T-Shaped Ionic Liquid Crystals Based on the Imidazolium Motif: Exploring Substitution of the C-2 Imidazolium Carbon Atom

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Abstract: In this contribution the first examples of so-called rigid-core, Tshaped imidazolium ionic liquid crystals, in which the C-2 atom of the imidazolium ring is substituted with an aryl moiety decorated with one or two alkoxy chains, are described. The length of the alkoxy chain(s) was varied from six to eighteen carbon atoms (n=6, 10, 14–18). Whereas the compounds with one long alkoxy chain display only smectic A phases, the salts containing two alkoxy chains exhibit smectic A, multicontinuous cubic, as well as hexagonal columnar phases, as evidenced by polarising optical microscopy, differential scanning calorimetry, and powder X-ray diffraction. Structural models are proposed for the self-assembly of the molecules within the mesophases. The imidazolium head

Keywords: cubic phases • imidazolium cations • ionic liquids • liquid crystals • self-assembly groups and the iodide counterions were found to adopt a peculiar orientation in the central part of the columns of the hexagonal columnar phases. The enantiotropic cubic phase shown by the 1,3-dimethyl-2-[3,4-bis(pentadecyloxy)phenyl]imidazolium iodide salt has a multicontinuous $Pm\bar{3}m$ structure. To the best of our knowledge, this is the first example of a thermotropic cubic mesophase of this symmetry.

Introduction

Ionic liquid crystals are a fascinating class of molecular materials. They combine the characteristics of liquid crystals (anisotropy of physical properties) with those of ionic liquids (ionic conductivity, thermal stability, tuning possibilities, etc.).^[1] One of the most frequently used cations to obtain ionic mesogens is the 1,3-disubstituted imidazolium core. By attaching one or two relatively long alkyl chains to the heterocyclic cation, mesomorphism is induced.^[2-9] These mesogens can be considered as flexible amphiphiles. The alkyl chains might additionally be decorated with mesogenic groups to influence the phase behaviour.^[10-16] In this way, rare nematic ionic liquid crystals could be obtained.^[16,17] Alternatively, a benzene ring was incorporated into the aliphatic chain(s) (benzyl substituent(s)).^[18] By attachment of multiple alkyl chains to this benzene ring, taper-shaped cations were obtained.[19-25]

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Kouwer and Swager recognised that the imidazolium fragment is a polarisable rigid group that is suitable as part of a mesogenic core rather than being placed at one end of a flexible alkyl chain.^[26] However, the mesomorphism of ionic mesogens, wherein the imidazolium group is an integral part of the rigid core, remained virtually unexplored until very recently when reports appeared in the literature about 1aryl-3-alkylimidazolium salts^[26-29] and 1,3-diarylimidazolium salts.^[30,31] However, no examples exist of 2-arylsubstituted imidazolium ionic liquid crystals (i.e., with a substituted aryl group directly connected to the carbon atom in the 2-position of the imidazolium ring). Kouwer and Swager,^[26] and Kato et al.^[21,32] did investigate the influence of a methyl, ethyl, pentyl or phenyl group in the 2-position on the phase behaviour of imidazolium salts, but these substituents only lowered the transition temperatures in some cases, led to a disappearance of the liquid-crystalline properties or had only a minor influence. Mukai et al. also reported on a protonated 2-heptadecylimidazolium tetrafluoroborate salt showing a smectic A (SmA) phase over a rather narrow temperature range.^[33] In a report by Aida et al., a methyl group in the 2-position of the six imidazolium groups situated at the periphery of triphenylene discotic liquid crystals had an influence on the phase behaviour.^[34]

It is remarkable that no attempts have been made to prepare 2-arylsubstituted imidazolium mesogens, since these structures might show different intermolecular interactions (e.g., hydrogen bonding) and thus a different phase behaviour than the imidazolium ionic liquid crystals previously reported. Most likely, this is due to the fact that the required precursors are not commercially available. To be able to

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attach a substituted aryl moiety to the imidazolium cation in its 2-position, one has to 'build up' the cationic core oneself.

Results and Discussion

Synthesis: Imidazolium salts **1–3** (with a 4-(OC_nH_{2n+1}) phenyl moiety, n=6, 10, 14) and **5–6** (with a 3,4-bis-(OC_nH_{2n+1}) phenyl moiety, n=6, 10) were prepared by reacting the appropriate alkoxy-substituted benzaldehyde with ethylenediamine to obtain an imidazoline compound,^[35,36] and by oxidising (Swern oxidation^[37]) the latter to the corresponding imidazole compound,^[38] which was finally alkylated and quaternised (Menschutkin reaction^[39]) by using NaH and an excess of CH₃I (Scheme 1). CH₃I was chosen as the



Scheme 1. Synthesis of 2-arylsubstituted imidazolium salts **1–3** and **5–6**. i) $C_nH_{2n+1}Br$, K_2CO_3 , KI, 2-butanone, reflux, Ar; ii) ethylenediamine, *N*-bromosuccinimide (NBS), dry CH₂Cl₂, 0°C \rightarrow RT, Ar; iii) 1) oxalyl chloride, DMSO, dry CH₂Cl₂, -78°C, Ar; 2) Et₃N, -78°C \rightarrow RT, Ar; iv) NaH, CH₃I (excess), dry THF, RT \rightarrow reflux, Ar.

Abstract in Dutch: In deze bijdrage beschrijven we de eerste voorbeelden van T-vormige ionische vloeibare kristallen gebaseerd op een kationische imidazoliumgroep, die deel uitmaakt van een ruimere rigide kern doordat het koolstofatoom in de 2-positie van de imidazoliumring gesubstitueerd is met een arylgroep die één of twee alkoxyketens bevat. De lengte van de alkoxyketen(s) werd gevarieerd van zes tot achttien koolstofatomen (n=6, 10, 14-18). Terwijl de verbindingen met slechts één-voldoende lange-alkylketen enkel smectische A fasen vertonen, werden zowel smectische A, kubische als hexagonaal-kolomvormige mesofasen gevonden voor de zouten die twee alkylketens bevatten. Voor de studie van de vloeibaar-kristallijne eigenschappen werd gebruik gemaakt van gepolariseerde optische microscopie, differentiëlescanning calorimetrie, en X-stralenpoederdiffractie. We geven een nauwkeurige beschrijving van de spontane ordening van de moleculen in de mesofasen. De imidazoliumkopgroepen en de jodide-anionen blijken een bijzondere oriëntatie te vertonen in het centrale gedeelte van de kolommen in de hexagonaal-kolomvormige fasen. De enantiotrope kubische fase vertoond door het 1,3-dimethyl-2-[3,4-bis(pentadecyloxy)fenyl]imidazoliumjodidezout heeft een multicontinue Pm3m-structuur. Voor zover wij weten, is dit het eerste voorbeeld van een thermotrope kubische mesofase met deze symmetrie.

alkylating agent instead of CH₃Cl or CH₃Br, because the last two compounds are gases at room temperature.

This procedure appeared not to be suitable to obtain compounds **4** (with a 4-(OC_nH_{2n+1}) phenyl moiety, n=18) and **7–11** (with a 3,4-bis(OC_nH_{2n+1}) phenyl moiety, n=14-18): the intermediate imidazoline compounds did not sufficiently dissolve in either CH₂Cl₂ or DMSO to transform them into the corresponding imidazole compounds by using literature procedures.^[38,40] Dehydrogenation of the imidazolines in toluene at reflux in the presence of Pd/C (5 wt %)^[41] gave the imidazole compounds only in very low yields. Therefore, an alternative synthetic route was followed (Scheme 2). Precur-



Scheme 2. Synthesis of 2-arylsubstituted imidazolium salts **4** and **7–11**. i) ethylenediamine, NBS, dry CH_2Cl_2 , 0°C \rightarrow RT, Ar; ii) diacetoxyiodobenzene (DIB), K₂CO₃, DMSO, RT, Ar; iii) NaH, CH₃I, dry THF, RT, Ar; iv) pyridinium chloride, 200°C; v) $C_nH_{2n+1}Br$, K₂CO₃, KI, 2-butanone, reflux, Ar; vi) CH₃I (excess), dry THF, RT \rightarrow reflux, Ar.

sors **4a** and **7a** were oxidised to the corresponding imidazole compounds **4b** and **7b** in DMSO by means of DIB.^[40] Compounds **4b** and **7b** were then monoalkylated with CH₃I to afford **4c** and **7c**, which were then deprotected in pyridinium chloride at 200 °C.^[42] Finally, the hydroxyl groups of **4d** and **7d** were alkylated, followed by quaternisation with CH₃I.

Single-crystal X-ray diffraction: Crystal structure of 2c: Crystals of the neutral precursor 2c suitable for single-crystal X-ray structure determination could be obtained by slowly evaporating a solution of the compound in chloroform. The asymmetric unit contains two 2-[4-(decyloxy)phenyl]-1*H*-imidazole molecules. The imidazole rings are at an angle to the benzene rings (34.8(1)° and 33.5(1)° between planes through the respective ring atoms). The alkyl chains of both molecules in the asymmetric unit are completely staggered and almost planar with respect to the benzene rings.

Intermolecular hydrogen bonds exist between the protonated imidazole nitrogen atom of one molecule and the nonprotonated imidazole nitrogen atom of another molecule (N2(H)···N3 and N4(H)···N1 distances of 2.888(2) and 2.922(2) Å, respectively). These interactions link the molecules together in the [001] direction and result in layers par-

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Figure 1. Packing in the crystal structure of compound **2c**, showing the linkage of the molecules in the [001] direction through intermolecular hydrogen bonds.

allel with the (010) plane (Figure 1). In the crystal structures of 2-[4-(methoxy)phenyl]-4,5-dihydro-1*H*-imidazole^[43] and 2-[4-(methoxy)phenyl]-1*H*-benzimidazole,^[44] similar N(H)...N hydrogen bonds that link the molecules into one-dimensional chains (extending in the [100] and [001] directions, respectively) were found. In the packing diagram, C–H... π ring interactions were observed between H(C24) and an imidazole ring C20–C22,N3,N4 (C–H...ring centroid distance of 2.88 Å), and between H(C5) and H(C27) and benzene rings C23–C28 and C4–C9, respectively (C–H...ring centroid distances of 2.84 and 2.93 Å, respectively).

