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Polycatenar 1*H*-imidazole amphiphiles, consisting of a 1*H*-imidazole head connected through a benzene ring to a trialkyloxyphenyl tail, were synthesized and their self-assembling properties investigated. The ¹H NMR and fluorescence spectroscopy studies showed that in nonpolar solvents, the amphiphiles formed reverse micelles in which the hydrophilic imidazole heads aggregated inside the micelles through intermolecular hydrogen bonding and the nonpolar alkyl chains were located at the periphery of the micelles. In concentrated solutions, they formed lyotropic liquid crystals having columnar hexagonal structures. The molecules were arranged in a disk *via* hydrogen bonding between successive imidazole moieties. When dilute solutions of the amphiphiles in *n*-hexane (0.1 wt%) were spin-coated on to a plasma-cleaned Si wafer, a band-like structure with a width of 60–100 nm was imaged by AFM. Microscopic fiber bundles with a diameter as large as 13 μm were observed by SEM when the lyotropic liquid crystals in 30 wt% hexane solution were dried on the glass.

Introduction

The self-assembly of amphiphilic molecules consisting of a hydrophilic head and one or more hydrophobic tails has been extensively studied for the synthesis of molecular and supramolecular materials.¹ Depending on their molecular structure and the environment, these amphiphilic molecules form various ordered aggregates. For example, amphiphilic molecules self-assemble into spherical micelles, cylindrical worm-like micelles and bilayers in aqueous solution. They form reverse aggregates such as a reverse micelle in nonpolar organic solvents.

There have also been reports of amphiphilic aromatic molecules containing polar substituents and flexible chains that order into columnar liquid crystalline phases. Columnar mesophases represent highly ordered supramolecular structures, generally obtained by self-organization of disk shaped molecules.² Certain molecules with non disk-like shape can also form discotic mesophases through supramolecular assembly.³ The driving forces for the self-assembly of a nondiscotic molecule to form a disk-like structure include hydrogen bonding, charge-transfer and ionic interactions.

1*H*-Imidazole and its derivatives are of great interest due to their important roles in biological systems, particularly in enzymes, as a proton donor and/or acceptor, ligands of coordination systems and the base of charge-transfer processes. Unlike pyrrole as a proton donor and pyridine as a proton acceptor, 1*H*-imidazole has both proton donor and acceptor properties.^{4,5} Imidazole functionalities have been

used for complexation reactions with different molecular components such as carboxylic acids to obtain liquid crystal-line assemblies.⁶ Recently we reported the self-assembly of linear 1*H*-imidazole amphiphiles in a one component system.⁷ The amphiphiles, where an imidazole head was connected to a hydrophobic alkyloxyphenyl group through an ester linkage, formed organogels. In the gel state, the intermolecular hydrogen bonding between 1*H*-imidazole heads was observed by ¹H NMR analysis, which could be a driving force for the gelation. The strong self-assembly tendency of the 1*H*-imidazole amphiphiles to build supramolecular structures led us to further study their self-assembling behavior with varying structures.

In this paper, we report the synthesis and self-assembling properties of polycatenar 1*H*-imidazole amphiphiles, consisting of a 1*H*-imidazole head connected through a benzene ring to a trialkyloxyphenyl tail. Polycatenar mesogens have attracted a considerable amount of attention because they are considered intermediates between rod-like and disk-like mesogenic compounds. Studies showed that the compounds should have at least three benzene rings to exhibit mesophases.⁸ Despite the fact that 1*H*-imidazole amphiphiles prepared in this work contain only two benzene rings, they form columnar liquid crystals in a concentrated solution and aggregate into bundles at the surface of silicon.

