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#### Highlights

- 1-Alkyl-3-methylimidazolium perfluorinated sulfonylimide ionic liquid crystals.
- Smectic A liquid crystalline mesophase was observed.
- Layered structure was determined for the crystalline phase by single-crystal XRD.
- Perfluorinated sulfonylimide anion is relatively difficult to form liquid crystal.

#### **Graphical Abstract**

Thermal and Structural Properties of 1-Alkyl-3-methylimidazolium Perfluorinated Sulfonylimide Ionic Liquid Crystals, and explanation for why ionic liquid crystals based on perfluorinated sulfonylimide anions are rare.



# Ionic Liquid Crystals Based on 1-Alkyl-3-

# methylimidazolium Cations and Perfluorinated

Sulfonylimide Anions

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#### Abstract

In contrast to the studies on ionic liquids based on perfluorinated sulfonylimide anions, their ionic liquid crystals were seldom reported. In the present study, four 1-alkyl-3-methylimidazolium perfluorinated sulfonylimide salts ( $[C_xMIm][N(SO_2R_F)_2]$ , x = 18 and 22;  $R_F = F$  (FSI) and CF<sub>3</sub> (TFSI)) have been synthesized and characterized. [ $C_{22}MIm][FSI]$ , [ $C_{18}MIm][FSI]$ , and [ $C_{22}MIm][TFSI]$  show smectic A<sub>2</sub> liquid crystalline mesophase. Single-crystal XRD revealed that [ $C_{18}MIm][FSI]$  and [ $C_{22}MIm][TFSI]$  show layered structures of low-polar and high-polar layers alternate with each other in the crystalline phase. It is suggested that perfluorinated sulfonylimide anions have weak interactions with imidazolium headgroups, making them relatively difficult to form mesophase.

#### Keywords

Ionic liquids, Liquid crystals, Mesophases, Smectic, Perfluorinated sulfonylimide

#### Introduction

Ionic liquid crystals (ILCs) are substances that possess the properties of both ionic liquids (ILs) and liquid crystals.<sup>1,2</sup> Ionic liquid crystals have an anisotropic structural organization composed of only ionic species, which makes them superior candidates to design one-dimensional.<sup>3-5</sup> two-dimensional.<sup>6,7</sup> or three-dimensional<sup>8,9</sup> ion-conductive materials, as well as anisotropic reaction media.<sup>10</sup> Because of the widespread use of imidazolium-based ILs with low melting point and low viscosity, imidazolium-based ILCs are frequently studied by combination with various functional groups to form different liquid crystalline (LC) mesophases.<sup>1,2</sup> In particular, ILCs based on 1-alkyl-3-methylimidazolium cations  $(C_x MIm^+)$ , where x denotes the carbon number of the alkyl chain) attract special research interest, not only because of their potential application in dye-sensitized solar cells,<sup>11–14</sup> but also due to their structural simplicity to investigate the effects of alkyl chain length and anionic species on the properties. For example, 1-alkyl-3-methylimidazolium cations with long alkyl chains were combined with a variety of anions such as chloride  $(Cl^{-})$ ,<sup>15</sup> bromide  $(Br^{-})$ ,<sup>16</sup> tetrachlorometallate  $(CoCl_4^{-} \text{ and } NiCl_4^{-})$ ,<sup>15</sup> tetrafluoroborate  $(BF_4^-)$ ,<sup>17</sup> hexafluorocomplex  $(PF_6^-)$ ,<sup>18,19</sup> AsF<sub>6</sub>, SbF<sub>6</sub>, NbF<sub>6</sub>, and TaF<sub>6</sub>),<sup>20</sup> trifluoromethylsulfonate  $(OSO_2CF_3^-)$ ,<sup>16</sup> fluorohydrogenate  $((FH)_nF^-)$ ,<sup>21,22</sup> perhalogeno carborane  $(B_{10}Cl_{10}^{2-} \text{ and } B_{12}Cl_{12}^{2-})^{23}$  bromoeuropate  $([EuBr_6]^{3-}Br^{-})^{24}$  hexabromoterbate  $(TbBr_6^{3-})^{25}$ fluoroaluminate  $(Al_2F_9^{3-})$ ,<sup>26</sup> and hexanitratolanthanate  $(La(NO_3)_6^{3-})$ .<sup>27</sup> The temperature range of LC mesophase observed for these salts increases with increasing alkyl chain length, although the alkyl chain length where mesophase appears depends on the anionic species.

