}H NMR measurements of *m*-**3b·Cl** with concentrations varying from 0.83 to 2.50 mg μL^{-1} were carried out. The N–H signal shift of 0.1 ppm turned out to be negligible with respect to the strong dependence of the NH signal on the anion (see Supplementary Material for details). This effect rather might be due to either the interaction of the anion with the anisotropic cone of the aryl ring than due to the conjugation between the guanidinium cation and the aryl ring. Previous DFT calculations of several guanidinium salts revealed no or only very little conjugation, i.e. the guanidinium moiety behaves like an isolated cation.[39] In agreement with these studies, the N–H signal shifted upfield with increasing anion radii[64,65] with an almost linear correlation (Fig. 2).

Mesomorphic Properties of Guanidinium ILCs

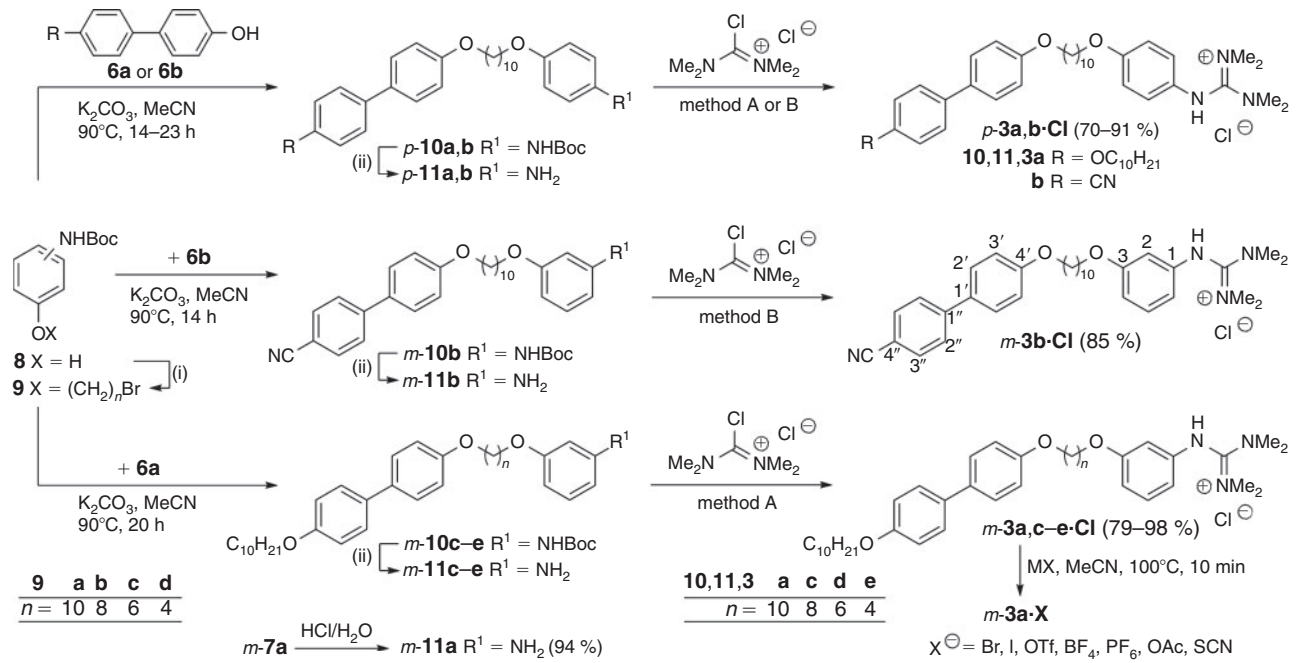
The mesomorphic properties of guanidinium salts **3** were studied by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (XRD).

The results of DSC investigations are summarised in Table 1. Whereas both cyanobiphenyl guanidinium chlorides *p*- and *m*-**3b·Cl** as well as *m*-**3e·Cl** with a butyl spacer were non-mesomorphic (entries 2, 3, and 9), the other chlorides revealed mesophases and some crystal-to-crystal transitions. ILCs *m*-**3c·Cl** and *m*-**3d·Cl** with spacer lengths < C10 showed monotropic phase behaviour, forming small SmA phases upon first cooling (entries 5, 7). As recently reported,[35] bending of the cationic core by *meta*-substitution (*m*-**3a·Cl**) decreased melting and clearing points compared with the *para*-substituted analogue *p*-**3a·Cl**. Their mesophase widths ranged from 16 to 23 K (entries 1, 8).

Upon successive heating and cooling cycles, however, melting and clearing points of the guanidinium chloride *m*-**3a·Cl** were shifted to lower temperatures after each cycle, indicating thermal decomposition (Fig. 3a). *Para*-substituted **3a·Cl** behaved similarly. Replacement of chloride by other anions giving *m*-**3a·X** not only led to lower clearing temperatures as compared with *m*-**3a·Cl**, but also decomposition was suppressed and clearing transitions stayed constant at the same temperature (Fig. 3b), as recently reported for guanidinium phenylalkoxybenzoates.[37] Guanidinium salts *m*-**3a·X** (X = Br, BF_4) formed reproducible enantiotropic mesophases (Table 1, entries 10, 14). In contrast, *m*-**3a·I** and *m*-**3a·SCN** showed only monotropic phase behaviour (entries 12, 18) and salts *m*-**3a·X** (X = OTf, OAc, PF_6) were non-mesogenic.

Under POM, the liquid crystalline guanidinium salts **3** exhibited strong tendencies for a homeotropic alignment, which could be distinguished from the isotropic phase by shearing textures. It should be noted that a homeotropic alignment is a typical feature of SmA phases.[45] As exemplarily shown for guanidinium chlorides **3a**, focal-conic textures (*m*-**3a·Cl**) and Maltese crosses (*p*-**3a·Cl**) were observed, indicating the presence of SmA mesophases (Fig. 4).

XRD experiments (wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS)) of both decyloxybiphenyl guanidinium chlorides *p*- and *m*-**3a·Cl** supported the assignment of phase geometry. For example, at 130°C the chloride *m*-**3a·Cl** exhibited a typical smectic diffraction pattern



Scheme 2. Synthesis of guanidinium ionic liquid crystals **3** from precursors **9**. (i) **8**, $Br(CH_2)_nBr$, K_2CO_3, 70°C (for *p*-**8**), 100°C (for *m*-**8**), 16–21 h; (ii) methane sulfonic acid, $CHCl_3$, r.t., 20–27 h or 2 h (for *p*- and *m*-**10b**). Method A: NEt_3, KOH; method B: $NaHCO_3$. Numbering for NMR assignment.

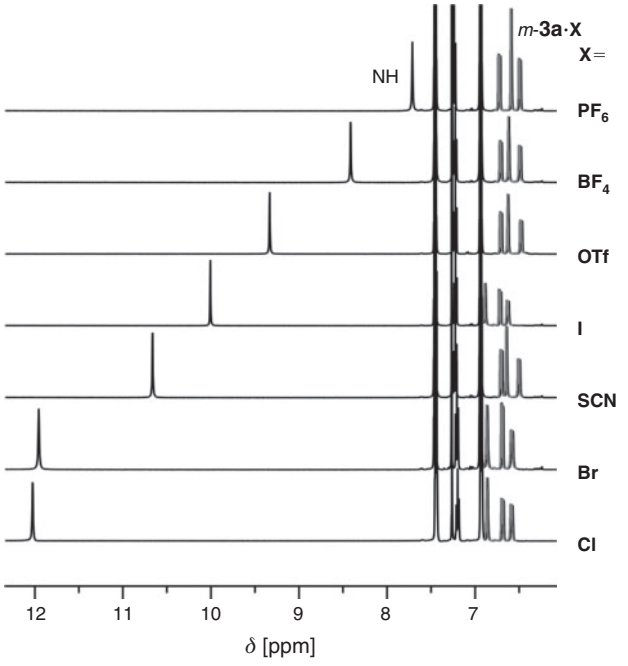


Fig. 1. Anion-dependent chemical shift of the N–H proton and protons of the phenyl moiety (grey) in ^1H NMR spectra (in $CDCl_3$) of decyloxybiphenyl guanidinium salts *m*-**3a·X**.

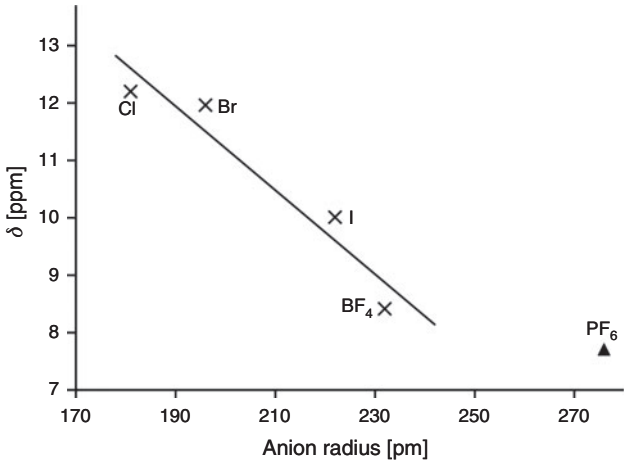


Fig. 2. Correlation of the chemical shift of the N–H proton with the corresponding anion radii for guanidinium salts *m*-**3a·X** (in $CDCl_3$).

with a sharp (10) reflection in the small-angle region together with a diffuse halo which is generated by the fluidity of the alkoxy chains (Fig. 5, black line). By measuring this sample in a magnetic field, an oriented sample could be obtained. Radial integration of the (10) reflection with the software *Datasqueeze* and the halo led to an angle of 90° between these two signals. This is a very strong indicator for the presence of a SmA phase.

Upon further cooling to 128°C (Fig. 5, grey line) a much sharper diffraction peak at wide angles in the region of the halo is visible indicating crystallization. Due to structural similarities and indication by POM textures, all mesophases of liquid crystalline guanidinium salts **3** were assigned to the SmA phase as well.

In order to obtain a greater understanding of the formed SmA phase, temperature-dependent SAXS measurements were carried out in the mesophases of *para*- and *meta*-substituted guanidinium chlorides **3a·Cl**. Based on these measurements, layer spacings were determined through Gaussian fitting of the (10) signal (software QtiPlot) and Bragg's equation. To get good comparability of the layer spacing L_{XRD}, all calculations were extrapolated from a reduced temperature ($T_{red} = 0.95\ T_{iso}$).[66] The experimental values of *p*-**3a·Cl** ($L_{XRD} = 5119$ pm) and *m*-**3a·Cl** ($L_{XRD} = 5162$ pm) can be compared with the calculated all-*trans* lengths $L_{cal} = 4330$ pm and $L_{cal} = 4070$ pm, respectively (*Chem3D 13.0*). Regarding $L_{cal} < L_{XRD} < 2L_{cal}$ and the electrostatic repulsion between the ionic head groups, a proposed interdigitation of the terminal decyloxy chain with

Table 1. Phase transition temperatures (T) and enthalpies (ΔH) of guanidinium ionic liquid crystals 3·X upon first heating

Phase transitions and enthalpies were determined by DSC. Heating/cooling rate: 5 K min^{-1}. Cr, crystalline; SmA, smectic A; I, isotropic; +, observed; −, not observed

Entry	Compd	Cr[A]	T [°C] (ΔH [kJ mol^{-1}])	SmA	T [°C] (ΔH [kJ mol^{-1}])	I
1	*p*-**3a·Cl**	+	144 (19.0)	+	167 (6.8)	+
2	*p*-**3b·Cl**	+	135 (37.1)	−		+
3	*m*-**3e·Cl**	+	184 (63.2)	−		+
4	*m*-**3d·Cl**	+	150 (58.3)	−		+
5		+	129 (52.7)	+	141 (3.4)[B]	+
6	*m*-**3c·Cl**	+	154 (60.7)	−		+
7		+	131 (39.6)	+	136 (7.5)[B]	+
8	*m*-**3a·Cl**	+	133 (8.6)	+	149 (13.5)	+
9	*m*-**3b·Cl**	+	149 (47.0)	−		+
10	*m*-**3a·Br**	+	123 (6.2)	+	128 (8.4)	+
11	*m*-**3a·I**	+	124 (16.9)	−		+
12		+	124 (14.8)	+	127 (3.4)[B]	+
13	*m*-**3a·OTf**	+	117 (28.5)	−		+
14	*m*-**3a·BF$_4$**	+	129 (15.2)	+	135 (4.0)	+
15	*m*-**3a·PF$_6$**	+	127 (27.5)	−		+
16	*m*-**3a·OAc**	+	87 (91.4)	−		+
17	*m*-**3a·SCN**	+	125 (28.7)	−		+
18		+	124 (18.6)	+	127 (4.4)[B]	+

[A]For further crystal-to-crystal transitions, see *Experimental*.
[B]Upon first cooling.

