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p-Alkoxybiphenyls with guanidinium head groups displaying smectic mesophases

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Novel calamitic guanidinium salts with p-alkoxybiphenyl or p-alkoxyphenyl core unit (**7**, **11**, **12**) have been synthesised, utilising the corresponding nitro compounds as synthetic intermediates. Differential scanning calorimetry (DSC), polarising optical microscopy (POM) and temperature-dependent X-ray diffraction studies reveal smectic A (SmA) mesophases for all series. Whereas the p-alkoxybiphenyl guanidinum chlorides **7** display SmA phases with a minimum chain lengths of C8 and broad mesophase width from 80°C (for C8 derivative **7b**) up to 180°C (for C16 derivative **7g**), the corresponding p-alkoxyphenyl guanidinium chlorides **11** display much smaller mesophase width from 4°C (for C10 derivative **11c**) up to 72°C (for C16 derivative **11e**). For the series **12** a large influence of the anion on the clearing point is observed, with clearing points ranging from 209°C for the guanidinium chloride **7f** down to 127°C for guanidinium hexafluorophosphate **12d**.

Keywords: ionic liquid crystal; guanidinium salts; smectic; X-Ray experiments; calamitic

1. Introduction

Ionic liquids have steadily turned from an academic curiosity to 'designer solvents', reagents and ligands for laboratory and industrial applications (*1–13*). If the ionic liquids are equipped with thermotropic mesomorphic properties, ordered materials with interesting features such as ionic conductivity and high thermal stability can be obtained, as was initially shown by various groups (*14–45*). Most of the work in this area has focused on ionic liquid crystals containing imidazolium (*46–56*) or pyridinium ions (*57–66*), whereas liquid crystalline guanidinium salts have been much less investigated (*67–69*). We have recently reported that tetramethylguanidinium salts which are tethered to a pentaalkyloxytriphenylene moiety via an alkyl spacer display rectangular columnar mesophases with different symmetries depending on the chain lengths and temperature (*70*). With respect to calamitic ionic liquid crystals containing p-cyanobiphenyl or p-alkoxybiphenyl units, the biphenyl moiety is often tethered to the cationic group via an alkyl spacer (*47*, *53*, *71*). However, Kouwer and Swager (*72*) has shown that rigid core ionic liquid crystals where the p-alkoxybiphenyl unit is directly attached to the imidazolium ion display smectic A (SmA) phases with increased mesophase stability as compared with the corresponding derivatives with smaller core size (e.g. p-alkoxyphenyl). In contrast, Ster *et al.* (*73*) reported that mesogenic 4-phenylpyridinium salts usually display a decreased mesophase width in comparison with 4-methylpyridinium salts. (See also examples for dikationic or H-bonding biaryl derivatives (*74–77*).) We were therefore interested in the study of guanidinium ions as an alternative head group with directly attached p-alkoxybiphenyl or p-alkoxyphenyl unit with regard to their mesomorphic properties. The results are described in the following.

2. Results and discussion

2.1 Synthesis of p-alkoxybiphenyl guanidinium chlorides

Following a procedure by Kelley *et al.* (*78*) 4-hydroxybiphenyl **1** was treated with benzoyl chloride in pyridine at 0°C to yield the benzoate **2** in 91%. Subsequent nitration in a mixture of HNO_3/HOAc at 85°C gave 54% of the 4′-nitrobiphenyl-4-yl benzoate **3b** together with 40% of the corresponding 2′-nitro derivative **3a** as a byproduct which could be separated by recrystallisation from acetic acid. Removal of the benzoate was achieved by refluxing compound **3b** with K_2CO_3 in aqueous EtOH to give the phenol **4** in 90% yield, followed by alkylation with various alkyl bromides in the presence of K_2CO_3 in acetone under reflux. The 4-alkoxy-4′-nitrobiphenyls **5** were isolated in moderate to good yields (55–89%). Nitro compounds **5** were then submitted to hydrogenation using Pd/C in CH_2Cl_2 at room temperature to yield the amines **6** in 49–62%. Treatment with N,N,N′,N′-tetramethylchloroamidinium chloride (*79*) in the presence of NEt_3 followed by treatment with NaOH gave the desired guanidinium chlorides **7** in moderate to good yields (56–75%). The complete synthesis is given in Scheme 1.

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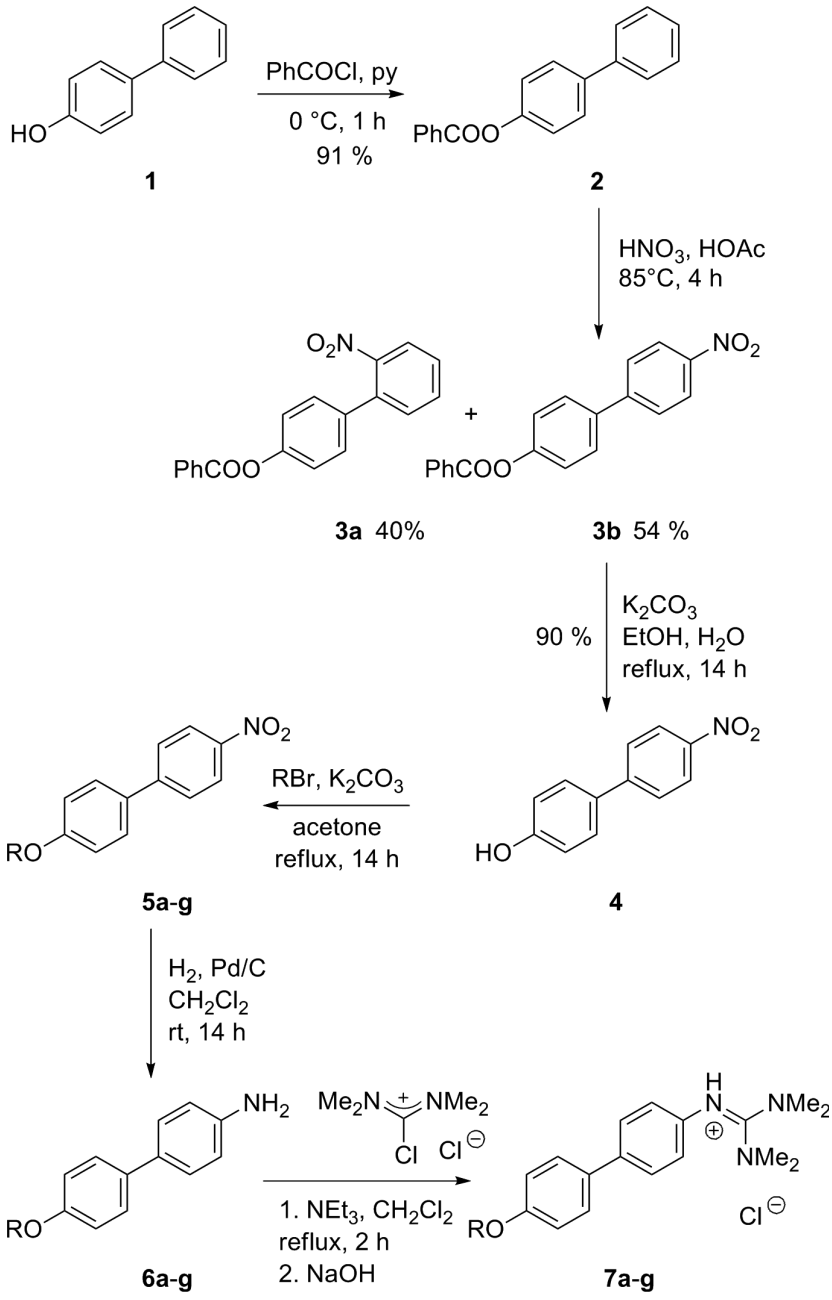


5 - 7	R	5 [%]	6 [%]	7 [%]
a	C_7H_{15}	76	78	72
b	C_8H_{17}	83	38	73
c	C_9H_{19}	89	55	56
d	$C_{10}H_{21}$	55	55	75
e	$C_{11}H_{23}$	45	32	75
f	$C_{12}H_{25}$	81	62	74
g	$C_{16}H_{33}$	76	49	68

Scheme 1. Synthesis of p-alkoxybiphenyl guanidinium chlorides.

2.2 Synthesis of p-alkoxyphenyl guanidinium chlorides

First p-nitrophenol was alkylated with various alkyl bromides to give the 4-alkoxy-nitrobenzenes **9a–e** in good yields (80–93%), followed by reduction of the nitro group with Pd/C under hydrogen atmosphere to the corresponding amines **10a–e**. Guanidinium chlorides **11a–e** were obtained in good yields (63–74%) from the amines using the procedure described previously. The reaction scheme is given in Scheme 2.

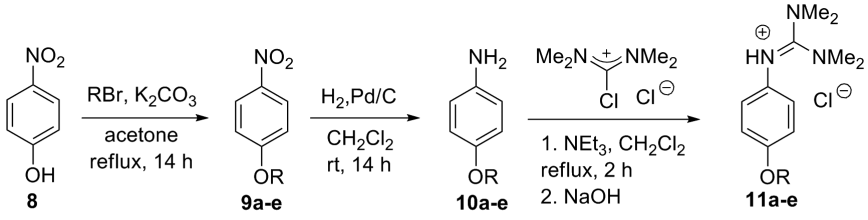
2.3 Anion exchange by Finkelstein reaction

The sodium or potassium salts with the desired anions were mixed in acetonitrile with a solution of p-alkoxybiphenyl-guanidinium chloride **7f**. The mixture was heated under reflux for 1 h and the resulting precipitate of sodium or potassium chloride was removed. The guanidinium salts **12a–e** were obtained in good yields (84–94%). The reaction scheme is given in Scheme 3.

2.4 Mesomorphic properties of guanidinium salts

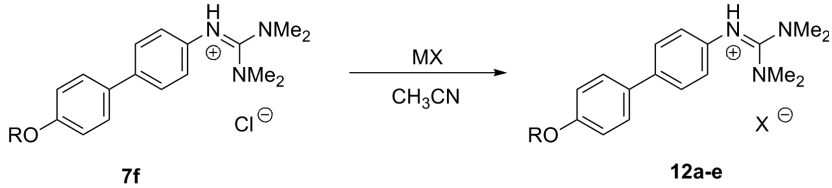
All derivatives **7**, **11** and **12** were investigated by differential scanning calorimetry (DSC) and polarising optical microscopy (POM). The phase transition temperatures and enthalpies for the p-alkoxybiphenyl and the p-alkoxyphenyl guanidinium salts are given in Table 1. A typical DSC trace of compound **7f** is shown in Figure 1. The first heating run displayed a crystal-to-crystal transition at 124°C, a melting point at 147°C and a clearing point at 222°C. Upon first cooling a clearing point at 209°C was observed and crystallisation was suppressed. Upon second heating a glass transition at 42°C and a clearing point at 208°C were detected.

Generally DSC traces for the compounds **7**, **11** and **12** showed two transitions during second heating run, i.e. a glass transition and a clearing point. During the first heating only, the pristine solids showed a melting transition into a mesophase followed by the clearing point (Figure 1). During the subsequent cooling run the mesosphase reappeared but recrystallisation was



9 - 11	R	9 [%]	10 [%]	11 [%]
a	C_8H_{17}	93	85	74
b	$C_{10}H_{21}$	96	55	70
c	$C_{11}H_{23}$	83	80	72
d	$C_{12}H_{25}$	80	94	70
e	$C_{16}H_{33}$	93	53	63

Scheme 2. Synthesis of p-alkoxybiphenyl guanidinium chlorides.



12	MX	12 [%]
a	NaBr	84
b	NaI	94
c	$NaBF_4$	95
d	KPF_6	92
e	KSCN	91

Scheme 3. Anion exchange by salt metathesis.

Table 1. Phase transition temperatures (°C) and enthalpies (kJ mol^{-1}) of p-alkoxybiphenyl guanidinium chlorides **7**, p-alkoxyphenyl guanidinium chlorides **11** and p-alkoxybiphenyl guanidinium salts **12**. The following phases were observed: crystalline phase (Cr), glass transition (G), smectic A phase (SmA), isotropic liquid (I), spontaneous recrystallisation (rCr). Heating/cooling rate 5 K min^{-1}.

Compound	Phase transitions (onset (°C)) and transition enthalpies (given in parentheses) (kJ mol^{-1})	
7a	1. Heating	Cr 145 (43.5) I
7b	1. Heating	G 39 SmA 119 (0.6) I
	1. Cooling	I 121 (–0.5) SmA
	2. Heating	G 39 SmA 119 (0.6) I
7c	1. Heating	G 24 SmA 180 (1.0) I
	1. Cooling	I 180 (–1.1) SmA
	2. Heating	G 26 SmA 180 (0.9) I
7d	1. Heating	Cr_1 38 (26.6) Cr_2 148 (36.3) SmA 195 (1.0) I
	1. Cooling	I 182 (–0.8) SmA
	2. Heating	G 46 rCr 111 (–8.0) Cr 133 (4.5) SmA 181 (0.8) I
7e	1. Heating	Cr_1 121 (32.8) Cr_2 143 (13.8) SmA 198 (1.1) I
	1. Cooling	I 196 (–0.9) SmA
	2. Heating	G 40 SmA 193 (1.0) I
7f	1. Heating	Cr_1 124 (54.4) Cr_2 147 (8.9) SmA 222 (0.9) I
	1. Cooling	I 209 (–1.1) SmA
	2. Heating	G 42 SmA 208 (1.0) I
7g	1. Heating	Cr 118 (51.9) SmA 238 (1.1) I
	1. Cooling	I 230 (–0.3) SmA 51 G 43 (–1.7) Cr
	2. Heating	Cr 43 (14.1) SmA 223 (0.6) I
11a	1. Heating	Cr_1 44 (22.7) Cr_2 96 (13.2) I
11b	1. Heating	Cr 95 (22.4) I
	1. Cooling	I 95 (–0.6) Cr
	2. Heating	Cr 93 (0.4) I
11c	1. Heating	Cr 117 (43.8) I
	1. Cooling	I 104 (–0.6) SmA
	2. Heating	G 103 SmA 107 (5.9) I
11d	1. Heating	Cr 121 (29.9) SmA 128 (0.7) I
	1. Cooling	I 129 (–0.9) SmA
	2. Heating	rCr 54 (–32.6) Cr 110 (34.0) SmA 128 (0.8) I
11e	1. Heating	Cr_1 56 (18.4) rCr 76 (–50.1) Cr_2 113 (40.0) SmA 188 (1.4) I
	1. Cooling	I 180 (–1.1) SmA 43 (–13.8) Cr_2 35 (–2.5) Cr_1
	2. Heating	Cr_1 53 (16.0) rCr 82 (–28.3) Cr_2 108 (34.6) SmA 180 (1.1) I
12a	1. Heating	Cr 122 (34.7) SmA 219 (1.1) I
	1. Cooling	I 206 (–1.4) SmA
	2. Heating	G 19 SmA 204 (1.0) I
12b	1. Heating	Cr_1 48 (5.7) Cr_2 66 (32.9) SmA 188 (1.4) I
	1. Cooling	I 186 (–1.1) SmA 7 G
	2. Heating	G 16 SmA 187 (0.9) I
12c	1. Heating	Cr 111 (22.7) SmA 170 (0.7) I
	1. Cooling	I 170 (–0.6) SmA 75 (–8.6) Cr_1 –2 (–1.0) Cr_2
	2. Heating	Cr_1 –7 (0.8) rCr 48 (–16.4) Cr_2 112 (23.8) SmA 169 (0.6) I
12d	1. Heating	Cr 106 (45.1) SmA 128 (0.4) I
	1. Cooling	I 127 (–0.4) SmA
	2. Heating	rCr 67 (–45.1) Cr 105 (44.3) SmA 127 (0.4) I
12e	1. Heating	Cr 116 (33.0) SmA 136 (0.5) I
	1. Cooling	I 154 (–0.6) SmA
	2. Heating	G 99 SmA 153 (0.7) I

kinetically hindered and in most cases completely suppressed. Since in all cases the observed mesophases appeared during heating and cooling processes the compounds **7**, **11** and **12** displayed enantiotropic behaviour. In the second heating run, the derivatives showed a glass transition from the solid phase to the mesophase but some derivatives (**7d**, **11d**, **12d**) displayed a cold crystallisation process preceding the melting transition. Only the guanidinium salt **7g** and **11e** with long chain length displayed a transition from the mesophase to the crystalline phase during the first cooling run. Looking at series **12** only iodine **12b** (X = I^-)

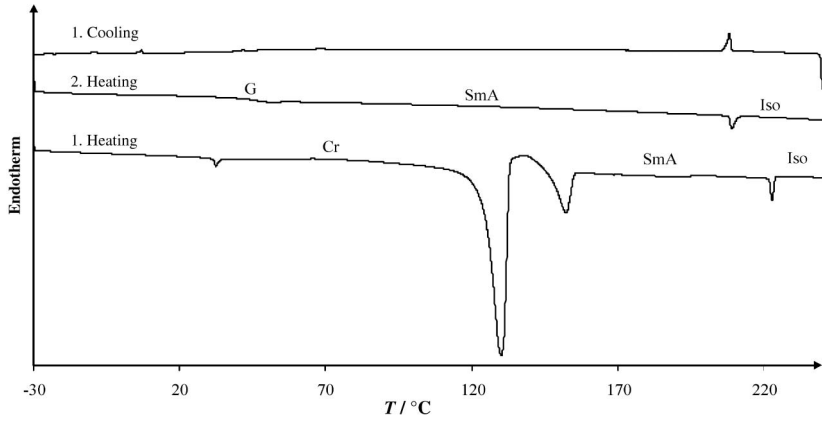


Figure 1. DSC trace of guanidinium salt **7f** (heating/cooling rate 10 K min^{-1}).

and **12c** (X = BF_4^-) showed a crystallisation during the first cooling run. For the other salts the recrystallisation was suppressed.