Crystal structure of 2: Single crystals of imidazolium salt 2 were obtained by slowly evaporating a solution of the compound in ethanol. Although the obtained structural model is very clear, the anisotropical refinement suffered from severe absorption effects and the attained R and wR_2 values are currently not sufficient for deposition of the crystal structure in the Cambridge Structural Database. Nevertheless, the structure is presented in the Supporting Information (Figures S1-S3 in the Supporting Information). The asymmetric unit contains two 1,3-dimethyl-2-[4-(decyloxy)phenyl]imidazolium iodide molecules. The imidazolium rings are at an angle to the benzene rings. The alkyl chains of both molecules in the asymmetric unit are completely staggered. The alkyl chain of one of the two molecules is almost planar with respect to the benzene ring, whereas the alkyl chain of the other molecule is non-planar with respect to this aromatic ring. The iodide anions link the imidazolium cations together through short contacts in the [010] direction (Figures S1 and S2 in the Supporting Information). In this way, layers parallel with the (100) plane are formed (Figure S3 in the Supporting Information).

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Crystal structure of **6**: Single crystals of imidazolium salt **6** could be obtained by slowly evaporating a solution of the compound in ethanol. The asymmetric unit contains two 1,3-dimethyl-2-[3,4-bis-

(decyloxy)phenyl]imidazolium iodide molecules. As in the crystal structure of 2, the imidazolium rings are at an angle to the benzene rings (88.8(2)° and 51.5(2)° between planes through the respective ring atoms). The alkyl chains of both molecules in the asymmetric unit are completely staggered, but they are not lying in the same plane as the benzene rings (37.5° and 71.5° between planes through the respective atoms for the first molecule, and 52.7° and 44.9° between

planes through the respective atoms for the second molecule).

As in the case of **2**, the iodide anions link the imidazolium cations together through short contacts in the [100] direction (Figure 2). Iodide anion I1 shows short contacts with hydrogen atoms of two methyl groups attached to two different imidazolium rings, and with the benzene ring belonging to a third molecule (C–H···I distances ranging from 3.00 to 3.17 Å). Iodide anion I2 shows short contacts with an imidazolium ring hydrogen atom belonging to a fourth cation (C–H···I distance of 3.03 Å), and with an imidazolium ring hydrogen atom belonging to a fourth cation (C–H···I distance of 3.03 Å), and with an imidazolium ring hydrogen atom of a methyl group that both belong to a cation that is already involved in the interactions with iodide anion I1 (C–H···I distances of 3.13 and 3.15 Å, respectively). In the packing diagram, C–H···π ring interactions were observed between H(C43) and benzene ring C6–C11 (C–H···ring centroid distance of 2.84 Å).

Thermal behaviour: The thermal properties of all compounds were examined by polarising optical microscopy (POM) and differential scanning calorimetry (DSC), and most mesophases were additionally investigated by X-ray diffraction on powder samples (powder XRD) at various temperatures (see below). Table 1 summarises the transition temperatures and thermal data. Representative DSC traces and thermogravimetric analysis (TGA) thermograms can be found in the Supporting Information.

All of the reported imidazolium salts were liquid crystalline, except for compound **1**, which has only a single hexyl chain. The SmA phases could be easily identified by their defect textures: focal conic fan and oily streak textures were observed, as well as large homeotropic areas and the formation of bâtonnets on cooling from the isotropic liquid (Figure 3a). The rather lowly viscous SmX phase shown by **5**



Figure 2. Top: intermolecular short contacts observed in the crystal structure of compound **6**. Iodide anions are labelled. Bottom: packing in the crystal structure of compound **6**, showing the linkage of the molecules in the [100] direction through intermolecular short contacts.

could not be identified by its optical texture (see the Supporting Information). The hexagonal columnar (Col_h) phases were identified by their pseudo-focal conic fanshaped texture and the appearance of homeotropic areas (Figure 3b–d). The cubic (Cub) phases were identified by their optical isotropy, in combination with the slow formation of the texture through the typical appearance of square edges and black polygonal areas growing across the preceding texture (Figure 3e and f).

The alkyl chain length has only a very minor influence on the melting point. The clearing point, however, is largely determined by this parameter, especially for the series 1–4. This has also been found for simple 1-alkyl-3-methylimid-azolium halide salts.^[6] It is not clear why **6** displays a slightly higher clearing point than **7**.

knowledge, this is the first example of a thermotropic mesogen showing a Cub $Pm\bar{3}m$ phase.

The appearance of smectic, cubic as well as hexagonal columnar phases for the same homologous series of bis-(alkoxy)-substituted thermotropic ionic mesogens is quite exceptional. The only other examples of such behaviour for imidazolium ionic liquid crystals have only very recently been reported.^[23,29] A transition from lamellar mesophases (with flat interfaces) to columnar mesophases (with curved interfaces), via an intermediate cubic structure, is typically found for tetracatenar liquid crystals.^[46–51] This is explained by the increase in the aliphatic volume fraction with temperature and/or chain length. To compensate for this increase, the rigid cores will tilt to the extent that tilting is no longer sufficient, and undulations start to occur. These undulations result in transitions to multicontinuous cubic and columnar

The type of mesophase is highly dependent on the number of alkyl chains (and the length). For the homologous series 1-4, containing one alkyl chain, only SmA phases were found. No smectic phases of higher order-as observed, for example, for N-alkyl-N-methylpyrrolidinium ionic liquid crystals^[45]-could be detected. A longer chain results in a higher clearing point due to a more efficient microsegregation (see also below).

For compounds 5, 6 and 7, with alkyl chains up to 14 carbon atoms, lamellar SmA phases were also observed. For 5, an underlying highly ordered smectic phase was found by POM and DSC in the second and subsequent heating runs. On heating a fresh sample of 5, however, the compound rapidly recrystallised at 106°C to melt only at 124 °C (see the Supporting Information). Salts 8, 9, 10 and 11, with fairly long alkyl chains $(C_{15}-C_{18})$, exhibited Col_h phases as a result of the increased curvature at the aromatic/ionic-aliphatic interface (see also below).^[46] Compounds 8 and 9 also exhibited a lowerphase. temperature Cub Powder XRD revealed that the enantiotropic Cub phase of salt 8 most probably has a multicontinuous $Pm\bar{3}m$ symmetry (see below). To the best of our

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Table 1.	Transition t	empera	tures	and	thermal	data for	the 2-aryls	substitut
ed imida	zolium salts	•						
				n 1	-	f -]	-	. 1-

	Subst.	Transition ^[b]	$T [^{\circ}C]^{[c]}$	$\Delta H [\mathrm{kJ}\mathrm{mol}^{-1}]$
	pattern ^[a]			$(\Delta S [J K^{-1} mol^{-1}])$
1	$4-C_6$	$Cr \rightarrow I$	123	24.3 (61)
2	$4-C_{10}$	$Cr \rightarrow SmA$	122	40.4 (102)
		$SmA \rightarrow I$	152	0.7 (2)
3	$4-C_{14}$	$Cr \rightarrow SmA$	120 ^[d]	41.6 (106)
		$SmA \rightarrow I$	220	1.2 (2)
4	$4-C_{18}$	$Cr \rightarrow SmA$	122	72.7 (184)
		$SmA \rightarrow I$	243	1.5 (3)
5	3,4-C ₆	$Cr_1 \rightarrow Cr_2$	33 ^[d]	0.8 (3)
		$Cr_2 \rightarrow Cr_3$	99 ^[e]	4.7 (13)
		$Cr_3 \rightarrow SmX^{[f]}$	106	19.6 (52)
		$SmX \rightarrow SmA$	124	0.5 (1.4)
		$SmA \rightarrow I$	147	1.7 (4)
6	$3,4-C_{10}$	$Cr_1 \rightarrow Cr_2$	66 ^[d]	0.5 (1.4)
		$Cr_2 \rightarrow Cr_3$	75	0.5 (1.3)
		$Cr_3 \rightarrow SmA$	113	38.0 (98)
		$SmA \rightarrow I$	164	0.7 (1.7)
7	3,4-C ₁₄	$Cr_1 \rightarrow Cr_2$	91	7.8 (21)
		$Cr_2 \rightarrow SmA$	115	46.9 (121)
		$SmA \rightarrow I$	159	0.2 (0.4)
8	3,4-C ₁₅	$Cr_1 \rightarrow Cr_2$	103 ^[d]	3.8 (10)
		$Cr_2 \rightarrow Cub$	118	47.8 (122)
		$Cub \rightarrow Col_h$	139	0.5 (1.2)
		$Col_h \rightarrow I$	172	0.2 (0.5)
9	3,4-C ₁₆	$Cr_1 \rightarrow Cr_2$	94	6.9 (19)
		$(Cub \rightarrow Col_h)$	96 ^[d,g]	$0.3 (0.9)^{[g]}$
		$Cr_2 \rightarrow Col_h$	118	55.0 (141)
		$Col_h \rightarrow I$	190	0.5 (1.0)
10	3,4-C ₁₇	$Cr_1 \rightarrow Cr_2$	108	11.6 (30)
		$Cr_2 \rightarrow Col_h$	120	58.4 (148)
		$Col_h \rightarrow I$	204	0.7 (1.5)
11	3,4-C ₁₈	$Cr_1 \rightarrow Cr_2$	98	0.1 (0.4)
		$Cr_2 \rightarrow Cr_3$	103	9.7 (26)
		$Cr_3 \rightarrow Col_h$	121	63.9 (162)
		$Col_h \rightarrow I$	208	0.7 (1.5)

[a] Substitution pattern of the aryl substituent: 4-(alkoxy) or 3,4-bis-(alkoxy). [b] Abbreviations: Cr=crystalline phase; SmX=unidentified smectic phase; SmA = smectic A phase; Cub=cubic phase, most probably of $Pm\bar{3}m$ symmetry (see text); Col_h = hexagonal columnar phase; I=isotropic liquid. Transitions between parentheses indicate transitions to a monotropic mesophase. [c] Onset temperatures obtained by DSC at heating/cooling rates of 10°C min⁻¹ (He atmosphere). Values were taken from the first heating run for 1, 2, 3, 4, 7, 9 and 10, and from the second heating run for 5, 6, 8 and 11 (first heating run up to 180°C). [d] Peak temperature. [e] Prior to this endothermic transition, an exothermic recrystallisation process took place at 85°C (peak temperature). [f] This phase does not appear during the first heating run, in contrast to all subsequent heating runs. [g] From the first cooling run.