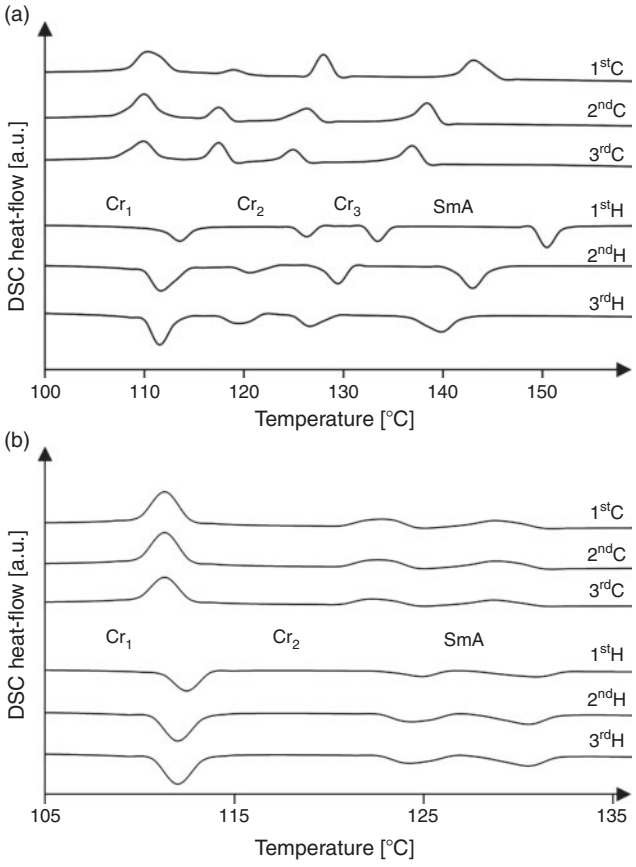


Fig. 3. Comparison of differential scanning calorimetry curves of decyloxybiphenyl guanidinium ionic liquid crystals *m*-**3a·Cl** (a) and *m*-**3a·Br** (b). C = cooling, H = heating, Cr$_x$ = crystalline, SmA = smectic A.

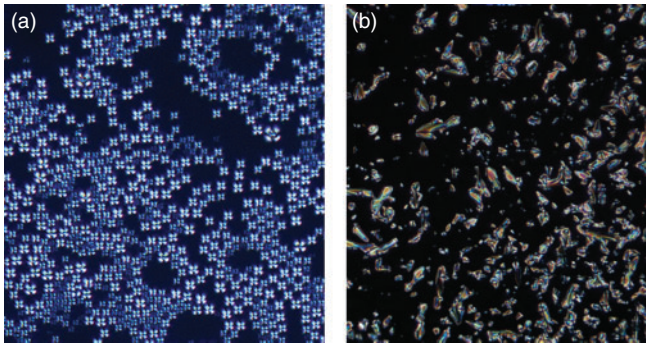


Fig. 4. Polarizing optical microscopy image of (a) Maltese crosses of *p*-**3a·Cl** at 157°C; (b) focal-conic textures of *m*-**3a·Cl** at 135°C upon cooling (magnification × 200; cooling rate: 5 K min^{-1}).

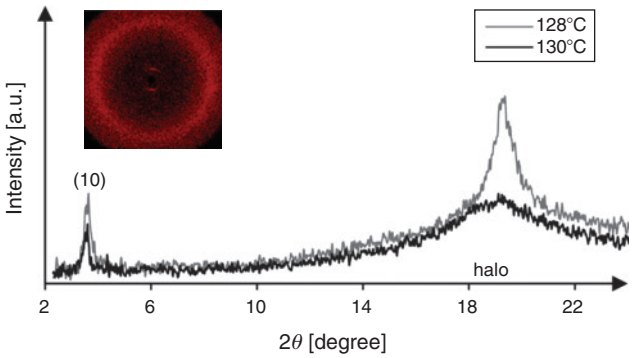


Fig. 5. X-Ray diffraction profile of *m*-**3a·Cl** at 130°C (black line) illustrating a SmA mesophase, and at 128°C (grey line) indicating crystallization. Inset: wide-angle X-ray scattering (WAXS) diffraction pattern of an oriented sample of *m*-**3a·Cl** at 130°C.

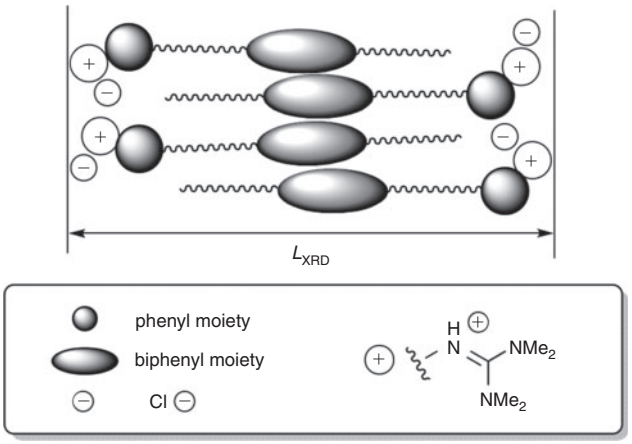


Fig. 6. Model of the proposed bilayer structure of the guanidinium chlorides **3a·Cl**.

the alkoxy spacer between the biphenyl and the head group within a bilayer structure is in good agreement with the experimental values (Fig. 6).

Conclusions

We successfully prepared a class of ILCs **3** consisting of a bent or linear phenylguanidinium moiety tethered via an alkoxy spacer to a biphenyl mesogen starting from *N*-Boc-protected hydroxyanilines **8**. All mesomorphic representatives self-assembled

into smectic A (SmA) mesophases, as was indicated by POM and further confirmed by XRD. Prerequisites for mesophase formation are a tether length of at least C6 and the 4-alkoxybiphenyl unit. The symmetry of the head group did not affect the mesophase properties but melting and clearing points. The molecules seem to form a bilayer structure with interdigitation of the terminal decyloxy substituent and the alkoxy spacer. Most surprisingly, ILCs **3b·Cl** with 4-cyanobiphenyl unit were not liquid crystalline at all. Regardless of the symmetry of the phenylguanidinium head group the molecular architecture of ILCs **3** strongly favours SmA phases while neither SmE nor SmC phases could be detected in contrast to structural analogues **1** and **2**. Thus, further studies are necessary to elucidate the parameters that favour SmC over SmA mesophases in ILCs. This current work contributes to the understanding of structure–property relationships in ILCs which are required for applications such as electrolytes in dye-sensitized solar cells.[67–69]

Experimental

Materials

All reagents were used as purchased from the suppliers. Silica 60 (40–63 µm) was purchased from Fluka. Solvents were dried following known methods, hexanes and EtOAc were distilled before use.

General Procedure for the Williamson Etherification with 1,ω-Dibromoalkanes[70]

The respective 1,ω-dibromoalkane (20.2 mmol) was added to a solution of the appropriate *p*- or *m*-**8** (3.36 mmol) and K_2CO_3 (10.7 mmol) in MeCN (30 mL), and the reaction mixture heated at reflux for the given time. Workup is given for the respective product.

tert-*Butyl 4-[(10-Bromodecyl)oxy] phenylcarbamate* (p-***9a***)

After heating for 21 h at 70°C, the precipitate was filtered off and washed with EtOAc (50 mL), silica was added to the filtrate, the solvent removed under reduced pressure, and the residue purified by chromatography (silica; 10 : 1 hexanes/EtOAc) to afford *p*-**9a** (1.56 g, 76 %) as a colourless solid. mp 110°C. ν_{max}/cm^{-1} 3358, 3008, 2988, 2938, 2921, 2902, 2869, 2851, 1692, 1618, 1596, 1521, 1434, 1443, 1414, 1390, 1366, 1316, 1296, 1249, 1228, 1156, 1115, 1057, 1040, 1017, 941, 924, 906, 889, 835, 806, 772, 761, 739, 722, 641, 624, 592, 562, 517. δ_H (500 MHz, $CDCl_3$) 1.26–1.47 (m, 12H, 6 × CH_2), 1.50 (s, 9H, $C(CH_3)_3$), 1.71–1.78 (m, 2H, $BrCH_2CH_2$), 1.81–1.89 (m, 2H, OCH_2CH_2), 3.40 (t, *J* 6.9, 2H, $BrCH_2$), 3.91 (t, *J* 6.6, 2H, OCH_2), 6.35 (s, 1H, NH), 6.82 (d, *J* 8.9, 2H, 3-H), 7.22–2.26 (m, 2H, 2-H). δ_C (126 MHz, $CDCl_3$) 26.0, 28.2, 28.4, 28.7, 29.3, 29.4, 32.8, 34.1, 68.3, 80.2, 114.9, 120.5, 131.2, 153.2, 155.2. *m/z* (ESI) 450 [M + Na^+], 396, 372, 227. *m/z* (HRMS ESI) 450.1591. $C_{21}H_{34}BrNNaO_3^+$ $[M + Na]^+$ requires 450.1614. Anal. Calc. for $C_{21}H_{34}BrNO_3$: C 58.88, H 8.00, N 3.27. Found: C 58.90, H 8.01, 3.23 %.

tert-*Butyl 3-[(10-Bromodecyl)oxy] phenylcarbamate* (m-***9a***)

After heating for 16 h at 100°C, CH_2Cl_2 (30 mL) was added, the precipitate was filtered off, washed with CH_2Cl_2 (80 mL) and EtOAc (50 mL), the filtrate was concentrated under reduced pressure, and the residue purified by chromatography (silica; 40 : 1 → 8 : 1 hexanes/EtOAc) to afford *m*-**9a** (3.33 g, 55 %) as a colourless solid, mp 57°C. ν_{max}/cm^{-1} 3370, 2982, 2941, 2920, 2854, 1703, 1602, 1587, 1521, 1474, 1438, 1392, 1364, 1329, 1286, 1236, 1193, 1168, 1152, 1087, 1053, 1039, 1017, 987, 971, 881, 846, 832, 797, 771, 758, 737, 716, 680. δ_H (500 MHz, $CDCl_3$) 1.26–1.47 (m, 12H, 6 × CH_2), 1.51 (s, 9H, $C(CH_3)_3$), 1.71–1.79 (m, 2H, $BrCH_2CH_2$), 1.81–1.89 (m, 2H, OCH_2CH_2), 3.41 (t, *J* 6.9, 2H, $BrCH_2$), 3.94 (t, *J* 6.5, 2H, OCH_2), 6.44 (s, 1H, NH), 6.55–6.81 (m, 2H, 4-H, 6-H), 7.08–7.17 (m, 2H, 2-H, 5-H). δ_C (126 MHz, $CDCl_3$) 26.0, 28.2, 28.3, 28.7, 29.3, 29.4, 32.8, 34.1, 67.9, 80.5, 104.7, 109.3, 110.5, 129.6, 139.5, 152.6, 159.9. *m/z* (ESI) 450 $[M + Na]^+$, 428 $[M + H]^+$, 393, 372, 348, 311, 292. *m/z* (HRMS ESI) 450.1608. $C_{21}H_{34}BrNNaO_3^+$ $[M + Na]^+$ requires 450.1614. Anal. Calc. for $C_{21}H_{34}BrNO_3$: C 58.88, H 8.00, N 3.27. Found: C 59.18, H 8.02, N 3.19 %.

tert-*Butyl 3-[(8-Bromooctyl)oxy] phenylcarbamate* (m-***9c***)

After heating for 40 h at 100°C, CH_2Cl_2 (50 mL) was added, the precipitate was filtered off, washed with CH_2Cl_2 (50 mL) and EtOAc (50 mL), silica was added to the filtrate, the solvent removed under reduced pressure, and the residue purified by chromatography (silica; 40 : 1 → 10 : 1 hexanes/EtOAc) to afford *m*-**9c** (1.81 g, 45 %) as a colourless solid, mp 63°C. ν_{max}/cm^{-1} 3005, 2978, 2931, 2854, 1758, 1730, 1702, 1605, 1524, 1495, 1474, 1423, 1392, 1367, 1334, 1286, 1267, 1231, 1192, 1154, 1092, 1051, 1026, 992, 874, 851, 767, 723, 688, 646, 557, 528. δ_H (300 MHz, $CDCl_3$) 1.29–1.49 (m, 8H, 4 × CH_2), 1.51 (s, 9H, $C(CH_3)_3$), 1.71–1.91 (m, 4H, OCH_2CH_2, $BrCH_2CH_2$), 3.41 (t, *J* 6.8, 2H, $BrCH_2$), 3.94 (t, *J* 6.5, 2H, OCH_2), 6.46 (s, *J* 8.0, 1H, NH), 6.54–6.82 (m, 2H, 4-H, 6-H), 7.09–7.18 (m, 2H, 2-H, 5-H). δ_C (75 MHz, $CDCl_3$) 26.0, 27.7, 28.1, 28.3, 28.7, 29.2, 32.8, 34.0, 67.9, 80.5, 104.7, 109.3, 110.5, 129.6, 139.6, 152.6, 159.8. *m/z* (ESI) 422 $[M + Na]^+$, 402 $[M + H]^+$, 368, 332, 301, 266, 227. *m/z* (HRMS ESI) 422.1289. $C_{19}H_{30}BrNNaO_3^+$ $[M + Na]^+$ requires 422.1301. Anal. Calc. for $C_{19}H_{30}BrNO_3$: C 57.00, H 7.55, N 3.50. Found: C 57.00, H 7.56, N 3.41 %.

tert-*Butyl 3-[(6-Bromohexyl)oxy] phenylcarbamate* (m-***9d***)