Perfluorinated sulfonylimide anions ( $[N(SO_2R_F)_2]^-$ , where  $R_F$  denotes perfluoroalkylsulfonyl groups or F atoms) draw continuous research interest, because of their delocalized negative charge and high conformational degrees of freedom, originated from the electron-withdrawing perfluoroalkylsulfonyl groups or F atoms conjugated by the flexible S–N–S bonds. Such a weak coordinating nature makes them superior anions for designing IL electrolytes.<sup>28</sup> For example, ILs based on bis(trifluoromethanesulfonyl)imide ( $[N(SO_2CF_3)_2]^-$ , TFSI<sup>-</sup>) or bis(fluorosulfonyl)imide ( $[N(SO_2F)_2]^-$ , FSI<sup>-</sup>) anions show low viscosities, high conductivities, and wide electrochemical windows, which are advantageous for electrolytes used in lithium secondary batteries.<sup>29–32</sup> Besides, mixtures of alkali salts

based on FSF or TFSF anions have also been demonstrated to be superior intermediate-temperature IL electrolytes for sodium or lithium secondary batteries.<sup>33,34</sup> However, in contrast to the numerous researches on the ILs, reports on ILCs based on perfluorinated sulfonylimide anions are relatively fewer.<sup>35,36</sup> For example, for the 1-alkyl-3-methylimidazolium cations, although some attempts have been made by the combination of it with TFSF anion,<sup>37–43</sup> ILCs were only encountered in quite limited cases.<sup>42,43</sup> Hence, it is necessary to investigate why the perfluorinated sulfonylimide anions are relatively more difficult to form ILCs.

Herein, four 1-alkyl-3-methylimidazolium perfluorinated sulfonylimide salts ( $[C_xMIm][N(SO_2R_F)_2]$ , x = 18 and 22;  $R_F = F$  (FSI) and CF<sub>3</sub> (TFSI)) were synthesized and characterized. The imidazolium cations with a normal alkyl chain were chosen because such a simple cation structure is preferable to investigate the effects of the anion on the thermal and structural properties, especially when compared with previous reported C<sub>x</sub>MIm-based ILCs. Physicochemical properties and structures of the obtained salts were studied by differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction (XRD). Crystal structures of two salts,  $[C_{18}MIm][FSI]$  and  $[C_{22}MIm][TFSI]$ , were also determined.

#### **Results and discussion**

**Thermal properties.** All the four salts are white hydrophobic solid at room temperature. Figure 1 shows the DSC curves of the four salts (heating process), and Figures 2 and 3 show the detailed DSC curves of  $[C_{18}MIm][FSI]$  and  $[C_{22}MIm][TFSI]$ , respectively. Table 1 summarizes the obtained DSC data (phase transition temperature,  $\Delta H$ , and  $\Delta S$ ). Identical DSC curves are observed during the first and second heating processes for all the four salts, suggesting they are thermally stable up to 200 °C. As shown in Figure 1, the largest endothermic peak corresponds to melting (phase transition from crystal to liquid crystal or isotropic liquid). The relatively large  $\Delta H$  (and thus  $\Delta S$ ) at the melting point is ascribed to the breakup of a three-dimensionally positional order of the crystal lattice. The small peak corresponding to clearing (phase transition from liquid crystal to isotropic liquid) above the melting point is observed for  $[C_{22}MIm][FSI]$ , indicating the formation of LC mesophase. The small  $\Delta H$  (and