phases (with the cubic phases having rather slow formation kinetics due to the large structural rearrangements that occur). However, the compounds presented herein do not possess a typical polycatenar structure in the sense that they only contain flexible alkyl chains on one side of the rigid core, which is moreover very short (only two ring structures). One can imagine the formation of some supramolecular polycatenar mesogens by head-to-head coupling of the imidazolium groups through hydrogen-bonding interactions between the imidazolium H-4 and H-5 atoms and the halide anions. Such an arrangement has already been found in the crystal structure of an imidazolium bromide salt with a

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pendant mesogenic group,^[16] and linkage of imidazolium cations in the solid state through non-classical C-H...X hydrogen bonds is well known.^[52,53] This would effectively enlarge the central rigid core from two rings to four rings. Nevertheless, these C-H···X hydrogen bonds are rather weak, a fortiori when $X^- = I^-$ instead of Cl^- or Br^{-} .^[54] In the crystal structures of compounds 2 and 6, intermolecular short C-H-I contacts were indeed found to link the imidazolium moieties together, but it is difficult to distinguish any dimer formation, especially in the case of 6 (Figure 2 and Figures S1-S3 in the Supporting Information). Therefore, the concept of a supramolecular polycatenar mesogen being formed seems to be false (it should also be noted that for tetracatenar mesogens with shorter chain lengths, SmC (and nematic) phases are generally expected instead of SmA phases). Indeed, as will be shown below, the mesophase structures are governed by microsegregation, space filling and, in particular, by strong electrostatic interactions. It is striking that none of the neutral imidazole precursors (1c-3c, 5c-6c, 4e, 7e-11e) are mesomorphic (despite the phasesegregated lamellar structure already present in the crystalline solid state, see Figure 1), which emphasises the importance of electrostatic interactions. Hydrogen bonding (through the N-H moiety) cannot induce mesomorphism in precursors 1b-3b, 5b-6b, 1c-3c and 5c-6c, due to too low a degree of amphiphilicity in these compounds (in contrast to the compounds reported for example by Seo et al.^[55]). Unlike the models developed for polycatenar mesogens, the well-established Israelachvili theory concerning the self-assembly of hydrocarbon amphiphiles can be used to explain the phase behaviour and the observed molecular arrangements in the mesophases (see below).^[56] In the past, a SmA-Cub-Col_b phase sequence in a homologous series has often been observed for non-ionic, amphiphilic compounds, and microsegregation has been shown to play a crucial role in the mesomorphism.^[57-60] Analogies to lyotropic systems have already been drawn in these earlier investigations.^[61,62]

Powder XRD: The enantiotropic mesophases were investigated by powder XRD to obtain more information about the molecular packing in these phases. Table 2 summarises the Bragg reflections collected from the X-ray diffractograms.

Before discussing the powder XRD results, we will give a brief overview of the imidazolium-based ionic liquid crystals exhibiting thermotropic cubic mesophases that have been reported up to now. To the best of our knowledge, only six examples exist. 1) Bielawski et al. reported one benzobis-(imidazolium) salt that showed a Cub phase between 188 and 238 °C.^[63] 2) Kato et al. synthesised an imidazolium bromide salt containing an L-glutamic acid moiety that exhibited a micellar Cub $Pm\bar{3}n$ phase above 136 °C (a lower-temperature Col_h phase was found as well) with thermal degradation occurring at about 180 °C.^[64] [The authors showed that the anisotropic ionic conductivity measured parallel to the aligned columnar axes in the low-temperature Col_h phase decreased by one order of magnitude when heating





Figure 3. Defect textures observed by polarising optical microscopy (POM): a) formation of bâtonnets and fan-shaped texture of the SmA phase of **5** at 143 °C on cooling $(100 \times)$; b) pseudo-focal conic fan-shaped texture of the Col_h phase of **11** at 205 °C on cooling $(200 \times)$; c) homeotropic domains and fan-shaped texture of the Col_h phase of **9** at 182 °C on cooling $(200 \times)$; d) fan-shaped texture of the Col_h phase of **9** at 150 °C on cooling $(200 \times)$; e) development of the Cub phase of **8** at 132 °C on cooling from the Col_h phase $(200 \times)$; f) development of the monotropic Cub phase of **9** at 96 °C after fast cooling from the Col_h phase $(200 \times)$.

the sample into the micellar Cub phase: the ionic moieties became confined within the micelles and insulated by the lipophilic parts and this prevented fast, long-range ion conduction. A similar decrease in proton conductivity was found for the micellar Cub phases shown by amphiphilic *N*-(2,3-dihydroxypropyl)benzamides.^[65] 3) Douce et al. prepared 1-[3,4-bis(dodecyloxy)benzyl]-3-methylimidazolium chloride and bromide salts.^[23] These two compounds showed a bicontinuous Cub *Ia*3*d* phase. 4) Percec et al. reported two dendrons containing 3-methylimidazolium chloride and

hexafluorophosphate at their apex, respectively.^[66] These dendrons self-assembled into micellar Cub $Pm\bar{3}n$ phases. 5) Aida et al. synthesised triphenylene discotic liquid crystals with 3-methylimidazolium groups at the ends of the six peripheral chains.^[34] Some of the compounds showed a bicontinuous Cub $Ia\bar{3}d$ phase. One compound (namely, that with peripheral tetradecyl chains and tetrafluoroborate counterions) additionally showed a bicontinuous Cub $Pn\bar{3}m$ phase. We believe this represents the first example of a thermotropic ionic liquid crystal showing this type of Cub phase.

Table 2. Bragg reflections collected from the	he X-ray diffractograms o	of the different enantiotropic mesophases.
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	$d_{ m meas} \ [m \AA]^{[a]}$	$I^{[\mathrm{b}]}$	hkl ^[c]	$d_{ m calcd} \ [{ m \AA}]^{[{ m a}]}$	Parameters of the mesophase ^[d]		$d_{ m meas} \ [m \AA]^{[a]}$	<i>I</i> ^[b]	hkl ^[c]	$d_{ m calcd} \ [{ m \AA}]^{[{ m a}]}$	Parameters of the mesophase ^[d]
2	31.11	М	001	31.11	SmA: T=140 °C	8 ^[f]	42.89	W	200	43.05	Cub: <i>T</i> =124 °C
					$V_{\rm M} = 823 \text{ Å}^3$		35.32	VS	211	35.15	$V_{\rm M} = 1343 \text{ Å}^3$
					$A_{\rm M} = 52.9 {\rm \AA}^2$		30.02	VW	220	30.44	$a_{\rm Cub} = 86.1 {\rm ~\AA}$
					d/L = 1.42		29.15	VW	221	28.70	$V_{\rm Cub} = 638253{\rm \AA}^3$
							27.54	W	310	27.23	$N_{\rm Cub} = 475$
3	34.51	S	001	34.51	SmA: T=140 °C		26.57	W	311	25.96	
					$V_{\rm M} = 925 {\rm ~\AA}^3$		25.23	W	222	24.85	
					$A_{\rm M} = 53.6 {\rm \AA}^2$		23.46	VW	320	23.88	
					d/L = 1.36		22.58	VW	321	23.01	
							21.45	VW	400	21.52	
4	38.49	VS	001	38.74	SmA: $T = 140 ^{\circ}\text{C}$		21.00	VW	322	20.88	
	19.50	W	002	19.37	$V_{\rm M} = 1026 {\rm \AA}^3$		20.15	VW	411	20.29	
					$A_{\rm M} = 53.0 {\rm \AA}^2$		19.62	VW	331	19.75	
					d/L = 1.34		19.12	VW	420	19.25	
							18.77	VW	421	18.79	
5 ^[e]	26.81	М	001	26.81	SmA: $T = 129 ^{\circ}\text{C}$		18.31	VW	332	18.36	
					$V_{\rm M} = 896 {\rm \AA}^3$		17.56	W	422	17.57	
					$A_{\rm M} = 66.8 {\rm \AA}^2$		34.31	S	10	34.31	$\operatorname{Col}_{h}: T = 155 ^{\circ}\mathrm{C}$
					d/L = 1.58		6.61	VW (br)	h_1		$V_{\rm M} = 1371 {\rm A}^3$
											$a_{\rm Col} = 39.6 {\rm A}$
6	30.64	VS	001	30.68	SmA: $T = 140 ^{\circ}\text{C}$						$S = 1359 \text{ A}^2$
	15.36	VW	002	15.34	$V_{\rm M} = 1104 {\rm A}^{3}$						$N_{\rm slice} = 7.2$
					$A_{\rm M} = 72.0 {\rm A}^2$						
					d/L = 1.39	9	34.91	VS	10	34.91	$\operatorname{Col}_{h}: T = 155 ^{\circ}\mathrm{C}$
_		_					6.61	W (br)	h_1		$V_{\rm M} = 1423 {\rm A}^3$
7	34.91	S	001	34.91	SmA: $T = 140 ^{\circ}\text{C}$						$a_{\rm Col} = 40.3 \rm A$
					$V_{\rm M} = 1308 {\rm A}^3$						$S = 1407 A^2$
					$A_{\rm M} = 74.9 {\rm A}^2$						$N_{\rm slice} = 7.2$
					d/L = 1.39	10	26.17	0	10	26.17	C 1 T 14(0C
						10	36.17	5	10	36.17	$Col_h: I = 146 {}^{\circ}C$
							20.71	W VW (ha)	11	20.88	$V_{\rm M} = 1405 {\rm A}^2$
							0.01	v w (01)	n_1		$u_{\rm Col} = 41.0 \text{ A}$ S = 1511 Å ²
											S = 1511 A
											$N_{\rm slice} = 7.4$
						11	36.39	S	10	36.39	Col.: $T = 155$ °C
							21.92	w	11	21.51	$V_{\rm M} = 1525 \text{ Å}^3$
							18.65	vw	20	18.20	$a_{\rm Cal} = 42.0 \text{ Å}$
							6.61	W (br)	h_1	10.20	$S = 1529 \text{ Å}^2$
							0.01	(01)	1		$N_{\rm w} = 7.2$