After heating for 40 h at 100°C, CH_2Cl_2 (50 mL) was added, the precipitate was filtered off, washed with CH_2Cl_2 (50 mL) and EtOAc (50 mL), silica was added to the filtrate, the solvent removed under reduced pressure, and the residue purified by chromatography (silica; 60 : 1 → 12 : 1, hexanes/EtOAc) to afford *m*-**9d** (1.82 g, 49 %) as a colourless solid, mp 89°C. ν_{max}/cm^{-1} 3338, 3005, 2978, 2936, 2859, 1729, 1699, 1604, 1537, 1523, 1494, 1474, 1442, 1423, 1392, 1367, 1286, 1267, 1231, 1192, 1153, 1092, 1050, 1027, 990, 943, 872, 849, 767, 733, 688, 645, 597, 560. δ_H (300 MHz, $CDCl_3$) 1.42–1.50 (m, 4H, 2 × CH_2), 1.51 (s, 9H, $C(CH_3)_3$), 1.72–1.94 (m, 4H, OCH_2CH_2, $BrCH_2CH_2$), 3.38–3.45 (m, 2H, $BrCH_2$), 3.95 (t, *J* 6.4, 2H, OCH_2), 6.46 (s, 1H, NH), 6.54–6.81 (m, 2H, 4-H, 6-H), 7.10–7.19 (m, 2H, 2-H, 5-H). δ_C (75 MHz, $CDCl_3$) 25.3, 27.9, 28.3, 29.1, 32.7, 33.8, 67.7, 80.5, 104.7, 109.3, 110.5, 129.6, 139.6, 152.6, 159.8. *m/z* (ESI) 394 $[M + Na]^+$, 338, 316, 266, 248, 154. *m/z* (HRMS ESI) 394.0999. $C_{17}H_{26}BrNNaO_3^+$ $[M + Na]^+$ requires 394.0988. Anal. Calc. for $C_{17}H_{26}BrNO_3$: C 54.84, H 7.04, N 3.76. Found: C 54.59, H 6.95, N 3.50 %.

tert-*Butyl 3-[(4-Bromobutyl)oxy] phenylcarbamate* (m-***9e***)

After heating for 40 h at 100°C, CH_2Cl_2 (50 mL) was added, the precipitate was filtered off, washed with CH_2Cl_2 (50 mL)

and EtOAc (50 mL), silica was added to the filtrate, the solvent removed under reduced pressure, and the residue purified by chromatography (silica; 60 : 1 → 40 : 1 hexanes/EtOAc) to afford *m*-**9e** (1.97 g, 54 %) as a colourless solid, mp 74°C. ν_{max}/cm^{-1} 2978, 2930, 2872, 1729, 1698, 1604, 1523, 1494, 1474, 1442, 1422, 1392, 1367, 1286, 1232, 1191, 1151, 1092, 1049, 1028, 990, 965, 823, 850, 768, 726, 688, 651, 598, 559. δ_H (300 MHz, $CDCl_3$) 1.51 (s, 9H, $C(CH_3)_3$), 1.86–2.12 (m, 4H, OCH_2CH_2, $BrCH_2CH_2$), 3.49 (m, 2H, $BrCH_2$), 3.99 (t, *J* 5.9, 2H, OCH_2), 6.47 (s, 1H, NH), 6.53–6.82 (m, 2H, 4-H, 6-H), 7.11–7.27 (m, 2H, 2-H, 5-H). δ_C (75 MHz, $CDCl_3$) 27.9, 28.3, 29.5, 33.5, 66.8, 80.6, 104.7, 109.2, 110.7, 129.6, 139.6, 152.6, 159.6. *m/z* (ESI) 368 $[M + Na]^+$, 332, 310, 288, 266, 249, 173, 137. *m/z* (HRMS ESI) 366.0686. $C_{15}H_{22}BrNNaO_3^+$ $[M + Na]^+$ requires 366.0675. Anal. Calc. for $C_{15}H_{22}BrNO_3$: C 52.34, H 6.44, N 4.07. Found: C 52.00, H 6.32, N 3.90 %.

*General Procedure for the Williamson Etherification with Biphenyl-4-ols **6** Analogous to Das et al.*[71]

Biphenyl-4-ol **6a** or **6b** (1.54 mmol), the respective bromide **9** (1.40 mmol), and K_2CO_3 (4.90 mmol) were suspended in MeCN (40 mL) and the reaction mixture heated at 90°C for the given time. The precipitate was filtered off and washed with MeCN (50 mL) (for **10c**–**e**) before suspension in $CHCl_3$ (50 mL). The remaining solid was filtered off, washed, and dried under vacuum. In the case of **10b**, H_2O (50 mL) was added, the solid filtered off, washed, and recrystallized (EtOAc) (*p*-**10b**) or dried under vacuum (*m*-**10b**).

tert-*Butyl 4-[(10-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy}decyl)oxy]phenylcarbamate* (p-***10a***)

Reaction time 23 h. Washing with $CHCl_3$ (3 × 10 mL) and drying afforded *p*-**10a** (766 mg, 90 %) as a colourless solid, mp 143°C. ν_{max}/cm^{-1} 3333, 3041, 2937, 2920, 2873, 2851, 1696, 1607, 1595, 1569, 1536, 1521, 1500, 1474, 1462, 1445, 1414, 1392, 1366, 1329, 1314, 1295, 1273, 1245, 1232, 1174, 1110, 1060, 1045, 1032, 1012, 981, 952, 936, 908, 824, 800, 774, 759, 742, 719, 646, 595, 545. δ_H (500 MHz, $CDCl_3$) 0.88 (t, *J* 7.0, 3H, CH_2CH_3), 1.23–1.49 (m, 26H, 13 × CH_2), 1.50 (s, 9H, $C(CH_3)_3$), 1.72–1.84 (m, 6H, 3 × OCH_2CH_2), 3.87–4.00 (m, 6H, 3 × OCH_2), 6.32 (s, 1H, NH), 6.80–6.85 (m, 2H, 3-H), 6.91–6.96 (m, 4H, 3′-H, 3″-H), 7.21–7.27 (m, 2H, 2-H), 7.43–7.48 (m, 4H, 2′-H, 2″-H). δ_C (126 MHz, $CDCl_3$) 14.1, 22.7, 26.0, 26.1, 28.4, 29.3, 29.4, 29.5, 29.6, 31.9, 68.1, 68.1, 68.3, 114.7, 114.9, 120.5, 127.6, 131.2, 133.3, 153.2, 155.3, 158. *m/z* (ESI) 696 $[M + Na]^+$, 673 $[M]^+$, 579, 443, 350. *m/z* (HRMS ESI) 696.4591. $C_{43}H_{63}NNaO_5^+$ $[M + Na]^+$ requires 696.4598. Anal. Calc. for $C_{43}H_{63}NO_5$: C 76.74, H 9.42, N 2.05. Found: C 76.63, H 9.42, N 2.08 %.

tert-*Butyl 4-({10-[(4′-Cyano-1,1′-biphenyl-4-yl)oxy]decyl}oxy)phenylcarbamate* (p-***10b***)

Reaction time 14 h. The solid washed with H_2O (3 × 10 mL) and 9 : 1 H_2O/MeCN (10 mL); recrystallization afforded *p*-**10b** (600 mg, 78 %) as a colourless solid, mp 160°C. ν_{max}/cm^{-1} 3362, 3073, 3042, 3014, 2990, 2974, 2945, 2924, 2906, 2855, 2224, 1690, 1599, 1578, 1520, 1493, 1473, 1413, 1392, 1368, 1318, 1289, 1268, 1251), 1230), 1180, 1157, 1117, 1075, 1054, 1027, 1012, 989, 934, 903, 855, 836, 821, 806, 773, 748, 735, 721, 660, 636, 622, 560. δ_H (300 MHz, $CDCl_3$) 1.26–1.48 (m, 12H, 6 × CH_2), 1.50 (s, 9H, $C(CH_3)_3$), 1.69–1.88 (m, 4H, 2 × OCH_2CH_2), 3.87–4.04 (m, 4H, 2 × OCH_2), 6.34 (s, 1H, NH), 6.79–6.86 (m, 2H, 3-H), 6.95–7.02 (m, 2H, 3′-H), 7.22–7.25 (m, 2H, 2-H), 7.49–7.57 (m, 2H, 2′-H), 7.60–7.73 (m, 4H, 2″-H, 3″-H). δ_C (75 MHz, $CDCl_3$) 26.0, 28.4, 29.2, 29.3, 29.4, 29.5, 68.2, 68.3, 80.2, 110.0, 114.9, 115.1, 119.1, 120.6, 127.1, 128.3, 131.3, 132.6, 145.3, 153.2, 155.2, 159.8. *m/z* (ESI) 565 $[M + Na^+]$ 543 $[M + H^+]$, 509, 487, 443, 393, 298. *m/z* (HRMS ESI) 565.3024. $C_{34}H_{42}N_2NaO_4^+$ $[M + Na^+]$ requires 565.3037. Anal. Calc. for $C_{34}H_{42}N_2O_4$: C 75.25, H 7.80, N 5.16. Found: C 74.32, H 7.69, N 5.01 %.

tert-*Butyl 3-({10-[(4′-Cyano-1,1′-biphenyl-4-yl)oxy]decyl}oxy)phenylcarbamate* (m-***10b***)

Reaction time 14 h. Filtration at 0°C, suspension (sonification), filtration, washing with H_2O (3 × 10 mL) and MeCN (2 mL), and drying afforded *m*-**10b** (1.13 g, 86 %) as a colourless solid, mp 122°C. ν_{max}/cm^{-1} 3327, 3139, 3036, 2983, 2945, 2922, 2852, 2224, 1690, 1604, 1583, 1536, 1493, 1467, 1438, 1393, 1369, 1315, 1285, 1243, 1196, 1179, 1154, 1116, 1093, 1054, 1031, 999, 946, 868, 848, 821, 806, 783, 770, 718, 694, 616, 647, 593, 562, 531. δ_H (500 MHz, $CDCl_3$) 1.28–1.50 (m, 12H, 6 × CH_2), 1.51 (s, 9H, $C(CH_3)_3$), 1.71–1.85 (m, 4H, 2 × OCH_2CH_2), 3.91–4.03 (m, 4H, 2 × OCH_2), 6.45 (s, 1H, NH), 6.54–6.80 (m, 2H, 4-H, 6-H), 6.97–7.01 (m, 2H, 3′-H), 7.10–7.13 (m, 1H, 2-H), 7.13–7.17 (m, 1H, 5-H), 7.50–7.53 (m, 2H, 2′-H), 7.61–7.65 (m, 2H, 2″-H), 7.66–7.70 (m, 2H, 3″-H). δ_C (126 MHz, $CDCl_3$) 26.0, 28.3, 29.2, 29.3, 29.5, 67.9, 68.2, 80.5, 104.7, 109.3, 110.0, 110.5, 115.1, 119.1, 127.1, 128.3, 129.6, 131.2, 132.6, 139.6, 145.3, 152.6, 159.8, 159.9. *m/z* (ESI) 565 $[M + Na]^+$. *m/z* (HRMS ESI) 565.3024. $C_{34}H_{42}N_2NaO_4^+$ $[M + Na]^+$ requires 565.3037. Anal. Calc. for $C_{34}H_{42}N_2O_4$: C 75.25, H 7.80, N 5.16. Found: C 75.30, H 7.82, N 5.09 %.

tert-*Butyl 3-[(8-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy}octyl)oxy]phenylcarbamate* (m-***10c***)

Reaction time 20 h. Washing with $CHCl_3$ (3 × 10 mL) and drying afforded *m*-**10c** (701 mg, 87 %) as a colourless solid, mp 107°C. ν_{max}/cm^{-1} 3360, 3041, 2979, 2957, 2935, 2919, 2874, 2852, 1737, 1702, 1608, 1527, 1501, 1475, 1441, 1423, 1393, 1367, 1328, 1273, 1250, 1226, 1197, 1177, 1156, 1068, 1037, 1013, 992, 936, 911, 884, 844, 824, 808, 772, 760, 734, 723, 685, 644, 627, 596, 573, 552. δ_H (300 MHz, $CDCl_3$) 0.88 (t, *J* 6.7, 3H, CH_2CH_3), 1.24–1.49 (m, 22H, 11 × CH_2), 1.51 (s, 9H, $C(CH_3)_3$), 1.71–1.86 (m, 6H, 3 × OCH_2CH_2), 3.91–4.01 (m, 6H, 3 × OCH_2), 6.44 (s, 1H, NH), 6.54–6.82 (m, 2H, 4-H, 6-H), 6.90–6.98 (m, 4H, 3′-H, 3″-H), 7.08–7.11 (m, 1H, 2-H), 7.12–7.18 (m, 1H, 5-H), 7.40–7.50 (m, 4H, 2′-H, 2″-H). δ_C (75 MHz, $CDCl_3$) 14.1, 22.7, 26.0, 26.1, 28.3, 29.3, 29.4, 29.6, 31.9, 67.9, 68.0, 68.1, 80.5, 104.7, 109.4, 110.5, 114.7, 127.7, 129.6, 133.3, 139.5, 152.6, 158.2, 159.9. *m/z* (ESI) 668 $[M + Na]^+$, 590, 546, 465, 393, 327. *m/z* (HRMS ESI) 668.4266. $C_{41}H_{59}NNaO_5^+$ $[M + Na]^+$ requires 668.4285. Anal. Calc. for $C_{41}H_{59}NO_5$: C 76.24, H 9.21, N 2.17. Found: C 76.02, H 9.23, N 2.07 %.

tert-*Butyl 3-[(6-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy}hexyl)oxy]phenylcarbamate* (m-***10d***)

Reaction time 20 h. Washing with $CHCl_3$ (3 × 10 mL) and drying afforded *m*-**10d** (854 mg, 87 %) as a colourless solid, mp 121°C. ν_{max}/cm^{-1} 3360, 3038, 2980, 2956, 2938, 2922, 2910, 2872, 2848, 1734, 1702, 1689, 1605, 1528, 1499, 1473, 1442, 1427, 1392, 1366, 1326, 1287, 1271, 1245, 1197, 1176, 1156, 1069, 1051, 1033, 1018, 996, 983, 936, 883, 844, 823, 804, 773, 759, 734, 682, 646, 592, 547. δ_H (300 MHz, $CDCl_3$) 0.88 (t, *J*