thus  $\Delta S$ ) at the clearing point illustrates liquid crystal is a state of high disorder, namely more like liquid rather than crystal. It is noteworthy that a small exothermic peak appeared for  $[C_{18}MIm][FSI]$  around 70 °C during the cooling process (Figure 2). This transition is guite near the melting point and can only be observed in the heating process at a lower scan rate of 0.5  $^{\circ}$ C min<sup>-1</sup> (Figure 2, insert), similar with the previously reported  $[C_{14}MIm][PF_6]^{20}$  Although a small peak was also found in the cooling step for [C<sub>22</sub>MIm][TFSI] (Figure 3), the phase transition temperature (65.4 °C, Table 1) is slightly lower than the melting point (65.9 °C, Table 1), and no peak was found above the melting point during the heating process even at a scan rate as low as 0.5 °C min<sup>-1</sup> (Figure 3, insert). The results above demonstrate [C<sub>18</sub>MIm][FSI] shows a narrow enantiotropic LC mesophase whereas [C<sub>22</sub>MIm][TFSI] shows a monotropic one. As listed in Table 1, the C<sub>22</sub>MIm salts have a higher melting point than the corresponding  $C_{18}$ MIm ones. This can be interpreted by their special crystal structures (see the crystal structure section). Extension of the alkyl chain of the amphipathic cation enhances a clear phasesegregation of high-polar (imidazolium headgroups and anions) and low-polar (long alkyl chains) regions, leading to a higher packing order and thus higher melting point.<sup>17,18,20</sup> Similar phenomena were also observed for other C<sub>x</sub>MIm-based ILCs and such a packing mode is not an uncommon case.<sup>18–</sup> <sup>20,24,44,45</sup> For a given anion, extension of the alkyl chain (from [C<sub>18</sub>MIm][FSI] to [C<sub>22</sub>MIm][FSI]) strengthens the van der Waals interaction and increases the clearing point considerably, resulting in a wider LC mesophase.<sup>15,17,18,20,21</sup> For a given cation, [C<sub>22</sub>MIm][FSI] shows a wider LC mesophase (51.4 °C) than [C<sub>22</sub>MIm][TFSI] (9.2 °C, but not thermodynamically stable), due to the smaller anion and thus stronger coulombic interaction.



Figure 1. Differential scanning calorimetric curves (heating process) for the four salts at 5 °C min<sup>-1</sup>.



**Figure 2.** Differential scanning calorimetric curves of heating and cooling processes for  $[C_{18}MIm][FSI]$  at 5 °C min<sup>-1</sup> and heating process at 0.5 °C min<sup>-1</sup> (insert).



**Figure 3.** Differential scanning calorimetric curves of heating and cooling processes for  $[C_{22}MIm][TFSI]$  at 5 °C min<sup>-1</sup> and heating process at 0.5 °C min<sup>-1</sup> (insert).

	Transition <sup><i>a</i></sup>	<i>T</i> (°C)	$\Delta H (\mathrm{kJ} \mathrm{mol}^{-1})$	$\Delta S (\text{J mol}^{-1} \text{ K}^{-1})$
[C <sub>22</sub> MIm][FSI]	Cryst1–Cryst2	67.1	6.5	19.0
	Cryst2–SmA <sub>2</sub>	77.9	41.2	117.0
	SmA <sub>2</sub> –Iso	129.3	0.6	1.4
[C <sub>22</sub> MIm][TFSI]	Cryst–Iso	65.9	45.5	134.1
	Iso–SmA <sub>2</sub> <sup>b</sup>	65.4	0.6	1.8
	SmA <sub>2</sub> –Cryst <sup>b</sup>	56.2	44.8	136.0
[C <sub>18</sub> MIm][FSI]	Cryst1–Cryst2	40.1	0.2	0.6
	Cryst2–Iso	65.7	4.1	12.1
	Cryst2–SmA <sub>2</sub> <sup>c</sup>	65.6	3.9	11.5
	SmA <sub>2</sub> –Iso <sup>c</sup>	69.6	0.03	0.09
[C <sub>18</sub> MIm][TFSI]	Cryst–Iso	52.2	39.9	122.7

Table 1. Summary of the DSC data

<sup>*a*</sup>The symbols, Cryst, Iso, and SmA<sub>2</sub> denote crytstal, isotropic liquid, and smectic A<sub>2</sub> liquid crystal, respectively. <sup>*b*</sup>These transitions were determined from the cooling process. <sup>*c*</sup>These transitions were determined from DSC recorded at 0.5 °C min<sup>-1</sup>.

