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1. Introduction

Ionic liquids are salts with melting points below 100 °C, and they are intriguing from the viewpoint of fundamental physical chemistry and electrochemistry.¹ Most ionic liquids are formed from organic onium cations such as imidazolium, ammonium, and phosphonium cations, and their modifications have led to various functionalities.² As the counter anion, fluorinated anions such as bis(trifluoromethanesulfo-

Organometallic ionic liquids from alkyloctamethylferrocenium cations: thermal properties, crystal structures, and magnetic properties†

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(trifluoromethanesulfonyl)amide) were prepared, and their ionic liquid properties, thermal properties, crystal structures, and magnetic properties were investigated. The melting points of the Tf₂N salts were near room temperature, and decreased with increasing alkyl chain length up to n = 8 and then increased. The salts with PF₆ and NO₃ anions were also prepared. The melting points of the PF₆ salts were higher than 100 °C. Most of these salts exhibited phase transitions in the solid state. The sum of the entropies of the melting and solid phase transitions was nearly independent of the alkyl chain length for salts with short alkyl chains, whereas those for salts with longer alkyl chains ($n \ge 10$ for Tf₂N salts, $n \ge 6$ for PF₆ salts) increased with increasing alkyl chain length. Crystal structure determinations revealed that the short chain salts form simple alternately packed structures of cations and anions in the solid state, and that the long chain salts form lamellar structures, in which the alkyl chains are aligned parallel between the layers. The effects of magnetic fields on the crystallization of the paramagnetic ionic liquids were investigated, and revealed that the Tf₂N salts with n = 4 exhibited magnetic orientation when solidified under magnetic fields. The magnetic orientation was shown to be a bulk phenomenon, and the importance of the magnetic anisotropy of the crystal structure was suggested in comparison with the response of other Tf₂N salts.

nyl)amide (Tf₂N) are frequently used, and magnetic anions such as MX_n (M = metal, X = anionic ligands),³ organic radicals,⁴ and metal complexes⁵ are used to add magnetic functions to the liquids.

Recently, several interesting examples of onium-free ionic liquids composed of cationic metal complexes have been reported.⁶ We have recently developed ionic liquids containing metallocenium cations⁷ and cationic chelate complexes,⁸ which exhibit interesting properties such as magnetic orientation,^{7b,d} color changes,^{8a} gas absorption,^{7e,8a} and chemical reactivities.^{7e} Ferrocenium cations are interesting from the viewpoint of magnetism,⁹ and they are suitable components of ionic liquids because of their bulkiness and charge delocalization. However, ferrocenium ionic liquids are highly sensitive to air.^{7a,d} In this study, alkyloctamethylferrocenium cations were used to obtain air-stable ferrocenium ionic liquids. There are a few examples of liquid-like peralkylated ferrocenium salts, such as alkali metal podates with ether substituents¹⁰ and liquid crystal salts with mesogenic substituents.¹¹

In this paper, we report the preparation and physical properties of alkyloctamethylferrocenium salts with the Tf_2N anion ([Fe(C₅Me₄C_nH_{2n+1})(C₅Me₄H)][Tf₂N], Scheme 1), which are air-

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Scheme 1 Structural formulae of alkyloctamethylferrocenium salts prepared in this study. Abbreviations for the salts are also shown.

stable paramagnetic ionic liquids. 1-Pentenyloctamethylferrocene was also used as the cation, and several nitrate (NO₃) and hexafluorophosphate (PF₆) salts were prepared for comparison. The discussion of the crystal structure is useful in elucidating the nature of ionic liquids.¹² Although structural data were not available for the ferrocenium ionic liquids, structural determination of the present salts was possible. The thermal properties of $[C6Fc][Tf_2N]^{7c}$ and the effects of magnetic fields on the crystallization of $[C4Fc][Tf_2N]^{7b}$ have been reported previously. A detailed investigation of magnetic phenomena in the latter salt is described here, and compared with those of other Tf_2N salts.