6.7, 3H, CH_2CH_3), 1.23–1.49 (m, 18H, 9 × CH_2), 1.51 (s, 9H, $C(CH_3)_3$), 1.73–1.88 (m, 6H, 3 × OCH_2CH_2), 3.93–4.03 (m, 6H, 3 × OCH_2), 6.44 (s, 1H, NH), 6.55–6.82 (m, 2H, 4-H, 6-H), 6.90–6.98 (m, 4H, 3′-H, 3″-H), 7.09–7.12 (m, 1H, 2-H), 7.12–7.19 (m, 1H, 5-H), 7.42–7.50 (m, 4H, 2′-H, 2″-H). δ_C (75 MHz, $CDCl_3$) 14.1, 22.7, 25.9, 26.1, 28.3, 29.3, 29.4, 29.6, 31.9, 67.8, 67.9, 68.1, 80.5, 104.7, 109.4, 110.5, 114.7, 127.7, 129.6, 133.3, 133.4, 139.6, 152.6, 158.2, 158.2, 159.8. *m/z* (ESI) 640 $[M + Na]^+$, 612 $[M + H]^+$, 481. *m/z* (HRMS ESI) 640.3958. $C_{39}H_{55}NNaO_5^+$ $[M + Na]^+$ requires 640.3972. Anal. Calc. for $C_{39}H_{55}NO_5$: C 75.81, H 8.97, N 2.27. Found: C 75.99, H 9.03, N 2.09 %.

tert-Butyl 3-[(4-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy}butyl)oxy]phenylcarbamate (m-**10e**)

Reaction time 20 h. Washing with $CHCl_3$ (3 × 10 mL) and drying afforded *m*-**10e** (987 mg, 88 %) as a colourless solid, mp 140°C. ν_{max}/cm^{-1} 3337, 3039, 2956, 2920, 2873, 2851, 1702, 1606, 1535, 1501, 1475, 1442, 1426, 1390, 1366, 1324, 1289, 1271, 1234, 1194, 1175, 1159, 1072, 1048, 1032, 1012, 995, 956, 890, 847, 814, 779, 759, 724, 688, 644, 595, 540. δ_H (300 MHz, $CDCl_3$) 0.88 (t, *J* 6.7, 3H, CH_2CH_3), 1.22–1.48 (m, 14H, 7 × CH_2), 1.51 (s, 9H, $C(CH_3)_3$), 1.73–2.01 (m, 6H, 3 × OCH_2CH_2), 3.93–4.09 (m, 6H, 3 × OCH_2), 6.45 (s, 1H, NH), 6.56–6.82 (m, 2H, 4-H, 6-H), 6.90–6.98 (m, 4H, 3′-H, 3″-H), 7.12–7.13 (m, 1H, 2-H), 7.13–7.19 (m, 1H, 5-H), 7.41–7.49 (m, 4H, 2′-H, 2″-H). δ_C (75 MHz, $CDCl_3$) 14.1, 22.7, 26.0, 26.1, 28.4, 29.3, 29.4, 29.6, 31.9, 67.4, 67.6, 68.1, 80.5, 104.8, 109.3, 110.6, 114.8, 127.7, 127.7, 129.6, 133.3, 133.5, 139.6, 152.6, 158.1, 158.3, 159.7. *m/z* (ESI) 612 $[M + Na]^+$, 578, 556, 481. *m/z* (HRMS ESI) 612.3644. $C_{37}H_{51}NNaO_5^+$ $[M + Na]^+$ requires 612.3659. Anal. Calc. for $C_{37}H_{51}NO_5$: C 75.35, H 8.72, N 2.37. Found: C 75.65, H 8.79, N 2.20 %.

General Procedure for the Deprotection of Boc-Protected Derivatives **10**

A solution of the respective **10** (985 μmol) in $CHCl_3$ (30 mL) was stirred with methane sulfonic acid (3.25 mmol) at room temperature for the given time. After neutralization with K_2CO_3 or $NaHCO_3$ (9.85 mmol) in H_2O (20 mL), the phases were separated, and the aqueous layer was extracted with $CHCl_3$ (4 × 75 mL). The combined organic layers were concentrated under reduced pressure and the remaining solid was dried under vacuum. With exception of *p*-**11a**, all other products **11** were further purified by column chromatography (silica).

4-[(10-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy}decyl)oxy]aniline (p-**11a**)

Reaction time 27 h. Extraction with hot $CHCl_3$ (4 × 75 mL) afforded *p*-**11a** (664 mg, 92 %) as a colourless solid, mp 149°C. ν_{max}/cm^{-1} 3575, 3379, 3318, 3041, 2957, 2935, 2918, 2874, 2850, 1605, 1569, 1515, 1499, 1473, 1462, 1393, 1329, 1298, 1273, 1248, 1177, 1128, 1124, 1096, 1047, 1032, 1010, 994, 979, 930, 824, 808, 798, 736, 719, 644, 593, 556, 519, 507. δ_H (500 MHz, DMSO, 100°C) 0.86 (t, *J* 6.8, 3H, CH_3), 1.20–1.47 (m, 26H, 13 × CH_2), 1.59–1.75 (m, 6H, 3 × OCH_2CH_2), 3.81 (t, *J* 6.5, 2H, C4-OCH_2), 3.99 (t, *J* 6.5, 4H, 2 × biphenyl-OCH_2), 4.23 (s, 2H, NH_2), 6.49–6.65 (m, 4H, 2-H, 3-H), 6.91–6.97 (m, 4H, 3′-H, 3″-H), 7.43–7.49 (m, 4H, 2′-H, 2″-H). δ_C (126 MHz, DMSO, 100°C) 12.0, 21.3, 24.9, 27.9, 28.0, 28.1, 28.2, 28.3, 28.4, 30.6, 67.5, 68.2, 114.6, 114.8, 115.4, 126.6, 132.1, 141.6, 150.1, 157.5. *m/z* (EI) (%) 573 (100) $[M + H]^+$, 466 (5), 433 (1), 326 (1), 287 (3), 216 (2), 186 (14), 157 (1), 109 (13), 83 (2), 55 (2). *m/z* (HRMS EI) 573.4196. $C_{38}H_{56}NO_3^+$ $[M + H]^+$ requires 573.4182. Anal. Calc. for $C_{38}H_{55}NO_3$: C 79.53, H 9.66, N 2.44. Found: C 78.16, H 9.52, N 2.32 %.

4′-{[10-(4-Aminophenoxy)decyl]oxy}-1,1′-biphenyl-4-carbonitrile (p-**11b**)

Reaction time 2 h. Chromatography (3 : 1 → 1 : 1 hexanes/EtOAc) afforded *p*-**11b** (253 mg, 58 %) as a colourless solid, mp 145°C. ν_{max}/cm^{-1} 3375, 2935, 2919, 2851, 2225, 1630, 1601, 1580, 1511, 1493, 1474, 1462, 1494, 1293, 1269, 1254, 1233, 1182, 1120, 1047, 1025, 1012, 981, 817, 799, 770, 746, 717, 662, 621. δ_H (500 MHz, $CDCl_3$) 1.28–1.51 (m, 12H, 6 × CH_2), 1.70–1.85 (m, 4H, 2 × OCH_2CH_2), 3.41 (s, 2H, NH_2), 3.85–4.04 (m, 4H, 2 × OCH_2), 6.61–6.76 (m, 4H, 2-H, 3-H), 6.97–7.01 (m, 2H, 3′-H), 7.50–7.54 (m, 2H, 2′-H), 7.62–7.70 (m, 4H, 2″-H, 3″-H). δ_C (126 MHz, $CDCl_3$) 26.0, 26.1, 29.2, 29.3, 29.4, 29.5, 68.2, 68.7, 110.0, 115.1, 115.6, 116.4, 119.1, 127.1, 128.3, 131.2, 132.6, 139.8, 145.3, 152.3, 159.8. *m/z* (ESI) 465 $[M + Na]^+$, 443 $[M + H]^+$, 393. *m/z* (HRMS ESI) 443.2699. $C_{29}H_{35}N_2O_2^+$ $[M + H]^+$ requires 443.2693. Anal. Calc. for $C_{29}H_{34}N_2O_2$: C 78.70, H 7.74, N 6.33. Found: C 78.45, H 7.82, N 6.14 %.

4′-{[10-(3-Aminophenoxy)decyl]oxy}-1,1′-biphenyl-4-carbonitrile (m-**11b**)

Reaction time 2 h. Chromatography (70 : 13 : 1 hexanes/EtOAc/MeCN) afforded *m*-**11b** (623 g, 94 %) as a colourless solid, mp 107°C. ν_{max}/cm^{-1} 3457, 3370, 2934, 2918, 2851, 2224, 1627, 1600, 1580, 1525, 1494, 1473, 1462, 1395, 1337, 1290, 1269, 1252, 1216, 1182, 1160, 1116, 1182, 1045, 1025, 1012, 985, 953, 822, 772, 759, 717, 691, 662. δ_H (500 MHz, $CDCl_3$) 1.29–1.51 (m, 12H, 6 × CH_2), 1.71–1.84 (m, 4H, 2 × OCH_2CH_2), 3.63 (s, 2H, NH_2), 3.85–4.02 (m, 4H, 2 × OCH_2), 6.23–6.25 (m, 1H, 2-H), 6.26–6.33 (m, 2H, 4-H, 6-H), 6.96–7.01 (m, 2H, 3′-H), 7.02–7.06 (m, 1H, 5-H), 7.49–7.55 (m, 2H, 2′-H), 7.61–7.65 (m, 2H, 2″-H), 7.66–7.71 (m, 2H, 3″-H). δ_C (126 MHz, $CDCl_3$) 26.0, 29.2, 29.3, 29.4, 29.5, 67.7, 68.2, 101.7, 104.6, 107.7, 110.0, 115.1, 119.1, 127.1, 128.3, 130.0, 131.2, 132.6, 145.3, 147.7, 159.8, 160.3. *m/z* (ESI) 465 $[M + Na]^+$, 443 $[M + H]^+$, 393, 339, 279, 246, 228. *m/z* (HRMS ESI) 443.2699. $C_{29}H_{35}N_2O_2^+$ $[M + H]^+$ requires 443.2693. Anal. Calc. for $C_{29}H_{34}N_2O_2$: C 78.70, H 7.74, N 6.33. Found: C 78.95, H 7.83, N 6.24 %.

3-[(8-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy}octyl)oxy]aniline (m-**11c**)

Reaction time 20 h. Chromatography (800 : 55 : 20, hexanes/EtOAc/NEt_3 → 100 : 3, EtOAc/NEt_3) afforded *m*-**11c** (485 g, 86 %) as a colourless solid, mp 157°C. ν_{max}/cm^{-1} 3438, 3402, 3207, 3069, 3040, 2955, 2933, 2918, 2873, 2850, 1630, 1598, 1566, 1497, 1470, 1442, 1390, 1329, 1318, 1289, 1272, 1247, 1196, 1177, 1157, 1136, 1119, 1049, 1031, 1014, 996, 985, 962, 907, 823, 808, 770, 740, 720, 688, 645, 592, 552. δ_H (500 MHz, $CDCl_3$) 0.88 (t, *J* 6.9, 3H, CH_3), 1.21–1.51 (m, 22H, 11 × CH_2), 1.71–1.84 (m, 6H, 3 × OCH_2CH_2), 3.63 (s, 2H, NH_2), 3.91 (t, *J* 6.5, 2H, C3-OCH_2), 3.96–4.00 (m, 4H, 2 × biphenyl-OCH_2), 6.23–6.25 (m, 1H, 2-H), 6.26–6.33 (m, 2H, 4-H, 6-H), 6.92–6.96 (m, 4H, 3′-H, 3″-H), 7.02–7.06 (m, 1H, 5-H), 7.43–7.48 (m, 4H, 2′-H, 2″-H). δ_C (126 MHz, $CDCl_3$) 14.1, 22.7, 26.0, 26.1, 29.3, 29.4, 29.6, 31.9, 67.7, 68.0, 68.1, 101.7, 104.6, 107.7, 114.7, 127.7, 130.1, 133.3, 133.3, 147.7, 158.2, 158.2, 160.3. *m/z* (ESI)

546 $[M+H]^+$, 512, 490, 393, 381. Anal. Calc. for $C_{36}H_{51}NO_3$: C 79.22, H 9.42, N 2.57. Found: C 78.27, H 8.77, N 2.71 %.

3-[(6-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy}hexyl) oxy]aniline (m-***11d***)

Reaction time 20 h. Chromatography (300 : 10 → 0 : 1 hexanes/EtOAc) afforded *m*-**11d** (550 mg, 78 %) as a colourless solid, mp 142°C. ν_{max}/cm^{-1} 3425, 3344, 3068, 3040, 2958, 2938, 2919, 2874, 2850, 1630, 1600, 1567, 1497, 1473, 1462, 1395, 1329, 1316, 1293, 1271, 1248, 1200, 1177, 1158, 1138, 1121, 1072, 1032, 1013, 993, 951, 889, 824, 805, 776, 756, 740, 728, 718, 690, 645, 587, 550. δ_H (500 MHz, $CDCl_3$) 0.88 (t, *J* 6.9, 3H, CH_3), 1.24–1.58 (m, 18H, 9 × CH_2), 1.75–1.86 (m, 6H, 3 × OCH_2CH_2), 3.62 (s, 2H, NH_2), 3.90–4.02 (m, 6H, 3 × OCH_2), 6.23–6.25 (m, 1H, 2-H), 6.26–6.33 (m, 2H, 4-H, 6-H), 6.92–6.96 (m, 4H, 3′-H, 3″-H), 7.02–7.07 (m, 1H, 5-H), 7.43–7.48 (m, 4H, 2′-H, 2″-H). δ_C (126 MHz, $CDCl_3$) 14.1, 22.7, 26.0, 26.1, 29.3, 29.4, 29.6, 31.9, 67.7, 68.0, 68.1, 101.7, 104.6, 107.7, 114.7, 127.7, 130.1, 133.3, 133.3, 147.7, 158.2, 158.2, 160.3. *m/z* (ESI) 518 $[M+H]^+$, 393. *m/z* (HRMS ESI) 518.36. $C_{34}H_{48}NO_3^+$ $[M+H]^+$ requires 518.36. Anal. Calc. for $C_{34}H_{47}NO_3$: C 78.87, H 9.15, N 2.71. Found: C 78.77, H 9.06, N 2.60 %.