In order to compare the mesophase stabilities of p-alkoxybiphenyl guanidinium chlorides **7** and p-alkoxyphenyl guanidinium chlorides **11** the dependence of the mesophase range on the chain lengths is schematically depicted in Figures 2 and 3, respectively. p-Alkoxybiphenyl derivatives **7** with chain lengths from 8 atoms up to 16 carbon atoms display a broad mesophase range of up to ΔT (SmA) 180°C for **7g** with a clearing point at 223°C. With increasing chain lengths the clearing temperature is rising and the mesophase is further stabilised. For compound **7a** with a chain length of C7 only isotropic melting was observed. So for the biphenyl guanidinium chlorides a minimum chain length of 8 carbon atoms is required to build up mesophases. In contrast, for the corresponding p-alkoxyphenyl derivatives **11** a minimum chain length of C11 is required in order to obtain a mesophase (Figure 3). Furthermore, the mesophase widths of the C11, C12 and C16 derivatives **11c,d,e** are much smaller as compared with the corresponding p-alkoxybiphenyl derivatives **7e,f,g**. The direct comparison is shown in Figure 4. Thus, the additional phenyl ring in the rigid core unit resulted in increased mesophase stabilities in agreement with Kouwer and Swager's report (*72*).

Ionic liquid crystals have a unique opportunity to influence the liquid crystalline properties. By changing the counterion it is possible to adjust the mesomorphic behaviour. Therefore, the chloride anion of p-dodecyloxybiphenyl-tetramethyl guanidinium salt **7f** was exchanged by bromide, iodine, tetrafluoroborate, hexafluorophosphate and thiocyanate. The results are summarised in Figure 5.

For the halides Cl^- (**7f**), Br^- (**12a**), I^- (**12b**) and the pseudo halide SCN^- (**12e**) a decrease of the clearing temperatures from 209°C for Cl^- to 187°C for I^- was observed. The pseudo halide SCN^- displayed an even lower clearing temperature of 153°C. Presumably with increasing anion radius the mesophase is destabilised

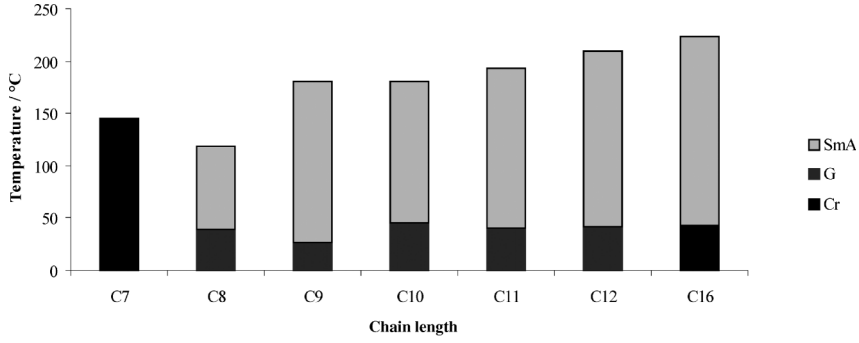


Figure 2. Mesophase widths of p-alkoxybiphenyl guanidinium chlorides **7a–g** depending on the chain lengths. For details see Table 1.

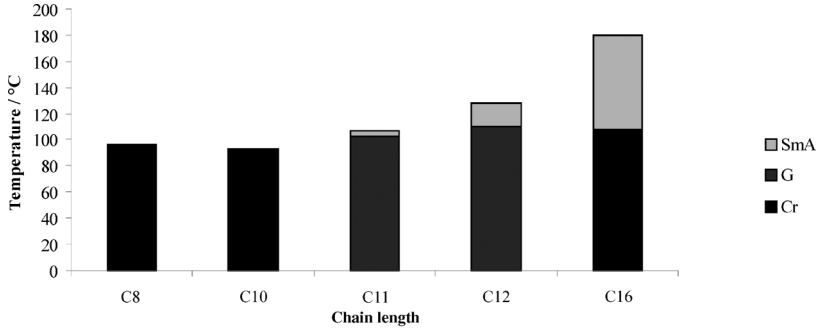


Figure 3. Mesophase widths of p-alkoxyphenyl guanidinium chlorides **11a–e** depending on the chain lengths. For details see Table 1.

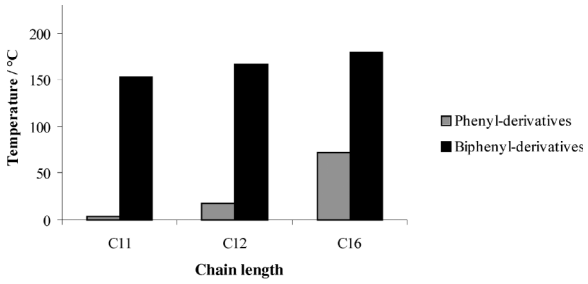


Figure 4. Comparison of the temperature range of SmA mesophases from guanidinium salts **11c,d,e** and **7e,f,g**.

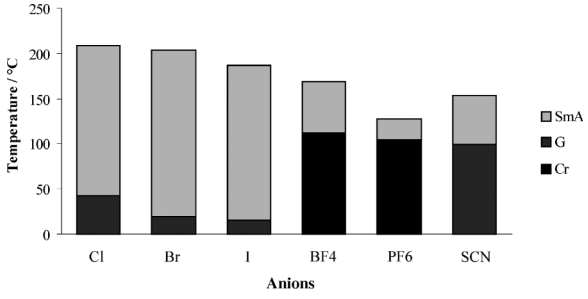


Figure 5. Mesophase widths of p-alkoxyphenyl guanidinium salts **7f** (X = Cl^-) and **12a–e** (X ≠ Cl^-) depending on the different anions. For details see Table 1.

resulting in a lower clearing temperature. The melting points decrease in the halides series from Cl^- to I^-. SCN^- exhibits a different behaviour. In this case the melting point is at 99°C, which is much higher than for the halides, resulting in a decreased mesophase range of only 54°C. The bulky anions BF_4^- (**12c**) and PF_6^- (**12d**) destabilise the smectic mesophases even further. For BF_4^- the clearing point of the guanidinium salt drops to 169°C and the mesophase range to ΔT = 58°C. PF_6^- exhibits a clearing point of only 127°C and a mesophase width of ΔT = 22°C. The clearing points decrease in the order: $Cl^- > Br^- > I^- > BF_4^- > SCN^- > PF_6^-$. Thus, the guanidinium salts display a similar behaviour as compared with the imidazolium salts described by Kouwer and Swager (*72*).

The mesophases of compounds **7b–g**, **11c–e** and **12a–e** were studied by POM. Typical POM pictures are shown in Figures 6–8. The derivatives **7**, **11** and **12** display spontaneous homeotropic alignment over large areas during cooling from isotropic melt into the smectic mesophases resulting in homeotropic textures. This is characteristic for SmA mesophases (*80*). Regarding the shape of the guanidinium salts they have a surfactant-like structure. The polar guanidinium head group interacts with the lower and upper glass plates inducing homeotropic alignment. This strong alignment could be suppressed by removing the upper glass plate from the sample (Figure 7) resulting in focal conical textures which are typical for SmA phases (*80*).

X-ray diffraction (XRD) studies of the mesophases revealed for all investigated compounds **7**, **11** the typical diffraction pattern for smectic mesophases, with a strong fundamental diffraction peak (001), in some cases a small second-order peak (002), and the diffuse scattering from the alkyl chains around 4.8 Å. For compounds **7c** and **7g** aligned samples were obtained by slowly cooling from isotropic melt into the smectic mesophase. The corresponding diffraction patterns are shown in Figure 9 with a strong first-order peak, a smaller second-order peak and the orientation of the director along the magnetic field. The (001) peaks were fit with a Gaussian distribution to obtain the layer exact spacings d_{001}. Looking at the diffraction pattern of the aligned samples SmA mesophases are proposed, since the first-order peak is parallel to the magnetic field and the wide angle scattering is perpendicular to the (001) reflection.

Unfortunately, for most of the other guanidinium salts no clear orientation along the magnetic field could be obtained. Instead the temperature-dependent behaviour of the layer spacings in the smectic

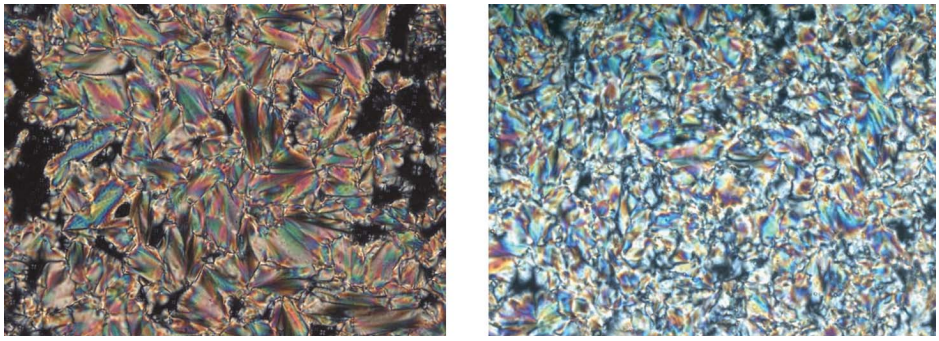


Figure 6. Focal conical textures from p-alkoxybiphenyl guanidinium chloride **7c** (left) and **11d** (right) under crossed polarisers at 145°C and 125°C, respectively, upon cooling from the isotropic phase (cooling rate 10 K min^{-1}, magnification 200×).

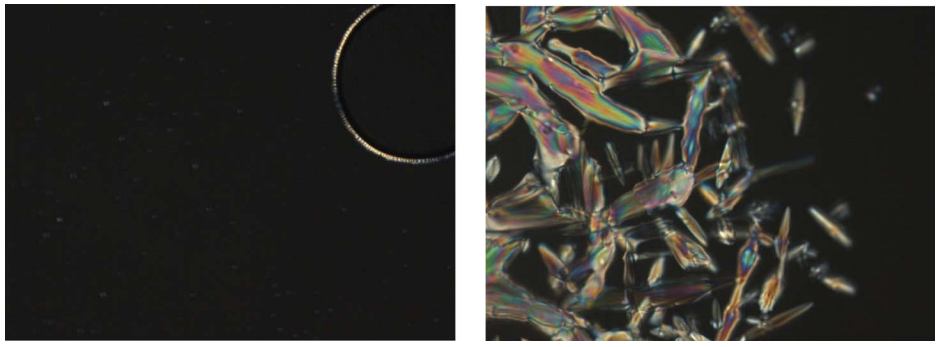


Figure 7. p-alkoxybiphenyl guanidinium chloride **7f** (left, between two glass plates; right, sample on slide without upper glass plate) under crossed polarisers at 200°C upon cooling from isotropic phase (cooling rate 10 K min^{-1}, magnification 200×) shows homeotropic alignment and focal conical texture of a SmA phase.

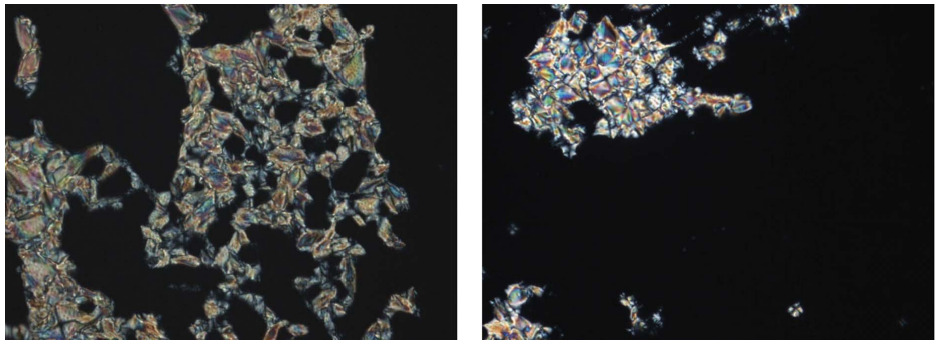


Figure 8. p-dodecyloxybiphenly guanidinium thiocyanate **12e** (left) at 140°C and guanidinium tetrafluoroborat **12c** (right) at 130°C by cooling from isotropic melt showing focal conical textures and large black areas of homeotropic alignment indicating SmA mesophases (cooling rate 10 K min^{-1}, magnification 200×).

mesophases of the guanidinium chlorides **7**, **11** was investigated. A typical small-angle X-ray scattering (SAXS) diffraction pattern and the temperature-dependent SAXS profiles are shown in Figure 10.

The first-order reflexions move to higher 2Θ values resulting in decreasing d_{001} values. The results are summarised in Figure 11 (see also Tables 2 and 3) for the p-alkoxybiphenyl guanidinium chlorides **7** and in Figure 12 (see also Tables 4 and 5) for the p-alkoxyphenyl guanidinium chlorides **11**.

The smectic layer spacings of **7** and **11** showed a similar linear temperature dependence to that Kouwer and Swager (*72*) showed for the imidazolium salts. With increasing temperature shrinkage of the layer spacing was observed. This negative thermal expansion is typical of SmA phases and related to the decrease of

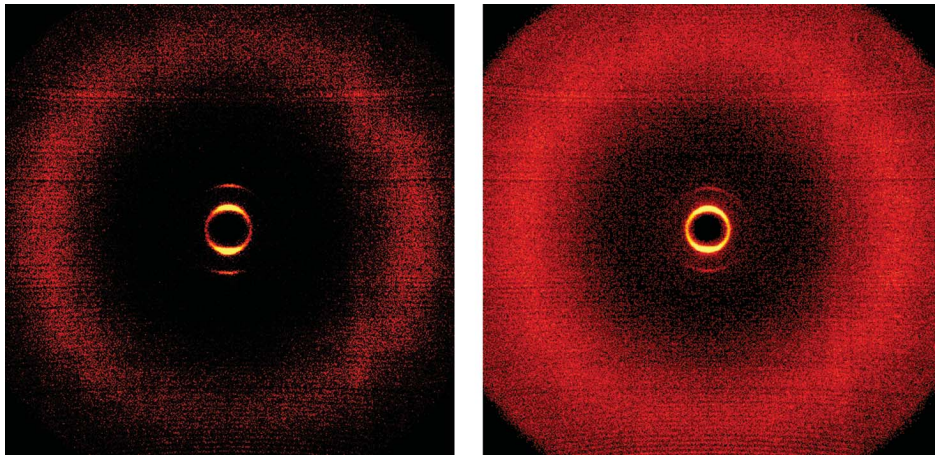


Figure 9. XRD patterns of the aligned samples of **7c** at 140°C and **7g** at 200°C (vertical magnetic field director).