2. Results and discussion

Preparation and properties

The alkyloctamethylferrocenium salts were prepared according to Scheme 2. Octamethylformylferrocene was reacted with Grignard reagents, and the resultant alcohols were reduced to give alkyloctamethylferrocenes as yellow-orange oils, which were further reacted with AgX (X = Tf_2N , PF₆, and NO₃) to give the desired salts. The Tf_2N salts ([C3Fc][Tf_2N]–[C17Fc][Tf_2N])



Scheme 2 Scheme for the preparation of alkyloctamethylferrocenium salts.

were obtained as dark-green oils or solids, which were stable under air. The 1-pentenyl derivative $[C5'Fc][Tf_2N]$ was prepared similarly. The melting points (T_m) of the Tf_2N salts were in the range 15–70 °C. The PF₆ salts ([C4Fc][PF₆], [C6Fc][PF₆], and [C10Fc]-[PF₆]) and NO₃ salts ([C6Fc][NO₃] and [C10Fc][NO₃]) were obtained as dark-green solids. The melting points of these salts were above 100 °C except for [C10Fc][NO₃], which melted at about 80 °C.

Melting points of Tf₂N salts and their precursors

The melting points, melting entropies, and glass transition temperatures of the Tf₂N salts are listed in Table 1. The melting points are plotted in Fig. 1 as a function of the alkyl chain length. Compared with $[Fe(C_5Me_4H)_2][Tf_2N]$ (T_m = 213 °C),¹³ introduction of alkyl chains significantly decreased the melting points. The melting points decreased with increasing chain length up to n = 8 and then increased, where n is the number of carbon atoms in the chain. This tendency is similar to that observed in ionic liquids of alkylimidazolium salts.¹⁴ The melting points of the present salts are higher by 10-30 °C than those of [Rmim][Tf₂N] (Rmim = 1-alkyl-3-methylimidazo- $(1)^{14b}$ and $[Fe(C_5H_4R)(C_5H_5)][Tf_2N]^{7a,d}$ with the same alkyl chain lengths, which is consistent with the larger molecular weights and volumes of the cations. The melting point of the alkenyl derivative [C5'Fc][Tf₂N] ($T_m = 56.9 \text{ °C}$) was higher than that of the alkyl derivative [C5Fc][Tf₂N] (T_m = 30.0 °C and 20.2 °C, vide infra) as a result of the decreased flexibility of the substituent.

The thermal properties of alkyloctamethylferrocenes, which are the precursors of the salts, were also examined (Table 2). They melted at around 20 °C, and exhibited glass transitions at around -85 °C when cooled from the liquid state. Crystallization was observed in the heating process from the glassy state, except for the pentyl and 1-pentenyl derivatives. It is interesting that the melting points of alkyloctamethylferrocenes (open circles) and their Tf₂N salts (filled circles) are comparable (Fig. 1).

The ratios of the melting points and glass transition temperatures (T_g/T_m) for the alkyloctamethylferrocenes were 0.61–0.65. In the Tf₂N salts, the glass transition was only observed in the pentenyl derivative $[C5'Fc][Tf_2N]$ ($T_g = -67 \text{ °C}$) when the liquid was cooled at a rate faster than 10 °C min⁻¹. The T_g/T_m ratio for this salt was 0.62. These ratios are consistent with the empirical relationship ($T_g/T_m \approx 2/3$) known for general molecular compounds¹⁵ and also for alkylimidazolium ionic liquids.¹⁶

Phase transitions in the Tf₂N salts

The phase sequences of the Tf_2N salts are shown in Fig. 2. $[C4Fc][Tf_2N]$, $[C5'Fc][Tf_2N]$, and $[C17Fc][Tf_2N]$ exhibited no phase transitions in the solid state (Fig. 2a). $[C3Fc][Tf_2N]$, $[C10Fc][Tf_2N]$, and $[C12Fc][Tf_2N]$ exhibited one phase transition and $[C8Fc][Tf_2N]$ exhibited two phase transitions in the solid state (Fig. 2b). The large values of ΔS indicate that extensive molecular motions occur above the phase transition