Results and discussion

Synthesis

Synthesis of the 1*H*-imidazole amphiphiles (**5–7**) is outlined in Scheme 1. Alkyloxy tails were introduced to 3,4,5-trihydroxybenzoate by reaction with 1-bromoalkane (*n* = 8, 10, 12) in DMF to yield compounds **1**. After hydrolysis, the resulting trialkyloxybenzoic acids (**2**) were converted to the corresponding benzoyl chlorides (**3**) with thionyl chloride and reacted with

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Scheme 1 Synthesis of 1H-imidazole amphiphiles.

hydroquinone in THF to give the corresponding hydroxyphenyl trialkoxybenzoates (**4**). Esterification of compounds **4a–c** with 4-chlorocarbonyl imidazole under basic conditions gave compounds **5–7**.

Solution properties

4-Chlorocarbonyl imidazole and hydroxyphenyl trialkoxybenzoates **4a–c**, the reactants in the synthesis of compounds **5–7**, showed poor solubility in nonpolar organic solvents; in contrast, the resulting 1H-imidazole amphiphiles (**5–7**) were soluble in hydrocarbons, CHCl_3 , methylene chloride and THF. These amphiphiles were insoluble in polar solvents such as methanol, H_2O , DMF and DMSO. High solubilities of the amphiphiles in nonpolar solvents suggest that the polar imidazole groups aggregate toward the interior to prevent their exposure to the solvent.

To further understand the behavior of these amphiphiles, the aggregation behavior of **6** in nonpolar solvents was investigated by ^1H NMR spectroscopy. The ^1H NMR spectrum of **6** recorded in chloroform- d_1 (1 wt%) showed the signals corresponding to all its protons (The ^1H NMR data are summarized in the experimental section). However, when the spectrum was taken in cyclohexane- d_{12} (1 wt%) at 20 °C, only the alkyl peaks appeared at 0.8–1.9 ppm (Fig. 1). At 60 °C, the characteristic signals associated with imidazole, the phenyl rings and the oxymethylene protons appeared at 7.7, 7.0 and 3.9 ppm, respectively. As the temperature was increased, the signals of these protons became shaper and stronger. These results suggest that in cyclohexane compound **6** formed reverse micelles in which the hydrophilic imidazole head groups were confined to the interior while the nonpolar alkyl chains were located at the periphery of the micelle. The hydrogen bonding

between 1H-imidazole groups in combination with solvophobic interactions between aromatic groups along with favorable interactions between cyclohexane and the alkyl tails would lead to the formation of a micelle. ^1H NMR studies on amphiphiles **5** and **7** showed the same results.

To further shed light on the self-assembly of **6** in nonpolar solvents, fluorescence emission spectra ($\lambda_{\text{ex}} = 279$ nm) in *n*-hexane were measured at room temperature. In a very dilute solution (1.00×10^{-6} M), the compound showed weak photoluminescence emission. Upon increasing the concentration gradual bathochromic shifts from $\lambda_{\text{max}} = 347$ to 435 nm were observed along with a strong enhancement of fluorescence intensity (Fig. 2), suggesting that the molecules were being aggregated into a micelle. The critical micelle

Fig. 1 ^1H NMR spectra of compound **6** taken in cyclohexane- d_{12} (1 wt%) at 20 and 60 °C.

Fig. 2 Fluorescence emission spectra of compound **6** in *n*-hexane at various concentrations ($\lambda_{\text{ex}} = 279$ nm).

concentration (cmc) was determined to be 1.25×10^{-5} M, based on the λ_{max} shift according to the concentration.

Liquid crystalline behavior

Compounds **5–7** showed birefringent mesophases in concentrated *n*-hexane solutions under a polarizing optical microscope, indicating that lyotropic liquid crystals formed. These solutions (30 wt% in *n*-hexane) were allowed to evaporate under ambient conditions to generate viscous residues for characterization by X-ray scattering measurements. The X-ray analysis showed that compounds **5–7** formed columnar hexagonal structures. For example, in the small angle X-ray diffractogram of compound **5**, four reflections corresponding to d spacings of 44.2, 25.4, 22.3 and 16.9 Å were obtained, which are indexed in sequence as (100), (110), (200) and (210) of a columnar hexagonal lattice with the lattice parameter of $a = 51.0$ Å. A summary of the X-ray data for amphiphiles **5–7** is given in Table 1.