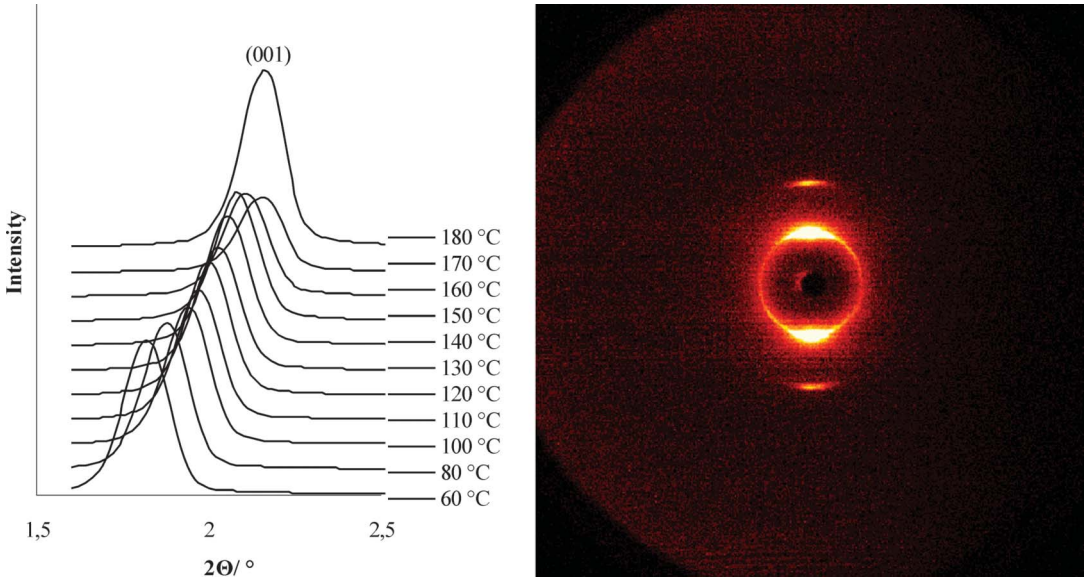


Figure 10. SAXS experiment (intensity versus scattering angle) of **7f** at different temperatures (left) diffraction pattern of **7f** at 100°C (right).

the orientational order parameter at increasing temperature (*81*, *82*). In analogy to the XRD results of the aligned samples **7c** and **7g**, together with the textures of the compounds, we propose SmA mesophases for the other guanidinium salts as well. This assumption is further confirmed by similar behaviour of the layer spacings with increasing temperature for all investigated compounds. Since the layer spacing is temperature dependent, the L_{XRD} values were determined at reduced temperature ($T = 0.95T_{iso}$) by linear interpolation of the experimental data of d_{001} (see Tables 6 and 7).

For the series **12**, first XRD experiments were performed. The results are summarised in Figure 13 and Tables 8 and 9. The observed diffraction patterns revealed smectic mesophases similarly to the compounds **7** and **11**, with a strong first-order (001), a weak second-order reflection (002) and a broad halo of the alkyl chains. The XRD results together with the homeotropic textures of compounds **12** indicate that the observed mesophases are SmA phases. An exchange of counterions showed no influence on the character of the mesophases only on the range and stability of the mesophases.

Upon comparing the experimental layer spacing values L_{XRD} with the molecular lengths L_{calc} of the guanidinium chlorides **7**, **11** and **12**, which were obtained by molecular modelling with Chem3D Ultra© (*all-trans*

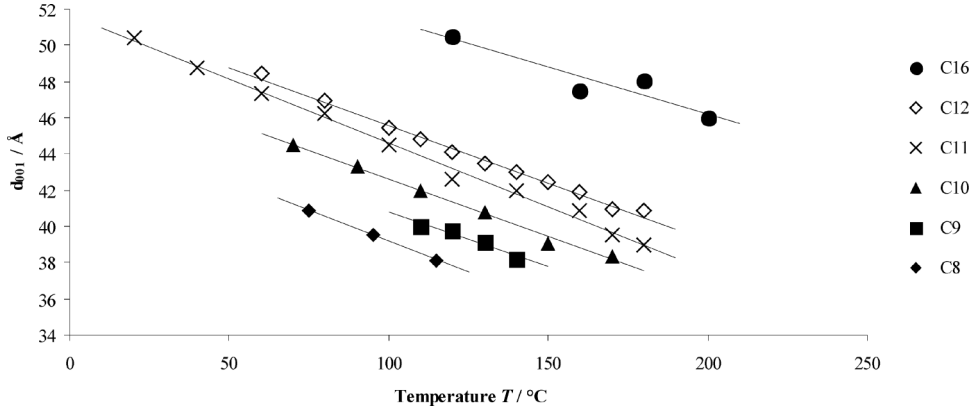


Figure 11. Temperature-dependent layer spacings in the SmA phase of **7** determined by XRD upon cooling from the isotropic melt. For details see Tables 2 and 3.

Table 2. XRD data obtained from compounds **7b–d** by cooling from isotropic melt.

C8		C9		C10	
Temperature T/(°C)	Layer spacing d_{001}/(Å)	Temperature T/[°C]	Layer spacing d_{001}/(Å)	Temperature T/(°C)	Layer spacing d_{001}/(Å)
115	38.14	140	38.19	170	38.38
95	39.5	130	39.13	150	39.05
75	40.88	120	39.80	130	40.79
		110	39.97	110	42.01
				90	43.33
				70	44.49
WAXS: 75	4.60	WAXS: 140	4.75	WAXS: 150	4.88

Table 3. XRD data obtained from compounds **7e–g** by cooling from isotropic melt.

C11		C12		C16	
Temperature T/(°C)	Layer spacing d_{001}/(Å)	Temperature T/(°C)	Layer spacing d_{001}/(Å)	Temperature T/(°C)	Layer spacing d_{001}/(Å)
180	39.00	180	40.83	200	46.01
170	39.49	170	40.96	180	48.07
160	40.87	160	41.89	160	47.52
140	42.00	150	42.43	120	50.53
120	42.61	140	42.98		
100	44.48	130	43.50		
80	46.22	120	44.14		
60	47.35	110	44.81		
40	48.74	100	45.44		
20	50.43	80	46.95		
		60	48.45		
WAXS: 150	4.84	WAXS: 158	4.73	WAXS: 160	4.81

configuration), we propose that the SmA phases of **7**, **11** and **12** consist of bilayers, with polar head groups pointing towards each other. A model of the suggested bilayer structure is shown in Figure 14.

The experimental layer spacing is increasing from shorter chain lengths to longer chains, owing to the increasing bulkiness of the alkyl chains. However, looking at the ratio of L_{XRD} to L_{calc} values from 1.9

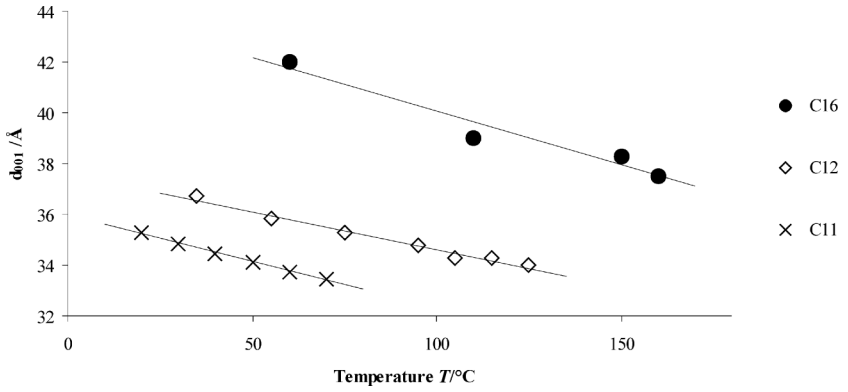


Figure 12. Temperature-dependent layer spacings in the SmA phase of **11** determined by XRD upon cooling from the isotropic melt. For details see Tables 4 and 5.

Table 4. XRD data obtained from compounds **11c–e** by cooling from isotropic melt.

C11		C12		C16	
Temperature *T*/(°C)	Layer spacing d_{001}/(Å)	Temperature *T*/(°C)	Layer spacing d_{001}/(Å)	Temperature *T*/(°C)	Layer spacing d_{001}/(Å)
70	33.47	125	34.01	160	37.51
60	33.74	115	34.26	150	38.27
50	34.09	105	34.26	110	39.02
40	34.45	95	34.76	60	42.02
30	34.86	75	35.26		
20	35.30	55	35.81		
		35	36.71		
WAXS: 70	4.76	WAXS: 110	4.76	WAXS: 130	4.87

Table 5. XRD data obtained from compounds **12a–c** by cooling from isotropic melt.

C12 bromide		C12 iodide		C12 tetrafluoroborate	
Temperature *T*/(°C)	Layer spacing d_{001}/(Å)	Temperature *T*/(°C)	Layer spacing d_{001}/(Å)	Temperature *T*/(°C)	Layer spacing d_{001}/(Å)
180	42.62	180	42.43	170	40.91
160	42.59	160	43.71	160	41.23
140	43.47	140	44.59	150	41.75
120	44.68	120	45.29	140	42.04
100	46.02			130	42.41
80	47.88			120	42.49
60	49.97			110	43.45
				100	43.97

for **7b** down to 1.5 for **7g** were found. In the case of a perfectly ordered bilayer structure the determined layer spacing should be approximately $2L_{calc}$. The guanidinium moiety results in a tilt of the head group (relative) with respect to the aromatic core unit. Owing to their orientational and conformational disorder (*83*) the alkyl chains occupy on average a more or less cone-shaped cylindrical volume in order to compensate for the bulky head group. This is particular true for short alkyl chains (e.g. **7b**), where the alkyl chain lengths are of a similar size as compared with the length of the biphenyl unit. Therefore, the

Table 6. XRD data of **7**.

Compound	L_{calc}/Å[a]	L_{XRD}/Å[b,c]	L_{XRD}/L_{calc}[c]
7a	18.6	–[d]	–[d]
7b	20.0	38.3	1.9
7c	21.1	38.5	1.8
7d	22.4	38.1	1.7
7e	23.5	38.8	1.7
7f	24.9	39.4	1.6
7g	29.8	45.6	1.5

[a]Length of the stretched molecule, determined by molecular modelling.
[b]Layer spacing, determined by XRD experiments.
[c]L_{XRD} was determined at $T = 0.95T_{iso}$ (after interpolation of the data).
[d]No mesophase observed.

Table 7. XRD data of **11**.

Compound	L_{calc}/Å[a]	L_{XRD}/Å[b,c]	L_{XRD}/L_{calc}[c]
11a	16.3	–[d]	–[d]
11b	18.8	–[d]	–[d]
11c	22.5	32.3	1.4
11d	23.9	34.0	1.4
11e	26.4	37.1	1.4

[a]Length of the stretched molecule, determined by molecular modelling.
[b]Layer spacing, determined by XRD experiments.
[c]L_{XRD} was determined at $T = 0.95T_{iso}$ (after interpolation of the data).
[d]No mesophase observed.

experimentally observed layer spacing L_{XRD} is about twice the calculated molecule length L_{calc}. In contrast, for long alkyl chains (e.g. **7g**) interdigitation becomes more pronounced owing to increased Van der Waals interactions, resulting in a layer spacing which is only 1.5 times longer than calculated maximum length of a fully extended molecule. It should be noted that Goosens *et al.* (*84*) and Guillon, Donnio and coworkers (*85–87*) have carried out a very detailed analysis of molecular volumes and areas for imidazolium ionic liquid crystals with pendant mesogenic groups and dendrimers.

We were able to obtain a single-crystal structure from **7f**. The crystal structure and the cell unit are shown in Figure 15 and 16. The crystallographic data of **7f** are shown in Table 10. The whole molecule is almost planar with the guanidinium group being slightly twisted out of the plane and the two aromatic rings of the biphenyl core are slightly twisted towards each other, owing to the steric hindrance of the hydrogen atoms. The alkyl chains are *all-trans* orientated and the anion is located near the N–H moiety of the guanidinium group forming a hydrogen bond. A monoclinic unit cell with $a = 23.2$ Å, $b = 9.4$ Å, $c = 13.5$ Å, $\alpha = \gamma = 90°$ and $\beta = 101°$ was found. As shown in Figure 16 the crystal structure exhibits a tilted highly interdigitated bilayer structure with almost fully overlapping alkyl chains. Since the crystal structure of smectic mesogenes is often related to the smectic mesophases the bilayer structure is in accordance with our proposed model for the observed mesophases. The fact that a tilt of the bilayer was found for the crystal in contrast to the non-tilted SmA mesophases is caused by crystal packing effects where the molecules have a fixed position in the unit cell and free rotation is limited, leading to a macroscopic tilted structure motive. Dobbs *et al.* (*88*) showed in their work about dodecyloxybenzyl-methyl-imidazolium dicyanoargentates, which form lamellar SmA phases, that X-ray crystal structures could give some

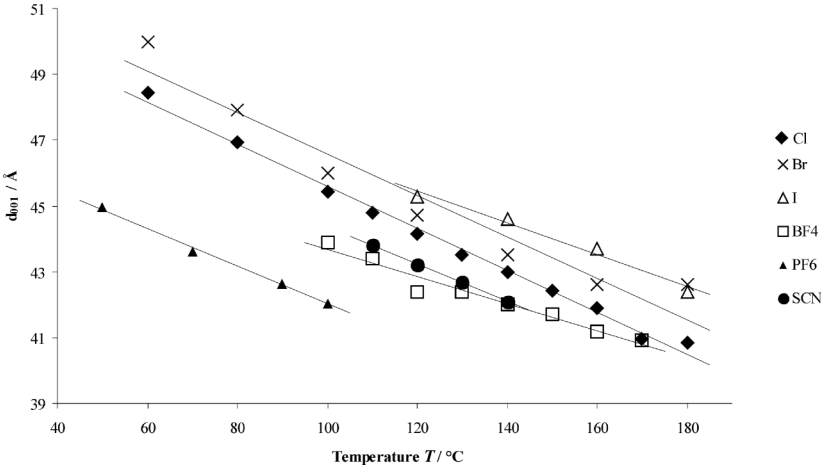


Figure 13. Temperature-dependent layer spacings in the SmA phase of **12** determined by XRD upon cooling from the isotropic melt. For details see Table 9.

Table 8. XRD data of **12**.

Compound	L_{XRD}/Å[a,b]
7f	39.4
12a	40.7
12b	42.7
12c	41.2
12d	40.9
12e	41.8

[a]Layer spacing, determined by XRD experiments.
[b]L_{XRD} was determined at $T = 0.95T_{iso}$ (after interpolation of the data).

Table 9. XRD data obtained from compounds **12d–e** by cooling from isotropic melt.

C12 hexafluorophosphate		C12 thiocyanate	
Temperature T/(°C)	Layer spacing d_{001}/(Å)	Temperature T/(°C)	Layer spacing d_{001}/(Å)
100	42.06	140	41.26
90	42.65	130	42.67
70	43.61	120	43.21
50	44.97	110	43.76
		100	43.78

information to analyse mesophases. Although such companions should be handled with care, X-ray crystal structures can be used as tool to analyse mesophases structures (*89*).