Table 1 Melting points (T_m), melting entropies (ΔS_m), phase transition temperatures (T_{c1} , T_{c2}), phase transition entropies (ΔS_{c1} , ΔS_{c2}), and the sums of the phase transition entropies (ΔS_{total}) of the Tf₂N, PF₆, and NO₃ salts

	$T_{\rm m}/^{\rm o}{\rm C}$	$\Delta S_{\rm m}/{ m J~K^{-1}~mol^{-1}}$	$T_{\rm c1}/^{\rm o}{\rm C}$	$\Delta S_{\rm c1}/{ m J~K}^{-1}~{ m mol}^{-1}$	$T_{\rm c2}/^{\rm o}{\rm C}$	$\Delta S_{c2}/J \text{ K}^{-1} \text{ mol}^{-1}$	$\Delta S_{\text{total}} {}^{a}/\text{J} \text{ K}^{-1} \text{ mol}^{-1}$
[C3Fc][Tf ₂ N]	67.4	16.6	45.4	90.5			107.1
C4Fc Tf ₂ N	34.4	86.3					86.3
C5Fc Tf ₂ N	30.0	98.5					98.5
	20.2^{b}	20.4	0.5^{b}	44.0^{b}			_
[C5'Fc][Tf ₂ N]	56.9	80.7					80.7
[C6Fc][Tf ₂ N]	27.7	27.4	$21.4 - 1.6^{b}$	55.2 39.7 ^{<i>b</i>}			84.6
[C8Fc][Tf ₂ N]	16.9	12.5	1.7	19.9	11.5	2.5	34.9
C10Fc Tf ₂ N	17.5	12.5	11.0	14.7			27.2
C12Fc Tf ₂ N	26.2	18.0	8.7	36.5			54.5
C17Fc Tf ₂ N	56.8	97.3					93.6
C4Fc PF6	166.8	26.1	-53.8	4.4	108.1	28.6	59.1
C6Fc PF6	142.1	26.7	109.9	1.1	132.2	7.3	35.1
[C10Fc][PF ₆]	201.4	39.8	$-44.5 \\ 54.2^{b}$	$20.5 \\ 32.9^{b}$	49.2	7.0	64.3
[C6Fc][NO ₃]	109.4	26.6					26.6





Fig. 1 Melting points of Tf_2N salts (\bullet) and alkyloctamethylferrocenes (O) plotted as a function of the alkyl-chain length. The values for octamethylferrocene and its Tf_2N salt (n = 0) are also shown.

Table 2 Melting points (T_m), melting entropies (ΔS_m), and glass transition temperatures (T_g) of alkyloctamethylferrocenes

	$T_{\rm m}/^{\rm o}{\rm C}$	$\Delta S_{\mathrm{m}}/\mathrm{J}~\mathrm{K}^{-1}~\mathrm{mol}^{-1}$	$T_{\rm g}/^{\rm o}{\rm C}$	
C3Fc	17.5	68.9	-97	
C4Fc	27.6	80.6	-88	
C5Fc	_	_	-86	
C5'Fc	_	_	-84	
C6Fc	22.1	84.7	-83	
C8Fc	23.8	34.7	-84	

temperatures, not merely rotational and/or conformational disorder of anions.