It was illustrated in previous reports that for the  $C_x$ MIm-based ILCs, both the van der Waals interaction between the alkyl chains and the interaction between the imidazolium headgroup and anion assist the formation of LC mesophase.<sup>15–18,20,21</sup> Consequently, the shortest alkyl chain needed to form

LC mesophase reflects the strength of the interaction between the anion and imidazolium headgroup. For example,  $[C_xMIm][BF_4]$ ,  $[C_xMIm][PF_6]$ , and  $[C_xMIm][AsF_6]$  shows LC mesophase from x = 12,<sup>17</sup> 14,<sup>18–20</sup> and 16,<sup>20</sup> respectively, which is in good agreement with the decreasing coulombic interaction with increasing anion size. Usually, *n*-octadecyl (x = 18) is long enough for the  $C_xMIm^+$  cation to form LC mesophase with most anions.<sup>15–18,20,21</sup> However,  $[C_{18}MIm][FSI]$  only gives a narrow LC mesophase (4.0 °C, Table 1), and  $[C_{18}MIm][TFSI]$  shows no LC properties. This result indicates that the perfluorinated sulfonylimide anions has a weak cation-anion interaction with the imidazolium headgroups, and calls for a longer alkyl chain (x = 22, and thus stronger van der Waals interaction) to form LC mesophase. On the other hand, a comparison of  $\Delta H$  at the clearing point can also shed light on the strength of the cation-anion interactions. For instance,  $[C_{18}MIm][FSI]$  gives a  $\Delta H$  of 0.03 kJ mol<sup>-1</sup> (Table 1), which is much lower than other  $C_{18}MIm$ -based ILCs (e.g., 1.7 kJ mol<sup>-1</sup> for  $[C_{18}MIm][CI]$ ,<sup>16</sup> 1.0 kJ mol<sup>-1</sup> for  $[C_{18}MIm][BF4]$ ,<sup>17</sup> and 1.1 kJ mol<sup>-1</sup> for  $[C_{18}MIm][PF6]$ ).<sup>20</sup> This is also indicative of the weak cation-anion interaction between FS $\Gamma$  anion and imidazolium headgroup. It is thus suggested from the results above that, the weak cation-anion interaction between the perfluorinated sulfonylimide anions and imidazolium headgroup. It is thus suggested from the results above that, the weak cation-anion interaction between the perfluorinated sulfonylimide anions and imidazolium headgroups makes them relatively difficult to form LC mesophase.<sup>37-43</sup>

**Structural properties.** The crystal structures of  $[C_{18}MIm][FSI]$  (25 °C, cryst1 in Table 1) and  $[C_{22}MIm][TFSI]$  (-100 °C) are determined, which are the first cases for ILCs based on perfluorinated sulfonylimide anions to the best of our knowledge. Determination of the crystal structure for  $[C_{18}MIm][FSI]$  at -100 °C was relatively difficult, as the crystal collapsed upon the crystal-crystal phase transition (40 °C) during the cooling process. Table 2 gives the crystallographic data and refinement results. Figure 4 shows the crystal structure of  $[C_{18}MIm][FSI]$  at 25 °C (see Figure 4a for the asymmetric unit with atom labelling). The long alkyl chain of the cation keeps an all-*trans* conformation from C6 to C23. The FSI<sup>-</sup> anion shows a *cis* conformation, where *cis* or *trans* indicate the F atoms locate on the same or opposite sides, respectively, relative to the plane defined by the S–N–S bonds. Although the *trans* conformer is more stable than the *cis* one according to the gas-phase computation, <sup>46–48</sup> the energy barrier is small and both conformers could be found in previous reports. <sup>49–56</sup> The bond lengths and bond angles for the FSI<sup>-</sup> anion here are generally in good agreement with previously