3. Experimental details

All reagents and solvents were purchased from commercial sources and used without further purification unless otherwise indicated. All reactions were carried out under the standard Schlenk technique unless otherwise noted. Column chromatography separations were performed on silica gel 60 (40–63 μm) from *Fluka*. Thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel 60 F_{254} (*Merck*) and visualised by ultraviolet (UV) light spectroscopy. Mass spectra were obtained on a MAT 711 from *Varian* under Electron Impact (EI) conditions at 70 eV and on a *Bruker Daltonics* microTOFq under Electron Spray Ionization (ESI) and Atmospheric Pressure Chemical Ionization (APCI) conditions. The intensities are given as a percentage of the base peak. Melting points were determined on SMP-20 from *Büchi*. Nuclear magnetic resonance (NMR; 500 MHz) spectra were recorded on a *Bruker* Advance 500. Chemical shifts (δ) are given relative to tetramethylsilane in parts per million, coupling constants (J) are given in Hertz. Measurements were performed in $CDCl_3$ at room temperature. Infrared (IR) spectroscopy was performed on a *Bruker* Fourier transform infrared (FT-IR) spectrometer Vektor22 with MKII Golden Gate Single Reflection Diamant ATR-system. DSC was performed on a *Mettler-Toledo* DSC822e (heating rates were 2, 5 or 10 K min^{-1}). POM was carried out

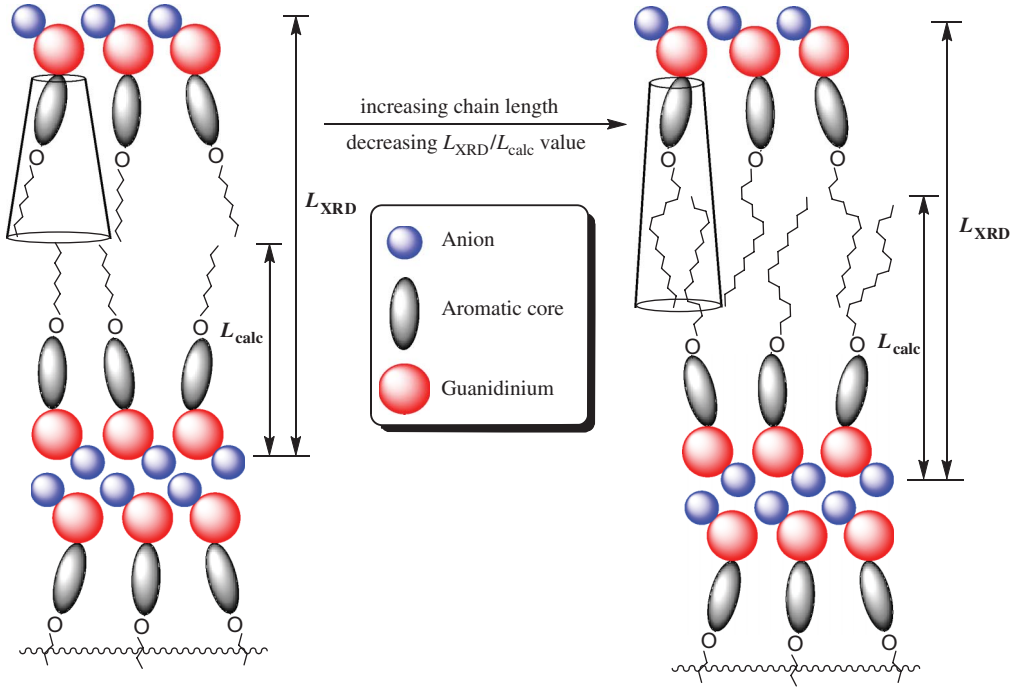


Figure 14. Model of the bilayer structure of the guanidinium chlorides. Increase in the chain length leads to coiling and interdigitation of the aliphatic tails.

Table 10. Crystallographic data of **7f**.

Wavelength (Å)	0.71073
Crystal system	Monoclin
Space group	P2(1) /c
Unit cell [Å]	
A	23.206(6)
B	9.357(2)
C	13.485(2)
Angle	
A	90
B	100.614(14)
Γ	90
Volume (unit cell) (Å^3)	2877.8(11)
Molecules per unit cell	4
Density (calculated) (g cm^{-3})	1.127
Crystal size (mm)	$0.4 \times 0.4 \times 0.05$
Θ-range	1.79–23.00
Reflections collected	4113
Unique reflections	4000
Used reflections for refining	4000
Refining parameters	312
R (%)	9.43
R_w (%)	14.74
Abs. structure parameter	–
Identification code	s1588rm

on an *Olympus* BX50 polarising microscope combined with a *Linkam* TP93 central processor. X-ray experiments were performed with a *Bruker AXS* Nanostar C diffractometer employing Ni-filtered $Cu_{K\alpha}$ radiation (λ = 1.5418 Å). Single crystal structure was performed on a Nicolet P3- with graphite monochromator applying Mo-K_α-radiation using the ω-scan method. Measurements were performed at 293(2) K.

3.1 Biphenyl-4-yl benzoate (2)

To a solution of 4-hydroxybiphenyl **1** (17.2 g, 101 mmol) in pyridine (170 ml), 11.7 ml benzoyl chloride (14.2 g, 101 mmol) was slowly added at 0°C. After 1 h the reaction was quenched by adding water (250 ml) and 1 N HCl_{aq} (150 ml) to the mixture. The resulting white solid was filtered off and washed with saturated $NaHCO_3$ solution in water. The crude product was dissolved in CH_2Cl_2 and the organic phase was washed three times with 100 ml of water. The organic phase was dried with $MgSO_4$ and the solvent was removed under vacuum. Purification was done by recrystallisation from n-butanol to yield 25.5 g (93.0 mmol, 92%) of a white solid. Melting point 149°C; CHN analysis: $C_{19}H_{14}O_2$ (M = 274.31 g mol^{-1}) calculated C 83.19%, H 5.14%, found C 83.05%, H 5.27%. High-resolution mass spectrometry (HRMS; under ESI conditions): found (M^+), 274.1014. $C_{19}H_{14}O_2$ requires M, 274.0994. ν_{max}(solid)/cm^{-1} 3061vw, 1729s, 1597w, 1519w, 1484m, 1450w, 1262m, 1218m, 1191m,

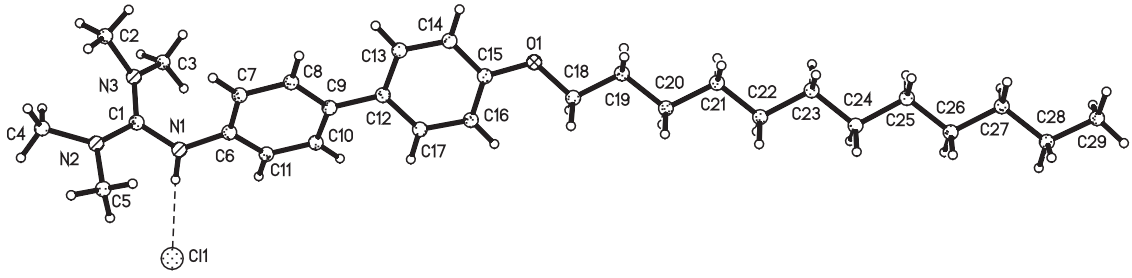


Figure 15. X-Ray structure of **7f**.

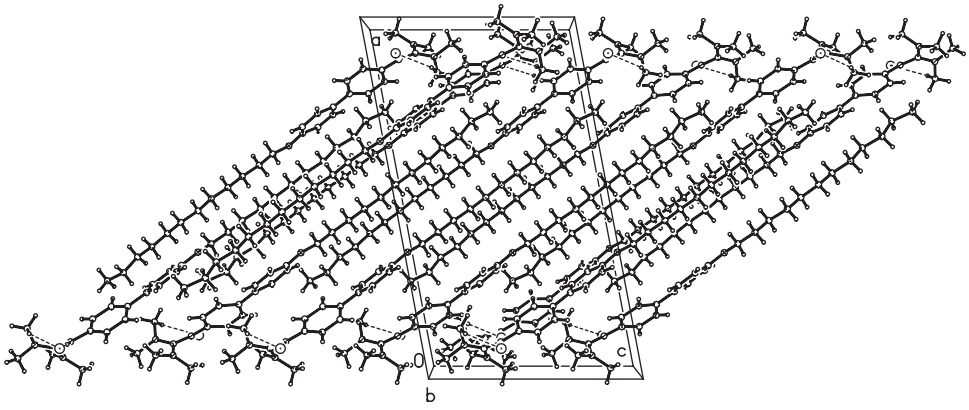


Figure 16. Unit cell of **7f**.

1170m, 1083m, 1063m, 1021w, 1005w, 875m, 820w, 757s; δ_H (500 MHz; $CDCl_3$; Me_4Si) 7.27–7.33 (m, 2H, 7-H), 7.33–7.39 (m, 1H, 13-H), 7.41–7.49 (m, 2H), 7.50–7.57 (m, 2H), 7.57–7.62 (m, 2H), 7.62–7.69 (m, 3H), 8.20–8.28 (m, 2H, 3-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 122.0 (C-7), 127.2 (C-11), 127.4 (C-13), 128.4 (C-12), 128.6 (C-3), 128.8 (C-8), 129.5 (C-4), 130.2 (C-2), 133.7 (C-1), 139.1 (C-9), 140.4 (C-10), 150.4 (C-6), 163.3 (C-5); *m/z* (ESI) 274 (M^+).

3.2 4′-nitrobiphenyl-4-yl benzoate (3b)

A solution of biphenyl-4-yl benzoate **2** (5.25 g, 19.2 mmol) in glacial acetic acid (50 ml) was heated to 85°C. Fuming nitric acid (13 ml) was then added slowly to the reaction flask keeping the temperature between 85 and 90°C. The solution was left to stir for 1.5 h then allowed to cool to room temperature. The obtained yellow solid was filtered and collected, washed in turn with distilled water (5 ml) and methanol (5 ml). The crude product was recrystallised from glacial acetic acid and dried under vacuum. The 4′-nitrobiphenyl-4-yl benzoate **3b** was obtained as a yellow solid (3.24 g, 10.2 mmol) in 53% yield. CHN analysis: $C_{19}H_{13}NO_4$ (M = 319.08 g mol^{-1}) calculated C 71.47%, H 4.10%, N 4.39%, found C 71.34%, H 4.25%, N 4.37%. ν_{max}(solid)/cm^{-1} 3075w, 2360w, 1733vs, 1598m, 1513vs, 1486m, 1343s, 1268m, 1253m, 1220m, 1165m, 1114w, 1081w, 1061s, 943w, 858s, 809m, 754m, 712vs; δ_H (500 MHz; $CDCl_3$; Me_4Si) 7.34–7.39 (m, 2H, 7-H), 7.51–7.57 (m, 2H, 2-H), 7.64–7.71 (m, 3H, 1-H, 11-H), 7.72–7.77 (m, 2H, 8-H), 8.21–8.25 (m, 2H, 3-H), 8.29–8.34 (m, 2H, 12-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 122.7 (C-7), 124.2 (C-12), 127.8 (C-8), 128.6 (C-11), 128.7 (C-2), 129.2 (C-4), 130.3 (C-3), 133.9 (C-1), 136.5 (C-9), 146.8 (C-13), 147.2 (C-10), 151.7 (C-6), 165.1 (C-5); *m/z* (ESI) 319 (M^+).

3.3 4′-nitrobiphenyl-4-ol (4)

A mixture of 4′-nitrobiphenyl-4-yl-benzoate **3b** (1.50 g, 4.7 mmol) and K_2CO_3 (0.92 g, 16.4 mmol) in water (75 ml) and ethanol (150 ml) was heated to 100°C for 24 h. The solvent mixture was vaporised until half the amount was left. Water (50 ml) was added followed by concentrated hydrochloric acid (drop wise) until a pH of 1 was obtained (solution turned from red to bright yellow). The aqueous phase was extracted three times with CH_2Cl_2 (100 ml). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under vacuum. The crude product was purified by recrystallisation from ethanol to yield 0.92 g (4.30 mmol, 91%) of 4′-nitrobiphenyl-4-ol **4** as a yellow solid. CHN analysis: $C_{12}H_9NO_3$ (M = 215.20 g mol^{-1}) calculated C 66.97%, H 4.22%, N 6.51%, found C 66.79%, H 4.25%, N 6.45%. ν_{max}(solid)/cm^{-1} 3416br, 1732w, 1586s, 1503s, 1485m, 1403w, 1332s, 1267m, 1189m, 1104m, 856m, 828s; δ_H (500 MHz; $CDCl_3$; Me_4Si) 4.98 (s, 1H, O*H*), 6.93–6.98 (m, 2H, 2-H), 7.51–7.56 (m, 2H, 3-H), 7.66–7.70 (m, 2H, 6-H), 8.25–8.30 (m, 2H, 7-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 116.1 (C-2), 124.2 (C-7), 127.1 (C-3), 128.9 (C-6), 128.4 (C-4), 129.4 (C-3), 131.4 (C-5), 147.2 (C-8), 156.5 (C-1); *m/z* (ESI) 215 (M^+).

3.4 General procedure for the synthesis of 4-(alkyloxy)-4′-nitrobiphenyl and 4-(alkyloxy)-nitrophenyl (5/9)

To a mixture of 4′-nitrobiphenyl-4-ol **4** (1.00 g, 4.70 mmol), respectively 4-nitrophenyl **8** (0.65 g, 4.70 mmol), and potassium carbonate (1.29 g, 9.30 mmol) in acetone (100 ml), alkylbromine (14.0 mmol) was added. The reaction mixture was heated to temperature 80°C for 48 h. The reaction was then quenched with water (100 ml) and extracted three time with dichloromethane (100 ml). Combined organic layers were washed in turns with 2 M NaOH (30 ml) and brine (30 ml) and dried over $MgSO_4$. The solvent was removed under vacuum. The product was purified by column chromatography on silica (PE/EtOAc; 10:1).

*3.4.1 4-(Heptyloxy)-4′-nitrobiphenyl (*5a*)*

Compound **5a** was prepared from 1.00 g (4.70 mmol) of compound **4**. Yield 1.12 g (76%). CHN analysis: $C_{19}H_{23}NO_3$ (313.39 g mol^{-1}) calculated C 72.82%, H 7.40%, N 4.47%, found C 72.72%, H 7.38%, N 4.33%. HRMS (ESI): found (M^+ + H), 314.1742. $C_{19}H_{24}NO_3$ requires M, 314.1751. ν_{max}(solid)/cm^{-1} 2960m, 2934s, 2906m, 2851m, 1598m, 1571w, 1512s, 1485w, 1473m, 1340s, 1300m, 1274m, 1243s, 1180m, 1170m, 1107m, 1039w, 1011m, 864m, 831s; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.90 (t, J 7.0 Hz, 3H, CH_2CH_3), 1.30–1.40 (m, 6H, CH_2), 1.44–1.50 (m, 2H, CH_2), 1.79–1.84 (m, 2H, CH_2), 4.01 (t, J 6.6 Hz, 2H, OCH_2), 6.99–7.02 (m, 2H, 7-H), 7.55–7.58 (m, 2H, 3-H), 7.67–7.69 (m, 2H, 6-H), 8.24–8.27 (m, 2H, 2-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.6 (CH_2CH_3), 26.0 ($OCH_2CH_2CH_2$), 29.1, 29.2, 31.8 (CH_2), 68.2 (OCH_2), 115.1 (C-2), 124.1 (C-7), 127.0 (C-3), 128.5 (C-6), 130.8 (C-4), 146.5 (C-8), 147.3 (C-5), 160.1 (C-1); *m/z* (ESI) 314 (M^+ + H).

*3.4.2 4-(Octyloxy)-4′-nitrobiphenyl (*5b*)*

Compound **5b** was prepared from 1.00 g (4.70 mmol) of compound **4**. Yield 1.32 g (83%). CHN analysis: $C_{20}H_{25}NO_3$ (M = 327.42 g mol^{-1}) calculated C

73.37%, H 7.70%, N 4.28% found C 73.54%, H 7.73%, N 4.27%. HRMS (ESI): found (M^+ + H), 328.1900. $C_{20}H_{26}NO_3$ requires *M*, 328.1907. ν_{max}(solid)/cm^{-1} 2920m, 2853m, 1718w, 1596m, 1574w, 1507s, 1487w, 1469m, 1336w, 1272w, 1246m, 1184w, 1110w, 1042w, 1031w, 996w, 855m, 828s; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.89 (t, *J* 7.0 Hz, 3H, CH_2CH_3), 1.27–1.40 (m, 8H, CH_2); 1.45–1.51 (m, 2H, CH_2), 1.79–1.84 (m, 2H, CH_2), 4.00 (t, *J* 6.6 Hz, 2H, OCH_2), 6.99–7.02 (m, 2H, 7-H), 7.55–7.58 (m, 2H, 3-H), 7.68–7.70 (m, 2H, 6-H), 8.25–8.28 (m, 2H, 2-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.0 ($OCH_2CH_2CH_2$), 29.1, 29.4 (CH_2), 31.8 (CH_2), 68.2 (OCH_2), 115.1 (C-2), 124.2 (C-7), 127.0 (C-3), 128.5 (C-6), 130.8 (C-4), 146.5 (C-8), 147.3 (C-5), 160.1 (C-1); *m*/*z* (ESI) 328 (M^+ +H).