The high-temperature phases in these salts are orientationally disordered phases with small melting entropies ($\Delta S < 20 \text{ J}$ K⁻¹ mol⁻¹).¹⁷ Among them, [**C10Fc**][Tf₂N] showed a glass transition in the crystal phase (phase II) at -40 °C, where the



Fig. 2 Phase sequences of Tf_2N salts. Different crystal phases are represented as I–III. The asterisks indicate metastable phases.

motions of the alkyl chains are probably frozen to form a glassy crystal. $[C5Fc][Tf_2N]$ and $[C6Fc][Tf_2N]$ exhibited three crystal phases, including metastable phases (Fig. 2c). The differential scanning calorimetry (DSC) traces for $[C5Fc][Tf_2N]$ are shown in Fig. S1 in the ESI.[†] The Gibbs free energy diagram for this salt derived from the data is shown in Fig. 3. The melting points of the stable phase (phase III) and the metastable phase (phase I) were 30.0 °C and 20.2 °C, respectively, and their melting entropies (ΔS_m) were 98.5 J K⁻¹ mol⁻¹ and 20.4 J K⁻¹ mol⁻¹, respectively. The latter small entropy indicates that phase I is a highly disordered phase. [C6Fc]-[Tf_2N] showed a similar but slightly different behavior, which we have reported previously.^{7c}

The sums of the entropies of the melting and solid phase transitions for the Tf₂N salts (ΔS_{total}) are shown in Fig. 4. The values for the salts with n = 3, 4, 5, and 6 were comparable (80–110 J K⁻¹ mol⁻¹), whereas the salt with n = 8 exhibited a much smaller value and the salts with $n \ge 10$ displayed an



Fig. 3 Schematic Gibbs free energy diagram for [C5Fc][Tf₂N]. The free energy curves are approximated by straight lines for simplicity.



Fig. 4 Sums of phase transition entropies of Tf_2N salts. The dark-gray areas are the entropies of solid phase transitions, and the others are the melting entropies.

increase with elongation of the alkyl chain. For molecules consisting of a rigid core and alkyl chains, such as mesogens and alkylimidazolium ionic liquids, conformational changes of the alkyl chains provide an entropy change of about 10 J K⁻¹ mol⁻¹ per methylene unit.¹⁸ The Tf₂N salts with $n \ge 10$ followed this tendency well, which indicates that the motion of the alkyl groups dominates the phase change entropies in these salts. The absence of such a tendency in the salts with $n \le 6$ is partly because the entropy contributions from the alkyl moieties are small in the short chain salts and, moreover, is probably the result of different packing structures (*vide infra*). The total phase transition entropy in [C5'Fc][Tf₂N] (80.7 J K⁻¹ mol⁻¹) was smaller by about 20 J K⁻¹ mol⁻¹ than that in [C5Fc][Tf₂N] (98.5 J K⁻¹ mol⁻¹), which is consistent with the loss of rotational freedom of two methylene groups.

It is interesting to note that the total phase transition entropies of alkyloctamethylferrocenes and the Tf_2N salts are comparable (Fig. 4 and Table 2), as well as the melting points, as noted above. A linear correlation between the melting points of the salts and the precursors has also been observed in alkylferrocenium Tf_2N salts.^{7d} These results demonstrate that the thermodynamic properties of the Tf_2N salts reflect those of their precursors.

Thermal properties of PF₆ and NO₃ salts

The melting points of [C4Fc][PF₆], [C6Fc][PF₆], and [C10Fc]-[PF₆] were 166.8 °C, 142.1 °C, and 201.4 °C respectively, and they first decreased and then increased with increasing chain length. The melting points of the PF₆ salts were higher by 100-150 °C than those of the corresponding Tf₂N salts. The PF₆ salts exhibited two phase transitions in the solid state, showing three stable crystalline phases (phase I-III). Their phase transition data are shown in Table 1. [C10Fc][PF₆] was obtained as a metastable glassy crystal, which was transformed to the stable phase (phase I) by heating (Fig. S2 in the ESI[†]). The sums of the phase transition entropies for the salts with n = 4, 6, and 10 were 59.1 J K⁻¹ mol⁻¹, 35.1 J K⁻¹ mol⁻¹, and 64.3 J K^{-1} mol⁻¹, respectively. The dependence on *n* is similar to that observed in the Tf₂N salts shown above. The increase in the value for the last salt is accounted for by the increased alkyl chain length, and the different tendency for the salt with n = 4 is ascribed to different packing structures, as shown below.