3-[(4-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy}butyl) oxy]aniline (m-***11e***)

Reaction time 24 h. Chromatography (1 : 1 hexanes/EtOAc, then 10 : 1 CH_2Cl_2/MeOH) afforded *m*-**11e** (688 mg, 86 %) as a colourless solid, mp 159°C. ν_{max}/cm^{-1} 3434, 3402, 3308, 3210, 3070, 3040, 2956, 2934, 2918, 2873, 2850, 1630, 1601, 1567, 1497, 1470, 1442, 1390, 1329, 1317, 1290, 1272, 1247, 1196, 1177, 1158, 1136, 1120, 1049, 1031, 1014, 996, 985, 962, 907, 823, 807, 771, 741, 720, 688, 645, 614, 592, 531. δ_H (500 MHz, $CDCl_3$) 0.88 (t, *J* 6.9, 3H, CH_3), 1.23–1.50 (m, 14H, 7 × CH_2), 1.75–2.00 (m, 6H, 3 × OCH_2CH_2), 3.60 (s, 2H, NH_2), 3.96–4.08 (m, 6H, 3 × OCH_2), 6.22–6.24 (m, 1H, 2-H), 6.26–6.33 (m, 2H, 4-H, 6-H), 6.91–6.96 (m, 4H, 3′-H, 3″-H), 7.01–7.06 (m, 1H, 5-H), 7.42–7.48 (m, 4H, 2′-H, 2″-H). δ_C (126 MHz, $CDCl_3$) 14.1, 22.7, 26.1, 26.2, 29.3, 29.4, 29.4, 29.6, 29.6, 31.9, 67.4, 67.7, 68.2, 101.9, 104.8, 108.0, 114.9, 127.7, 127.7, 130.1, 133.4, 133.6, 147.8, 158.2, 158.4, 160.3. *m/z* (ESI) 490 $[M+H]^+$, 459, 319, 290, 262, 222. *m/z* (HRMS ESI) 490.3316. $C_{32}H_{44}NO_3^+$ $[M+H]^+$ requires 490.3316. Anal. Calc. for $C_{32}H_{43}NO_3$: C 78.49, H 8.85, N 2.86. Found: C 78.33, H 8.79, N 2.78 %.

3-[(10-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy}decyl) oxy]aniline (m-***11a***) *Analogous to Lee et al.*[62]

Aqueous HCl (37 %, 2.8 mL) was added to a suspension of *m*-**7a** (567 mg, 921 µmol) in EtOH (30 mL), and the reaction mixture heated for 2.5 days at 100°C. After cooling to room temperature, an aqueous solution of $NaHCO_3$ (20 mL) was carefully added (gas formation!) until a pH of 8–9. The suspension was filtered off, the solid washed with H_2O (20 mL) and dried under vacuum to afford *m*-**11a** (496 mg, 94 %) as a colourless solid, mp 138°C. ν_{max}/cm^{-1} 3069, 3041, 2957, 2936, 2919, 2875, 2850, 1625, 1602, 1567, 1500, 1474, 1461, 1394, 1330, 1315, 1292, 1273, 1248, 1196, 1177, 1159, 1138, 1122, 1082, 1047, 1032, 1010, 994, 980, 950, 913, 890, 824, 808, 798, 777, 759, 718, 689, 645, 594, 520. δ_H (500 MHz, DMSO) 0.85 (t, *J* 6.8, 3H, CH_3), 1.21–1.48 (m, 26H, 13 × CH_2), 1.63–1.78 (m, 6H, 3 × OCH_2CH_2), 3.86 (t, *J* 6.4, 2H, C3-OCH_2), 3.99 (t, *J* 6.4, 4H, 2 × biphenyl-OCH_2), 4.59 (br s, 2H, NH_2), 6.06–6.21 (m, 3H, 2-H, 4-H, 6-H), 6.83–6.89 (m, 1H, 5-H), 6.91–7.00 (m, 4H, 3′-H, 3″-H), 7.41–7.51 (m, 4H, 2′-H, 2″-H). δ_C (126 MHz, DMSO) 13.6, 21.9, 25.5, 25.6, 28.6, 28.7, 28.9, 31.2, 67.6, 68.1, 101.2, 103.2, 107.3, 115.3, 127.2, 129.4, 132.8, 149.7, 158.1, 160.1. *m/z* (ESI) 612 $[M+K]^+$, 596 $[M+Na]^+$, 574 $[M+H]^+$, 490, 441, 393, 371, 327. *m/z* (HRMS ESI) 574.4241. $C_{38}H_{56}NO_3^+$ $[M+H]^+$ requires 574.4255. Anal. Calc. for $C_{38}H_{55}NO_3$: C 79.53, H 9.66, N 2.44. Found: C 79.48, H 9.61, N 2.40 %.

General Procedure for the Linkage of the Guanidinium Head Group Analogous to Butschies et al.[39]

A solution of chloro-*N*,*N*,*N*′,*N*′-tetramethylformamidinium chloride (502 µmol) in CH_2Cl_2 was added dropwise to a stirred suspension or solution of the respective **11** (418 µmol) in dry THF (20 mL) followed by addition of NEt_3 (1.88 mmol) (method A) or $NaHCO_3$ (method B) and the reaction mixture stirred for the given time at room temperature. After addition of an excess of H_2O and stirring for 15 min, purification with HCl-treated silica was carried out. Organic byproducts were separated by elution with EtOAc and the product eluted with CH_2Cl_2/MeOH. The eluate was filtered to remove trace amounts of silica, and the filtrate concentrated under reduced pressure. In the case of NEt_3 (method A), the remaining colourless solid was dissolved or suspended in MeOH (10 mL) and a solution of KOH (5.44 mmol) in MeOH (5 mL) added and the mixture stirred for 15 min. The solvent was removed under reduced pressure and the residue dried under high vacuum. Under N_2 atmosphere, the solid was then dissolved or suspended in Et_2O and HCl in Et_2O added until pH 1. After stirring for 15 min, all volatile materials were removed under vacuum.

N″-{4-[(10-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy} decyl)oxy]phenyl}-N,N,N′,N′-tetramethyl Guanidinium Chloride (p-***3a·Cl***)

Method A: reaction time 3 days. Chromatography with 20 : 1 CH_2Cl_2/MeOH afforded *p*-**3a·Cl** (270 mg, 91 %) as a colourless solid. ν_{max}/cm^{-1} 2935, 2917, 2849, 2360, 1631, 1607, 1562, 1516, 1500, 1474, 1397, 1327, 1274, 1247, 1177, 1166, 1111, 1068, 1034, 1011, 914, 825, 808, 728, 594, 565. δ_H (500 MHz, $CDCl_3$) 0.88 (t, *J* 7.0, 3H, CH_3), 1.19–1.51 (m, 26H, 13 × CH_2), 1.71–1.83 (m, 6H, 3 × OCH_2CH_2), 2.90 (m, 12H, $N(CH_3)_2$), 3.90–4.01 (m, 6H, 3 × OCH_2), 6.83–6.88 (m, 2H, 3-H), 6.91–6.96 (m, 4H, 3′-H, 3″-H), 7.06–7.11 (m, 2H, 2-H), 7.43–7.47 (m, 4H, 2′-H, 2″-H), 11.94 (s, 1H, NH). δ_C (126 MHz, $CDCl_3$) 14.1, 22.7, 26.0, 26.1, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9, 40.6, 68.1, 68.1, 68.3, 114.7, 115.5, 122.3, 127.6, 130.6, 133.3, 133.3, 156.8, 158.2, 158.2, 158.8. *m/z* (ESI) 673 $[M]^+$. *m/z* (HRMS ESI) 672.5082. $C_{43}H_{66}N_3O_3^+$ $[M]^+$ requires 672.5099. Anal. Calc. for $C_{43}H_{66}ClN_3O_3$: C 72.90, H 9.39, N 5.93. Found: C 69.73, H 9.09, N 5.30 %. DSC: Cr_1 119 (15.6 kJ mol^{-1}), Cr_2 144 (19.0 kJ mol^{-1}), SmA 167 (6.8 kJ mol^{-1}), I.

N″-[4-({10-[(4′-Cyano-1,1′-biphenyl-4-yl)oxy]decyl} oxy)phenyl]-N,N,N′,N′-tetramethyl Guanidinium Chloride (p-***3b·Cl***)

Method B: reaction time 2 days. Chromatography with 10 : 1 CH_2Cl_2/MeOH afforded *p*-**3b·Cl** (185 mg, 70 %) as a colourless solid, mp 185°C. ν_{max}/cm^{-1} 3038, 3005, 2942, 2920, 2850, 2803, 2771, 2222, 1620, 1596, 1564, 1510, 1493, 1471, 1453, 1426, 1414, 1399, 1323, 1290, 1267, 1239, 1228, 1204, 1178, 1170, 1153, 1113, 1067, 1040, 1012, 982, 959, 911, 855, 825, 799, 746, 721, 687, 661, 635, 608, 565, 551. δ_H (300 MHz,

$CDCl_3$) 1.27–1.53 (m, 12H, 6 × CH_2), 1.70–1.88 (m, 4H, 2 × OCH_2CH_2), 2.86 (s, 12H, $N(CH_3)_2$), 3.85–4.05 (m, 4H, 2 × OCH_2), 6.86 (m, 2H, 3-H), 6.96–7.02 (m, 2H, 3′-H), 7.06–7.15 (m, 2H, 2-H), 7.49–7.56 (m, 2H, 2′-H), 7.62–7.72 (m, 4H, 2″-H, 3″-H), 11.94 (s, 1H, NH). δ_C (75 MHz, $CDCl_3$) 26.0, 29.2, 29.4, 29.5, 40.6, 68.2, 68.3, 110.0, 115.1, 115.5, 119.1, 122.3, 127.1, 128.3, 130.6, 131.2, 132.6, 145.3, 156.8, 158.8, 159.8. *m/z* (ESI) 541 $[M]^+$. *m/z* (HRMS ESI) 541.3530. $C_{34}H_{45}N_4O_2^+$ $[M]^+$ requires 541.3537. Anal. Calc. for $C_{34}H_{45}ClN_4O_2$: C 70.75, H 7.86, N 9.71. Found: C 70.08, H 7.86, N 9.66 %. DSC: Cr 135 (37.1 kJ mol^{-1}) I.

N″-*{3-[(10-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy}decyl)oxy]phenyl}*-N,N,N′,N′-tetramethyl Guanidinium Chloride (m-***3a·Cl***)

Method A: reaction time 3 days. Chromatography with 10 : 1 CH_2Cl_2/MeOH afforded *m*-**3a·Cl** (440 mg, 97 %) as a colourless solid. ν_{max}/cm^{-1} 2936, 2918, 2849, 1630, 1605, 1562, 1556, 1501, 1473, 1463, 1431 8, 1395, 1329, 1315, 1273, 1249, 1226, 1179, 1159, 1067, 1033, 1011, 995, 951, 906, 848, 824, 808, 917, 690, 641, 621, 594, 573. δ_H (500 MHz, $CDCl_3$) 0.88 (t, *J* 6.9, 3H, CH_3), 1.22–1.51 (m, 26H, 13 × CH_2), 1.72–1.84 (m, 6H, 3 × OCH_2CH_2), 3.01 (s, 12H, $N(CH_3)_2$), 3.93–4.01 (m, 6H, 3 × OCH_2), 6.55–6.60 (m, 1H, 4-H), 6.66–6.71 (m, 1H, 6-H), 6.85–6.89 (m, 1H, 2-H), 6.92–6.97 (m, 4H, 3′-H, 3″-H), 7.18–7.23 (m, 1H, 5-H), 7.43–7.49 (m, 4H, 2′-H, 2″-H), 12.07 (s, 1H, NH). δ_C (126 MHz, $CDCl_3$) 14.1, 22.7, 26.0, 26.1, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9, 40.7, 68.1, 68.2, 107.2, 111.7, 112.2, 114.7, 127.6, 130.2, 133.3, 139.0, 158.2, 158.7, 160.3. *m/z* (ESI) 673 $[M]^+$. *m/z* (HRMS ESI) 672.5078. $C_{43}H_{66}N_3O_3^+$ $[M]^+$ requires 672.5099. Anal. Calc. for $C_{43}H_{66}ClN_3O_3$: C 72.90, H 9.39, N 5.93. Found: C 69.54, H 9.29, N 5.23 %. DSC: Cr_1 112 (14.7 kJ mol^{-1}), Cr_2 125 (5.7 kJ mol^{-1}), Cr_3 133 (8.6 kJ mol^{-1}), SmA 149 (13.5 kJ mol^{-1}), I.