reported values (Tables S1 and S2, Supporting Information).<sup>51–56</sup> As shown in Figures 4b and 4c, the packing mode is described as a layered structure of high-polar and low-polar domains. The high-polar domain is consisted of a double layered imidazolium headgroups and FSI<sup>–</sup> anions, and in each layer the anion is located in the center of four imidazolium headgroups (Figure 4d). The high-polar domains are separated by interdigitated alkyl chains (low-polar domains) tilted relative to the ionic layers (see Table S3, Supporting Information, for the calculated tilted angles). This packing mode is quite similar with previously reported [C<sub>14</sub>MIm]Cl·H<sub>2</sub>O,<sup>44</sup> [C<sub>12</sub>MIm]Br·H<sub>2</sub>O, and [C<sub>14</sub>MIm]Br·H<sub>2</sub>O,<sup>45</sup> only with different low-polar layer thickness, because of the different alkyl chain lengths. Table S4 lists the *D*-H···A interactions for [C<sub>18</sub>MIm][FSI]. All the O and N atoms of the FSI<sup>–</sup> anion are involved in short contacts (below the sum of van der Waals radii) with H atoms of the imidazolium ring (O1, O2, O3, and N11) or that of the alkyl side-chains (O3 and O4). Bifurcation of the *D*-H···A bonds is observed for H atoms (H2 and H5) which interacts with two atoms (O1 and O3, O2 and N11, respectively) of FSI<sup>–</sup>. No *D*-H···A interaction is observed for the two F atoms of the FSI<sup>–</sup> anion.

Table 2. Summary of crysta	l data and refinement	results for [C <sub>18</sub> MIm][]	FSI] and [C <sub>22</sub> MIm][TFSI]
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	[C <sub>18</sub> MIm][FSI]	[C <sub>22</sub> MIm][TFSI]
Formula	$C_{22}H_{43}F_2N_3O_4S_2$	$C_{28}H_{51}F_6N_3O_4S_2\\$
Fw	515.71	671.84
crystal size (mm)	0.30×0.28×0.14	0.36×0.30×0.12
<i>T</i> (°C)	25	-100
crystal system	Triclinic	Triclinic
space group	<i>P</i> –1	<i>P</i> –1
<i>a</i> (Å)	5.4261(9)	8.0810(12)
<i>b</i> (Å)	8.0014(13)	13.337(2)
<i>c</i> (Å)	32.313(5)	31.734(5)
α (°)	85.694(3)	89.084(4)
β (°)	85.871(3)	84.378(3)
γ (°)	81.293(3)	88.172(3)
$V(\text{\AA}^3)$	1380.2(4)	3401.7(9)
Ζ	2	4
$ ho_{ m calcd} ({ m g \ cm^{-3}})$	1.241	1.312
F(000)	556	1432
$\mu (\mathrm{mm}^{-1})$	0.237	0.225
$\lambda$ (Å)	0.71073	0.71073

11788/5365	11836/11836
0.0922	0.0566
0.2692	0.1573
0.0580	0 <sup>c</sup>
	11788/5365 0.0922 0.2692 0.0580

 ${}^{a}\overline{R_{1}} = \sum_{i} ||F_{o}| - |F_{c}|| / \sum_{i} |F_{o}| \text{ for } I > 2\sigma(I). {}^{b}wR_{2} = \{\sum_{i} [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum_{i} [w(F_{o}^{2})^{2}] \}^{1/2} \text{ for } I > 2\sigma(I). {}^{c}\text{Crystal twinning.}$ 



**Figure 4.** Crystal structure of [C<sub>18</sub>MIm][FSI] at 25 °C. Thermal ellipsoids are drawn at the 50% probability level. a) Asymmetric unit with atom labelling scheme, b) packing diagram along *a* axis, c) packing diagram along *b* axis, d) configuration of imidazolium headgroups and FSI<sup>-</sup> anions along *c* axis.

Figure 5 shows the crystal structure of  $[C_{22}MIm][TFSI]$  at -100 °C. The asymmetric unit contains two pairs of cations and anions, which show quite similar structures (Figures 5a and 5b). For both cations (Cation 1 in Figure 5a and Cation 2 in Figure 5b), the long alkyl chain keeps an all-*trans* conformation, but the C–N bond which links the imidazolium headgroup (N1–C6 and N31–C36) shows a *gauche* conformation relative to the alkyl chain, similar with a previously reported  $[C_6MIm][TFSI]$ .<sup>57</sup> Both anions (Anion 1 in Figure 5a and Anion 2 in Figure 5b) show a *trans* conformation (–CF<sub>3</sub> groups locate on the opposite sides of the plane defined by the S–N–S bonds), which is more stable than the *cis* conformer due to the bulky –CF<sub>3</sub> group.<sup>58,59</sup> The bond lengths and bond angles for the TFSI<sup>–</sup> anion here