3.4.3 4-(Nonyloxy)-4′-nitrobiphenyl (**5c**)

Compound **5c** was prepared from 0.50 g (2.30 mmol) of compound **4**. Yield 0.71 g (89%). CHN analysis: $C_{21}H_{27}NO_3$ (*M* = 341.44 g mol^{-1}) calculated C 73.87%, H 7.97%, N 4.10%, found C 73.88%, H 8.02%, N 3.91%. HRMS (ESI): found (M^+ + Na) 364.1874. $C_{21}H_{27}NNaO_3$ requires *M*, 364.1883. ν_{max}(solid)/cm^{-1} 2921s, 2361m, 1594s, 1514s, 1339s, 1251m, 1193m, 1110m, 827w, 756m; δ_H(500 MHz; $CDCl_3$; Me_4Si) 0.89 (t, *J* 7.0 Hz, 3H, $-CH_2CH_3$), 1.24–1.53 (m, 12H, CH_2), 1.75–1.86 (m, 2H, CH_2), 4.01 (t, *J* 6.6 Hz, 2H, OCH_2), 6.97–7.03 (m, 2H, 7-H), 7.59–7.53 (m, 2H, 3-H), 7.66–7.71 (m, 2H, 6-H), 8.23–8.29 (m, 2H, 2-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.0 ($OCH_2CH_2CH_2$), 29.2, 29.3, 29.4, 29.5 (CH_2), 31.9 (CH_2), 68.2 (OCH_2), 115.1 (C-2), 124.2 (C-7), 127.0 (C-3), 128.5 (C-6), 130.8 (C-4), 146.5 (C-8), 147.3 (C-5), 160.1 (C-1); *m*/*z* (ESI) 364 (M^+ + Na).

3.4.4 4-(Decyloxy)-4′-nitrobiphenyl (**5d**)

Compound **5d** was prepared from 0.50 g (2.30 mmol) of compound **4**. Yield 0.45 g (55%). HRMS (ESI): found (M^+ + Na) 378.2037. $C_{22}H_{29}NNaO_3$ requires *M*, 378.2040. ν_{max}(solid)/cm^{-1} 2922s, 1594s, 1508vs, 1331s, 1248s, 830s, 475 m; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.89 (t, *J* 6.9 Hz, 3H, CH_2CH_3), 1.23–1.52 (m, 14H, CH_2), 1.76–1.90 (m, 2H, CH_2), 4.01 (t, *J* 6.6 Hz, 2H, OCH_2), 6.97–7.03 (m, 2H, 7-H), 7.54–7.59 (m, 2H, 3-H), 7.66–7.71 (m, 2H, 6-H), 8.23–8.29 (m, 2H, 2-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.0 ($OCH_2CH_2CH_2$), 29.2, 29.3, 29.4, 29.57, 29.6 (CH_2), 31.9 (CH_2), 68.2 (OCH_2), 115.1 (C-2), 124.1 (C-7), 127.0 (C-3), 128.5 (C-6), 130.8 (C-4), 146.5 (C-8), 147.3 (C-5), 160.1 (C-1); *m*/*z* (ESI) 378 (M^+ + Na).

3.4.5 4-(Undecyloxy)-4′-nitrobiphenyl (**5e**)

Compound **5e** was prepared from 1.50 g (7.00 mmol) of compound **4**. Yield 1.17 g (45%). HRMS (ESI): found (M^+ + Na) 392.2189. $C_{23}H_{31}NNaO_3$ requires *M*, 392.2202. ν_{max}(solid)/cm^{-1} 3361w, 3261w, 2924s, 2854s, 1719m, 1596m, 1519m, 1453m, 1344m, 1299m, 1271s, 1250s, 1172m, 1069m, 1027m, 975m, 931m, 827m; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, *J* 6.9 Hz, 3H, CH_2CH_3), 1.26–1.35 (m, 14H, CH_2), 1.37–1.50 (m, 2H, CH_2), 1.78–1.88 (m, 2H, CH_2), 4.01 (t, *J* 6.6 Hz, 2H, OCH_2), 6.99–7.02 (m, 2H, 7-H), 7.55–7.58 (m, 2H, 3-H), 7.68–7.70 (m, 2H, 6-H), 8.25–8.28 (m, 2H, 2-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.0 ($OCH_2CH_2CH_2$–), 29.2, 29.3, 29.4, 29.5, 29.6 (CH_2), 31.9 (CH_2), 68.2 (OCH_2), 115.2 (C-2), 124.1 (C-7), 127.0 (C-3), 128.5 (C-6), 130.8 (C-4), 146.5 (C-8), 147.3 (C-5), 160.1 (C-1); *m*/*z* (EI) 369 (M^+).

3.4.6 4-(Dodecyloxy)-4′-nitrobiphenyl (**5f**)

Compound **5f** was prepared from 0.92 g (4.30 mmol) of compound **4**. Yield 1.33 g (81%). CHN analysis: $C_{24}H_{33}NO_3$ (*M* = 383.52 g mol^{-1}) calculated C 75.16%, H 8.67%, N 3.65%, found C 75.04%, H 8.54%, N 3.69%. ν_{max}(solid)/cm^{-1} 2921s, 2850m, 1596m, 1509s, 1471m, 1339s, 1250m, 1181w, 1001w, 829s, 757w, 723w, 511w; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, *J* 6.9 Hz, 3H, CH_2CH_3), 1.24–1.51 (m, 18H, CH_2), 1.78–1.85 (m, 2H, CH_2), 3.99 (t, *J* 6.6 Hz, 2H, OCH_2), 6.99–7.02 (m, 2H, 7-H), 7.55–7.59 (m, 2H, 3-H), 7.67–7.70 (m, 2H, 6-H), 8.25–8.28 (m, 2H, 2-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.2 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.2, 29.4, 29.41, 29.6, 29.63, 29.67, 29.7 (CH_2), 32.0 (CH_2), 68.2 (OCH_2), 115.2 (C-2), 124.2 (C-7), 127.0 (C-3), 128.6 (C-6), 130.8 (C-4), 146.5 (C-8), 147.3 (C-5), 160.1 (C-1); *m*/*z* (EI) 383 (M^+).

3.4.7 4-(Hexadecyloxy)-4′-nitrobiphenyl (**5g**)

Compound **5g** was prepared from 1.00 g (4.70 mmol) of compound **4**. Yield 1.56 g (76%). CHN analysis: $C_{28}H_{41}NO_3$ (*M* = 439.63 g mol^{-1}) calculated C 76.50%, H 9.40%, N 3.19%, found C 76.41%, H 9.51%, N 3.08%. HRMS (EI): found (M^+) 439.3091. $C_{28}H_{41}NO_3$ requires *M*, 439.3089. ν_{max}(solid)/cm^{-1} 2917vs, 2849s, 2360w, 1596m, 1509s, 1471m, 1344s, 1252m, 1194w, 857w, 829m; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, *J* 6.6 Hz, 3H, CH_2CH_3), 1.22–1.43 (m, 26H, CH_2), 1.79–1.86 (m, 2H, CH_2), 4.01 (t, *J* 6.6 Hz, 2H, OCH_2), 6.98–7.03 (m, 2H, 2-H), 7.54–7.60 (m, 2H, 6-H), 7.70–7.72 (m, 2H, 3-H), 8.24–8.29 (m, 2H, 7-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3),

22.7 (CH_2CH_3), 26.0 ($OCH_2CH_2CH_2$), 29.2, 29.4, 29.6, 29.7 (CH_2), 31.9 (CH_2), 68.2 (OCH_2), 115.1 (C-2), 124.2 (C-7), 127.0 (C-3), 128.5 (C-6), 130.8 (C-4), 146.5 (C-8), 147.3 (C-5), 160.1 (C-1); *m/z* (EI) 439 (M^+).

*3.4.8 4-(Octyloxy)-nitrophenyl (***9a***)*

Compound **9a** was prepared from 1.00 g (7.19 mmol) of 4-nitrophenol. Yield 1.69 g (93%). HRMS (ESI): found (M^+ + H) 252.1597. $C_{14}H_{22}NO_3$ requires *M*, 252.1594. ν_{max}(solid)/cm^{-1} 2924s, 2855m, 1967w, 1592s, 1510s, 1497s, 1467m, 1331vs, 1297m, 1258vs, 1172s, 1110s, 1016m 843s, 752s, 654s; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.89 (t, *J* 7.0 Hz, 3H, CH_2CH_3), 1.23–1.40 (m, 8H, CH_2), 1.42–1.51 (m, 2H, CH_2), 1.77–1.86 (m, 2H, CH_2), 4.05 (t, *J* 6.6 Hz, 2H, OCH_2), 6.91–6.96 (m, 2H, 2-H), 8.16–8.21 (m, 2H, 3-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 25.9 ($OCH_2CH_2CH_2$), 29.0, 29.2, 29.3 (CH_2), 31.8 (CH_2), 68.9 (OCH_2), 114.4 (C-2), 125.9 (C-3), 141.3 (C-4), 164.3 (C-1); *m/z* (ESI) 252 (M^+ + H).

*3.4.9 4-(Decyloxy)-nitrophenyl (***9b***)*

Compound **9b** was prepared from 1.00 g (7.19 mmol) of 4-nitrophenol. Yield 1.95 g (96%). HRMS (ESI): found (M^+ + H) 280.1914. $C_{16}H_{26}NO_3$ requires *M*, 280.1907. ν_{max}(solid)/cm^{-1} 2916s, 2848s, 1971w, 1589s, 1496vs, 1465m, 1332vs, 1258vs, 1172m, 1112s, 1068m, 845s, 752s, 656s; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.89 (t, *J* 6.9 Hz, 3H, CH_2CH_3), 1.22–1.38 (m, 12H, CH_2), 1.41–1.50 (m, 2H, CH_2), 1.77–1.83 (m, 2H, CH_2), 4.04 (t, *J* 6.6 Hz, 2H, OCH_2), 6.90–6.96 (m, 2H, 2-H), 8.15–8.22 (m, 2H, 3-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 25.9 ($OCH_2CH_2CH_2$), 29.0, 29.3, 29.5 (CH_2), 31.9 (CH_2), 68.9 (OCH_2), 114.4 (C-2), 125.9 (C-3), 141.3 (C-4), 164.3 (C-1); *m/z* (ESI) 280 (M^+ + H).

*3.4.10 4-(Undecyloxy)-nitrophenyl (***9c***)*

Compound **9c** was prepared from 2.00 g (14.38 mmol) of 4-nitrophenol. Yield 3.50 g (83%). HRMS (ESI): found (M^+ + H) 294.2072. $C_{17}H_{28}NO_3$ requires *M*, 294.2064. ν_{max}(solid)/cm^{-1} 2917s, 2849s, 1974w, 1590s, 1508s, 1465m, 1332s, 1258vs, 1114m, 1023m, 843vs, 752s, 688m, 657m; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, *J* 6.9 Hz, 3H, CH_2CH_3), 1.22–1.38 (m, 14H, CH_2), 1.42–1.50 (m, 2H, CH_2), 1.78–1.86 (m, 2H, CH_2), 4.04 (t, *J* 6.6 Hz, 2H, OCH_2), 6.91–6.96 (m, 2H, 2-H), 8.17–8.22 (m, 2H, 3-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 25.9 ($OCH_2CH_2CH_2$), 29.0, 29.3, 29.33, 29.5, 29.58, 29.6 (CH_2), 31.9 (CH_2), 68.9 (OCH_2), 114.4 (C-2), 125.9 (C-3), 141.3 (C-4), 164.3 (C-1); *m/z* (EI) 293 (M^+).

*3.4.11 4-(Dodecyloxy)-nitrophenyl (***9d***)*

Compound **9d** was prepared from 1.00 g (7.19 mmol) of 4-nitrophenol. Yield 0.71 g (80%). HRMS (ESI): found (M^+ + H) 308.2224 $C_{18}H_{30}NO_3$ requires *M*, 308.2220. ν_{max}(solid)/cm^{-1} 2919s, 2849s, 1909w, 1590m, 1503vs, 1469m, 1335s, 1268s, 1173m, 1113m, 998m, 842s, 753s, 688m 655m; δ_H(500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, *J* 6.9 Hz, 3H, CH_2CH_3), 1.23–1.51 (br, 18H, CH_2), 1.77–1.87 (m, 2H, CH_2), 4.04 (t, *J* 6.5 Hz, 2H, OCH_2), 6.91–6.97 (m, 2H, 2-H), 8.16–8.22 (m, 2H, 3-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.4, 29.5, 29.6, 29.62, 29.65, 29.7, 30.9 (CH_2), 31.9 (CH_2), 68.6 (OCH_2), 115.7 (C-2), 125.4 (C-2), 141.6 (C-4), 159.3 (C-1); *m/z* (EI) 307 (M^+).

*3.4.12 4-(Hexadecyloxy)-nitrophenyl (***9e***)*

Compound **9e** was prepared from 1.00 g (7.19 mmol) of 4-nitrophenol. Yield 2.45 g (93%). HRMS (EI): found (M^+) 363.2768. $C_{22}H_{37}NO_3$ requires *M*, 363.2773. ν_{max}(solid)/cm^{-1} 2916vs, 2847s, 1972w, 1590s, 1500vs, 1467m, 1338s, 1259vs, 1173m, 1113s, 1019m, 845s, 753s, 656s; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, *J* 6.9 Hz, 3H, CH_2CH_3), 1.22–1.38 (m, 24H, CH_2), 1.42–1.49 (m, 2H, CH_2), 1.78–1.85 (m, 2H, CH_2), 4.04 (t, *J* 6.5 Hz, 2H, OCH_2), 6.91–6.96 (m, 2H, 2-H), 8.17–8.21 (m, 2H, 3-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 25.9 ($OCH_2CH_2CH_2$), 29.0, 29.3, 29.4, 29.5, 29.6, 29.67, 29.7 (CH_2), 31.9 (CH_2), 68.9 (OCH_2), 114.4 (C-2), 125.9 (C-3), 141.3 (C-4), 164.3 (C-1); *m/z* (EI) 363 (M^+).

*3.5 General procedure for the synthesis of 4-(alkyloxy)-4′-aminobiphenyl and 4-(alkyloxy)-aminophenyl (***6/10***)*

Palladium on activated charcoal (10%), (100 mg) was placed in a reaction flask, followed by a solution of 4-(alkyloxy)-4′-nitrobiphenyl **5** (3.20 mmol), respectively 4-(alkyloxy)-aminophenyl **9**, in dichloromethane (25 ml). The mixture was left to stir at room temperature for 3 h under hydrogen atmosphere. The suspension was then filtered through Celite®, and solvent was evaporated from the filtrate. The residue was dissolved in dichloromethane (30 ml) and washed three times with water (30 ml). The organic phase was dried over magnesium sulphate and the solvent was removed under vacuum. The product was purified by column chromatography on silica (PE/EtOAc; 5:2).

*3.5.1 4-(Heptyloxy)-4′-aminobiphenyl (**6a**)*

Compound **6a** was prepared from 1.00 g (3.20 mmol) of compound **5a**. Yield 0.70 g (78%). CHN analysis: $C_{19}H_{25}NO$ (M = 283.41 g mol^{-1}) calculated C 80.52%, H 8.89%, N 4.49%, found C 80.57%, H 8.99%, N 4.82%. HRMS (ESI): found (M^+ + H), 284.1936. $C_{19}H_{26}NO$ requires *M*, 284.2009. ν_{max}(solid)/cm^{-1} 3418w, 3382w, 3278wb, 3026w, 2953m, 2933s, 2922s, 2857m, 1603m, 1496s, 1462s, 1393m, 1243s, 1177m, 1039w, 1011w, 987w, 824s, 811m; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.89 (t, *J* 6.9 Hz, 3H, CH_2CH_3), 1.28–1.39 (m, 6H, CH_2), 1.42–1.48 (m, 2H, CH_2), 1.76–1.81 (m, 2H, CH_2), 3.66 (s, 2H, NH_2), 3.96 (t, *J* 6.6 Hz, 2H, OCH_2), 6.70–6.73 (m, 2H, 7-H); 6.90–6.93 (m, 2H, 2-H), 7.34–7.36 (m, 2H, 6-H, 5), 7.41–7.45 (m, 2H, 3-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.0 (CH_2CH_3), 22.6 (CH_2CH_3), 26.0 ($OCH_2CH_2CH_2$), 29.1, 29.3 (CH_2), 31.8 (CH_2), 68.1 (OCH_2), 114.7 (C-2), 115.4 (C-7), 127.3 (C-3), 127.6 (C-6), 131.4 (C-4), 133.6 (C-5), 145.2 (C-8), 158.0 (C-1); *m*/*z* (ESI) 284 (M^+ + H).