Since the structures of the amphiphiles are not disk-like, it is quite natural to assume that a slice of column comprises more than one molecule. The number (n) of molecules constituting a single disk of the column can be estimated according to eqn (1).⁹

$$n = (a^2) \sqrt{3/2} h [N_A / (M + mM_{\text{hexane}})] \rho \quad (1)$$

The parameter a is the hexagonal lattice parameter, N_A Avogadro's number, M the molecular mass of the amphiphile

Table 1 Small angle X-ray diffraction data for the lyotropic columnar mesophases of compounds **5**, **6** and **7** in *n*-hexane

Compound	Phase	$d_{\text{obs}}/\text{\AA}$	$h\ k\ l$	Lattice constant/ $\text{\AA}$
5	Col_h	44.2	1 0 0	$a = 51.0$
		25.4	1 1 0	
		22.3	2 0 0	
		16.9	2 1 0	
6	Col_h	46.9	1 0 0	$a = 54.2$
		26.9	1 1 0	
		23.6	2 0 0	
7	Col_h	53.2	1 0 0	$a = 61.4$
		31.5	1 1 0	
		26.7	2 0 0

Fig. 3 Schematic representation of the hexagonal columnar structure.

and mM_{hexane} is the mass of the solvent molecules surrounding the amphiphile molecule. The thickness (h) of a slice is about 0.45 nm, calculated based on wide angle X-ray diffractograms. Assuming a density (ρ) of 1 g cm^{-3} and neglecting mM_{hexane} in the case of the highly concentrated sample used for the X-ray measurements, the estimated values of the number of molecules (n) constituting a slice were about nine to ten. The lengths of the molecules were calculated to be 25 Å for **5**, 27 Å for **6** and 29 Å for **7** by using a MM2 method, which were close to the radii of the corresponding disks determined by X-ray analysis. Judging from these results and considering that a polycatenar molecule should have at least three benzene rings to exhibit mesophases,⁸ it is very likely that the molecules are arranged in a disk to form longer mesogens *via* hydrogen bonding between successive imidazole moieties as shown in Fig. 3.¹⁰ Another possible model has the circular aggregated structure in which head groups are hydrogen bonded to be localized in the central core. We prefer the former since the circular aggregation of several molecules will form a spherical rather than a disk-like structure. This disk-like orientation should maximize stacking between aromatic compounds in contrast to micellar-like spherical structures. In addition, chain structures of hydrogen bonded imidazole molecules have been found in the crystal state and in the solution state.⁵

Self-assembly at interfaces

The dilute solutions of compounds **5** and **6** (0.1 wt%) in *n*-hexane were spin-coated on a plasma-cleaned Si wafer and examined by AFM (Fig. 4). AFM imaging showed worm-like bundles in the phase images that had a rather band-like structure with width of 60–100 nm and height of 3–4 nm in the height images. Samples prepared by solution dip-coating showed similar AFM images, but with smaller aggregates. In contrast, when the solutions were spin-coated on a gold-coated Si wafer, only spheres with a diameter of 300–500 nm formed [Fig. 4(d)] indicating that the surface has a strong effect on the assembly. These results suggest that the amphiphilic molecules

Fig. 4 AFM images of compounds **5** and **6**: (a) height and (b) phase images of **5** spin-coated on a plasma-cleaned silicon wafer, (c) phase image of **6** spin-coated on a plasma-cleaned silicon wafer and (d) phase image of **6** spin-coated on a gold-coated silicon wafer. The specimens were prepared from a solution in *n*-hexane (0.1 wt%).

were most likely adsorbed on the hydrophilic surface of silica initially through interactions with their 1*H*-imidazole head groups. We presume that the columnar liquid crystalline phase developed as the concentration was increased by solvent evaporation and that columns aligned parallel to the silica surface to form the bundles. The height of the bundle was slightly smaller than the diameter of the column from X-ray analysis, which can be attributed to deformation of the cylinder adsorbed onto the silica surface.