are generally in good agreement with previously reported values (Tables S1 and S2, Supporting Information).<sup>57,59-62</sup> Phase-segregation of high-polar (imidazolium headgroups and anions) and lowpolar (long alkyl chains) regions is also observed in the packing mode (Figures 5c and 5d). The double layered ion configuration of imidazolium headgroups and anions resembles that of  $[C_{18}MIm][FSI]$  case (Figure S1). It is interesting to note that  $[C_{22}MIm][TFSI]$  has a smaller c cell parameter (31.734 Å, Table 2) than [C<sub>18</sub>MIm][FSI] (32.313 Å, Table 2), in spite of a longer alkyl chain and a larger anion, indicating a larger tilted angle for the alkyl chains (Table S3, Supporting Information). The increase in tilted angle is due to the larger TFSI<sup>-</sup> anion and weaker cation-anion interaction, since it is revealed in  $[C_rMIm][PF_6]$  series that extension of the alkyl chain will not change the tilted angle or ion configuration (the imidazolium cations and anions) significantly.<sup>18–20</sup> Table S5 lists D–H···A interactions for [C<sub>22</sub>MIm][TFSI]. All the O and N atoms of the TFSI<sup>-</sup> anion are involved in short contacts with H atoms of the imidazolium ring (O3, O5, and O7) or that of the alkyl side-chains (O1, O2, O3, O4, O6, O8, N11, and N41), and only one F atom (F5) is found to form D-H···A interactions. Bifurcation of the  $D-H\cdots A$  bonds is not observed. The results of  $D-H\cdots A$  interactions for [C<sub>18</sub>MIm][FSI] and [C<sub>22</sub>MIm][TFSI] suggest the negative charge is mainly located on the N and O atoms of the FSI<sup>-</sup> and TFSI<sup>-</sup> anions.



**Figure 5.** Crystal structure of  $[C_{22}MIm][TFSI]$  at -100 °C. Thermal ellipsoids are drawn at the 50% probability level. a) Atom labelling scheme for Cation 1 and Anion 1, b) atom labelling scheme for Cation 2 and Anion 2, c) packing diagram along *b* axis, d) packing diagram along *a* axis.

Figure 6 shows the polarized optical microscopic (POM) textures of  $[C_{22}MIm][FSI]$ ,  $[C_{18}MIm][FSI]$ , and  $[C_{22}MIm][TFSI]$ . Smooth fan-like or focal conic defect textures were seen in the mesophase, along with black pseudo-isotropic regions, indicating the formation of uniaxial smectic A LC mesophase. The broken fan-like texture which is indicative of the smectic C mesophase was not observed in the LC mesophase on cooling from the isotropic phase to the crystalline phase.<sup>42,63</sup> These results of POM combined with the XRD study below suggest that the LC mesophase is assigned to smectic A type.<sup>1,15,17,18,21</sup> Such a smectic A LC mesophase is common for the C<sub>x</sub>MIm-based ILCs, since the cation is much larger than the anion and dominates the formation of the smectic layers.<sup>15–18,21</sup> Monotropic mesophase was confirmed for  $[C_{22}MIm][TFSI]$ , on the basis that the textures were observed only in the cooling process (Figure 6c), in good accordance with the DSC results.





**Figure 6.** Polarized optical microscopic texture of a)  $[C_{22}MIm][FSI]$  at 100 °C (heating from the crystal phase), b)  $[C_{18}MIm][FSI]$  at 68 °C and c)  $[C_{22}MIm][TFSI]$  at 65 °C (cooling from the isotropic phase).