N″-*[3-({10-[(4′-Cyano-1,1′-biphenyl-4-yl)oxy]decyl}oxy)phenyl]*-N,N,N′,N′-tetramethyl Guanidinium Chloride (m-***3b·Cl***)

Method B: reaction time 38 h. Chromatography with 10 : 1 CH_2Cl_2/MeOH afforded *m*-**3b·Cl** (225 mg, 85 %) as a colourless solid. ν_{max}/cm^{-1} 3193, 3054, 3032, 2941, 2923, 2852, 2778, 2220, 1630, 1597, 1560, 1521, 1492, 1471, 1449, 1425, 1414, 1396, 1330, 1313, 1296, 1266, 1249, 1228, 1178, 1116, 1085, 1067, 1047, 1025, 1013, 998, 950, 904, 870, 854, 824, 780, 756, 723, 691, 660, 630, 606, 590, 565. δ_H (500 MHz, $CDCl_3$) 1.28–1.52 (m, 12H, 6 × CH_2), 1.72–1.85 (m, 4H, 2 × OCH_2CH_2), 3.02 (s, 12H, $N(CH_3)_2$), 3.94–4.03 (m, 4H, 2 × OCH_2), 6.51–6.56 (m, 1H, 4-H), 6.66–6.70 (m, 1H, 6-H), 6.89–6.95 (m, 1H, 2-H), 6.98–7.03 (m, 2H, 3′-H), 7.18–7.23 (m, 1H, 5-H), 7.50–7.54 (m, 2H, 2′-H), 7.62–7.66 (m, 2H, 2″-H), 7.66–7.71 (m, 2H, 3″-H), 12.04 (s, 1H, NH). δ_C (126 MHz, $CDCl_3$) 26.0, 29.2, 29.3, 29.4, 29.5, 40.7, 68.2, 68.2, 107.2, 110.0, 111.7, 112.1, 115.1, 119.2, 127.1, 128.3, 130.2, 131.2, 132.6, 139.1, 145.3, 158.7, 159.8, 160.4. *m/z* (ESI) 541 $[M]^+$. *m/z* (HRMS ESI) 541.3534. $C_{34}H_{45}N_4O_2^+$ $[M]^+$ requires 541.3537. Anal. Calc. for $C_{34}H_{45}ClN_4O_2$: C 70.75, H 7.86, N 9.71. Found: C 70.70, H 7.86, N 9.76 %. DSC: Cr 149 (47.0 kJ mol^{-1}) I.

N″-*{3-[(8-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy}octyl)oxy]phenyl}*-N,N,N′,N′-tetramethyl Guanidinium Chloride (m-***3c·Cl***)

Method A: reaction time 1.5 h. Chromatography with 400 : 15 CH_2Cl_2/MeOH afforded *m*-**3c·Cl** (211 mg, 98 %) as a colourless solid. ν_{max}/cm^{-1} 2934, 2918, 2851, 1629, 1606, 1563, 1499, 1417, 1431, 1399, 1327, 1314, 1272, 1247, 1226, 1177, 1159, 1066, 1036, 1014, 994, 905, 825, 807, 725, 649, 595, 564. δ_H (500 MHz, $CDCl_3$) 0.88 (t, *J* 7.0, 3H, CH_3), 1.23–1.53 (m, 22H, 11 × CH_2), 1.73–1.84 (m, 6H, 3 × OCH_2CH_2), 3.01 (s, 12H, $N(CH_3)_2$), 3.94–4.01 (m, 6H, 3 × OCH_2), 6.55–6.60 (m, 1H, 4-H), 6.66–6.70 (m, 1H, 6-H), 6.86–6.90 (m, 1H, 2-H), 6.91–6.96 (m, 4H, 3′-H, 3″-H), 7.18–7.23 (m, 1H, 5-H), 7.43–7.48 (m, 4H, 2′-H, 2″-H), 12.12 (s, 1H, NH). δ_C (126 MHz, $CDCl_3$) 14.1, 22.7, 26.0, 26.1, 29.2, 29.3, 29.4, 29.6, 31.9, 40.7, 68.1, 68.1, 68.2, 107.2, 111.7, 112.2, 114.7, 127.7, 130.2, 133.3, 139.0, 158.2, 158.8, 160.3. *m/z* (ESI) 644 $[M]^+$. *m/z* (HRMS ESI) 644.4779. $C_{41}H_{62}N_3O_3^+$ $[M]^+$ requires 644.4786. Anal. Calc. for $C_{41}H_{62}ClN_3O_3$: C 72.38, H 9.18, N 6.18. Found: C 71.55, H 8.81, N 5.98 %. DSC: Cr [131 (39.6 kJ mol^{-1}) SmA 136 (7.5 kJ mol^{-1})] 154 (60.7 kJ mol^{-1}) I.

N″-*{3-[(6-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy}hexyl)oxy]phenyl}*-N,N,N′,N′-tetramethyl Guanidinium Chloride (m-***3d·Cl***)

Method A: reaction time 5 h. Chromatography with 20 : 1 CH_2Cl_2/MeOH afforded *m*-**3d·Cl** (139 mg, 79 %) as a colourless solid. ν_{max}/cm^{-1} 2924, 2853, 1624, 1606, 1563, 1498, 1470, 1431, 1400, 1314, 1289, 1269, 1241, 1174, 1158, 1065, 1036, 1013, 905, 824, 806, 723, 687, 641, 595, 519. δ_H (500 MHz, $CDCl_3$) 0.88 (t, *J* 6.9, 3H, CH_3), 1.23–1.58 (m, 18H, 9 × CH_2), 1.76–1.87 (m, 6H, 3 × OCH_2CH_2), 3.01 (s, 12H, $N(CH_3)_2$), 3.94–4.02 (m, 6H, 3 × OCH_2), 6.55–6.60 (m, 1H, 4-H), 6.67–6.71 (m, 1H, 6-H), 6.87–6.91 (m, 1H, 2-H), 6.92–6.96 (m, 4H, 3′-H, 3″-H), 7.19–7.23 (m, 1H, 5-H), 7.43–7.48 (m, 4H, 2′-H, 2″-H), 12.11 (s, 1H, NH). δ_C (126 MHz, $CDCl_3$) 14.1, 22.7, 25.9, 26.1, 29.1, 29.2, 29.3, 29.4, 29.6, 31.9, 40.7, 67.9, 68.1, 68.1, 107.2, 111.7, 112.2, 114.8, 127.7, 127.7, 130.2, 133.3, 133.4, 139.0, 158.2, 158.2, 158.7, 160.3. *m/z* (ESI) 616 $[M]^+$. *m/z* (HRMS ESI) 616.4459. $C_{39}H_{58}N_3O_3^+$ $[M]^+$ requires 616.4473. Anal. Calc. for $C_{39}H_{58}ClN_3O_3$: C 71.81, H 8.96, N 6.44. Found: C 72.19, H 9.10, N 5.97 %. DSC: Cr [129 (52.7 kJ mol^{-1}) SmA 141 (3.4 kJ mol^{-1})] 150 (58.3 kJ mol^{-1}) I.

N″-*{3-[(4-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy}butyl)oxy]phenyl}*-N,N,N′,N′-tetramethyl Guanidinium Chloride (m-***3e·Cl***)

Method A: reaction time 22 h. Chromatography with 200 : 15 CH_2Cl_2/MeOH afforded *m*-**3e·Cl** (113 mg, 80 %) as a colourless solid, mp 150°C. ν_{max}/cm^{-1} 2956, 2934, 2919, 2850, 1629, 1605, 1563, 1499, 1470, 1431, 1400, 1315, 1272, 1246, 1226, 1177, 1159, 1067, 1050, 1035, 1014, 907, 826, 806, 729, 688, 646, 593. δ_H (300 MHz, $CDCl_3$) 0.88 (t, *J* 6.6, 3H, CH_3), 1.20–1.51 (m, 14H, 7 × CH_2), 1.73–2.04 (m, 6H, 3 × OCH_2CH_2), 3.02 (s, 12H, $N(CH_3)_2$), 3.95–4.12 (m, 6H, 3 × OCH_2), 6.55–6.63 (m, 1H, 4-H), 6.67–6.73 (m, 1H, 6-H), 6.88–6.91 (m, 1H, 2-H), 6.91–6.98 (m, 4H, 3′-H, 3″-H), 7.17–7.25 (m, 1H, 5-H), 7.42–7.50 (m, 4H, 2′-H, 2″-H), 12.13 (s, 1H, NH). δ_C (126 MHz, $CDCl_3$) 14.1, 22.7, 25.9, 26.1, 29.3, 29.4, 29.6, 31.9, 40.7, 67.5, 67.8, 68.1, 107.2, 111.7, 112.3, 114.8, 127.6, 127.7, 130.3, 133.3, 133.5, 139.1, 158.1, 158.3, 158.7, 160.2. *m/z* (ESI) 588 $[M]^+$. *m/z* (HRMS ESI) 588.4152. $C_{37}H_{54}N_3O_3^+$ $[M]^+$ requires 588.4160. Anal. Calc. for $C_{37}H_{54}ClN_3O_3$: C 71.18, H 8.72, N 6.73. Found: C 71.17, H 8.59, N 6.59 %. DSC: Cr 184 (63.2 kJ mol^{-1}) I.

General Procedure for the Salt Metathesis Analogous to Butschies et al.[39]

Chloride *m*-**3a·Cl** (30 µmol) was suspended with the respective salt (44 µmol) in MeCN (5 mL) and the reaction mixture heated for 10 min at reflux. The solvent was removed under reduced pressure, the residue taken up in CH_2Cl_2 and filtered. The filtrate was concentrated under reduced pressure and the product dried under vacuum.

N″-{3-[(10-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy}decyl)oxy]phenyl}-N,N,N′,N′-tetramethyl Guanidinium Bromide (m-***3a·Br***)

Yield 22 mg (quant.) of a colourless solid. ν_{max}/cm^{-1} 2960, 2919, 2851, 1625, 1606, 1563, 1499, 1470, 1431, 1399, 1314, 1272, 1248, 1227, 1177, 1159, 1066, 1034, 1011, 995, 905, 846, 824, 807, 730, 688, 648, 595, 556. δ_H (500 MHz, $CDCl_3$) 0.88 (t, *J* 7.0, 3H, CH_3), 1.23–1.50 (m, 26H, 13 × CH_2), 1.72–1.83 (m, 6H, 3 × OCH_2CH_2), 3.02 (s, 12H, $N(CH_3)_2$), 3.94–4.00 (m, 6H, 3 × OCH_2), 6.54–6.61 (m, 1H, 4-H), 6.67–6.71 (m, 1H, 6-H), 6.84–6.88 (m, 1H, 2-H), 6.92–6.97 (m, 4H, 3′-H, 3″-H), 7.18–7.23 (m, 1H, 5-H), 7.42–7.49 (m, 4H, 2′-H, 2″-H), 11.96 (s, 1H, NH). δ_C (126 MHz, $CDCl_3$) 14.1, 22.7, 26.0, 26.1, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9, 40.7, 68.1, 68.3, 107.2, 111.7, 112.2, 114.7, 127.6, 130.2, 133.3, 139.0, 158.2, 158.7, 160.3. *m/z* (ESI) 673 $[M]^+$. *m/z* (HRMS ESI) 672.5090. $C_{43}H_{66}N_3O_3^+$ $[M]^+$ requires 672.5099. Anal. Calc. for $C_{43}H_{66}BrN_3O_3$: C 68.60, H 8.84, N 5.58. Found: C 69.48, H 9.34, N 4.94 %. DSC: Cr_1 111 (17.9 kJ mol^{-1}), Cr_2 123 (6.2 kJ mol^{-1}), SmA 128 (8.4 kJ mol^{-1}), I.

N″-{3-[(10-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy}decyl)oxy]phenyl}-N,N,N′,N′-tetramethyl Guanidinium Iodide (m-***3a·I***)

Yield: 24 mg (quant.) of a colourless solid. ν_{max}/cm^{-1} 2956, 2934, 2917, 2849, 1629, 1605, 1555, 1500, 1473, 1463, 1430, 1394, 1327, 1313, 1273, 1249, 1226, 1178, 1158, 1137, 1067, 1033, 1011, 995, 951, 920, 906, 846, 824, 808, 769, 723, 689, 643, 594, 566, 550. δ_H (500 MHz, $CDCl_3$) 0.88 (t, *J* 6.9, 3H, CH_3), 1.23–1.50 (m, 26H, 13 × CH_2), 1.72–1.82 (m, 6H, 3 × OCH_2CH_2), 3.06 (s, 12H, $N(CH_3)_2$), 3.94–4.01 (m, 6H, 3 × OCH_2), 6.60–6.64 (m, 1H, 4-H), 6.69–6.73 (m, 1H, 6-H), 6.86–6.89 (m, 1H, 2-H), 6.91–6.96 (m, 4H, 3′-H, 3″-H), 7.20–7.24 (m, 1H, 5-H), 7.43–7.48 (m, 4H, 2′-H, 2″-H), 10.01 (s, 1H, NH). δ_C (126 MHz, $CDCl_3$) 14.1, 22.7, 26.0, 26.1, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9, 41.2, 68.1, 68.1, 68.4, 107.1, 112.0, 112.3, 114.7, 127.6, 130.4, 133.3, 133.3, 138.3, 158.2, 158.3, 160.4. *m/z* (ESI) 673 $[M]^+$. *m/z* (HRMS ESI) 672.5115. $C_{43}H_{66}N_3O_3^+$ $[M]^+$ requires 672.5099. Anal. Calc. for $C_{43}H_{66}IN_3O_3$: C 64.57, H 8.32, N 5.25. Found: C 64.49, H 8.49, N 4.87 %. DSC: Cr_1 115 (10.0 kJ mol^{-1}), Cr_2 124 (16.9 kJ mol^{-1}), [SmA 127 (3.4 kJ mol^{-1})], I.