These small bundles formed by spin-coating were found to be much larger upon drying the lyotropic liquid crystals in 30 wt% hexane solution on glass slides. Fig. 5 shows scanning electron microscopy (SEM) images of dried lyotropic liquid crystals of compounds **5** and **6**. Fiber bundles with a diameter as large as 13 μm are clearly visible as shown in Fig. 5 (left). At a very high magnification, much smaller diameter bundles were also observed [Fig. 5 (right)]. This may suggest that the bundles observed by AFM further self-assemble into these microscopic fibers at higher concentrations.

Fig. 5 SEM images of compound **5** (left) and compound **6** (right) dried from their lyotropic liquid crystalline phases.

Conclusions

The polycatenar 1*H*-imidazole amphiphiles showed a strong tendency to self-assemble in solution, owing to their capability of acting as both a proton donor and acceptor in forming hydrogen bonding. ¹H NMR and fluorescence spectroscopy studies suggested that in nonpolar solvents, the amphiphiles formed reverse micelles where hydrophilic imidazole head groups were aggregated inside the micelle through intermolecular hydrogen bonding and the nonpolar alkyl chains were located at the periphery. In concentrated solutions, they formed lyotropic liquid crystals having columnar hexagonal structures as confirmed by X-ray analysis. Fiber bundles were found when the liquid crystals were dried on glass, while band-like structures were formed when dilute solutions of the amphiphiles were spin-coated on to a plasma-cleaned Si wafer. The connection between these band-like bundles and microscopic fibers remains to be elucidated but it seems likely that it is hierarchical self-assembly. The 1*H*-imidazole amphiphiles are versatile building blocks for supramolecular assembly and further studies to determine the influence of structural variation on their self-assembling behavior are in progress.

Experimental

Materials and instrumentations

4-Imidazole carboxylic acid, 1-bromooctane, 1-bromodecane, 1-bromododecane, hydroquinone and sodium hydride were purchased from Aldrich and used as received. Reagent grade

solvents were dried and purified as follows. Triethylamine (TEA) and methylene chloride (MC) were distilled over calcium hydride. Tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) were dried over sodium metal and distilled. Ethanol (EtOH) and methanol (MeOH) were dried over molecular sieves 4 Å and distilled. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DPX 300 (^1H : 300 MHz and ^{13}C NMR: 75 MHz) spectrometer. Fourier transform infrared (FT-IR) measurements were recorded on a PERKIN ELMER Spectrum GX I using KBr pellets. Scanning electron microscopy (SEM) images were taken by a JEOL JSM6330F microscope. X-Ray diffraction (XRD) patterns were recorded by a Bruker Xps GADDS (Cu K α radiation, $\lambda = 1.54$ Å). An optical microscopy study was performed by a Leica DM LP equipped with a Mettler Toledo FP 82HT heating stage and Mettler Toledo FP 90 central process controller. Elemental analyses were performed at the National Center for Inter-University Research Facilities of Seoul National University, Seoul, Korea. Fluorescence spectra were recorded on a RF-5301PC spectrofluorimeter (Shimadzu) with a 150 W Xenon lamp and a 1 cm quartz cell. The excitation and emission band-widths were both 3 nm. UV absorption spectra were obtained using a scinco S-3150 UV-vis spectrophotometer. Atomic force microscopy (AFM) images were recorded in ambient atmosphere at room temperature with a Digital Instruments Dimension 3000 atomic force microscope in tapping mode with etched silicon tips (Nanoprobe). Topographic and phase images were obtained simultaneously. The spring constant of the tips was 40–66 N m $^{-1}$ as specified by the manufacturer.

Preparation of the gold-coated substrate

An atomically flat Au surface was prepared by controlled vacuum deposition of Au onto an oriented Si wafer deposited with 1.5 nm of chromium as an adhesion layer.

Film preparation for AFM on the substrate

The solutions (0.1 wt%) in *n*-hexane were spin-coated at 2000 rpm on to a plasma-cleaned Si wafer and 2.5 nm gold-coated Si wafer. The thin films were analyzed after complete evaporation of *n*-hexane at room temperature.