Figure S2 shows the XRD patterns ( $2^{\circ} < 2\theta < 30^{\circ}$ ) of [C<sub>22</sub>MIm][FSI] (100 °C) and [C<sub>18</sub>MIm][FSI] (68 °C) in the LC mesophase (See Figure S3, Supporting Information, for XRD patterns of the crystalline phase). Measurement below 2° was prevented to protect the detector. Patterns of the LC mesophase were difficult to obtain for [C<sub>22</sub>MIm][TFSI], as the monotropic LC mesophase is thermodynamically unstable. As seen in Figure S2, no peak is observed in the  $2\theta$  range of  $2^{\circ}$ - $30^{\circ}$  for [C<sub>22</sub>MIm][FSI] and [C<sub>18</sub>MIm][FSI]. This result combined with the POM observation indicates the peak ascribed to the smectic layered structure is in the range lower than  $2^{\circ}$ , and thus the interlayer spacing is larger than 44.1 Å, which is larger than the fully extended length of the cation (about 32 Å for C<sub>22</sub>MIm<sup>+</sup> and 25 Å for C<sub>18</sub>MIm<sup>+</sup>). Hence, it is suggested that the cations form a bilayer structure in the smectic A mesophase (smectic A<sub>2</sub>) for [C<sub>22</sub>MIm][FSI].<sup>16</sup> Absence of peaks in the high-angle region suggests the loss of positional order within the smectic layer plane, which fits the characteristics of smectic A mesophase. To the best of our knowledge, all the C<sub>x</sub>MIm-based ILCs show the same type of LC mesophase. <sup>15-18,20,21</sup>

#### Conclusions

Thermal and structural properties of four 1-alkyl-3-methylimidazolium perfluorinated sulfonylimide salts were investigated. [ $C_{22}MIm$ ][FSI] and [ $C_{18}MIm$ ][FSI] show enantiotropic LC mesophases, and [ $C_{22}MIm$ ][TFSI] shows a monotropic one. It is suggested by a comparison with previous reported  $C_xMIm$ -based ILCs that, the weak cation-anion interaction between the perfluorinated sulfonylimide anions and imidazolium headgroups makes them relatively difficult to form LC mesophase. All the present LC mesophases are determined as smectic  $A_2$  bilayer structures. X-ray crystallography reveals that [ $C_{18}MIm$ ][FSI] and [ $C_{22}MIm$ ][TFSI] have layered structures in the crystalline phase, where the low-polar layer (interdigitated alkyl chains) and high-polar layer (imidazolium headgroups and anions) alternate with each other. The alkyl chains tilt relative to the high-polar layer, and [ $C_{22}MIm$ ][TFSI] has a larger tilted angle than [ $C_{18}MIm$ ][FSI], due to the larger anion size and weaker cation-anion interaction.

#### Experimental

**Apparatus and Materials.** All the solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (China) or Shanghai Chemical Reagent Co., Ltd. (China), and dried and purified with standard procedures prior to use. The 1-alkyl-3-methylimidazolium bromides,  $[C_xMIm]Br$  (x = 18 and 22), were prepared by reactions of 1-methylimidazole (Shanghai Chemical Reagent Co., Ltd., 98%) and equimolar quantities of the corresponding bromoalkanes (1-bromooctadecane (Shanghai Chemical Reagent Co., Ltd., 98%) and 1-bromodocosane (TCI, 98%)) at 80 °C for three days. Purification of the bromides was performed by dissolving the bromide salts in acetonitrile and then precipitating from the solution by adding ethyl acetate. Potassium bis(trifluoromethylsulfonyl)imide (K[TFSI]) was purchased from Rhodia. Potassium bis(fluorosulfonyl)imide (K[FSI]) were purchased from Dai-ichi Kogyo Seiyaku Co., Ltd..

Synthesis of [C<sub>18</sub>MIm][FSI]. The two starting materials, [C<sub>18</sub>MIm]Br (2.493 g, 6.00 mmol) and K[FSI] (1.381 g, 6.30 mmol), were dissolved in acetone (30 mL), and the mixture was stirred vigorously overnight. A slightly excess amount of K[FSI] was used for the thorough removal of Br<sup>-</sup>. The solution was separated from the mixture, and the acetone was removed under vacuum. Testing for the presence of residual bromide impurities with a 1M AgNO<sub>3</sub> aqueous solution gave no precipitation of AgBr. The product was dissolved in 30 mL of dichloromethane and the mixture was stirred vigorously overnight. The dichloromethane solution was separated from the precipitate, and dichloromethane was removed under vacuum up to 50 °C. (2.830 g, 5.49 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.65 (s, 1H), 7.31 (dd, *J* = 11.1, 1.7 Hz, 2H), 4.19 (t, *J* = 7.5 Hz, 2H), 3.97 (s, 3H), 1.42–1.21 (m, 32H), 0.90 (t, *J* = 6.8 Hz, 3H). <sup>19</sup>F NMR (376 MHz, DMSO): 53.28–53.09 (m).