[a] d_{meas} and d_{calcd} are the measured and calculated diffraction spacings, respectively. [b] *I* is the intensity of the reflections: VS, very strong; S, strong; M, medium; W, weak; VW, very weak; br, broad reflection. [c] *hkl* are the Miller indices of the reflections. h_1 denotes the medium-angle reflection that probably corresponds to the stacking periodicity along the columnar axes (see text). [d] *T* is the temperature at which the X-ray diffractogram was recorded. V_M is the molecular volume (estimated to be $V_M = (M/0.6022)f$, in which *M* is the molecular mass [gmol⁻¹] and *f* is a temperature-correcting factor ($f=0.9813+7.474\times10^{-4}T$ with *T* in °C)^[16]); A_M is the molecular area (calculated from $A_M = 2V_M/d$). a_{Cub} is the lattice parameter of the Cub phase ($=[\Sigma_{hk}d_{hkl}(h^2+k^2+t^2)^{1/2}]/N_{hkb}$, in which N_{hkl} = the number of (*hkl*) reflections); V_{Cub} is the volume of the cubic cell ($=a_{\text{Cub}}^{-3}$); N_{Cub} is the number of molecules within the cubic cell (estimated to be V_{Cub}/V_M). a_{Cu} is the lattice parameter of molecules within the Col_h phase ($=[(2/\sqrt{3})[\Sigma_{hk}d_{hk}(h^2+k^2+th)^{1/2}]/N_{hk}$, in which $N_{hk}=$ the number of one column in the Col_h phase ($=((\sqrt{3}/2)a_{\text{Col}}^{-2})$; N_{slice} is the number of molecules within one slice of a column in the Col_h phase, with a height h_1 of about 6.6 Å (simplified model, see text). N_{slice} was estimated by using the following equation and assuming a density of $\rho=1.0 \text{ gcm}^{-3}$: $N_{\text{slice}}=h_1S(N_A/M)\rho$, in which N_A =Avogadro constant and M =molecular mass [gmol⁻¹]. *L* is the calculated length of the 2-arylsubstituted imidazolium cation in its most extended conformation (estimated with the Chem3D program; the structure of the imidazolium cation in its most extended conformation (estimated with the Chem3D program; the structure of the imidazolium cation within Chem3D). [e] No diffraction data could be obtained for the SmX phase

6) Finally, Tschierske et al. reported four rod-like imidazolium bromide compounds containing three tetradecyl or hexadecyl chains that exhibited micellar Cub $Pm\bar{3}n$ phases.^[29]

The following sections describe the X-ray diffraction data that were obtained for our 2-arylsubstituted imidazolium salts. The crystalline nature of the solid phases at room temperature was confirmed by the presence of several sharp Bragg reflections at both small and wide angles. The equidistant small-angle reflections indicated that the molecules are arranged in a lamellar fashion (see also the section about single-crystal X-ray diffraction).

The diffractograms of the SmA phases showed one sharp reflection, indexed as the (001) reflection, in the small-angle region. In some cases the much weaker (002) reflection

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could be observed as well. These reflections are related to the consecutive smectic layers of a specific layer thickness d (Table 2). In the wide-angle region, a diffuse signal centred at about 4.7 Å was observed, corresponding to the lateral short-range order of the disordered (molten) aliphatic chains.

The diffractograms of the Col_h phases showed one sharp reflection in the small-angle region, indexed as the (10) reflection of the two-dimensional hexagonal lattice (for which $d_{hk} = a_{\text{Col}}/[(4/3)(h^2+k^2+hk)]^{\frac{1}{2}}$, in which a_{Col} is the lattice parameter of the hexagonal lattice). For compound 11 both the (11) and (20) reflections (reciprocal spacings of the (10), (11) and (20) reflections in the characteristic ratio of $1:\sqrt{3:2}$) could be observed. For compound 10, the characteristic (11) reflection was found at 146°C, but not the (20) reflection. For 8 and 9, the Col_h phase type was assigned based on the textural similarities with 10 and 11. At 155°C, the lattice parameter a_{Col} of the Col_h phase was found to be 39.6, 40.3, 41.3 and 42.0 Å for compounds 8, 9, 10 and 11, respectively. In addition, all diffractograms showed a diffuse wide-angle scattering centred at about 4.6 Å, indicating the liquid-like nature of the mesophases (molten aliphatic chains). Along with this broad scattering, another weak halo was seen at about 6.6 Å for 8, 9, 10 and 11. This signal probably corresponds to the stacking periodicity along the columnar axes (see below). The presence of this signal for all of the compounds in the series 8-11 is additional support of the Col_b phase type assignment.

The diffractogram of the Cub phase exhibited by compound **8** showed one very intense reflection, as well as multiple weak reflections in the small- and medium-angle region (Figure 4). The reciprocal spacings of the reflections within the 2–5° 2θ angular region were in the ratios of $\sqrt{4}:\sqrt{6}:\sqrt{8}:\sqrt{9}:\sqrt{10}:\sqrt{11}:\sqrt{12}:\sqrt{13}:\sqrt{14}:\sqrt{16}:\sqrt{17}:\sqrt{18}:\sqrt{19}:$ $\sqrt{20}:\sqrt{21}:\sqrt{22}:\sqrt{24}$. In the wide-angle region, a weak and diffuse scattering centred at about 4.7 Å was found, corre-



Figure 4. X-ray diffractogram of **8** in the Cub phase at 124 °C, represented as the scattering intensity (in counts) versus the scattering angle, 2θ . The broad diffraction signal between $2\theta \approx 5.6^{\circ}$ and 7.6° is due to the covering foil used in the experimental setup.

sponding to the liquid-like order of the molten aliphatic chains. The small-angle reflections could be indexed as the (200), (211), (220), (221), (310), (311), (222), (320), (321),(400), (322), (411), (331), (420), (421), (332) and (422) reflections of a cubic lattice (for which $d_{hkl} = a_{Cub}/(h^2 + k^2 + l^2)^{\frac{1}{2}}$, with a_{Cub} = the lattice parameter of the cubic lattice). Although an unequivocal space group determination of a thermotropic cubic mesophase is possible only by X-ray studies on aligned monodomain samples, the initial number of theoretical possibilities (36 cubic space groups) can be reduced by logical analysis of the data.^[23,29,51] First of all, because the presence or absence of a centre of symmetry cannot be detected on the basis of standard powder diffraction measurements (Friedel's law), all non-centrosymmetric groups (groups with Laue classes 23, 432, or 4m) can be disregarded.^[67] This leaves only 17 cubic space groups to consider. The observed reflections and the ratios of the corresponding reciprocal spacings are not compatible with a face-centred cubic network (F), nor with a body-centred cubic network (I) (for F: h+k=2n, h+l=2n, k+l=2n; for I: h+k+l=2n2n). This leaves 7 cubic space groups with a primitive Bravais lattice (P). However, the reflection conditions that apply for the space groups $Pm\bar{3}n^{223}$ (*hhl*: l=2n; 00*l*: l=2n), $Pa\bar{3}^{205}$ (0kl: k=2n; h0l: l=2n; hk0: h=2n; 00l: l=2n) and $Pn\bar{3}n^{222}$ (0kl: k+l=2n; hhl: l=2n; 00l: l=2n) are not compatible with the observed reflections. Then, the space groups $Pm\bar{3}^{200}$, $Pm\bar{3}m^{221}$, $Pn\bar{3}^{201}$ and $Pn\bar{3}m^{224}$ are theoretically still possible. But the (320) reflection is not allowed in $Pn\bar{3}$ or $Pn\bar{3}m$ symmetry. This leaves only $Pm\bar{3}$ and $Pm\bar{3}m$. Aggregation into the highest symmetry is generally assumed, and therefore, the $Pm\bar{3}m$ space group is finally retained.^[68] We are not aware of any reports on thermotropic Cub mesophases with $Pm\bar{3}m$ symmetry. There have been reports on thermotropic bicontinuous Cub $Pn\bar{3}m$ phases shown by discotic liquid crystals,^[34,69] and bicontinuous Cub Pn3m phases are frequently found for lyotropic systems.^[70,71] Usually, rodlike and polycatenar mesogens tend to exhibit bicontinuous (or tricontinuous^[72]) thermotropic Cub phases of $Im\bar{3}m$ or $Ia\bar{3}d$ symmetry.^[51,70,73-78] Therefore, the observation of a Cub phase of $Pm\bar{3}m$ symmetry for compound 8 merits further investigation. Direct Fourier reconstruction of the electron density profile on the basis of the observed small-angle Xray scattering (SAXS) intensities might be difficult because the (211) reflection is too dominating. Synchrotron measurements, however, can provide an unambiguous confirmation of $Pm\bar{3}m$ as a new Cub phase structure. These experiments will be carried out in due course. It should be noted that judging from the position of the Cub phase in the phase sequence $Cub \rightarrow Col_h$ it is expected to have a multicontinuous structure, consisting of multiple interwoven, infinite threedimensional (columnar) networks (probably formed by the cationic rigid cores and the anions) separated from each other by lipophilic regions (formed by the molten aliphatic chains; the surfaces obtained by connecting all the midway points between the networks are referred to as infinite periodic minimum surfaces).^[79] The lattice parameter a_{Cub} was found to be about 86.1 Å for the Cub phase shown by 8. As deduced from the estimated molecular volume $V_{\rm M}$ ($V_{\rm M} \approx 1343 \text{ Å}^3$, $\rho \approx 1.0 \text{ g cm}^{-3}$ (Table 2)), the elementary cell of the Cub phase (volume $V_{\rm Cub} = a_{\rm Cub}^3$) contains about 475 molecules.

Mesophase structure of the SmA phases: As commonly observed, the layer thickness d of the SmA phases decreased with increasing temperature (Figure 5). This is due to the



Figure 5. Evolution of the layer thickness *d* of the SmA phases of 3 (\blacksquare) and 7 (\Box) as a function of temperature.

higher thermal mobility of the alkyl chains at higher temperatures, resulting in a compression of the smectic layers. The layer thickness also increases linearly with the number of carbon atoms n in the alkyl chain(s) [Eqs. (1) for the series **2–4** (at 140 °C) and (2) for the series **5–7** (at 140 °C), and Figure 6]:



Figure 6. Evolution of the layer thickness d of the SmA phase at 140 °C as a function of the number of carbon atoms n in the alkyl chain(s) for the series 2–4 (\blacksquare) and for the series 5–7 (\square).