N″-{3-[(10-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy}decyl)oxy]phenyl}-N,N,N′,N′-tetramethyl Guanidinium Triflate (m-***3a·OTf***)

Yield: 26 mg (96 %) of a colourless solid. ν_{max}/cm^{-1} 2934, 2920, 2852, 2252, 1639, 1607, 1563, 1499, 1471, 1433, 1400, 1288, 1271, 1242, 1223, 1175, 1158, 1066, 1030, 995, 905, 845, 824, 807, 726, 689, 650, 636, 595, 573. δ_H (500 MHz, $CDCl_3$) 0.88 (t, *J* 7.0, 3H, CH_3), 1.22–1.50 (m, 26H, 13 × CH_2), 1.72–1.83 (m, 6H, 3 × OCH_2CH_2), 2.98 (s, 12H, $N(CH_3)_2$), 3.91–4.01 (m, 6H, 3 × OCH_2), 6.46–6.49 (m, 1H, 4-H), 6.60–6.64 (m, 1H, 2-H), 6.68–6.72 (m, 1H, 6-H), 6.91–6.96 (m, 4H, 3′-H, 3″-H), 7.19–7.24 (m, 1H, 5-H), 7.43–7.48 (m, 4H, 2′-H, 2″-H), 9.33 (s, 1H, NH). δ_C (126 MHz, $CDCl_3$) 14.1, 22.7, 26.0, 26.1, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9, 40.4, 68.1, 68.1, 68.3, 106.7, 111.9, 111.9, 114.7, 120.6, 127.6, 130.6, 133.3, 133.3, 138.5, 158.2, 158.2, 158.7, 160.5. *m/z* (ESI) $C_{43}H_{66}N_3O_3^+$ 673 $[M]^+$. *m/z* (HRMS ESI) 672.5079. $C_{43}H_{66}N_3O_3^+$ $[M]^+$ requires 672.5099. *m/z* (ESI) $CF_3O_3S^-$ 149 $[M]^-$. *m/z* (HRMS ESI) 148.9519. $CF_3O_3S^-$ $[M]^-$ requires 148.9526. Anal. Calc. for $C_{44}H_{66}F_3N_3O_6S$: C 64.29, H 8.09, N 5.11. Found: C 64.63, H 8.12, N 4.87 %. DSC: Cr_1 105 (16.5 kJ mol^{-1}), Cr_2 117 (28.5 kJ mol^{-1}), I.

N″-{3-[(10-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy}decyl)oxy]phenyl}-N,N,N′,N′-tetramethyl Guanidinium Tetrafluoroborate (m-***3a·BF$_4$***)

Yield: 23 g (96 %) of a colourless solid. ν_{max}/cm^{-1} 2934, 2918, 2851, 2252, 1630, 1607, 1536, 1500, 1473, 1434, 1399, 1273, 1249, 1228, 1177, 1161, 1068, 1034, 1011, 995, 904, 824, 808, 725, 689, 649, 594, 549. δ_H (500 MHz, $CDCl_3$) 0.88 (t, *J* 6.9, 3H, CH_3), 1.21–1.49 (m, 26H, 13 × CH_2), 1.72–1.83 (m, 6H, 3 × OCH_2CH_2), 2.98 (s, 12H, $N(CH_3)_2$), 3.92–4.01 (m, 6H, 3 × OCH_2), 6.46–6.51 (m, 1H, 4-H), 6.59–6.63 (m, 1H, 2-H), 6.68–6.73 (m, 1H, 6-H), 6.90–6.96 (m, 4H, 3′-H, 3″-H), 7.20–7.25 (m, 1H, 5-H), 7.42–7.48 (m, 4H, 2′-H, 2″-H), 8.41 (s, 1H, NH). δ_C (126 MHz, $CDCl_3$) 14.1, 22.7, 26.0, 26.1, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9, 40.3, 68.1, 68.1, 68.3, 106.9, 111.9, 112.0, 114.7, 127.6, 130.6, 133.3, 133.3, 138.3, 158.2, 158.7, 160.6. *m/z* (ESI) $C_{43}H_{66}N_3O_3^+$ 673 $[M^+]$. *m/z* (HRMS ESI) 672.5102. $C_{43}H_{66}N_3O_3^+$ $[M^+]$ requires 672.5099. Anal. Calc. for $C_{43}H_{66}BF_4N_3O_3$: C 67.97, H 8.76, N 5.53. Found: C 67.85, H 8.87, N 5.36 %. DSC: Cr_1 115 (15.1 kJ mol^{-1}), Cr_2 129 (15.2 kJ mol^{-1}), SmA 135 (4.0 kJ mol^{-1}), I.

N″-{3-[(10-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy}decyl)oxy]phenyl}-N,N,N′,N′-tetramethyl Guanidinium Hexafluorophosphate (m-***3a·PF$_6$***)

Yield: 23 mg (quant.) of a colourless solid, mp (DSC) 123°C. ν_{max}/cm^{-1} 2926, 2854, 1630, 1608, 1562, 1499, 1470, 1434, 1399, 1270, 1242, 1175, 1160, 1036, 904, 842, 822, 723, 687, 649, 594, 557. δ_H (500 MHz, $CDCl_3$) 0.88 (t, *J* 6.9, 3H, CH_3), 1.21–1.50 (m, 26H, 13 × CH_2), 1.72–1.83 (m, 6H, 3 × OCH_2CH_2), 2.96 (s, 12H, $N(CH_3)_2$), 3.94 (t, *J* 6.5, 2H, C3-OCH_2), 3.96–4.00 (m, 4H, 2 × biphenyl-OCH_2), 6.47–6.50 (m, 1H, 4-H), 6.57–6.60 (m, 1H, 2-H), 6.70–6.74 (m, 1H, 6-H), 6.91–6.96 (m, 4H, 3′-H, 3″-H), 7.21–7.26 (m, 1H, 5-H), 7.42–7.49 (m, 4H, 2′-H, 2″-H), 7.71 (s, 1H, NH). δ_C (126 MHz, $CDCl_3$) 14.1, 22.7, 26.0, 26.1, 29.1, 29.3, 29.4, 29.5, 29.6, 31.9, 40.2, 68.1, 68.1, 68.3, 106.9, 112.2, 112.2, 114.7, 127.6, 130.7, 133.3, 133.3, 138.0, 158.2, 158.2, 158.6, 160.6. *m/z* (ESI) $C_{43}H_{66}N_3O_3^+$ 673 $[M^+]$. *m/z* (HRMS ESI) 672.5097. $C_{43}H_{66}N_3O_3^+$ $[M]^+$ requires 672.5099. *m/z* (ESI) F_6P^- 145 $[A]^-$. *m/z* (HRMS ESI) 144.9644. F_6P^- $[A]^-$ requires 144.9639. Anal. Calc. for $C_{43}H_{66}F_6N_3O_3P$: C 63.14, H 8.13, N 5.14. Found: C 69.98, H 8.26, N 4.71 %. DSC: Cr_1 111 (16.6 kJ mol^{-1}), Cr_2 127 (27.5 kJ mol^{-1}), I.

N″-{3-[(10-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy}decyl)oxy]phenyl}-N,N,N′,N′-tetramethyl Guanidinium Acetate (m-***3a·OAc***)

Yield: 26 mg (96 %) of a colourless solid, mp (DSC) 84°C. ν_{max}/cm^{-1} 3068, 3041, 2957, 2935, 2918, 2850, 2790, 1672,

1606, 1580, 1536, 1500, 1474, 1463, 1424, 1390, 1377, 1329, 1309, 1273, 1249, 1232, 1176, 1149, 1138, 1048, 1032, 1011, 994, 952, 916, 862, 842, 824, 808, 780, 729, 707, 689, 644, 595, 561, 549. δ_H (500 MHz, $CDCl_3$) 0.88 (t, *J* 6.9, 3H, CH_3), 1.21–1.50 (m, 26H, $13 \times CH_2$), 1.72–1.84 (m, 6H, $3 \times OCH_2CH_2$), 2.72 (s, 12H, $N(CH_3)_2$), 3.92 (t, *J* 6.6, 2H, C3-OCH_2), 3.96–4.02 (m, 4H, $2 \times$ biphenyl-OCH_2), 6.25–6.28 (m, 1H, 4-H), 6.31–6.35 (m, 1H, 2-H), 6.40–6.45 (m, 1H, 6-H), 6.89–6.97 (m, 4H, 3′-H, 3″-H), 7.04–7.11 (m, 1H, 5-H), 7.42–7.49 (m, 4H, 2′-H, 2″-H). δ_C (126 MHz, $CDCl_3$) 14.1, 22.7, 26.1, 29.3, 29.4, 29.5, 29.6, 31.9, 39.6, 67.8, 68.1, 68.1, 106.9, 107.8, 114.1, 114.7, 127.6, 129.2, 133.3, 152.5, 158.2, 159.9, 160.0. *m/z* (ESI) $C_{43}H_{66}N_3O_3^+$ 673 $[M]^+$. *m/z* (HRMS ESI) 672.5080. $C_{43}H_{66}N_3O_3^+$ $[M]^+$ requires 672.5099. Anal. Calc. for $C_{45}H_{69}N_3O_5$: C 73.83, H 9.50, N 5.74. Found: C 74.71, H 9.67, N 5.65 %. DSC: Cr 87 (91.4 kJ mol^{-1}) I.

N″-{3-[(10-{[4′-(Decyloxy)-1,1′-biphenyl-4-yl]oxy}decyl)oxy]phenyl}-N,N,N′,N′-tetramethyl Guanidinium Thiocyanate (m-***3a·SCN***)

Yield: 22 mg (quant.) of a colourless solid. ν_{max}/cm^{-1} 2958, 2934, 2918, 2850, 2252, 2055, 1629, 1606, 1563, 1500, 1472, 1431, 1397, 1328, 1314, 1272, 1249, 1227, 1178, 1159, 1066, 1034, 1011, 995, 905, 846, 824, 808, 728, 689, 648, 595, 554. δ_H (500 MHz, $CDCl_3$) 0.88 (t, *J* 6.9, 3H, CH_3), 1.19–1.51 (m, 26H, $13 \times CH_2$), 1.73–1.84 (m, 6H, $3 \times OCH_2CH_2$), 3.01 (s, 12H, $N(CH_3)_2$), 3.93–4.01 (m, 6H, $3 \times OCH_2$), 6.48–6.52 (m, 1H, 4-H), 6.62–6.65 (m, 1H, 2-H), 6.68–6.72 (m, 1H, 6-H), 6.91–6.96 (m, 4H, 3′-H, 3″-H), 7.20–7.25 (m, 1H, 5-H), 7.42–7.47 (m, 4H, 2′-H, 2″-H), 10.66 (s, 1H, NH). δ_C (126 MHz, $CDCl_3$) 14.1, 22.7, 26.0, 26.1, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9, 40.6, 68.1, 68.1, 68.4, 107.1, 111.7, 112.3, 114.7, 127.6, 130.5, 133.3, 138.7, 158.2, 158.6, 160.5. *m/z* (ESI) $C_{43}H_{66}N_3O_3^+$ 673 $[M]^+$. *m/z* (HRMS ESI) 672.5094. $C_{43}H_{66}N_3O_3^+$ $[M]^+$ requires 672.5099. Anal. Calc. for $C_{44}H_{66}N_4O_3S$: C 72.29, H 9.10, N 7.66. Found: C 71.74, H 9.29, N 6.95 %. DSC: Cr_1 113 (83.7 kJ mol^{-1}), Cr_2 125 (28.7 kJ mol^{-1}), [SmA 127 (4.4 kJ mol^{-1})], I.

Analysis

NMR Spectroscopy

NMR spectra were recorded on a Bruker Avance 300 or Avance 500 spectrometer operating at 300 or 500 MHz for ^{1}H and 75 or 126 MHz for ^{13}C using tetramethylsilane (TMS) as a reference. The chemical shift (δ) was measured in ppm downfield from TMS.

FT-IR Spectroscopy

IR spectra were recorded on a Bruker Vekor 22 apparatus with MKII Golden Gate Single Reflection Diamant ATR.

Mass Spectrometry

Mass spectra and high-resolution mass spectra were recorded on a Bruker micrOTOF-Q with electrospray ionisation or a Varian MAT711 spectrometer with EI ionisation.

Differential Scanning Calorimetry

DSC curves were recorded on a Mettler Toledo DSC822e with a heating/cooling rate of 5 K min^{-1} using the Software STAR to determine phase transition temperatures.

Polarizing Optical Microscopy

Textures were obtained using an Olympus BX 50 polarizing microscope with a Linkam LTS 350 hot stage.

Powder X-Ray Diffraction

Measurements were performed on a Bruker AXS Nanostar C with a monochromatic $Cu_{K\alpha 1}$ beam (λ 1.5405 Å), which was obtained by using a ceramic tube generator (1500 W) with cross-coupled Göbel mirrors as the monochromator. Samples were prepared using glass tubes (0.7 mm outside diameter) from Hilgenberg GmbH.

Supplementary Material

Further synthetic procedures, concentration-dependent ^{1}H NMR spectra of *m*-**3b·Cl** as well as spectroscopic (^{1}H, ^{13}C) and MS data of all new compounds are available on the Journal's website.

