## Branched quaternary ammonium amphiphiles: nematic ionic liquid crystals near room temperature<sup>†</sup>

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Branched quaternary ammonium molecules were synthesized and characterized by calorimetric, optical and X-ray diffraction studies; two of the molecules exhibited interesting nematic liquid crystalline behavior close to room temperature.

In this communication, we report nematic ionic liquid crystals (ILCs) formed near room temperature. ILCs that combine both the solvent properties of ionic liquids and the selforganization features of liquid crystals, have been of considerable interest in recent years because they present unique potential applications lacking in normal liquid crystals.<sup>1</sup> These kinds of liquid crystals have been expected to serve as anisotropic ion-conductors,<sup>2</sup> ordered reaction media<sup>3</sup> or templates for the synthesis of zeolites,<sup>4</sup> mesoporous materials<sup>5</sup> and nanomaterials.<sup>6</sup> Additionally, ILCs also possess potential as electrolytes in dye-sensitized solar cells.<sup>7</sup> The rich properties observed for these materials have inspired the synthesis of ILC materials and the hunt for new mesophases. Many ILCs have been designed, synthesized and characterized, such as ammonium, phosphonium, imidazolium, pyridinium, vinamidinium, and dithiolium salts, etc., and have been well reviewed.<sup>1d</sup> However, most of the ILCs reported up to date are smectic polymorphism<sup>1d,8</sup> or columnar phases.<sup>2,9</sup> The simple yet more significant nematic phase is still very rarely reported.<sup>10,11</sup> One of the main reasons is that most of the popular ILCs are linear molecules consisting of a single ionic head group connecting one or multiple long aliphatic tails. As can be easily understood, the microsegregation of incompatible units, the aggregation of compatible units, and the minimization of volume are the main driving forces that give rise to a general tendency for lamellar or columnar structures. From the technical point of view, a simple nematic ILC is more important, because it has the least order and possesses the lowest viscosity of all types of mesophase, making the nematic phase easier to realign under external stimulation. Therefore, creating nematic ILCs might allow the improvement of their applications in ion transport, or the development of new switchable liquid crystalline electrolytes.

In order to realize nematic ILCs, it is necessary to reduce the interactions existing between ionic molecules moderately. Recently, some reports demonstrated that T-shaped amphiphiles

consisting of rod-like mesogens with an oligo(oxyethylene) group at the lateral position could disturb the original layer structure and form new and complex LC structures.<sup>12</sup> In addition, calamitic liquid crystals connected with flexible lateral alkyl chains can result in the formation of nematic phases.<sup>13</sup> Such a strategy for obtaining a nematic phase has also been employed in polymer<sup>14</sup> and hybrid LCs<sup>15</sup> successfully. We believe that an ionic nematic mesophase can be achieved through a branched modification of charged molecules with mesogenic groups.

Based on this motivation, we designed a series of branched (close to T-shaped) quaternary ammonium molecules (B-*n*), by connecting an azobenzene mesogen with a flexible alkyl chain to the lateral benzoic group of an ammonium bromide molecule *via* esterification, as shown in Fig. 1. We expected to utilize the branched molecular geometry as well as the alkyl chain length (*n*) to adjust the interactions between molecules, and thus leading to a nematic phase near room temperature. B-*n* were synthesized according to modified routes from the literature.<sup>16–18</sup> The detailed preparation procedures, characterizations and instrumentation are all presented in the electronic supplementary information (ESI).<sup>†</sup>

The mesomorphic properties of the B-*n* series were characterized using differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and temperature dependent X-ray diffraction (XRD), in detail. The phase sequences and assignments, transition temperatures, associated enthalpies and entropies are summarized in Table 1.

By taking B-8 as a representative example, its DSC traces exhibit typical thermal properties in the first cooling and second heating runs, as shown in Fig. 2. Upon cooling, an



**Fig. 1** (a) Schematic molecular structure of quaternary ammonium bromides, B-*n*, and (b) proposed packing model of the nematic phase of B-6 and B-8.