$d_{\rm SmA} \ (\text{in Å}) = 21.4(\pm 0.9) + 0.95(\pm 0.06)n \tag{1}$

$$d_{\rm SmA}$$
 (in Å) = 20.7(±0.3) + 1.01(±0.03)n (2)

We assume that the cationic rigid cores and the iodide anions separate into a distinct sublayer (microphase) inside the smectic layers. From Equations (1) and (2), the thickness of the ionic sublayers d_0 can be estimated to be approximately 21.4 Å for the series 2-4, and 20.7 Å for the series 5-7. These values correspond well to twice the length of a 1,3dimethyl-2-(4-hydroxyphenyl)imidazolium cation (estimated from the crystal structure of 6 to be about 8.2 Å; a similar value is found by using Chem3D) when taking into account that, in addition, the iodide anions have an ionic radius of 2.15 Å. This supports our assumption that a sublayer is formed in which the cationic rigid cores and the iodide anions of different molecules interact in a head-to-head arrangement. The alkyl chains are homogeneously distributed on either side of this sublayer. Driving forces for this arrangement are microsegregation, electrostatic interactions and, to a lesser degree, intermolecular short contacts between the imidazolium cations and iodide anions (see also Figure 2).

Interestingly, an almost identical layer thickness d is found at 140 °C for both compounds 2 and 6 ($d \approx 30.9$ Å), which carry decyl chains, and for both compounds 3 and 7 $(d \approx 34.7 \text{ Å})$, which carry tetradecyl chains (Table 2 and Figure 6). Thus, while one might expect-intuitively and on the basis of the crystal structures of $\mathbf{2}$ and $\mathbf{6}^{[80]}$ —an arrangement with interdigitated alkyl chains in the case of the single-chain compounds 2 and 3, in contrast to an arrangement with non-interdigitated chains in the case of the double-chain compounds 6 and 7, all of the alkyl chains of the two molecules belonging to different ionic sublayers are always interdigitated in both series. When one subtracts the thickness of the ionic sublayers d_0 from the observed d values, one can see that the thickness of the aliphatic sublayers is even smaller than the length of one decyl or tetradecyl chain (Table 3). This means that the alkyl chains are not only interdigitated, but also highly folded.

One can estimate the cross-sectional area, σ_{chain} , of one fully stretched aliphatic chain as $\sigma_{\text{chain}} \approx (V_{\text{CH}}/1.27) \approx$

Table 3. Analysis of the layer thicknesses found for compounds 2, 6, 3 and 7.

	Subst. pattern ^[a]	d [Å] (at 140 ℃) ^[b]	$d_0 \ [m \AA]^{[c]}$	$\substack{(d-d_0)\ [{ m \AA}]^{[{ m d}]}}$	L _{chain} [Å] ^[e]
2	$4-C_{10}$	31.11	≈21.4	≈ 9.7	≈12.4
6	$3,4-C_{10}$	30.68	≈ 20.7	≈ 10.0	≈ 12.4
3	$4-C_{14}$	34.51	≈ 21.4	\approx 13.1	≈ 17.5
7	3,4-C ₁₄	34.91	≈ 20.7	≈ 14.2	≈ 17.5

[a] Substitution pattern of the aryl substituent: 4-(alkoxy) or 3,4-bis-(alkoxy). [b] *d* is the observed layer thickness of the SmA phase (Table 2). [c] d_0 is the estimated thickness of the ionic sublayer (see text). [d] $(d-d_0)$ corresponds to the thickness of the aliphatic sublayer (see text). [e] L_{chain} is the calculated length of one decyl or tetradecyl chain, respectively, in the most extended conformation (estimated with the Chem3D program, after energy minimisation by an MM2 calculation).

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[(26.5616 + 0.02023T)/1.27] (in which V_{CH_2} is the volume of one methylene group and T is the temperature in $^{\circ}C$).^[81] At 140 °C, σ_{chain} equals about 23.1 Å². Furthermore, the molecular volume, $V_{\rm M}$, can be estimated by using the relationship $V_{\rm M} = (M/0.6022)f$, in which M is the molecular mass (in $gmol^{-1}$) and f is a temperature-correcting factor (f= $0.9813 + 7.474 \times 10^{-4} T$ with T in °C).^[16] This allows us to calculate the molecular area, $A_{\rm M}$, as $2V_{\rm M}/d$, when considering a supramolecular assembly of two molecules with a head-tohead arrangement of ionic head groups. The following values were found at 140 °C: $A_{\rm M} \approx 52.9 \,\text{\AA}^2$ for 2, $A_{\rm M}$ \approx 53.6 Å² for **3**, $A_{\rm M} \approx$ 72.0 Å² for **6**, and $A_{\rm M} \approx$ 74.9 Å² for **7** (Table 2). This means that the fully interdigitated alkyl chains are folded to a larger extent in the case of 2 and 3 than in the case of 6 and 7, in which two and three alkyl chains, respectively, counterbalance the area occupied by the cationic head group and the iodide anion (see below).

Series 2-4: An $A_{\rm M}$ value of about 53 Å² is acceptable when one considers literature values for the cross-sectional areas of rod-like mesogenic groups (for example, 22-24 Å² for cyanobiphenyl groups) and for the area occupied by iodide anions (about 14.5 Å², since these anions have an ionic radius of 2.15 Å). Although the exact cross-sectional area of a 1,3-dimethyl-2-phenylimidazolium core is presently not known, it is clearly larger than that of a cyanobiphenyl group because of the protruding methyl groups. For compound 2, the values found for d, d_0 and A_M suggest that two orthogonally oriented ionic cores are arranged in a head-tohead manner in such a way that a strict alternation of positive and negative charges is maintained. However, a slight tilt of the rigid cores with respect to the layer normal cannot be excluded. Within the polar sublayers, the imidazolium cations are probably additionally linked by intermolecular short C-H.I contacts (see above). The alkyl chains attached to rigid cores that belong to adjacent polar sublayers need to interdigitate and fold to compensate for the crosssectional area of the ionic head groups (see above). Figure 7a shows a structural model of this system. When compared with the packing in the crystal structure of compound 2 (Figures S2 and S3 in the Supporting Information), this structure is reminiscent of the crystalline solid state. The SmA phases shown by compounds 3 and 4 have similar structures.

Series 5–7: In the case of compound 6, the calculated $A_{\rm M}$ value (\approx 72.0 Å² at 140 °C) is smaller than $4 \times \sigma_{\rm chain}$, but larger than $2 \times \sigma_{\rm chain}$. In fact, it is only slightly larger than $3 \times \sigma_{\rm chain}$ (\approx 69.3 Å² at 140 °C). Consequently, the cationic head group and the iodide anion are now counterbalanced by three alkyl chains (instead of two). Since 6 contains only two aliphatic chains, the third one originates from an imidazolium cation in the adjacent polar sublayer. The alkyl chains are folded to only a minor degree and the cationic head group is necessarily tilted (increase of $A_{\rm M}$ from 52.9 Å² for 2 to 72.0 Å² for 6). This also explains the slightly lower d_0 value found for 6 in comparison with 2. Figure 7b shows a



Figure 7. Structural models (idealised) for the SmA phases exhibited by a) 2 and b) 6. Iodide anions are represented by grey spheres (not in space-filling mode). The smectic layer thickness is indicated by d.

structural model. The SmA phases shown by compounds **5** and **7** have similar structures (slightly larger tilt for longer chain lengths). Of course, the SmA phase is an optically uniaxial mesophase, and therefore, there is no correlation in the direction of the tilt of the rigid cores. When compared with the crystal structure of compound **6** (Figure 2), the melting process involves softening of the alkyl chains to result in interdigitation, whereas the clearing process involves the breakdown of the polar sublayers. For longer rigid cores, SmC phases might appear instead of SmA phases (it should be noted that, surprisingly, the SmC phase is rarely found for ionic liquid crystals^[1,82]).

The proposed models are supported by an analysis based on Israelachvili's theory concerning the self-assembly of hydrocarbon amphiphiles.^[56] In this concept, packing constraints are considered by the critical parameter $P = V_{\rm alkyl}/(A_{\rm M}L_{\rm alkyl})$ (in which $V_{\rm alkyl}$ is the volume of the alkyl chain(s) and $L_{\rm alkyl}$ is the length of the alkyl chains in the most extended conformation). For a decyl chain, $L_{\rm alkyl}$ was estimated with Chem3D to be 12.37 Å (Table 3). At 140 °C, for the single-chain compound **2**, $P = [1 \times (9V_{\rm CH_2} + V_{\rm CH_3})]/[(52.9 Å^2)(12.37 Å)] \approx 0.46$, whereas for the doublechain compound **6**, $P = [2 \times (9V_{\rm CH_2} + V_{\rm CH_3})]/[(72.0 Å^2) (12.37 Å)] \approx 0.68$ ($V_{\rm CH_3}$ is the volume of one methyl group,

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estimated to be $27.14 \pm 0.01713T \pm 0.0004181T^2$, with *T* in °C ^[83]). Since for a lamellar arrangement *P* should be approximately 1, the aliphatic chains of opposing imidazolium head groups completely interdigitate and the theoretical number of chains per head group is two for $2 (2 \times 0.46 \approx 1)$, and three for $6 (1.5 \times 0.68 \approx 1)$, in agreement with the models in Figure 7.

Finally, it should be noted that $A_{\rm M}$ increases linearly as a function of temperature (Figure 8). This corresponds to an increased disordering of the molten aliphatic chains. Since compound 7 contains one alkyl chain more than compound 3, the slope of the $A_{\rm M}(T)$ curve is steeper in the case of 7. At the clearing point, the chain fluctuations have become so strong that the ionic layers collapse.



Figure 8. Evolution of $A_{\rm M}$ in the SmA phases of 3 (\blacksquare) and 7 (\square) as a function of temperature.

Mesophase structure of the Col_h phases: For longer chain lengths (n > 14), the double-chain compounds exhibit Col_h phases due to the increased curvature at the aromatic/ionicaliphatic interface. Indeed, the increased chain volume cannot be counterbalanced anymore by further tilting of the cationic rigid cores within a layer structure, and the layers collapse to form cylindrical superstructures. Conceptually, one can regard these cylinders as stacked slices that contain a certain number of molecules, which self-aggregate in such a way that the centre of one slice contains the polar moieties (microsegregation).^[19,23,29,84] In reality, for these tapershaped amphiphilic molecules there are no discrete slices (as known from the Col phases formed in lyotropic systems, and previously reported thermotropic systems^[61]), and the plane of the aromatic core can nearly freely rotate (no discrete π - π stacking distance has been observed by powder XRD in any of the Col phases formed by simple tapershaped amphiphilic compounds, and this is also the case for the compounds presented herein). However, in the following sections we will analyse the powder XRD data using a simplified/idealised model wherein the columnar structures

in the Col_h phases do consist of stacked slices that contain multiple taper-shaped molecules.