*3.5.2 4-(Octyloxy)-4′-aminobiphenyl (**6b**)*

Compound **6b** was prepared from 1.28 g (3.90 mmol) of compound **5b**. Yield 0.44 g (38%). CHN analysis: $C_{20}H_{27}NO$ (*M* = 297.43 g mol^{-1}) calculated C 80.76%, H 9.15%, N 4.17%, found C 80.64%, H 9.19%, N 4.56%. HRMS (ESI): found (M^+ + H), 298.2093. $C_{20}H_{28}NO$ requires *M*, 298.2165. ν_{max}(solid)/cm^{-1} 3419w, 3383w, 2955w, 2934w, 2921m, 2871w, 2854m, 1605m, 1497s, 1472m, 1463m, 1393w, 1290w, 1247s, 1177m, 1136w, 1116w, 1043w, 1033m, 996m, 856w, 823s, 815s; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.89 (t, *J* 6.9 Hz, 3H, CH_2CH_3), 1.26–1.37 (m, 8H, CH_2), 1.43–1.49 (m, 2H, CH_2), 1.76–1.82 (m, 2H, CH_2), 3.68 (s, 2H, NH_2), 3.98 (t, *J* 6.6 Hz, 2H, OCH_2), 6.72–6.75 (m, 2H, 7-H), 6.91–6.94 (m, 2H, 2-H), 7.34–7.37 (m, 2H, 6-H), 7.42-7.45 (m, 2H, 3-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.3, 29.3, 29.4 (CH_2), 31.8 (CH_2), 68.1 (OCH_2), 114.7 (C-2), 115.4 (C-7), 127.4 (C-3), 157.6 (C-6), 131.5 (C-4), 133.4 (C-5), 145.2 (C-8), 158.0 (C-1); *m*/*z* (ESI) 298 (M^+ + H).

*3.5.3 4-(Nonyloxy)-4′-aminobiphenyl (**6c**)*

Compound **6c** was prepared from 0.50 g (1.50 mmol) of compound **5c**. Yield 0.25 g (55%). HRMS (APCI): found (M^+ + H), 312.2321. $C_{21}H_{30}NO$ requires *M*, 312.2322. ν_{max}(solid)/cm^{-1} 3419w, 3382w, 3282m, 3173m, 3028w, 2921s, 2851s, 2050w, 1905w, 1606s, 1499s, 1462s, 1394m, 1249s, 1178m, 1013m, 811s, 719m, 566m; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, *J* 6.9 Hz, 3H, CH_2CH_3), 1.19–1.52 (m, 12H, CH_2), 1.72–1.84 (m, 2H, CH_2), 3.68 (s, 2H, $-NH_2$), 3.97 (t, *J* 6.6 Hz, 2H, OCH_2), 6.71–6.76 (m, 2H, 7-H), 6.90–6.95 (m, 2H, 2-H), 7.33–7.38 (m, 2H, 6-H), 7.41–7.46 (m, 2H, 3-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.3, 29.33, 29.4, 29.7 (CH_2), 31.9 (CH_2), 68.1 (OCH_2), 114.7 (C-2), 115.4 (C-7), 127.4 (C-3), 127.6 (C-6), 131.5 (C-4), 133.6 (C-5), 145.2 (C-8), 158.0 (C-1); *m*/*z* (APCI) 312 (M^+ + H).

*3.5.4 4-(Decyloxy)-4′-aminobiphenyl (**6d**)*

Compound **6d** was prepared from 0.40 g (1.10 mmol) of compound **5d**. Yield 0.20 g (55%). HRMS (APCI): found (M^+ + H), 326.2459. $C_{22}H_{32}NO$ requires *M*, 326.2478. ν_{max}(solid)/cm^{-1} 3419w, 3382w, 3283m, 3173m, 2920s, 2852s, 1971w, 1606s, 1498s, 1380m, 1248s, 1178m, 1015m, 824s, 717m, 566m; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, *J* 6.6 Hz, 3H, CH_2CH_3), 1.23–1.50 (m, 14H, CH_2), 1.73–1.85 (m, 2H, CH_2), 3.68 (s, 2H, NH_2), 3.98 (t, *J* 6.6 Hz, 2H, OCH_2), 6.71–6.76 (m, 2H, 7-H), 6.90–6.95 (m, 2H, 2-H), 7.33–7.38 (m, 2H, 6-H), 7.41–7.46 (m, 2H, 3-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.3, 29.4, 29.57, 29.6 (CH_2), 31.9 (CH_2), 68.1 (OCH_2), 114.7 (C-2), 115.4 (C-7), 127.4 (C-3), 127.6 (C-6), 131.5 (C-4), 133.6 (C-5), 145.2 (C-8), 158.0 (C-1); *m*/*z* (ESI) 326 (M^+ + H).

*3.5.5 4-(Undecyloxy)-4′-aminobiphenyl (**6e**)*

Compound **6e** was prepared from 4.00 g (10.8 mmol) of compound **5e**. Yield 1.17 g (32%). CHN analysis: $C_{23}H_{33}NO$ (*M* = 339.51 g mol^{-1}) calculated C 81.37%, H 9.80%, N 4.13%, found C 81.47%, H 9.75%, N 4.08%. HRMS (ESI): found (M^+ + H), 340.2601. $C_{23}H_{34}NO$ requires *M*, 340.2635. ν_{max}(solid)/cm^{-1} 3419w, 3382w, 3286w, 3026w, 2952m, 2934m, 2917s, 2849s, 1904w, 1638m, 1605s, 1567m, 1498s, 1473s, 1461s, 1393m, 1247s, 1178m, 1137w, 1031m, 986m, 824s, 811s; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.89 (t, *J* 6.9 Hz, 3H, CH_2CH_3), 1.30–1.37 (m, 14H, CH_2), 1.43–1.49 (m, 2H, CH_2), 1.76–1.82 (m, 2H, CH_2), 3.68 (s, 2H, NH_2), 3.98 (t, *J* 6.6 Hz, 2H, OCH_2), 6.72–6.75 (m, 2H, 7-H), 6.91–6.94 (m, 2H, 2-H), 7.34–7.37 (m, 2H, 6-H), 7.42–7.45 (m, 2H, 3-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.3, 29.4, 29.6 (CH_2), 31.9 (CH_2), 68.1 (OCH_2), 114.7 (C-2), 115.4 (C-7), 127.4 (C-3), 127.6 (C-6), 131.5 (C-4), 133.7 (C-5), 145.2 (C-8), 158.0 (C-1); *m*/*z* (ESI) 340 (M^+ + H).

*3.5.6 4-(Dodecyloxy)-4′-aminobiphenyl (***6f***)*

Compound **6f** was prepared from 1.00 g (2.60 mmol) of compound **5f**. Yield 0.76 g (62%). CHN analysis: $C_{24}H_{35}NO$ (M = 353.54 g mol^{-1}) calculated C 81.53%, H 9.98%, N 3.96%, found C 81.28%, H 9.92%, N 3.88%. HRMS (ESI): found (M^+ +H), 354.2775. $C_{24}H_{36}NO$ requires M, 354.2791. ν_{max}(solid)/cm^{-1} 3420w, 3381w, 3283m, 3179m, 2919s, 2851s, 2052w, 1905w, 1605s, 1498s, 1380m, 1248s, 1178m, 1032m, 813s, 716m, 566m; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, J 6.8 Hz, 3H, CH_2CH_3), 1.23–1.50 (m, 18H, CH_2), 1.73–1.85 (m, 2H, CH_2), 3.68 (s, 2H, NH_2), 3.98 (t, J 6.6 Hz, 2H, OCH_2), 6.71–6.77 (m, 2H, 7-H), 6.90–6.95 (m, 2H, 2-H), 7.33–7.38 (m, 2H, 6-H), 7.41–7.47 (m, 2H, 3-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.3, 29.36, 29.4, 29.6, 29.61, 29.65, 29.7 (CH_2), 31.9 (CH_2), 68.1 (OCH_2), 114.7 (C-2), 115.4 (C-7), 127.4 (C-3), 127.6 (C-6), 131.5 (C-4), 133.6 (C-5), 145.2 (C-8), 158.0 (C-1); m/z (ESI) 354 (M^+ + H).

*3.5.7 4-(Hexadecyloxy)-4′-aminobiphenyl (***6g***)*

Compound **6g** was prepared from 1.00 g (2.30 mmol) of compound **5g**. Yield 0.46 g (49%). CHN analysis: $C_{28}H_{43}NO$ (M = 409.65 g mol^{-1}) calculated C 82.09%, H 10.58%, N 3.42%, found C 81.55%, H 10.46%, N 3.50%. HRMS (ESI): found (M^+ + H), 410.3395. $C_{28}H_{44}NO$ requires M, 410.3417. ν_{max}(solid)/cm^{-1} 3421w, 3381w, 3286m, 3179m, 2917s, 2849s, 2050w, 1904w, 1605m, 1499s, 1474s, 1380m, 1248s, 1019m, 812s, 716m, 566m; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, J 6.6 Hz, 3H, CH_2CH_3), 1.22–1.51 (m, 26H, CH_2), 1.73–1.84 (m, 2H, CH_2), 3.04 (s, 2H, NH_2), 3.99 (t, J 6.6 Hz, 2H, OCH_2), 6.71–6.76 (m, 2H, 7-H), 6.90–6.96 (m, 2H, 2-H), 7.33–7.39 (m, 2H, 6-H), 7.41–7.47 (m, 2H, 3-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.3, 29.4, 29.43, 29.6, 29.62, 29.67, 29.70 (CH_2), 31.9 (CH_2), 68.1 (OCH_2), 114.7 (C-2), 115.4 (C-7), 127.4 (C-3), 127.6 (C-6), 131.5 (C-4), 133.6 (C-5), 145.2 (C-8), 158.0 (C-1); m/z (ESI) 410 (M^+ + H).

*3.5.8 4-(Octyloxy)-aminophenyl (***10a***)*

Compound **10a** was prepared from 1.59 g (6.33 mmol) of compound **9a**. Yield 1.19 g (85%). HRMS (ESI): found (M^+ - H) 222.1853. $C_{14}H_{24}NO$ requires M, 222.1851. ν_{max}(solid)/cm^{-1} 3402m, 3320w, 3221w, 2920s, 2847s, 1974w, 1633w, 1508vs, 1473m, 1227vs, 1177w, 1069m, 1020m, 967m, 822s, 691s; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, J 6.9 Hz, 3H,–CH_2CH_3), 1.22–1.36 (m, 8H, CH_2), 1.34–1.46 (m, 2H, CH_2), 1.69–1.77 (m, 2H, CH_2), 3.35 (s, 2H, NH_2), 3.87 (t, J 6.6 Hz, 2H, OCH_2), 6.61–6.66 (m, 2H, 3-H), 6.71–6.76 (m, 2H, 2-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.3, 29.4, 29.44 (CH_2), 31.8 (CH_2), 68.7 (OCH_2), 115.6 (C-2), 116.5 (C-3), 139.6 (C-4), 152.4 (C-1); m/z (ESI) 222 (M^+ - H).

*3.5.9 4-(Decyloxy)-aminophenyl (***10b***)*

Compound **10b** was prepared from 1.85 g (6.61 mmol) of compound **9b**. Yield 0.91 g (55%). HRMS (ESI): found (M^+ + H) 250.2158. $C_{16}H_{28}NO$ requires M, 250.2165. ν_{max}(solid)/cm^{-1} 3410w, 3330m, 2918vs, 2849vs, 1979w, 1605w, 1508s, 1473m, 1395w, 1243s, 1178m, 1030m, 818s, 717w; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, J 6.9 Hz, 3H, CH_2CH_3), 1.19–1.37 (m, 12H, CH_2), 1.37–1.47 (m, 2H, CH_2), 1.68–1.78 (m, 2H, CH_2), 3.37 (s, 2H, NH_2), 3.87 (t, J 6.6 Hz, 2H, OCH_2), 6.62–6.67 (m, 2H, 3-H), 6.71–6.76 (m, 2H, 2-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.3, 29.4, 29.57, 29.6 (CH_2), 31.9 (CH_2), 68.7 (OCH_2), 115.6 (C-2), 116.5 (C-3), 139.5 (C-4), 152.5 (C-1); m/z (ESI) 250 (M^+ + H).

*3.5.10 4-(Undecyloxy)-aminophenyl (***10c***)*

Compound **10c** was prepared from 3.50 g (11.9 mmol) of compound **9c**. Yield 2.51 g (80%). HRMS (ESI): found (M^+ + H) 264.2325 $C_{17}H_{30}NO$ requires M, 264.2322. ν_{max}(solid)/cm^{-1} 3384m, 3309m, 2916vs, 2848s, 1973w, 1603w, 1513s, 1463s, 1394w, 1296w, 1241s, 1094w, 1029m, 886m, 827s, 759m, 727m, 641w; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, J 6.9 Hz, 3H, CH_2CH_3), 1.20–1.36 (m, 14H, CH_2), 1.39–1.46 (m, 2H, CH_2), 1.69–1.77 (m, 2H, CH_2), 3.29 (s, 2H, NH_2), 3.87 (t, J 6.6 Hz, 2H, OCH_2), 6.60–6.67 (m, 2H, 3-H), 6.70–6.76 (m, 2H, 2-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.2 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.4, 29.5, 29.6, 29.64 (CH_2), 31.9 (CH_2), 68.7 (OCH_2), 115.7 (C-2), 116.5 (C-3), 139.7 (C-4), 152.4 (C-1); m/z (ESI) 264 (M^+ + H).

*3.5.11 4-(Dodecyloxy)-aminophenyl (***10d***)*

Compound **10d** was prepared from 0.50 g (1.60 mmol) of compound **9d**. Yield 0.43 g (94%). HRMS (ESI): found (M^+ + H) 278.2469. $C_{18}H_{32}NO$ requires M, 278.2478. ν_{max}(solid)/cm^{-1} 3366w, 3309m, 2916vs, 2849s, 1967w, 1603w, 1515s, 1462m, 1383w, 1299w, 1242s, 1097w, 1027m, 878m, 828s, 763m, 642w; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, J 6.9 Hz, 3H, CH_2CH_3), 1.22–1.47 (m, 18H, CH_2), 1.67–1.79 (m, 2H, CH_2), 3.40 (s, 2H, NH_2), 3.87 (t, J 6.6 Hz, 2H, OCH_2), 6.60–6.67 (m, 2H, 3-H), 6.71–6.77 (m, 2H, 2-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.4, 29.5, 29.6, 29.62, 29.65, 29.7

(CH_2), 31.9 (CH_2), 68.7 (OCH_2), 115.7 (C-2), 116.4 (C-3), 139.8 (C-4), 152.5 (C-1); *m/z* (EI) 277 (M^+).

*3.5.12 4-(Hexadecyloxy)-4′-aminophenyl (***10e***)*

Compound **10e** was prepared from 2.34 g (6.45 mmol) of compound **9e**. Yield 1.143 g (53%). HRMS (ESI): found (M^+ + H) 334.3110. $C_{22}H_{40}NO$ requires *M*, 334.3104. ν_{max}(solid)/cm^{-1} 3389w, 3309m, 2916vs, 2848vs, 1976w, 1606w, 1515s, 1462m, 1382w, 1242s, 1126w, 1028m, 880m, 815m,718m; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, *J* 7.0 Hz, 3H, CH_2CH_3), 1.20–1.36 (m, 24H, CH_2), 1.39–1.46 (m, 2H, $OCH_2CH_2CH_2$), 1.70–1.77 (m, 2H, CH_2), 3.39 (s, 2H, NH_2), 3.87 (t, *J* 6.6 Hz, 2H, OCH_2), 6.60–6.66 (m, 2H, 3-H), 6.71–6.77 (m, 2H, 2-H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.4, 29.5, 29.6, 29.62, 29.67, 29.7 (CH_2), 31.9 (CH_2), 68.7 (OCH_2), 115.6 (C-2), 116.4 (C-3), 139.8 (C-4), 152.3 (C-1); *m/z* (ESI) 334 (M^+ + H).

*3.6 General procedure for the synthesis of 4-(alkyloxy)-4′-(N,N,N′,N′-tetramethylguanidinium)-biphenyl chlorides and 4-(alkyloxy)-4′-(N,N,N′,N′-tetramethyl-guanidinium)-phenyl chlorides (***7***/***11***)*

To a solution of chloroformamidinium chloride (10.0 mg, 55.0 μmol, 1.30 M solution in CH_3CN) in CH_2Cl_2 (5 ml) was added a solution of primary amine **6/10** (55.0 μmol) and Et_3N (8 μl, 55.0 μmol) in CH_2Cl_2 (5 ml). The mixture was stirred under reflux for 1.5 h followed by evaporation of solvent under vacuum. The residue was treated with NaOH (6 μl, 55.0 μmol, 10 M solution in water) and water (2 ml) and stirred for 5 min. The solvents were removed under vacuum. The remaining salt was washed with hot CH_3CN (10 ml) and filtered. The filtrate was evaporated until dryness and the resulting salt was purified by column chromatography on silica (CH_2Cl_2/MeOH 10:1) to give waxy solids.