Methyl 3,4,5-tris(*n*-alkan-1-yloxy)benzoate (1a–1c)

To a solution of methyl 3,4,5-trihydroxybenzoate (5 g, 27.2 mmol) and potassium carbonate (18.8 g, 136.0 mmol) in DMF was added 1-bromoalkane ($n = 8, 10, 12$) (16.4 mL for 1-bromooctane, 19.8 mL for 1-bromodecane and 22.8 mL for 1-bromododecane, 95.2 mmol) at 60 °C. The mixture was stirred for 24 h at 60 °C. After filtration and evaporation, the product was isolated by column chromatography on silica gel (EA–*n*-hexane = 1 : 20 v/v); (91% yield for **1a**, 87% yield for **1b** and 86% yield for **1c**).

^1H NMR (300 MHz, CDCl_3): δ 7.24 (s, 2H, ArH), 4.00 (t, 6H, ArOCH_2), 3.88 (s, 3H, OCH_3), 1.83–1.26 (m, 36H, CH_2), 0.90 (t, 9H, CH_3) for **1a**; δ 7.24 (s, 2H, ArH), 4.00 (t, 6H, ArOCH_2), 3.88 (s, 3H, OCH_3), 1.83–1.26 (m, 48H, CH_2), 0.89 (t, 9H, CH_3) for **1b**; and δ 7.23 (s, 1H, ArH), 3.99 (t, 6H,

ArOCH_2), 3.88 (s, 3H, OCH_3), 1.83–1.26 (m, 60H, CH_2), 0.90 (t, 9H, CH_3) for **1c**.

3,4,5-Tris(*n*-alkan-1-yloxy)benzoic acid (2a–2c)

To a solution of compound **1** (5 g for **1a**, 5.8 g for **1b** and 6.8 g for **1c**, 9.6 mmol) in MeOH (100 mL) was added potassium hydroxide (1.6 g, 28.8 mmol). The mixture was refluxed for 2 h. Then, the crude product was acidified with HCl. After evaporation, the product was isolated by column chromatography on silica gel (EA–*n*-hexane = 1 : 5 v/v); (97% yield for **2a**, 95% yield for **2b** and 96% yield for **2c**).

^1H NMR (300 MHz, CDCl_3): δ 7.28 (s, 2H, ArH), 4.00 (t, 6H, ArOCH_2), 1.88–1.25 (m, 36H, CH_2), 0.90 (t, 9H, CH_3) for **2a**; δ 7.30 (s, 2H, ArH), 4.00 (t, 6H, ArOCH_2), 1.84–1.27 (m, 48H, CH_2), 0.88 (t, 9H, CH_3) for **2b**; and δ 7.30 (s, 2H, ArH), 4.00 (t, 6H, ArOCH_2), 1.82–1.26 (m, 60H, CH_2), 0.88 (t, 9H, CH_3) for **2c**.

3,4,5-Tris(*n*-alkan-1-yloxy)benzoyl chloride (3a–3c)

To a solution of compound **2** (3 g for **2a**, 3.5 g for **2b** and 4.1 g for **2c**, 6.0 mmol) in MC (30 mL) was added a catalytic amount of *N,N*-dimethylformamide. The reaction flask was cooled in an ice bath and thionyl chloride (0.5 mL, 6.6 mmol) was added dropwise. Then, the ice bath was removed and the reaction mixture was stirred for 4 h. After filtration and evaporation, the crude product was used for the next step without further purification.

4-Hydroxyphenyl 3,4,5-tris(*n*-alkan-1-yloxy)benzoate (4a–4c)

To a solution of hydroquinone (0.48 g, 4.4 mmol) in THF (50 mL) was added sodium hydride (0.14 g, 5.7 mmol). After stirring for 1 h at room temperature, compound **3** (2.0 g for **3a**, 2.3 g for **3b** and 2.6 g for **3c**, 3.7 mmol) was added under nitrogen. The reaction mixture was stirred for 10 h at room temperature. The product was isolated by column chromatography on silica gel (EA–*n*-hexane = 1 : 5 v/v); (65% yield for **4a**, 58% yield for **4b** and 61% yield for **4c**).