From the lattice parameter a_{Col} determined for **11** (\approx 42.0 Å at 155 °C), the cross-sectional area, *S*, of one column can be estimated as $(\sqrt{3}/2)a_{Col}^2 = 1529$ Å² (Table 2). Consequently, the column radius, *r*, is about 22.1 Å at 155 °C; the calculated length *L* of the 1,3-dimethyl-2-[3,4-bi-s(octadecyloxy)phenyl]imidazolium cation in its most extended conformation (estimated by using the Chem3D program; the structure of the imidazolium cation was energy-minimised by an MM2 calculation within Chem3D) is 32.1 Å. When comparing the values for *r* and *L*, it appears that the aliphatic chains of adjacent columns need to interdigitate. This is also required for an efficient filling of the space remaining at the periphery of a column slice (see below).^[29] The columnar cross-section, *S*, decreases with increasing temperature (Figure 9), indicating a shrinkage of



Figure 9. Evolution of the columnar cross-section, *S*. in the Col_h phases of **8** (\blacksquare), **9** (\square), **10** (\bigcirc) and **11** (\bigcirc) as a function of temperature.

the column slices due to the higher thermal mobility of the alkyl chains and increasing disorder at higher temperatures. The slope of the S(T) curves is comparable for all compounds in the series 8–11.

The area *S* also increases linearly with the number of carbon atoms *n* in the alkyl chains [Eq. (3) for the series **8**–**11** (at 155 °C) and Figure 10]:

$$S (in Å2) = 490(\pm 42) + 58(\pm 3)n$$
(3)

From Equation (3), the cross-sectional area S_0 of the nonaliphatic centre of the columns can be estimated to be approximately 490 Å² for the series **8–11** at 155 °C. Thus, the radius r_0 of the central part of the columns is about 12 Å.

With the data currently at our disposal, we cannot deduce the precise arrangement of the cationic rigid cores and the iodide anions within the central part of the columns. It is important to note, however, that our compounds must show a different arrangement in the Col_h phase than the *N*-alkyl-

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substituted imidazolium-based mesogens reported by the groups of Kato,^[19,21] Douce,^[23] Percec,^[66] and Tschierske.^[29] When one positions the imidazolium planes perpendicular to the columnar axes and the aliphatic chains in a slice radially pointing away from the column centre, the central part of the columns cannot be filled by the alkyl groups that are attached to the nitrogen atoms. Indeed, the H-4 and H-5 atoms of the imidazolium rings would point towards the centre in such an arrangement. At the same time, different molecules in a slice, with more or less co-planar imidazolium rings, cannot approach each other very closely because of steric hindrance between the protruding methyl groups of adjacent molecules. It is highly improbable that the resulting central void is completely filled by the iodide anions due to mutual repulsions. A model in which the long axes of the molecules in a slice (these axes coincide with the bond between the imidazolium ring and the aryl substituent) nearly coincide with tangent lines to the column centre, so that one or both methyl groups point towards the centre, also seems improbable. Therefore, we propose a model in which the imidazolium planes of adjacent ionic head groups are on average more or less perpendicular to the plane of the column slice (i.e., on average parallel to the columnar long axis). This allows a closer packing of the imidazolium groups because of a reduced steric hindrance between the protruding methyl groups, as well as an efficient charge alternation between cations and anions. Recently, a Col_h mesophase in which rod-like mesogenic units with hydrogenbonding polar groups lie parallel to the columnar long axes was reported, which supports the structure proposed in Figure 11.^[85] The aromatic rings connected to the imidazolium groups are assumed to lay more or less in the plane of the column slice (but let us recall that the concept of discrete slices is a simplification for taper-shaped amphiphilic molecules). As seen in the crystal structures of compounds 2 and 6, the imidazolium rings are at an angle to the benzene rings. The observation of a halo centred at about 6.6 Å in



Figure 11. Structural model (idealised) for one column in the Col_h phase exhibited by compound **11** (at 155 °C). The columns are arranged in a two-dimensional hexagonal lattice with the lattice parameter $a_{Col} = 42.0$ Å. The outer, solid circle indicates the imaginary edge of the column with a diameter of $r \approx 22.1$ Å. The inner, dashed circle indicates the imaginary edge of the non-aliphatic column centre with a diameter of $r_0 \approx 12$ Å. The imidazolium planes, on average perpendicular to the plane of the column slice, are represented by grey rectangles. The methyl groups and hydrogen atoms attached to the imidazolium rings are represented by small grey (C atoms) and white (H atoms) circles, respectively. Iodide anions are represented by grey spheres (not in space-filling mode).

the diffractograms of the Col_h phases (denoted as h_1 in Figure 12) completely supports the proposed model. Indeed, the width of a 1,3-dimethylimidazolium cation (with the methyl groups lying in the plane of the imidazolium ring) is about 6.2 Å (estimated from the crystal structure of **6**, and with Chem3D). Thus, the height h_1 of one column slice is about 6.6 Å. The influence of the replacement of one of the methyl groups by a longer alkyl chain is currently being investigated. This newly found cation–anion arrangement is



Figure 12. X-ray diffractogram of **11** in the Col_h phase at 155 °C, represented as the scattering intensity (in counts) versus the scattering angle, 2θ . The broad diffraction signal between $2\theta \approx 5.6^{\circ}$ and 7.6° is due to the covering foil used in the experimental setup.

expected to have an influence on the dynamic ionic conductivity measured parallel to the columnar axes of an aligned sample (experiments by Kato et al.^[19–21]).

The number of molecules that self-aggregate within one slice of height $h_1 \approx 6.6$ Å can be estimated as $N_{\text{slice}} = h_1 S(N_A/M)\rho$ (in which N_A is the Avogadro constant and M is the molecular mass (in g mol⁻¹); Table 2). By assuming a density of $\rho = 1.0 \text{ g cm}^{-3}$, this gives a value of 7.2 for **11** at 155 °C. The model that we propose for the Col_h phase shown by compound **11**, by considering the values for a_{Col} , S, S_0 , h_1 and N_{slice} , and the conclusions drawn above, is displayed in Figure 11. For the most efficient packing, the molecules in adjacent column slices are rotated by about 26° (=[360°/(7 molecules per slice)]/2). The Col_h phases shown by compounds **8**, **9** and **10** have a similar structure. The model presented in Figure 11 is different from the structure of the Col_h phases shown by polycatenar mesogens, which arrange into columns in a totally different way.^[49]

Again, a packing constraint analysis similar to that described above for 2 and 6 can be applied to the Col_h phase of compound 11. For an octadecyl chain, L_{alkyl} was estimated with the Chem3D program to be 22.57 Å (after energy minimisation by an MM2 calculation). At 155°C, the critical parameter $P = V_{alkyl} / (A_M L_{alkyl}) = [2 \times (17V_{CH_2} + V_{CH_3})] / [(54.5 \text{ Å}^2)]$ $(22.57 \text{ Å})] \approx 0.89$ [the value of $A_{\rm M} \approx 54.5 \text{ Å}^2$ is the one obtained for compound 4 in the SmA phase at 155°C; in Figure 11 the cross-sectional area of a cationic rigid core and an iodide anion in a tangent plane to the column formed by the polar moieties is comparable to that of the untilted head groups in the SmA phases of compounds 2-4]. Because of interdigitation (see above), the theoretical number of chains per head group is actually four, $P \approx 1.78$. A value for P that exceeds one indeed corresponds to an inverted micellar structure of amphiphiles (with the micellar structures having a cylindrical shape in the case of a columnar mesophase).

As noted by Douce et al., it is reasonable to assume that the columnar structure described above is retained during the Col_h-to-Cub phase transition on cooling the Col_h phase of compound **8** (i.e., the minicolumns forming the rod networks in the multicontinuous Cub phase reflect the structure of the columns in the higher-temperature columnar phase).^[23] They point out that molecular flexibility is important in this aspect and that this transformation may occur through regular column undulations and interconnections, which increase substantially with decreasing temperature.

Conclusion

Synthetic strategies were developed to prepare a homologous series of 1,3-dimethyl-2-[4-(alkoxy)phenyl]imidazolium and 1,3-dimethyl-2-[3,4-bis(alkoxy)phenyl]imidazolium salts. Whereas only SmA phases were found for the former compounds, the latter salts showed SmA, multicontinuous Cub as well as Col_h phases, depending on the chain length. To the best of our knowledge, the enantiotropic Cub phase of compound **8** is the first example of a thermotropic Cub mesophase of $Pm\bar{3}m$ symmetry. Structural models were proposed to describe the molecular organisation within the SmA and Col_h phases. It turned out that the imidazolium head groups and the iodide counterions adopt a peculiar orientation in the central part of the columns of the columnar phases.