Acknowledgements

Generous financial support by the Ministerium für Wissenschaft, Forschung und Kunst des Landes Baden-Württemberg, the Bundesministerium für Bildung und Forschung (shared instrumentation grant # 01 RI 05177) and the Fonds der Chemischen Industrie (Kekulé fellowship for S.B.) is gratefully acknowledged.

References

[1] T. Ishikawa, *Chem. Pharm. Bull. (Tokyo)* **2010**, *58*, 1555. doi:10.1248/CPB.58.1555
[2] M. P. Coles, *Chem. Commun.* **2009**, 3659. doi:10.1039/B901940E
[3] S. Herres-Pawlis, *Nachr. Chem.* **2009**, *57*, 20. doi:10.1002/NADC.200960857
[4] T. Ishikawa, T. Kumamoto, *Synthesis* **2006**, 737. doi:10.1055/S-2006-926325
[5] A. R. Katritzky, B. V. Rogovoy, *ARKIVOC* **2005**, *2005*, 49. doi:10.3998/ARK.5550190.0006.406
[6] J. Sundermeyer, V. Raab, E. Gaoutchenova, U. Garrelts, N. Abacilar, K. Harms, in *Activating Unreactive Substrates* (Eds C. Bolm, F. E. Hahn) **2009**, pp. 17–37 (Wiley-VCH Verlag GmbH: Weinheim).
[7] K. Vazdar, R. Kunetskiy, J. Saame, K. Kaupmees, I. Leito, U. Jahn, *Angew. Chem.* **2014**, *126*, 1459. doi:10.1002/ANGE.201307212
[8] O. Bienemann, A. Hoffmann, S. Herres-Pawlis, *Rev. Inorg. Chem.* **2011**, *31*, 83. doi:10.1515/REVIC.2011.003
[9] F. T. Edelmann, in *Advances in Organometallic Chemistry* (Eds A. F. Hill, M. J. Fink) **2008**, pp. 183–352 (Academic Press: London).
[10] M. P. Coles, *Dalton Trans.* **2006**, 985. doi:10.1039/B515490A
[11] A. Peters, E. Kaifer, H.-J. Himmel, *Eur. J. Org. Chem.* **2008**, 5907. doi:10.1002/EJOC.200800900
[12] P. Selig, *Synthesis* **2013**, *45*, 703. doi:10.1055/S-0032-1318154
[13] K. Nagasawa, Y. Sohtome, in *Science of Synthesis, Asymmetric Organocatalysis* (Eds B. List, K. Maruoka) **2012**, pp. 1–40 (Thieme Medical Publishers: New York, NY).
[14] J. E. Taylor, S. D. Bull, J. M. J. Williams, *Chem. Soc. Rev.* **2012**, *41*, 2109. doi:10.1039/C2CS15288F
[15] M. Odagi, K. Furukori, T. Watanabe, K. Nagasawa, *Chem. – Eur. J.* **2013**, *19*, 16740. doi:10.1002/CHEM.201303006
[16] D. Basavaiah, K. Venkateswara Rao, B. Sekhara Reddy, *Tetrahedron Asymmetry* **2006**, *17*, 1036. doi:10.1016/J.TETASY.2006.03.020
[17] J. Y. Quek, T. P. Davis, A. B. Lowe, *Chem. Soc. Rev.* **2013**, *42*, 7326. doi:10.1039/C3CS60065C
[18] C. C. Huval, S. R. Holmes-Farley, W. H. Mandeville, J. S. Petersen, R. J. Sacchiero, C. Maloney, P. K. Dhal, *J. Macromol. Sci. A* **2004**, *41*, 231. doi:10.1081/MA-120028203
[19] D. S. Kim, A. Labouriau, M. D. Guiver, Y. S. Kim, *Chem. Mater.* **2011**, *23*, 3795. doi:10.1021/CM2016164
[20] M. K. Rauf, Imtiaz-ud-Din, A. Badshah, *Expert Opin. Drug Dis.* **2014**, *9*, 39. doi:10.1517/17460441.2013.857308
[21] A. Mishra, S. Batra, *Curr. Top. Med. Chem.* **2013**, *13*, 2011. doi:10.2174/15680266113139990126
[22] F. Sączewski, Ł. Balewski, *Expert Opin. Ther. Pat.* **2013**, *23*, 965. doi:10.1517/13543776.2013.788645

[23] R. G. S. Berlinck, A. E. Trindade-Silva, M. F. C. Santos, *Nat. Prod. Rep.* **2012**, *29*, 1382. doi:10.1039/C2NP20071F
[24] S. S. Ebada, P. Proksch, *Mini Rev. Med. Chem.* **2011**, *11*, 225. doi:10.2174/138955711795049862
[25] R. G. S. Berlinck, A. C. B. Burtoloso, A. E. Trindade-Silva, S. Romminger, R. P. Morais, K. Bandeira, C. M. Mizuno, *Nat. Prod. Rep.* **2010**, *27*, 1871. doi:10.1039/C0NP00016G
[26] F. Saczewski, Ł. Balewski, *Expert Opin. Ther. Pat.* **2009**, *19*, 1417. doi:10.1517/13543770903216675
[27] R. G. S. Berlinck, A. C. B. Burtoloso, M. H. Kossuga, *Nat. Prod. Rep.* **2008**, *25*, 919. doi:10.1039/B507874C
[28] R. G. S. Berlinck, M. H. Kossuga, *Nat. Prod. Rep.* **2005**, *22*, 516. doi:10.1039/B209227C
[29] S. Su, I. B. Seiple, I. S. Young, P. S. Baran, *J. Am. Chem. Soc.* **2008**, *130*, 16490. doi:10.1021/JA8074852
[30] F. Mathevet, P. Masson, J.-F. Nicoud, A. Skoulios, *J. Am. Chem. Soc.* **2005**, *127*, 9053. doi:10.1021/JA051312A
[31] D. Kim, S. Jon, H.-K. Lee, K. Baek, N.-K. Oh, W.-C. Zin, K. Kim, *Chem. Commun.* **2005**, 5509. doi:10.1039/B511517E
[32] S. M. Martin, J. Yonezawa, M. J. Horner, C. W. Macosko, M. D. Ward, *Chem. Mater.* **2004**, *16*, 3045. doi:10.1021/CM049594L
[33] F. Mathevet, P. Masson, J.-F. Nicoud, A. Skoulios, *Chem. – Eur. J.* **2002**, *8*, 2248. doi:10.1002/1521-3765(20020517)8:10<2248::AID-CHEM2248>3.0.CO;2-B
[34] L. M. Antill, M. M. Neidhardt, J. Kirres, S. Beardsworth, M. Mansueto, A. Baro, S. Laschat, *Liq. Cryst.* **2014**, *41*, 976. doi:10.1080/02678292.2014.896052
[35] M. Butschies, M. Mansueto, J. C. Haenle, C. Schneck, S. Tussetschläger, F. Giesselmann, S. Laschat, *Liq. Cryst.* **2014**, *41*, 821. doi:10.1080/02678292.2014.885600
[36] M. Butschies, M. M. Neidhardt, M. Mansueto, S. Laschat, S. Tussetschläger, *Beilstein J. Org. Chem.* **2013**, *9*, 1093. doi:10.3762/BJOC.9.121
[37] M. Butschies, J. C. Haenle, S. Tussetschläger, S. Laschat, *Liq. Cryst.* **2013**, *40*, 52. doi:10.1080/02678292.2012.732617
[38] M. Butschies, W. Frey, S. Laschat, *Chem. – Eur. J.* **2012**, *18*, 3014. doi:10.1002/CHEM.201101925
[39] M. Butschies, S. Sauer, E. Kessler, H.-U. Siehl, B. Claasen, P. Fischer, W. Frey, S. Laschat, *ChemPhysChem* **2010**, *11*, 3752. doi:10.1002/CPHC.201000444
[40] S. Sauer, S. Saliba, S. Tussetschläger, A. Baro, W. Frey, F. Giesselmann, S. Laschat, W. Kantlehner, *Liq. Cryst.* **2009**, *36*, 275. doi:10.1080/02678290902850027
[41] S. Sauer, N. Steinke, A. Baro, S. Laschat, F. Giesselmann, W. Kantlehner, *Chem. Mater.* **2008**, *20*, 1909. doi:10.1021/CM702967C
[42] T. Kato, M. Yoshio, in *Electrochemical Aspects of Ionic Liquids* (Ed. H. Ohno) **2011**, pp. 375–392 (Wiley: Hoboken, NJ).
[43] K. V. Axenov, S. Laschat, *Materials* **2011**, *4*, 206. doi:10.3390/MA4010206
[44] T. Kato, N. Mizoshita, K. Kishimoto, *Angew. Chem. Int. Ed.* **2006**, *45*, 38. doi:10.1002/ANIE.200501384
[45] K. Binnemans, *Chem. Rev.* **2005**, *105*, 4148. doi:10.1021/CR0400919
[46] L. Douce, J.-M. Suisse, D. Guillon, A. Taubert, *Liq. Cryst.* **2011**, *38*, 1653. doi:10.1080/02678292.2011.610474
[47] *Ionic Liquids in Synthesis*, 2nd edn (Eds P. Wasserscheid, T. Welton) **2008** (Wiley-VCH: Weinheim).
[48] *Electrodeposition from Ionic Liquids* (Eds F. Endres, D. MacFarlane, A. Abbott) **2008** (Wiley-VCH: Weinheim).
[49] *Ionic Liquids IIIA: Fundamentals, Progress, Challenges, and Opportunities* (Eds R. D. Rogers, K. R. Seddon) **2005**, Vol. 901, ACS Symposium Series (American Chemical Society: Washington DC).
[50] *Ionic Liquids IIIB: Fundamentals, Progress, Challenges, and Opportunities* (Eds R. D. Rogers, K. R. Seddon) **2005**, Vol. 902, ACS Symposium Series (American Chemical Society: Washington DC).
[51] *Handbook of Liquid Crystals* (Eds J. W. Goodby, P. J. Collings, T. Kato, C. Tschierske, H. F. Gleeson, P. Raynes) **2014**, Vols 1–8 (Wiley-VCH: Weinheim).
[52] C. Tschierske, *Angew. Chem. Int. Ed.* **2013**, *52*, 8828. doi:10.1002/ANIE.201300872
[53] C. Tschierske, *Isr. J. Chem.* **2012**, *52*, 935. doi:10.1002/IJCH.201200053
[54] G. Ungar, X. Zeng, *Soft Matter* **2005**, *1*, 95. doi:10.1039/B502443A
[55] K. Goossens, P. Nockemann, K. Driesen, B. Goderis, C. Görller-Walrand, K. Van Hecke, L. Van Meervelt, E. Pouzet, K. Binnemans, T. Cardinaels, *Chem. Mater.* **2008**, *20*, 157. doi:10.1021/CM702321C
[56] S. K. Pal, S. Kumar, *Tetrahedron Lett.* **2006**, *47*, 8993. doi:10.1016/J.TETLET.2006.09.167
[57] S. Kumar, S. K. Gupta, *Tetrahedron Lett.* **2010**, *51*, 5459. doi:10.1016/J.TETLET.2010.08.022
[58] J. Motoyanagi, T. Fukushima, T. Aida, *Chem. Commun.* **2005**, 101. doi:10.1039/B414649B
[59] H. Yoshizawa, T. Mihara, N. Koide, *Mol. Cryst. Liq. Cryst.* **2004**, *423*, 61. doi:10.1080/15421400490502481
[60] L. Cui, V. Sapagovas, G. Lattermann, *Liq. Cryst.* **2002**, *29*, 1121. doi:10.1080/02678290210155589
[61] W. Davids, J. J. Roberts, W. C. J. Ross, *J. Chem. Soc.* **1955**, 890. doi:10.1039/JR9550000890
[62] S. K. Lee, Y. Naito, L. Shi, M. Tokita, H. Takezoe, J. Watanabe, *Liq. Cryst.* **2007**, *34*, 935. doi:10.1080/02678290701541538
[63] W. Kantlehner, E. Haug, W. W. Mergen, P. Speh, T. Maier, J. J. Kapassakalidis, H.-J. Bräuner, H. Hagen, *Liebigs Ann. Chem.* **1984**, 108. doi:10.1002/JLAC.198419840112
[64] J. N. Sarmousakis, M. J. D. Low, *J. Phys. Chem.* **1956**, *60*, 1139. doi:10.1021/J150542A028
[65] Y. Marcus, *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 713. doi:10.1039/FT9938900713
[66] P. H. J. Kouwer, T. M. Swager, *J. Am. Chem. Soc.* **2007**, *129*, 14042. doi:10.1021/JA075651A
[67] N. Yamanaka, R. Kawano, W. Kubo, N. Masaki, T. Kitamura, Y. Wada, M. Watanabe, S. Yanagida, *J. Phys. Chem. B* **2007**, *111*, 4763. doi:10.1021/JP0671446
[68] X. Pan, M. Wang, X. Fang, C. Zhang, Z. Huo, S. Dai, *Sci. China Chem.* **2013**, *56*, 1463. doi:10.1007/S11426-013-4904-Y
[69] W. S. Chi, H. Jeon, S. J. Kim, D. J. Kim, J. H. Kim, *Macromol. Res.* **2013**, *21*, 315. doi:10.1007/S13233-013-1097-3
[70] S. Balamurugan, P. Kannan, K. Yadupati, A. Roy, *J. Mol. Struct.* **2011**, *1001*, 118. doi:10.1016/J.MOLSTRUC.2011.06.027
[71] A. Das, B. Maity, D. Koley, S. Ghosh, *Chem. Commun.* **2013**, *49*, 5757. doi:10.1039/C3CC42808G