^1H NMR (300 MHz, CDCl_3): δ 7.37 (s, 2H, $\text{ArH}(\text{OCH}_2)_3$), 7.02, 6.84 (dd, 4H, ArH), 5.26 (s, 1H, HOAr), 4.02 (m, 6H, ArOCH_2), 1.86–1.24 (m, 36H, CH_2), 0.89 (t, 9H, CH_3) for **4a**; δ 7.39 (s, 2H, $\text{ArH}(\text{OCH}_2)_3$), 7.02, 6.82 (dd, 4H, ArH), 5.28 (s, 1H, HOAr), 4.04 (m, 6H, ArOCH_2), 1.83–1.20 (m, 48H, CH_2), 0.88 (t, 9H, CH_3) for **4b**; and δ 7.41 (s, 2H, $\text{ArH}(\text{OCH}_2)_3$), 7.04, 6.88 (dd, 4H, ArH), 5.31 (s, 1H, HOAr), 4.06 (m, 6H, ArOCH_2), 1.85–1.22 (m, 60H, CH_2), 0.90 (t, 9H, CH_3) for **4c**.

4-[1*H*-Imidazole-4-carboxyloxy]phenyl 3,4,5-tris(*n*-octan-1-yloxy)benzoate (5)

4-Imidazole carboxylic acid (1 g, 9 mmol) in benzene (10 mL) was stirred at room temperature, and then thionyl chloride (10 mL) dissolved in benzene (10 mL) was added slowly. The mixture was refluxed for 10 h. After evaporation, the product was dried and used for the next reaction without further purification. To a solution of compound **4a** (1 g, 1.7 mmol) in DMF (50 mL) was added sodium hydride (0.05 g, 2.0 mmol). After stirring for 1 h at room temperature, 4-chlorocarbonyl imidazole (1.24 g, 7.4 mmol) was added. The solution was

stirred for 24 h at 90 °C. After filtration and evaporation, the product was isolated by column chromatography on silica gel (THF–*n*-hexane = 2 : 1 v/v) and further purified by recrystallization from THF–*n*-hexane; (65% yield).

Elemental analysis. Calcd for C₄₁H₆₀N₂O₇: C, 71.07; H, 8.73; N, 4.04. Found: C, 71.34; H, 8.92; N, 3.83%. ¹H NMR (300 MHz, CDCl₃): δ 7.92, 7.84 (s, 2H, imidazole ring protons), 7.41 (s, 2H, ArH), 7.27 (dd, 4H, ArH), 4.05 (t, 6H, ArOCH₂), 1.29–1.86 (m, 36H, CH₂), 0.88 (t, 9H, CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 165.47, 161.30, 153.22, 148.69, 148.28, 143.41, 138.10, 123.80, 123.07, 122.98, 108.87, 73.87, 69.53, 32.11, 32.03, 31.12, 30.57, 29.72, 29.56, 29.53, 29.49, 26.31, 26.26, 22.90, 22.87, 13.80. IR (KBr pellet, cm^{−1}): 3113, 3078, 2925, 2663, 2598, 1732, 1504, 1336, 1178, 1127, 976.

4-[1*H*-Imidazole-4-carbonyloxy]phenyl 3,4,5-tris(*n*-decan-1-yloxy)benzoate (6)

This compound was prepared by a similar procedure to that described for compound **5** from compound **4b** and 4-chloro-carbonyl imidazole. The product was isolated by column chromatography on silica gel (THF–*n*-hexane = 2 : 1 v/v); (63% yield).