The new rigid-core structure offers opportunities as a versatile scaffold to synthesise more elaborate molecular architectures by using appropriately substituted benzaldehyde compounds. Substitution of the nitrogen atoms of the imidazolium ring and the choice of the anion will allow the transition temperatures and phase behaviour to be fine-tuned. Current research efforts focus on the replacement of the iodide anions by more asymmetric and/or functional anions. The mesomorphic behaviour of 2-arylsubstituted imidazolium salts with these anions and that of the corresponding 2arylsubstituted benzimidazolium salts will be published elsewhere. The thermal behaviour of 2-arylsubstituted imidazolium salts with an elongated aryl substituent (i.e., containing more than one aromatic ring, resulting in increasing shape anisotropy) is being investigated as well. The latter compounds might be interesting as materials displaying nonlinear optical properties because of the inherent donor-acceptor structure (provided that no centrosymmetric structure is formed in the mesophase).^[86]

Experimental Section

General: NMR spectra were recorded on a Bruker Avance 300 spectrometer (operating at 300 MHz for ¹H), a Bruker AMX-400 spectrometer (operating at 400 MHz for ¹H) or a Bruker Avance II⁺ 600 spectrometer (operating at 600 MHz for 1 H). Abbreviations used for the description of the spectra are s=singlet, d=doublet, dd=doublet of doublets, t=triplet and m=multiplet. Chemical shifts are given in ppm relative to tetramethylsilane (TMS) (when CDCl₃ or CD₃OD was used as a solvent) or to the solvent peak (when CD₂Cl₂ was used as a solvent). Elemental analyses (carbon, hydrogen and nitrogen) were obtained from a CE Instruments EA-1110 elemental analyser. The results in percentages were interpreted allowing a deviation of ± 0.4 %. ESI mass spectra were recorded on a Thermo Finnigan LCQ Advantage mass spectrometer. Optical textures of the mesophases were observed with an Olympus BX60 polarising optical microscope equipped with a LINKAM THMS600 heating stage and a LINKAM TMS93 programmable temperature controller. DSC traces were recorded under helium with a Mettler-Toledo DSC822e module. Heating/cooling rates are specified in the captions of the thermograms. Indium was used as a standard for temperature and enthalpy calibrations. Thermal stability was assessed by TGA under nitrogen with a TA Instruments SDT Q600 thermal analyser. Heating rates are specified in the captions of the thermograms. Powder XRD patterns were recorded with a Bruker AXS D8 Discover diffractometer mounted with a copper X-ray ceramic tube, working at 1.6 kW. The emitted $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å) was focused on the sample by a Göbel mirror. All of the samples were prepared by spreading the powders on a thin cleaned silicon wafer. Diffraction patterns were collected by using the Bragg-Brentano reflection geometry ($\theta/2\theta$ setup) at an angular resolution (in 2θ) of 0.03° per step. The scattered signal was recorded by a one-dimensional detector (LynxEye detector). Indexation of the powder X-ray diffractograms was performed with the WinX^{POW} program package, with the Index & Refine program by using Werner's TREOR algorithm pro-

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gram.^[87,88] Molecular models were obtained with the Chem3D software package from CambridgeSoft.

For the determination of the crystal structures of compounds 2c, 2 and 6, X-ray intensity data were collected at 100 K on a SMART 6000 diffractometer equipped with a CCD detector, using $Cu_{K\alpha}$ radiation ($\lambda =$ 1.5418 Å) and making use of ϕ and ω scans. The images were interpreted and integrated with the program SAINT from Bruker.^[89] All structures were solved by direct methods and refined by full-matrix least-squares techniques on F² by using the SHELXTL program package.^[90] Non-hydrogen atoms were refined anisotropically and hydrogen atoms in riding mode with isotropic temperature factors fixed at 1.2 U(eq) of the parent atoms (1.5 U(eq) for methyl groups). CCDC-782251 (2c) and 782252 (6) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The provisional crystal data for compound 2 are given in the Supporting Information. 2c: $C_{19}H_{28}N_2O; M = 300.44 \text{ gmol}^{-1}; \text{ monoclinic}; P2_1/c \text{ (no. 14)}; a = 24.064(1),$ 100(2) K; Z=8; $\rho_{\text{calcd.}}=1.179 \text{ g cm}^{-3}$; $\mu(\text{Cu}_{\text{K}\alpha})=0.561 \text{ mm}^{-1}$; F(000)=1312; crystal size $0.4 \times 0.15 \times 0.1$ mm; 5964 independent reflections ($R_{int} =$ 0.0887). Final R = 0.0552 for 3850 reflections with $I > 2\sigma(I)$ and $wR_2 =$ 0.1457 for all data. 6: $C_{31}H_{53}IN_2O_2$; $M = 612.67 \text{ g mol}^{-1}$; triclinic; $P\overline{1}$ (no. 2); a = 7.3299(4), b = 11.2460(5), c = 39.019(2) Å; a = 88.599(2), $\beta = 11.2460(5)$ 87.604(2), $\gamma = 88.138(3)^{\circ}$; $V = 3211.0(3) \text{ Å}^3$; T = 100(2) K; Z = 4; $\rho_{\text{calcd.}} =$ 1.267 g cm⁻³; μ (Cu_{K α}) = 8.032 mm⁻¹; F(000) = 1288; crystal size 0.4 × 0.3 × 0.15 mm; 11130 independent reflections ($R_{int}=0.0481$). Final R=0.0453for 10072 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.1159$ for all data.

General procedure for the synthesis of 1-3 and 5-6: A solution of the appropriate precursor (1c-3c, 5c-6c) (1 equiv) in dry THF was added dropwise to an ice-cooled stirred suspension of NaH (1.5 equiv of a 60 % dispersion in mineral oil) in dry THF in a three-necked round-bottomed flask. The mixture was stirred for 1 h at room temperature and for 1 h at 55°C under an argon atmosphere (the formation of hydrogen gas could be observed by the formation of bubbles in the solution). After cooling to room temperature, iodomethane (20 equiv) was added dropwise and the mixture was further stirred at the same temperature for 1 h, protected from light. Then the reaction mixture was quickly transferred from the round-bottomed flask to a screw-cap vial. The mixture was further stirred overnight at 70 °C, protected from light. After cooling to room temperature, dichloromethane was added and the reaction mixture was filtered. The solvent and excess iodomethane were removed under reduced pressure. The residue was dissolved in dichloromethane and washed with water. After removal of the solvent under reduced pressure, the product was stirred in n-hexane at 50 °C for 30 min. The precipitate was filtered off and washed with n-hexane. The pure compound was obtained as a pale yellow to yellow powder. It was dried in vacuo at 50 °C for 24 h, and stored in a container protected from light.

Compound **1**: Additional purification on a silica column with chloroform/ methanol (95:5) as the eluent gave **1** (0.68 g, 42%). ¹H NMR (300 MHz, CD₂Cl₂, 25°C): δ =0.90 (t, *J*=6.2 Hz, 3H; CH₃-CH₂), 1.28–1.46 (m, 6H; CH₂), 1.81 (quintet, *J*=6.9 Hz, 2H; O-CH₂-CH₂), 3.81 (s, 6H; N-CH₃), 4.05 (t, *J*=6.5 Hz, 2H; O-CH₂), 7.13 (d, *J*_o=8.6 Hz, 2H; H-aryl), 7.56 (d, *J*_o=8.6 Hz, 2H; H-aryl), 7.74 ppm (s, 2H; N-CH=CH-N); ¹³C NMR (100 MHz, CDCl₃, 25°C): δ =14.0, 22.6, 25.7, 29.0, 31.5, 36.8, 68.6, 100.0, 111.7, 115.9, 123.6, 132.4, 145.1, 162.5 ppm; ESI-MS (methanol): *m/z* (%): 273.5 (100) [*M*–I]⁺, 673.1 (5) [*M*+*M*–I]⁺; elemental analysis calcd (%) for C₁₇H₂₅IN₂O (400.30): C 51.01, H 6.29, N 7.00; found: C 50.90, H 6.61, N 6.91.

Compound **2**: Yield: 82% (0.50 g); ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ =0.87 (t, *J*=5.9 Hz, 3H; CH₃-CH₂), 1.23–1.51 (m, 14H; CH₂), 1.81 (quintet, *J*=6.8 Hz, 2H; O-CH₂-CH₂), 3.81 (s, 6H; N-CH₃), 4.05 (t, *J*=6.4 Hz, 2H; O-CH₂), 7.14 (d, *J*_o=8.3 Hz, 2H; H-aryl), 7.55 (d, *J*_o=8.3 Hz, 2H; H-aryl), 7.71 ppm (s, 2H; N-CH=CH-N); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ =14.2, 22.8, 26.1, 29.1, 29.38, 29.41, 29.6, 32.0, 37.0, 68.7, 111.7, 115.9, 123.6, 132.5, 145.3, 162.6 ppm; ESI-MS (methanol): *m/z* (%): 329.6 (100) [*M*–I]⁺, 785.1 (5) [*M*+*M*–I]⁺; elemental analysis calcd (%) for C₂₁H₃₃IN₂O·0.5H₂O (465.41): C 54.19, H 7.36, N 6.02; found: C 54.05, H 7.58, N 5.97.

Compound **3**: Yield: 92% (1.19 g); ¹H NMR (300 MHz, CDCl₃, 25 °C): δ =0.88 (t, *J*=6.0 Hz, 3H; CH₃-CH₂), 1.20–1.52 (m, 22 H; CH₂), 1.82 (quintet, *J* = 7.0 Hz, 2H; O-CH₂-CH₂), 3.87 (s, 6H; N-CH₃), 4.04 (t, *J* = 6.5 Hz, 2H; O-CH₂), 7.12 (d, *J*_o=7.9 Hz, 2H; H-aryl), 7.65 (d, *J*_o=7.9 Hz, 2H; H-aryl), 7.85 ppm (s, 2H; N-CH=CH-N); ¹³C NMR (75 MHz, CD₂Cl₂, 25 °C): δ =14.2, 22.8, 26.1, 29.1, 29.4, 29.6, 29.7, 29.8, 32.0, 37.0, 68.7, 111.7, 115.9, 123.6, 132.5, 145.2, 162.5 ppm; ESI-MS (methanol): *m/z* (%): 385.9 (100) [*M*–I]⁺; elemental analysis calcd (%) for C₂₅H₄₁IN₂O (512.51): C 58.59, H 8.06, N 5.47; found: C 58.37, H 8.36, N 5.55.

Compound **5**: Additional purification on a silica column with chloroform/methanol (95:5) as the eluent gave **5** (0.80 g, 55%). ¹H NMR (300 MHz, CD₂Cl₂, 25°C): δ =0.84–0.93 (m, 6H; CH₃-CH₂), 1.17–1.58 (m, 12H; CH₂), 1.81 (quintet, *J*=7.6 Hz, 4H; O-CH₂-CH₂), 3.81 (s, 6H; N-CH₃), 4.05 (t, *J*=5.9 Hz, 4H; O-CH₂), 7.00–7.40 (m, 3H; H-aryl), 7.74 ppm (s, 2H; N-CH=CH-N); ¹³C NMR (100 MHz, CDCl₃, 25°C): δ = 14.1, 22.6, 25.8, 29.0, 29.2, 31.56, 31.63, 36.8, 69.3, 70.1, 111.9, 113.4, 115.0, 123.5, 124.0, 145.2, 149.9, 152.7 ppm; ESI-MS (methanol): *m/z* (%): 373.7 (100) [*M*–I]⁺, 873.1 (5) [*M*+*M*–I]⁺; elemental analysis calcd (%) for C₂₃H₃₇IN₂O₂ (500.46): C 55.20, H 7.45, N 5.60; found: C 55.14, H 7.82, N 5.51.