*3.6.1 4-(Heptyloxy)-4′-(N,N,N′,N′-tetramethylguanidinium)-biphenyl chloride (***7a***)*

Compound **7a** was prepared from 1.04 g (3.69 mmol) of compound **6a**. Yield 1.02 g (72%). CHNCl analysis: $C_{24}H_{36}ClN_3O$ (*M* = 418.02 g mol^{-1}) calculated C 68.96%, H 8.68%, N 10.05%, Cl 8.48%, found C 68.80%, H 8.53%, N 10.15%, Cl 8.71%. HRMS (ESI): found (M^+), 382.2848. $C_{24}H_{36}N_3O$ requires *M*, 382.2853. ν_{max}(solid)/cm^{-1} 2940w, 2918w, 2848w, 1619m, 1574w, 1552m, 1498m, 1470m, 1427w, 1407m, 1243s, 1172m, 1152m, 1044m, 1011w, 831s; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.90 (t, *J* 6.9 Hz, 3H, CH_2CH_3), 1.30–1.40 (m, 6H, CH_2), 1.44–1.50 (m, 2H, CH_2), 1.77–1.83 (m, 2H, CH_2), 3.02 (br, 12H, N–CH_3), 3.99 (t, *J* 6.6 Hz, 2H, OCH_2), 6.94–6.97 (m, 2H, 2-H), 7.21–7.23 (m, 2H, 7-H), 7.45–7.48 (m, 2H, 3-H), 7.51–7.53 (m, 2H, 6-H), 12.05 (s, 1H, N–H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.6 (CH_2CH_3), 26.0 ($OCH_2CH_2CH_2$), 29.1, 29.2 (CH_2), 31.8 (CH_2), 40.8 (N–CH_3), 68.1 (OCH_2), 114.9 (C-2), 121.0 (C-7), 127.76 (C-3), 127.8 (C-6), 132.3 (C-4), 136.5 (C-5), 137.9 (C-8), 158.7 (C-9), 158.9 (C-1); *m/z* (ESI) 382 (M^+).

*3.6.2 4-(Octyloxy)-4′-(N,N,N′,N′-tetramethylguanidinium)-biphenyl chloride (***7b***)*

Compound **7b** was prepared from 0.81 g (2.73 mmol) of compound **6b**. Yield 0.79 g (73%). CHNCl analysis: $C_{25}H_{38}ClN_3O$ (*M* = 432.04 g mol^{-1}) calculated C 69.50%, H 8.87%, N 9.73%, Cl 8.21%, found C 69.65%, H 8.75%, N 9.76%, Cl 8.17%. HRMS (ESI): found (M^+), 396.3016. $C_{25}H_{38}N_3O$ requires *M*, 396.3009. ν_{max}(solid)/cm^{-1} 2920w, 2849w, 1616m, 1551s, 1498m, 1467m, 1407m, 1242s, 1173s, 1150m, 1116w, 1044s, 1033s, 999m, 915w, 822s; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.89 (t, *J* 6.9 Hz, 3H, CH_2CH_3), 1.29–1.38 (m, 8H, CH_2), 1.44–1.50 (m, 2H, CH_2), 1.77–1.83 (m, 2H, CH_2), 3.03 (br, 12H, N–CH_3), 3.99 (t, *J* 6.6 Hz, 2H, OCH_2), 6.93–6.96 (m, 2H, 2-H), 7.21–7.23 (m, 2H, 7-H), 7.45–7.47 (m, 2H, 3-H), 7.51–7.53 (m, 2H, 6-H), 11.95 (s, 1H, N–H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 29.25, 29.3, 29.4 (CH_2), 31.8 (CH_2), 40.7 (N-CH_3), 68.1 (OCH_2), 114.9 (C-2), 121.0 (C-7), 127.7 (C-3), 127.8 (C-6), 132.2 (C-4), 136.5 (C-5), 167.8 (C-8), 158.6 (C-9), 158.9 (C-1); *m/z* (ESI) 396 (M^+).

*3.6.3 4-(Nonyloxy)-4′-(N,N,N′,N′-tetramethylguanidinium)-biphenyl chloride (***7c***)*

Compound **7c** was prepared from 0.20 g (0.60 mmol) of compound **6c**. Yield 0.16 g (56%). CHNCl analysis: $C_{26}H_{40}ClN_3O$ (*M* = 446.07 g mol^{-1}) calculated C 70.01%, H 9.04%, N 9.42%, Cl 7.95%, found C 66.93%, H 8.91%, N 9.58%, Cl 8.00%. HRMS (ESI): found (M^+), 410.3155. $C_{26}H_{40}N_3O$ requires *M*, 410.3166. ν_{max}(solid)/cm^{-1} 2922m, 2853m, 2360w, 1626s, 1552s, 1498s, 1469m, 1407m, 1244s, 1175m, 1039w, 823m, 518w; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.89 (t, *J* 6.9 Hz, 3H, CH_2CH_3), 1.21–1.37 (m, 12H, CH_2), 1.75–1.90 (m, 2H, CH_2), 2.96–3.21 (br, 12H, N–CH_3), 3.99 (t, *J* 6.5 Hz, 2H, OCH_2), 6.91–6.99 (m, 2H, 2-H), 7.17–7.26 (m, 2H, 7-H), 7.43–7.56 (m, 4H, 3-H, 6-H), 11.99 (s, 1H, N–H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.3, 29.4, 29.5, 29.7 (CH_2), 31.9

(CH_2), 40.7 (N–CH_3), 68.2 (OCH_2), 114.9 (C-2), 121.0 (C-7), 127.8, 127.84 (C-6, C-3), 132.2 (C-4), 136.4 (C-5), 137.9 (C-8), 158.7, 158.9 (C-1, 9); *m/z* (ESI) 410 (M^+).

*3.6.4 4-(Decyloxy)-4′-(N,N,N′,N′-tetramethylguanidinium)-biphenyl chloride (***7d***)*

Compound **7d** was prepared from 0.15 g (0.50 mmol) of compound **6d**. Yield 0.16 g (75%). CHNCl analysis: $C_{27}H_{42}ClN_3O$ (M = 460.09 g mol^{-1}) calculated C 70.48%, H 9.20%, N 9.13%, Cl 7.71%, found C 69.77%, H 9.07%, N 9.09%, Cl 7.70%. HRMS (APCI): found (M^+), 424.3334. $C_{27}H_{42}N_3O$ requires M, 424.3322. ν_{max}(solid)/cm^{-1} 2922s, 2853m, 2361w, 1626s, 1552s, 1498s, 1468m, 1406m, 1244s, 1174m, 1039w, 909m, 822s, 729s; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, J 6.8 Hz, 3H, CH_2CH_3), 1.24–1.51 (m, 14H, CH_2), 1.74–1.85 (m, 2H, CH_2), 2.86–3.18 (br, 12H, N–CH_3), 3.98 (t, J 6.4 Hz, 2H, OCH_2), 6.91–6.98 (m, 2H, 2-H), 7.18–7.25 (m, 2H, 7-H), 7.43–7.55 (m, 4H, 3-H, 6-H), 12.07 (s, 1H, N–H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.3, 29.33, 29.4, 29.5, 29.6 (CH_2), 31.9 (CH_2), 40.7 (N–CH_3), 68.1 (OCH_2), 114.9 (C-2), 121.1 (C-7), 127.7, 127.8 (C-6, C-3), 132.2 (C-4), 136.5 (C-5), 137.9 (C-8), 158.7, 158.9 (C-1,C-9); *m/z* (APCI) 424 (M^+).

*3.6.5 4-(Undecyloxy)-4′-(N,N,N′,N′-tetramethylguanidinium)-biphenyl chloride (***7e***)*

Compound **7e** was prepared from 0.20 g (0.67 mmol) of compound **6e**. Yield 0.22 g (75%). CHNCl analysis: $C_{28}H_{44}ClN_3O$ (M = 474.12 g mol^{-1}) calculated C 70.93%, H 9.35%, N 8.68%, Cl 7.48%, found C 70.85%, H 9.25%, N 8.96%, Cl 7.53%. HRMS (ESI): found (M^+), 438.3485. $C_{28}H_{44}N_3O$ requires M, 438.3479. ν_{max}(solid)/cm^{-1} 2939w, 2916m, 2846m, 1618s, 1592m, 1575m, 1554s, 1497s, 1466s, 1427m, 1407m, 1323w, 1313w, 1243s, 1172s, 1152m, 1037m, 916m, 804s; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, J 6.8 Hz, 3H, CH_2CH_3), 1.27–1.36 (m, 14H, CH_2), 1.44–1.50 (m, 2H, CH_2), 1.77–1.83 (m, 2H, CH_2), 3.03 (br, 12H, N–CH_3), 3.99 (t, J 6.6 Hz, 2H, OCH_2), 6.94–6.97 (m, 2H, 2-H), 7.21–7.23 (m, 2H, 7-H), 7.45–7.48 (m, 2H, 3-H), 7.52–7.53 (m, 2H, 6-H); 12.16 (s, 1H, N–H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.3, 29.4, 29.6 (CH_2), 31.9 (CH_2), 40.7 (N-CH_3), 68.2 (OCH_2), 114.9 (C-2), 121.0 (C-7), 127.8 (C-3), 127.8 (C-6), 132.3 (C-4), 136.5 (C-5), 137.9 (C-8), 158.4 (C-9) 158.7 (C-1); *m/z* (ESI) 437 (M^+ – H).

*3.6.6 4-(Dodecyloxy)-4′-(N,N,N′,N′-tetramethylguanidinium)-biphenyl chloride (***7f***)*

Compound **7f** was prepared from 0.33 g (1.50 mmol) of compound **6f**. Yield 0.51 g (70%). CHNCl analysis: $C_{29}H_{46}ClN_3O$ (M = 488.15 g mol^{-1}) calculated C 71.35%, H 9.50%, N 8.61%, Cl 7.26%, found C 71.19%, H 9.35%, N 8.67%, Cl 7.31%. HRMS (ESI): found (M^+), 452.3640. $C_{29}H_{46}N_3O$ requires M, 452.3635. ν_{max}(solid)/cm^{-1} 2920s, 1627s, 1553s, 1499s, 1427m, 1407m, 1323w, 1245s, 1152m, 1037m, 916m, 824m; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, J 6.9 Hz, 3H, CH_2CH_3), 1.24–1.51 (m, 18H, CH_2), 1.74–1.85 (m, 2H, CH_2), 2.79–3.10 (br, 12H, N–CH_3), 3.99 (t, J 6.6 Hz, 2H, OCH_2), 6.91–6.98 (m, 2H, 2-H), 7.04–7.11 (m, 2H, 7-H), 7.44–7.52 (m, 4H, 3-H, 6-H), 11.99 (s, 1H, N–H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.3, 29.4, 29.42, 29.59, 29.6, 29.64, 29.7 (CH_2), 31.9 (CH_2), 40.7 (N-CH_3), 68.2 (OCH_2), 114.9 (C-2), 121.0 (C-7), 127.7, 127.8 (C-6, C-3), 132.2 (C-4), 136.5 (C-5), 137.9 (C-8), 158.7, 158.9 (C-9,C-1); *m/z* (ESI) 452 (M^+).

*3.6.7 4-(Hexadecyloxy)-4′-(N,N,N′,N′-tetramethylguanidinium)-biphenyl chloride (***7g***)*

Compound **7g** was prepared from 0.18 g (0.90 mmol) of compound **6g**. Yield 0.32 g (68%). CHNCl analysis: $C_{33}H_{54}ClN_3O$ (M = 544.25 g mol^{-1}) calculated C 72.82%, H 10.00%, N 7.72%, Cl 6.51%, found C 72.95%, H 10.04%, N 7.49%, Cl 6.25%. HRMS (ESI): found (M^+), 508.4240. $C_{33}H_{54}N_3O$ requires M, 508.4261. ν_{max}(solid)/cm^{-1} 2916s, 2849s, 2360m, 1633m, 1553m, 1499m, 1467w, 1246s, 1176w, 1034w, 828w, 727m, 488m; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, J 6.7 Hz, 3H, –CH_2CH_3), 1.18–1.53 (m, 26H, CH_2), 1.74–1.85 (m, 2H, CH_2), 2.75–3.38 (br, 12H, N–CH_3), 3.99 (t, J 6.6 Hz, 2H, OCH_2), 6.92–7.00 (m, 2H, 2-H), 7.18–7.25 (m, 2H, 7-H), 7.43–7.56 (m, 4H, 3-H, 6-H), 12.25 (s, 1H, N–H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.3, 29.4, 29.42, 29.6, 29.62, 29.67, 29.7 (CH_2), 31.9 (CH_2), 40.7 (N-CH_3), 68.1 (OCH_2), 114.9 (C-2), 121.0 (C-7), 127.76, 127.8 (C-6, C-3), 132.3 (C-4),136.5 (C-5), 137.8 (C-8), 158.7, 158.9 (C-9,C-1); *m/z* (ESI) 508 (M^+).

*3.6.8 4-(Octyloxy)-1-(N,N,N′,N′-tetramethylguanidinium)-phenyl chloride (***11a***)*

Compound **11a** was prepared from 1.19 g (5.38 mmol) of compound **10a**. Yield 1.42 g (74%). CHNCl analysis: $C_{19}H_{34}ClN_3O$ (M = 355.95 g mol^{-1}) calculated C 64.11%, H 9.63%, N 11.89%, Cl 9.96%, found C

63.52%, H 9.45%, N 11.71%, Cl 9.87%. HRMS (ESI): found (M^+), 320.2699. $C_{19}H_{34}N_3O$ requires *M*, 320.2696. ν_{max}(solid)/cm^{-1} 2961m, 2937m, 2919vs, 2815s, 2790m, 1970w, 1623m, 1560m, 1518s, 1417m, 1230s, 1166m, 1115m, 1032m, 909w, 837s, 715s; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.89 (t, *J* 7.0 Hz, 3H, –CH_2CH_3), 1.23–1.37 (m, 8H, CH_2), 1.38–1.48 (m, 2H, CH_2), 1.71–1.79 (m, 2H, CH_2), 2.96 (br, 12H, N–CH_3), 3.91 (t, *J* 6.6 Hz, 2H, OCH_2), 6.82–6.88 (m, 2H, 3-H), 7.04–7.10 (m, 2H, 2-H), 11.37 (s, 1H, N–H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.2, 29.4 (CH_2), 31.8 (CH_2), 40.6 (N-CH_3), 68.4 (OCH_2), 115.5 (C-2), 122.4 (C-3), 130.6 (C-4), 156.8 (C-1), 158.7 (C-5); *m/z* (ESI) 320 (M^+).

*3.6.9 4-(Decyloxy)-1-(N,N,N′,N′-tetramethylguanidinium)-phenyl chloride (***11b***)*

Compound **11b** was prepared from 0.91 g (3.35 mmol) of compound **10b**. Yield 0.90 g (70%). CHNCl analysis: $C_{21}H_{38}ClN_3O$ (*M* = 383.99 g mol^{-1}) calculated C 65.68%, H 9.97%, N 10.94%, Cl 9.23%, found C 65.51%, H 9.86%, N 10.92%, Cl 8.95%. HRMS (ESI): found (M^+), 348.3006. $C_{21}H_{38}N_3O$ requires *M*, 348.3009. ν_{max}(solid)/cm^{-1} 2958m, 2921vs, 2849s, 2795m, 1975w, 1622vs, 1560s, 1505s, 1400s, 1314m, 1232vs, 1171s, 1017m, 908w, 839s, 755s, 603w; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, *J* 7.0 Hz, 3H, CH_2CH_3), 1.21–1.37 (m, 12H, CH_2), 1.39–1.47 (m, 2H, CH_2), 1.71–1.80 (m, 2H, CH_2), 3.01 (br, 12H, N–CH_3), 3.91 (t, *J* 6.6 Hz, 2H, OCH_2), 6.83–6.88 (m, 2H, 3-H), 7.06–7.12 (m, 2H, 2-H), 11.77 (s, 1H, N–H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (–CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.2, 29.3, 29.4, 29.55, 29.6 (CH_2), 31.9 (CH_2), 40.6 (N–CH_3), 68.4 (OCH_2), 115.5 (C-2), 122.3 (C-3), 130.6 (C-4), 156.8 (C-1), 158.8 (C-5); *m/z* (ESI) 348 (M^+).