Elemental analysis. Calcd for C₄₇H₇₂N₂O₇: C, 72.64; H, 9.34; N, 3.60. Found: C, 72.82; H, 9.39; N, 3.46%. ¹H NMR (300 MHz, CDCl₃): δ 7.92, 7.84 (s, 2H, imidazole ring protons), 7.41 (s, 2H, ArH), 7.26 (dd, 4H, ArH), 4.05 (t, 6H, ArOCH₂), 1.29–1.86 (m, 48H, CH₂), 0.87 (t, 9H, CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 165.44, 160.82, 153.22, 148.70, 148.22, 143.42, 138.08, 123.78, 123.03, 122.96, 108.86, 73.85, 69.53, 32.15, 32.12, 30.56, 29.94, 29.90, 29.88, 29.84, 29.79, 29.61, 29.55, 29.52, 26.30, 26.27, 22.90, 14.31. IR (KBr pellet, cm^{−1}): 3113, 3068, 2852, 2666, 2600, 1735, 1502, 1338, 1180, 1122, 976.

4-[1*H*-Imidazole-4-carbonyloxy]phenyl 3,4,5-tris(*n*-dodecan-1-yloxy)benzoate (7)

This compound was prepared by a similar procedure to that described for compound **5** from compound **4c** and 4-chloro-carbonyl imidazole. The product was isolated by column chromatography on silica gel (THF–*n*-hexane = 2 : 1 v/v); (58% yield).

Elemental analysis. Calcd for C₅₃H₈₄N₂O₇: C, 73.91; H, 9.83; N, 3.25. Found: C, 73.83; H, 9.90; N, 3.14%. ¹H NMR (300 MHz, CDCl₃): δ 7.92, 7.84 (s, 2H, imidazole ring protons), 7.41 (s, 2H, ArH), 7.26 (dd, 4H, ArH), 4.05 (t, 6H, ArOCH₂), 1.29–1.86 (m, 60H, CH₂), 0.87 (t, 9H, CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 165.45, 160.65, 153.22, 148.71, 148.20, 143.43, 138.06, 123.77, 123.02, 122.96, 108.86, 73.85, 69.53, 32.15, 32.13, 30.57, 29.94, 29.91, 29.87, 29.85, 29.79, 29.62, 29.57, 29.53, 26.31, 26.28, 22.90, 14.3. IR (KBr pellet, cm^{−1}): 3113, 3078, 2852, 2664, 2598, 1733, 1504, 1337, 1177, 1121, 976.