Synthesis of [C<sub>18</sub>MIm][TFSI]. The same procedure as for [C<sub>18</sub>MIm][FSI] was used. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.82 (s, 1H), 7.30 (dd, J = 8.4, 6.7 Hz, 2H), 4.18 (dd, J = 14.6, 7.0 Hz, 2H), 3.97 (s, 3H), 1.31 (d, J = 27.7 Hz, 32H), 0.90 (t, J = 6.8 Hz, 3H). <sup>19</sup>F NMR (376 MHz, DMSO): -78.70 (d, J = 4.0 Hz).

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**Synthesis of [C<sub>22</sub>MIm][FSI].** The same procedure as for [C<sub>18</sub>MIm][FSI] was used. <sup>1</sup>H NMR (400 MHz, DMSO): 9.09 (s, 1H), 7.73 (dt, J = 26.0, 1.7 Hz, 2H), 4.15 (t, J = 7.2 Hz, 2H), 3.85 (s, 3H), 1.24 (s, 40H), 0.86 (t, J = 6.8 Hz, 3H). <sup>19</sup>F NMR (376 MHz, DMSO): 53.28–53.09 (m).

Synthesis of [C<sub>22</sub>MIm][TFSI]. The same procedure as for [C<sub>18</sub>MIm][FSI] was used. <sup>1</sup>H NMR (400 MHz, DMSO): 9.10 (s, 1H), 7.73 (d, J = 26.2 Hz, 2H), 4.34–3.96 (m, 2H), 3.85 (s, 3H), 1.24 (s, 40H), 0.86 (t, J = 6.7 Hz, 3H). <sup>19</sup>F NMR (376 MHz, DMSO): -78.70 (d, J = 4.0 Hz).

**Spectroscopic and thermal analyses.** The DSC curves were recorded under a dry Ar gas flow on a Shimadzu DSC-60, at a scanning rate of 5 or  $0.5 \,^{\circ}$ C min<sup>-1</sup>. The sample was placed in an Al sealed cell for DSC analysis. Polarized optical microscopy was carried out using an Olympus BX51 digital microscope under cross-polarized light at ×50 magnification. The sample was placed between two pieces of bare glass substrate (several micrometers apart). The temperature was controlled by Linkam HFS91 hot stage.

**X-Ray Diffraction Analyses. a. Powder Diffraction.** X-ray diffraction was performed using a Bruker D8 Advance diffractometer (Cu-K $\alpha$ ,  $\lambda = 1.542$  Å). The data were recorded in the 2 $\theta$  ranges of 2–30° (scanning rate of 2° per minute) with a step of 0.02°. The sample was sealed in a vacuum cell. The heating and cooling rate of 5 °C min<sup>-1</sup> was used.

**b.** Single-Crystal Diffraction. Crystals of  $[C_{18}MIm][FSI]$  and  $[C_{22}MIm][TFSI]$  were grown by slow evaporation of the solvent from the dichloromethane solution. Suitable crystals were fixed on an X-ray diffractometer (Bruker Smart Apex2) equipped with an imaging plate area detector and graphitemonochromated Mo K $\alpha$  radiation (0.71073 Å). Data collection was performed at -100 °C for  $[C_{22}MIm][TFSI]$  and 25 °C for  $[C_{18}MIm][FSI]$ , using  $\varphi$  and  $\omega$  scans. Integration, scaling, and absorption corrections were performed using Apex2 (Bruker, 2004). The structure was solved using SIR-92 and refined by SHELXL-97 linked to Win-GX. Anisotropic displacement factors were introduced for all atoms except for hydrogen.

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**Supporting Information Available:** Results of single-crystal XRD and powder XRD data are available free of charge.

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