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Table 1Summary of assignments of mesophases, transitiontemperatures, enthalpies and entropies of B-n by means of DSC(second heating run)

Amphiphiles	Transitions <sup>a</sup>	$T/^{\circ}\mathbf{C}$	$\Delta H/kJ mol^{-1}$	$\Delta S/J \ \mathrm{K}^{-1} \ \mathrm{mol}^{-2}$
B-6	g–N	23	_	_
	N–Iso	36	0.38	1.23
<b>B-</b> 8	g–N	25		
	N–Iso	68	1.17	3.43
B-10	g–SmA	32	_	
	SmA–Iso	87	1.90	5.31
B-12	g–SmA	31		
	SmA–Iso	92	2.63	7.23
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<sup>*a*</sup> g, N, SmA and Iso denote glass transition, nematic, smectic A and isotropic phases, respectively.

exothermal change appears at 60 °C, and the estimated transition enthalpy and entropy are quite low as compared to the normal phase transition from liquid crystal to the isotropic state (see Table 1). This result suggests a much smaller increase in ordering going from the isotropic liquid to the mesophase. With further decreasing temperature, a glass transition occurs at ca. 25 °C. Similar transition temperatures from the glass state to the mesophase and from the mesophase to the isotropic state are also observed upon second heating and following cycles, indicating that the transition behavior is reversible. The DSC curves of other B-*n* molecules (n = 6, 10, 12)exhibit similar phase transitions, as provided in the ESI.<sup>†</sup> The alkyl chain length of B-n has an influence on the phase transitions. With the increase in the alkyl chain length from B-6 to B-12, both the phase transition temperatures and the enthalpy changes tend to rise accordingly. Interestingly, the mesophases of all B-n molecules emerge at  $23 \sim 32$  °C, indicative of suitable candidates for an anisotropic ionic liquid at near room temperature.

The mesophases deduced from the DSC results can be further understood from the optical textures upon heating and cooling the samples. The isotropic liquid of B-8 placed between glass slides was examined through a slow cooling rate of 2 °C min<sup>-1</sup>. The appearance of distinct nematic droplets reveals the phase definitely (Fig. 3a). The texture flashed when the top glass slide was pressed gently. Upon cooling further, the nematic schlieren texture (Fig. 3b) with four-brush disclinations (strength S = 1) was persistent at the edges of the slide. The texture was maintained until it was cooled down to room temperature, indicating that the mesophase can freeze



Fig. 2 DSC thermograms of B-8 on the first cooling and second heating processes with a rate of 5  $^{\circ}$ C min<sup>-1</sup>.



Fig. 3 POM images of (a) nematic droplets of B-8 occurring just below the isotropic liquid phase, (b) a schlieren texture of the nematic phase of B-8 (thin), (c) marbled patterns of B-6 at 25  $^{\circ}$ C, and (d) orthogonal isogyre texture of B-10 at 60  $^{\circ}$ C with mechanical press.

into the glass state. B-6 shows marbled patterns even at lower temperature, which can be regarded as a room-temperature LC material (Fig. 3c). Notably, B-10 and B-12 show preferential homeotropic aligned areas in their mesophases, which are optically isotropic between crossed polarizers. The orthogonal isogyre texture of B-10 can be clearly viewed when the top glass slide was pressed, as presented in Fig. 3d, which implies the formation of smectic A phase.

In agreement with the POM observations, powder XRD results also support the assignment of the nematic phase, as seen in the data of B-8 (Fig. 4). When cooling from the isotropic state, diffuse diffractions at both low and wide angles were observed and assigned to the intermolecular short-range interactions which are parallel and perpendicular to the molecule long axis, respectively. The estimated distance from the low-angle diffraction is ca. 2.4 nm through Bragg's equation, which corresponds to the average length along the molecular long-axis. Meanwhile, the broad wide-angle diffraction indicates an average intermolecular separation of 0.46 nm, close to the typical value for liquid crystalline phases. At 25 °C, the two diffuse diffractions are still maintained, indicating the near room temperature mesophase, which is consistent with the data from POM and DSC. The XRD patterns of B-6 are similar to that of B-8, showing the presence



**Fig. 4** Variable-temperature X-ray diffractions of B-8 (inset: wide-angle X-ray diffraction of B-8).

of a nematic phase. For B-10 and B-12, strong low-angle diffraction peaks are observed, suggesting lamellar LC structures.<sup>†</sup> Combining the microscopic observations, DSC and XRD data, we conclude that B-6 and B-8 with shorter alkyl chains form nematic phases, and B-10 and B-12 form smectic A phases due to the increasing interactions. A schematic packing model of the nematic phase of B-6 and B-8 is proposed, as shown in Fig. 1b.

In summary, we have designed and synthesized branched quaternary ammonium amphiphiles. The special chemical structure can lead to the formation of nematic ILCs. The results obtained suggest a direct relationship between molecular structure and LC properties. Most importantly, the temperature at which the nematic phase occurs is low and close to room temperature, which is beneficial for functionalizations. Detailed research for more of these kinds of molecule is currently in progress in this laboratory.

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