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References

- G. Li, W. Fudickar, M. Skupin, A. Klyszcz, C. Draeger, M. Lauer and J.-H. Fuhrhop, *Angew. Chem., Int. Ed.*, 2002, **41**, 1828–1852; J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304–1319; V. Percec, A. E. Dulcey, V. S. K. Balagurusamy, Y. Miura, J. Smidrkal, M. Peterca, S. Nummelin, U. Edlund, S. D. Hudson, P. A. Heiney, H. Duan, S. N. Magonov and S. A. Vinogradov, *Nature*, 2004, **430**, 764–768; T. Mukai, M. Yoshio, T. Kato, M. Yoshizawa and H. Ohno, *Chem. Commun.*, 2005, 1333–1335; B.-K. Cho, A. Jain, S. M. Gruner and U. Wiesner, *Chem. Commun.*, 2005, 2143–2145; O. M. Martin, L. Yu and S. Mecozzi, *Chem. Commun.*, 2005, 4964–4966; V. Percec, A. E. Dulcey, M. Peterca, M. Ilies, S. Nummelin, M. J. Sienkowska and P. A. Heiney, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 2518–2523; L. J. M. Gaspar and G. Baskar, *Chem. Commun.*, 2005, 3603–3605; J.-H. Ryu, N.-K. Oh and M. Lee, *Chem. Commun.*, 2005, 1770–1772; M. Yoshio, T. Mukai, H. Ohno and T. Kato, *J. Am. Chem. Soc.*, 2004, **126**, 994–995; K. T. Kim, I. H. Lee, C. Park, Y. Song and C. Kim, *Macromol. Res.*, 2004, **12**, 528–533.
- P. J. Collings and M. Hird, *Introduction to Liquid Crystals Chemistry and Physics*, Taylor & Francis, London, 1997, pp. 79–92; L. Brunsveld, H. Zhang, M. Glasbeek, J. A. J. M. Veckmans and E. W. Meijer, *J. Am. Chem. Soc.*, 2000, **122**, 6175–6182; L. Douce, T. H. Diep, R. Ziessel, A. Skoulios and M. Césario, *J. Mater. Chem.*, 2003, **7**, 1533–1539; E. J. Foster, C. Lavigueur, Y.-C. Ke and V. E. Williams, *J. Mater. Chem.*, 2005, **37**, 4062–4068; J. Y. Chang, J. H. Baik, C. B. Le, M. J. Han and S.-K. Hong, *J. Am. Chem. Soc.*, 1997, **119**, 3197–3198; C. V. Yelamaggad, A. S. Achalkumar, D. S. Shankar Rao and S. K. Prasad, *J. Am. Chem. Soc.*, 2004, **126**, 6506–6507; M. Hashimoto, S. Ujije and A. Mori, *Adv. Mater.*, 2003, **15**, 797–800; D. L. Gin, W. Gu, B. A. Pindzola and W.-J. Zhou, *Acc. Chem. Res.*, 2001, **34**, 973–980; A. Kraft, A. Reichert and R. Kleppinger, *Chem. Commun.*, 2000, 1015–1016; W. Shu and S. Valiyaveetil, *Chem. Commun.*, 2002, 1350–1351; D. Goldmann, D. Janietz, C. Schmidt and J. H. Wendorff, *J. Mater. Chem.*, 2004, **10**, 1521–1525.
- T. Kato, N. Mizoshita and K. Kishimoto, *Angew. Chem., Int. Ed.*, 2006, **45**, 38–68; U. Beginn, *Prog. Polym. Sci.*, 2003, **28**, 1049–1105.
- R. Breslow, *Acc. Chem. Res.*, 1991, **24**, 317–324; M. T. Green, *J. Am. Chem. Soc.*, 2000, **122**, 9495–9499; X.-J. Song and A. E. McDermott, *Magn. Reson. Chem.*, 2001, **39**, S37–S43; F. Schneider, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 583–592; A. Katrusiak, *J. Mol. Struct.*, 1999, **474**, 125–133; T. Ueda, H. Masui and N. Nakamura, *Solid State Nucl. Magn. Reson.*, 2001, **20**, 145–155; R. J. Sundberg and R. B. Martin, *Chem. Rev.*, 1974, **74**, 471–517; Y. Tomoyose, D.-L. Jiang, R.-H. Jin, T. Aida, T. Yamashita, K. Horie, E. Yashima and Y. Okamoto, *Macromolecules*, 1996, **29**, 5236–5238.
- H. R. Flakus and A. Bryk, *J. Mol. Struct.*, 1995, **372**, 215–227; B. Brzezinski and G. Zundel, *J. Mol. Struct.*, 1998, **446**, 199–207.
- T. Kawakami and T. Kato, *Macromolecules*, 1998, **31**, 4475–4479; A. Kraft, A. Reichert and R. Kleppinger, *Chem. Commun.*, 2000, 1015–1016.
- S. H. Seo and J. Y. Chang, *Chem. Mater.*, 2005, **17**, 3249–3254.
- H.-T. Nguyen, C. Destradre and J. Malthête, *Adv. Mater.*, 1997, **9**, 375–388.
- K. Borisch, S. Diele, P. Göring, H. Kresse and C. Tschierske, *J. Mater. Chem.*, 1998, **8**, 529–543.
- Compounds **5**–**7** also exhibited thermotropic mesophases. A phase transition was observed from a columnar hexagonal phase to a cubic phase as the temperature increased on heating, and *vice versa* on cooling. Thermotropic hexagonal lattice structures were very similar to those of corresponding lyotropic liquid crystals. The calculated number of molecules constituting a disk in the thermotropic columnar state was close to that obtained in the lyotropic columnar state. The thermotropic liquid crystalline properties of the 1*H*-imidazole amphiphiles will be published in a subsequent paper.