*3.6.10 4-(Undecyloxy)-1-(N,N,N′,N′-tetramethylguanidinium)-phenyl chloride (***11c***)*

Compound **11c** was prepared from 2.51 g (9.53 mmol) of compound **10c**. Yield 2.73 g (72%). CHNCl analysis: $C_{22}H_{40}ClN_3O$ (*M* = 398.03 g mol^{-1}) calculated C 66.39%, H 10.13%, N 10.56%, Cl 8.91%, found C 66.45%, H 9.99%, N 10.56%, Cl 9.06%. HRMS (APCI): found (M^+), 362.3172. $C_{22}H_{40}N_3O$ requires *M*, 362.3166. ν_{max}(solid)/cm^{-1} 2920s, 2849s, 2795m, 1976w, 1623vs, 1560s, 1505s, 1400s, 1314m, 1232vs, 1171m, 1024m, 908w, 839s, 754s, 604w; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, *J* 6.9 Hz, 3H, CH_2CH_3), 1.20–1.38 (m, 14H, CH_2), 1.39–1.48 (m, 2H, CH_2), 1.71–1.80 (m, 2H, CH_2), 3.01 (br, 12H, N–CH_3), 3.91 (t, *J* 6.6 Hz, 2H, OCH_2), 6.82–6.88 (m, 2H, 3-H), 7.06–7.12 (m, 2H, 2-H), 11.76 (s, 1H, N–H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (–CH_2CH_3), 26.0 ($OCH_2CH_2CH_2$), 29.2, 29.3, 29.4, 29.56, 29.6 (CH_2), 31.9 (CH_2), 40.6 (N–CH_3), 68.3 (OCH_2), 115.4 (C-2), 122.3 (C-3), 130.6 (C-4), 156.7 (C-1), 158.7 (C-5); *m/z* (APCI) 362 (M^+).

*3.6.11 4-(Dodecyloxy)-1-(N,N,N′,N′-tetramethylguanidinium)-phenyl chloride (***11d***)*

Compound **11d** was prepared from 0.12 g (0.70 mmol) of compound **10d**. Yield 0.21 g (70%). CHN analysis: $C_{23}H_{42}ClN_3O$ (*M* = 412.05 g mol^{-1}) calculated C 67.04%, H 10.27%, N 10.20%, found C 66.32%, H 10.21%, N 9.98%. HRMS (ESI): found (M^+), 376.3326. $C_{23}H_{42}N_3O$ requires *M*, 376.3322. ν_{max}(solid)/cm^{-1} 2919s, 2849s, 1967w, 1623vs, 1560s, 1505s, 1469m, 1417s, 1314m, 1232vs, 1171m, 1027m, 837s, 755m, 718m, 538m; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, *J* 7.0 Hz, 3H, CH_2CH_3), 1.23–1.38 (m, 16H, CH_2), 1.39–1.50 (m, 2H, CH_2), 1.70–1.82 (m, 2H, CH_2), 3.12 (br, 12H, N–CH_3), 3.92 (t, *J* 6.6 Hz, 2H, OCH_2), 6.83–6.90 (m, 2H, 3-H), 7.06–7.12 (m, 2H, 2-H), 11.98 (s, 1H, N–H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.0 ($OCH_2CH_2CH_2$), 29.2, 29.4, 29.41, 29.58, 29.6, 29.64, 29.7 (CH_2), 31.9 (CH_2), 40.5 (N–CH_3), 68.4 (OCH_2), 115.5 (C-2), 122.3 (C-3), 130.6 (C-4), 156.7 (C-1), 158.9 (C-5); *m/z* (ESI) 376 (M^+).

*3.6.12 4-(Hexadecyloxy)-1-(N,N,N′,N′-tetramethylguanidinium)-phenyl chloride (***11e***)*

Compound **11e** was prepared from 1.14 g (3.43 mmol) of compound **10e**. Yield 1.17 g (73%). CHNCl analysis: $C_{27}H_{50}ClN_3O$ (*M* = 468.16 g mol^{-1}) calculated C 69.27%, H 10.76%, N 8.98%, Cl 7.57%, found C 69.17%, H 10.59%, N 9.06%, Cl 7.87%. HRMS (ESI): found (M^+), 432.3946. $C_{27}H_{50}N_3O$ requires *M*, 432.3948. ν_{max}(solid)/cm^{-1} 2967m, 2941m, 2922s, 2850m 2796m, 1980w, 1624vs, 1561s, 1480m, 1401s, 1233s, 1018m 840s, 753m, 604w; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, *J* 7.0 Hz, 3H, CH_2CH_3), 1.21–1.38 (m, 24H, CH_2), 1.40–1.48 (m, 2H, CH_2), 1.72–1.80 (m, 2H, CH_2), 3.01 (br, 12H, N–CH_3), 3.91 (t, *J* 6.6 Hz, 2H, OCH_2), 6.83–6.89 (m, 2H, 3-H), 7.06–7.11 (m, 2H, 2-H), 11.62 (s, 1H, N–H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.0 ($OCH_2CH_2CH_2$), 29.3, 29.4, 29.43, 29.58, 29.6, 29.66, 29.7 (CH_2), 31.9 (CH_2), 40.6 (N–CH_3), 68.4 (OCH_2), 115.5 (C-2), 122.3 (C-3), 130.6 (C-4), 156.8 (C-1), 158.8 (C-5); *m/z* (ESI) 432 (M^+).

*3.7 General procedure for anion exchange from 4-(dodecyloxy)-1-(N,N,N′,N′-tetramethylguanidinium)-biphenyl chloride (**7f**)*

To a solution of the desired sodium/potassium salt (1.23 mmol) in acetonitrile (15 ml) the guanidinium chloride **7f** (0.20 g, 0.41 mmol) was added and the mixture was heated to reflux for 1 h. The precipitated sodium/potassium chloride was removed by hot filtration and washed with 30 ml hot acetonitrile. The solvent was evaporated under vacuum and the resulting solid was dissolved in 20 ml CH_2Cl_2. The remaining residue was filtered and washed with 20 ml CH_2Cl_2. Subsequently the solvent was removed under vacuum and the desired guanidinium salt was obtained without further purification.

*3.7.1 4-(Dodecyloxy)-1-(N,N,N′,N′-tetramethylguanidinium)-biphenyl bromide (**12a**)*

Compound **12a** was prepared from 0.20 g (0.41 mmol) of compound **7f**. Yield 0.18 g (84%). CHNBr analysis: $C_{29}H_{46}BrN_3O$ (M = 532.60 g mol^{-1}) calculated C 65.40%, H 8.71%, N 7.89%, Br 15.00%, found C 64.98%, H 8.58%, N 7.70%, Br 15.39%. HRMS (ESI): found (M^+), 452.3638. $C_{29}H_{46}N_3O$ requires M, 452.3635. ν_{max}(solid)/cm^{-1} 3002w, 2918s, 2850m, 1622vs, 1552s, 1498m, 1468m, 1407m, 1246s, 1176m, 1036m, 1000w, 911w, 820s, 719m, 514m; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, J 6.9 Hz, 3H, CH_2CH_3), 1.21–1.40 (m, 16H, CH_2), 1.41–1.50 (m, 2H, CH_2), 1.76–1.84 (m, 2H, CH_2), 3.05 (br, 12H, N–CH_3), 3.98 (t, J 6.6 Hz, 2H, OCH_2), 6.93–6.97 (m, 2H, 2-H), 7.22–7.26 (m, 2H, 7-H), 7.43–7.47 (m, 2H, 3-H), 7.50–7.54 (m, 2H, 6-H), 11.15 (s, 1H, N–H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.3, 29.35, 29.4, 29.6, 29.61, 29.65, 29.7 (CH_2), 31.9 (CH_2), 40.9 (N–CH_3), 68.1 (OCH_2), 114.9 (C-2), 121.1 (C-7), 127.8, 127.83 (C-6, C-3), 132.1 (C-4), 136.1 (C-5), 138.1 (C-8), 158.5, 158.9 (C-9, C-1); m/z (ESI) 452 (M^+); m/z (ESI) 78 (Br^-).

*3.7.2 4-(Dodecyloxy)-1-(N,N,N′,N′-tetramethylguanidinium)-biphenyl iodide (**12b**)*

Compound **12b** was prepared from 0.20 g (0.41 mmol) of compound **7f**. Yield 0.22 g (94%). CHNI analysis: $C_{29}H_{46}IN_3O$ (M = 579.60 g mol^{-1}) calculated C 60.09%, H 8.00%, N 7.25%, I 21.90%, found C 60.18%, H 7.92%, N 7.29%, I 22.10%. HRMS (ESI): found (M^+), 452.3640. $C_{29}H_{46}N_3O$ requires M, 452.3635. ν_{max}(solid)/cm^{-1} 3426br, 3034w, 2920s, 2851m, 1980w, 1622vs, 1561vs, 1498s, 1466m, 1406m, 1243s, 1174m, 1038m, 820s, 720w, 609w, 518m; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, J 6.9 Hz, 3H, CH_2CH_3), 1.23–1.40 (m, 16H, CH_2), 1.43–1.50 (m, 2H, CH_2), 1.76–1.84 (m, 2H, CH_2), 3.07 (br, 12H, N–CH_3), 3.99 (t, J 6.6 Hz, 2H, OCH_2), 6.93–6.97 (m, 2H, 2-H), 7.22–7.27 (m, 2H, 7-H), 7.43–7.47 (m, 2H, 3-H), 7.51–7.55 (m, 2H, 6-H), 10.37 (s, 1H, N–H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.3, 29.4, 29.42, 29.6, 29.62, 29.64, 29.7 (CH_2), 31.9 (CH_2), 41.2 (N-CH_3), 68.2 (OCH_2), 114.9 (C-2), 121.2 (C-7), 127.8 (C-6, C-3), 132.0 (C-4), 135.8 (C-5), 138.3 (C-8), 158.4, 159.0 (C-9, C-1); m/z (ESI) 452 (M^+); m/z (ESI) 126 (I^-).

*3.7.3 4-(Dodecyloxy)-1-(N,N,N′,N′-tetramethylguanidinium)-biphenyl tetrafluoroborate (**12c**)*

Compound **12c** was prepared from 0.20 g (0.41 mmol) of compound **7f**. Yield 0.22 g (97%). CHN analysis: $C_{29}H_{46}BF_4N_3O$ (M = 539.50 g mol^{-1}) calculated C 64.56%, H 8.59%, N 7.79%, found C 64.49%, H 8.51%, N 7.80%. HRMS (ESI): found (M^+), 452.3630. $C_{29}H_{46}N_3O$ requires M, 452.3635. ν_{max}(solid)/cm^{-1} 3316br, 2918s, 2850m, 1980w, 1636s, 1557s, 1499m, 1468m, 1408w, 1245s, 1170m, 1037s, 998vs, 917m, 820s, 722m, 604w, 516m; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, J 6.9 Hz, 3H, CH_2CH_3), 1.22–1.41 (m, 16H, CH_2), 1.43–1.51 (m, 2H, CH_2), 1.76–1.83 (m, 2H, CH_2), 3.00 (br, 12H, N–CH_3), 3.98 (t, J 6.6 Hz, 2H, OCH_2), 6.92–6.96 (m, 2H, 2-H), 7.03–7.08 (m, 2H, 7-H), 7.42–7.46 (m, 2H, 3-H), 7.50–7.54 (m, 2H, 6-H), 8.49 (s, 1H, N–H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.3, 29.4, 29.43, 29.6, 29.62, 29.65, 29.7 (CH_2), 31.9 (CH_2), 40.3 (N–CH_3), 68.1 (OCH_2), 114.9 (C-2), 120.8 (C-7), 127.8, 127.9 (C-6, C-3), 131.9 (C-4), 135.7 (C-5), 138.2 (C-8), 158.6, 159.0 (C-9, C-1); m/z (ESI) 452 (M^+); m/z (ESI) 87 (BF_4^-).

*3.7.4 4-(Dodecyloxy)-1-(N,N,N′,N′-tetramethylguanidinium)-biphenyl hexafluorophosphate (**12d**)*

Compound **12d** was prepared from 0.20 g (0.41 mmol) of compound **7f**. Yield 0.23 g (92%). CHNP analysis: $C_{29}H_{46}F_6N_3OP$ (M = 597.66 g mol^{-1}) calculated C 58.28%, H 7.76%, N 7.03%, P 5.18%, found C 58.28%, H 7.66%, N 6.92%, P 4.97%. HRMS (ESI): found (M^+), 452.3628. $C_{29}H_{46}N_3O$ requires M, 452.3635. ν_{max}(solid)/cm^{-1} 3368br, 2918s, 2849m, 1980w, 1634s, 1556s, 1502m, 1426m, 1394m, 1242s, 1166m, 1037m, 820vs, 724m, 556m; δ_H (500 MHz;

$CDCl_3$; Me_4Si) 0.88 (t, *J* 6.7 Hz, 3H, CH_2CH_3), 1.23–1.39 (m, 16H, CH_2), 1.40–1.53 (m, 2H, CH_2), 1.74–1.86 (m, 2H, CH_2), 2.97 (br, 12H, N–CH_3), 3.98 (t, *J* 6.6 Hz, 2H, OCH_2), 6.91–6.97 (m, 2H, 2-H), 7.00–7.06 (m, 2H, 7-H), 7.41–7.46 (m, 2H, 3-H), 7.50–7.55 (m, 2H, 6-H), 7.59 (s, 1H, N–H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.3, 29.4, 29.43, 29.6, 29.62, 29.65, 29.7 (CH_2), 31.9 (CH_2), 40.3 (N–CH_3), 68.1 (OCH_2), 114.9 (C-2), 120.8 (C-7), 127.8, 128.0 (C-6, C-3), 131.9 (C-4), 135.9 (C-5), 138.3 (C-8), 158.7, 159.0 (C-9, C-1); *m*/*z* (ESI) 452 (M^+); *m*/*z* (ESI) 145 (PF_6^-).

*3.7.5 4-(Dodecyloxy)-1-(N,N,N′,N′-tetramethylguanidinium)-biphenyl thiocyanate (***12e***)*

Compound **12e** was prepared from 0.20 g (0.41 mmol) of compound **7f**. Yield 0.19 g (91%). CHNS analysis: $C_{30}H_{46}N_4OS$ (M = 510.78 g mol^{-1}) calculated C 70.54%, H 9.08%, N 10.97%, S 6.28%, found C 70.62%, H 8.99%, N 10.89%, S 5.99%. HRMS (ESI): found (M^+), 452.3640. $C_{29}H_{46}N_3O$ requires *M*, 452.3635. ν_{max}(solid)/cm^{-1} 2918s, 2850m, 2061vs, 1980w, 1633s, 1556s, 1496s, 1466m, 1243s, 1170m, 1039m, 917w, 820s, 717w, 518w; δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.88 (t, *J* 6.7 Hz, 3H, CH_2CH_3), 1.23–1.39 (m, 16H, CH_2), 1.43–1.51 (m, 2H, CH_2), 1.76–1.84 (m, 2H, CH_2), 3.03 (br, 12H, N–CH_3), 3.99 (t, *J* 6.6 Hz, 2H, OCH_2), 6.93–6.97 (m, 2H, 2-H), 7.08–7.12 (m, 2H, 7-H), 7.44–7.48 (m, 2H, 3-H), 7.50–7.55 (m, 2H, 6-H), 11.07 (s, 1H, N–H); δ_c (125 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_2CH_3), 22.7 (CH_2CH_3), 26.1 ($OCH_2CH_2CH_2$), 29.3, 29.4, 29.42, 29.6, 29.62, 29.65, 29.7 (CH_2), 31.9 (CH_2), 40.7 (N–CH_3), 68.2 (OCH_2), 114.9 (C-2), 121.0 (C-7), 127.8, 127.9 (C-6, C-3), 132.1 (C-4), 136.2 (C-5), 138.1 (C-8), 158.6, 159.0 (C-9,C-1); *m*/*z* (ESI) 452 (M^+).

4. Conclusion

We have developed an efficient synthetic route towards calamitic guanidinium salts which displayed broad SmA mesophases. Guanidinium salts with larger aromatic cores (biphenyl) exhibit broader and more stable mesophases than those with smaller cores (phenyl). Furthermore, increasing the chain lengths of the aliphatic tails of the molecules leads to an increase of mesophase range and clearing points. A strong influence of different counteranions on the mesophase behaviour was demonstrated. With halides displaying much broader mesophases and lower melting points as compared with the corresponding tetrafluoroborates, hexafluorophosphates and thiocyanates, respectively, making guanidinium halides attractive for applications.

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