Compound **6**: Yield: 81% (1.08 g); ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ =0.87 (t, *J*=5.6 Hz, 6H; CH₃-CH₂), 1.17–1.60 (m, 28 H; CH₂), 1.82 (quintet, *J*=7.5 Hz, 4H; O-CH₂-CH₂), 3.81 (s, 6H; N-CH₃), 4.03 (t, *J*=6.2 Hz, 2H; O-CH₂), 4.07 (t, *J*=6.3 Hz, 2H; O-CH₂), 7.00–7.40 (m, 3H; H-aryl), 7.70 ppm (s, 2H; N-CH=CH-N); ¹³C NMR (150 MHz, CDCl₃, 25 °C): δ =14.2, 22.8, 26.08, 26.14, 29.1, 29.3, 29.45, 29.46, 29.5, 29.66, 29.70, 32.0, 36.9, 69.3, 70.2, 111.9, 113.5, 115.2, 123.5, 124.0, 145.4, 150.0, 152.7 ppm; ESI-MS (methanol): *m*/*z* (%): 486.0 (100), [*M*–I]⁺; elemental analysis calcd (%) for C₃₁H₅₃IN₂O₂·0.5H₂O (621.68): C 59.89, H 8.76, N 4.51; found: C 59.93, H 8.89, N 4.40.

General procedure for the synthesis of 4, 7-11: Iodomethane (20 equiv) was added dropwise to a solution of the appropriate precursor (4e, 7e-11e) (1 equiv) in dry THF. The mixture was stirred for 1 h at room temperature under an argon atmosphere, protected from light. Then, it was transferred from the round-bottomed flask to a screw-cap vial, and was further stirred overnight at 70 °C, protected from light. The solvent and excess iodomethane were removed under reduced pressure. The pure product was obtained as a pale yellow to yellow powder and was dried in vacuo at 50 °C for 24 h, and stored in a container protected from light. Compound 4: Yield: 89% (0.60 g); ¹H NMR (400 MHz, CDCl₃, 25°C): $\delta = 0.83$ (t, J = 6.9 Hz, 3H; CH_3 -CH₂), 1.20–1.54 (m, 30H; CH₂), 1.78 (quintet, J = 7.1 Hz, 2H; O-CH₂-CH₂), 3.83 (s, 6H; N-CH₃), 4.00 (t, J =6.5 Hz, 2H; O-CH₂), 7.08 (d, $J_o = 8.7$ Hz, 2H; H-aryl), 7.61 (d, $J_o =$ 8.7 Hz, 2H; H-aryl), 7.81 ppm (s, 2H; N-CH=CH-N); ¹³C NMR $(100 \text{ MHz}, \text{ CDCl}_3, 25 \,^{\circ}\text{C}): \delta = 14.1, 22.7, 26.0, 29.1, 29.35, 29.37, 29.57,$ 29.61, 29.65, 29.69, 31.9, 36.9, 68.6, 111.7, 115.9, 123.5, 132.5, 145.2, 162.5 ppm; ESI-MS (methanol): m/z (%): 442.0 (100) $[M-I]^+$, 1009.3 (2) $[M+M-I]^+$; elemental analysis calcd (%) for C₂₉H₄₉IN₂O (568.62): C 61.26, H 8.69, N 4.93; found: C 60.98, H 8.84, N 4.91.

Compound 7: Yield: 96% (0.19 g); ¹H NMR (300 MHz, CDCl₃, 25 °C): δ =0.88 (t, *J*=6.4 Hz, 6H; CH₃-CH₂), 1.18–1.65 (m, 44H; CH₂), 1.77–1.93 (m, 4H; O-CH₂-CH₂), 3.85 (s, 6H; N-CH₃), 4.07 (t, *J*=6.4 Hz, 4H; O-CH₂), 7.04 (d, *J*_o=8.3 Hz, 1H; H-aryl), 7.17 (dd, *J*_o=8.3 Hz, *J*_m=1.7 Hz, 1H; H-aryl), 7.31 (d, *J*_m=1.7 Hz, 1H; H-aryl), 7.72 ppm (s, 2H; N-CH=CH-N); ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ =14.3, 22.8, 26.2, 29.2, 29.3, 29.5, 29.6, 29.78, 29.82, 29.9, 32.1, 36.9, 69.4, 70.2, 111.8, 113.4, 115.3, 123.4, 123.9, 145.6, 150.1, 152.8 ppm; ESI-MS (methanol): *m*/*z* (%): 598.1 (100) [*M*-I]⁺, 1321.5 (5) [*M*+*M*-I]⁺; elemental analysis calcd (%) for C₃₉H₆₉IN₂O₂ (724.88): C 64.62, H 9.59, N 3.86; found: C 64.41, H 9.90, N 4.01.

Compound **8**: Yield: 94% (0.58 g); ¹H NMR (300 MHz, CDCl₃, 25 °C): δ =0.88 (t, *J*=6.4 Hz, 6H; CH₃-CH₂), 1.17–1.62 (m, 48H; CH₂), 1.77–1.93 (m, 4H; O-CH₂-CH₂), 3.85 (s, 6H; N-CH₃), 4.07 (t, *J*=6.2 Hz, 4H; O-CH₂), 7.04 (d, *J*_o=8.3 Hz, 1H; H-aryl), 7.17 (dd, *J*_o=8.3 Hz, *J*_m= 1.6 Hz, 1H; H-aryl), 7.29 (d, *J*_m=1.6 Hz, 1H; H-aryl), 7.75 ppm (s, 2H; N-CH=CH-N); ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ =14.3, 22.8, 26.1, 26.2, 29.2, 29.3, 29.5, 29.6, 29.78, 29.81, 29.9, 32.1, 36.9, 69.4, 70.2, 111.9, 113.4, 115.2, 123.4, 123.9, 145.5, 150.0, 152.8 ppm; ESI-MS (methanol):

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m/z (%): 626.0 (100) $[M-I]^+;$ elemental analysis calcd (%) for $C_{41}H_{73}IN_2O_2$ (752.94): C 65.40, H 9.77, N 3.72; found: C 65.25, H 9.62, N 3.75.

Compound **9**: Yield: 92% (0.56 g); ¹H NMR (300 MHz, CDCl₃, 25 °C): δ =0.88 (t, *J*=6.4 Hz, 6H; CH₃-CH₂), 1.17–1.60 (m, 52H; CH₂), 1.78–1.96 (m, 4H; O-CH₂-CH₂), 3.84 (s, 6H; N-CH₃), 4.07 (t, *J*=6.4 Hz, 4H; O-CH₂), 7.04 (d, *J*_o=8.3 Hz, 1H; H-aryl), 7.16 (dd, *J*_o=8.3 Hz, *J*_m could not be determined because the doublet of doublets was not fully resolved, 1H; H-aryl), 7.31 (d, *J*_m=1.9 Hz, 1H; H-aryl), 7.69 ppm (s, 2H; N-CH=CH-N); ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ =14.3, 22.8, 26.15, 26.21, 29.2, 29.3, 29.5, 29.6, 29.8, 29.9, 32.1, 36.9, 70.2, 111.8, 113.4, 115.3, 123.4, 145.5, 150.1, 152.8 ppm; ESI-MS (methanol): *m/z* (%): 654.0 (100) [*M*–I]⁺; elemental analysis calcd (%) for C₄₃H₇₇IN₂O₂ (780.99): C 66.13, H 9.94, N 3.59; found: C 66.07, H 10.32, N 3.63.

Compound **10**: Yield: 95% (0.57 g); ¹H NMR (300 MHz, CDCl₃, 25 °C): δ =0.88 (t, *J*=6.5 Hz, 6H; CH₃-CH₂), 1.15–1.60 (m, 56H; CH₂), 1.78–1.95 (m, 4H; O-CH₂-CH₂), 3.84 (s, 6H; N-CH₃), 4.07 (t, *J*=6.4 Hz, 4H; O-CH₂), 7.04 (d, *J_o*=8.3 Hz, 1H; H-aryl), 7.17 (dd, *J_o*=8.3 Hz, *J_m*= 1.9 Hz, 1H; H-aryl), 7.32 (d, *J_m*=1.9 Hz, 1H; H-aryl), 7.70 ppm (s, 2H; N-CH=CH-N); ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ =14.3, 22.8, 26.2, 29.2, 29.3, 29.5, 29.6, 29.8, 29.9, 32.1, 36.9, 69.4, 70.2, 111.8, 113.4, 115.3, 123.4, 123.9, 145.6, 150.1, 152.8 ppm; ESI-MS (methanol): *m/z* (%): 682.0 (100) [*M*-I]⁺; elemental analysis calcd (%) for C₄₅H₈₁IN₂O₂ (809.04): C 66.81, H 10.09, N 3.46; found: C 67.03, H 10.42, N 3.49.

Compound **11**: Yield: 98 % (0.33 g); ¹H NMR (300 MHz, CDCl₃, 25 °C): δ =0.88 (t, *J*=6.5 Hz, 6H; CH₃-CH₂), 1.15–1.62 (m, 60H; CH₂), 1.78–1.95 (m, 4H; O-CH₂-CH₂), 3.85 (s, 6H; N-CH₃), 4.07 (t, *J*=6.4 Hz, 4H; O-CH₂), 7.04 (d, *J_o*=8.3 Hz, 1H; H-aryl), 7.17 (dd, *J_o*=8.3 Hz, *J_m* could not be determined because the doublet of doublets was not fully resolved, 1H; H-aryl), 7.30 (s, 1H; H-aryl), 7.72 ppm (s, 2H; N-CH=CH-N); ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ =14.3, 22.8, 26.15, 26.21, 29.2, 29.3, 29.5, 29.6, 29.8, 29.9, 32.1, 36.9, 69.4, 70.2, 111.8, 113.4, 115.3, 123.4, 123.9, 145.6, 150.1, 152.8 ppm; ESI-MS (methanol, *m/z*) (%): 710.2 (100) [*M*−I]⁺, 1545.6 (5) [*M*+*M*−I]⁺; elemental analysis calcd (%) for C₄₇H₈₅IN₂O₂ (837.09): C 67.44, H 10.23, N 3.35; found: C 67.33, H 10.51, N 3.41.

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