The melting point of $[C6Fc][NO_3]$ was 109.4 °C ($\Delta S = 26.6 \text{ J}$ K⁻¹ mol⁻¹), which is much higher than that of the corresponding Tf₂N salt ($[C6Fc][Tf_2N]$: $T_m = 27.7$ °C). Crystallization from the melt occurred at 23.5 °C when cooled at 2 °C min⁻¹, but a glass transition ($T_g = -35$ °C) was observed when the cooling rate was faster than 10 °C min⁻¹. [C10Fc][NO_3] melted at around 80–82 °C, but it is not a precise melting point because of the small amount of remaining solvate molecules.

Viscosities

The viscosities of [C6Fc][Tf₂N] and [C10Fc][Tf₂N] at 25 °C were 752 mPa s and 746 mPa s, respectively, and they were comparable. Both were Newtonian liquids, and they were much more viscous than the imidazolium ionic liquids (e.g., [bmim]- $[Tf_2N]$: 49 mPa s, bmim = 1-butyl-3-methylimidazolium)¹⁹ and ferrocenium ionic liquids (e.g., $[Fe(C_5H_4^nBu)(C_5H_5)][Tf_2N]$: 112.3 mPa s).^{7a,d} The temperature dependences of the viscosities were fitted using the Arrhenius plot from which activation energies (E_a) of 43.1 kJ mol⁻¹ and 44.9 kJ mol⁻¹, respectively, were derived. These values are comparable to those of [bmim]- $[Tf_2N] (31.3 \text{ kJ mol}^{-1})^{19} \text{ and } [Fe(C_5H_4^{\ n}Bu)(C_5H_5)][Tf_2N] (38.8 \text{ kJ})$ mol⁻¹).^{7a,d} The Vogel–Tammann–Fulcher (VTF) equation ($\eta =$ $\eta_0 \exp[DT_0/(T-T_0)]^{20}$ was also used to fit the data, where T_0 is the ideal glass transition temperature and D is a parameter that shows deviation from Arrhenius behavior. The values T_0 and D obtained for [C6Fc][Tf₂N] were -57.2 °C and 1.76, and those for [C10Fc][Tf₂N] were -53.6 °C and 1.63, respectively. The small D values, which are even smaller than that of [bmim][Tf₂N] (D = 4.65),²¹ suggest that they are strongly fragile liquids.22



Fig. 5 Packing diagrams of (a) $[C3Fc][Tf_2N]$, (b) $[C4Fc][PF_6]$, (c) $[C6Fc][PF_6]$, (d) $[C6Fc][NO_3]$, (e) $[C10Fc][PF_6]$, and (f) $[C10Fc][NO_3]$. Hydrogen atoms have been omitted for clarity.

Crystal structures

The crystal structures of [C3Fc][Tf₂N], [C4Fc][PF₆], [C6Fc][X], and [C10Fc][X] (X = PF₆, NO₃) were determined at -100 °C. Their packing diagrams are shown in Fig. 5. The structure of [C4Fc][Tf₂N] was reported previously.^{7b} [C3Fc][Tf₂N] belongs to space group C2/c, $[C4Fc][PF_6]$ and $[C10Fc][NO_3]$ belong to $P\overline{1}$, and the others belong to $P2_1/c$. In the alkyl chains of the salts, the C-C bond adjacent to the Cp ring exhibited the gauche conformation, whereas the other bonds exhibited the trans conformation. [C4Fc][PF₆] exhibited disorder in the alkyl chains. The intramolecular Fe-C(Cp) bond lengths, of which $Fe-C_H$ was the shortest, were comparable to those of substituted octamethylferrocenium cations.²³ In all the salts, the C₅ axes of the ferrocenium moieties were aligned in nearly the same direction in the crystal. Weak hydrogen bonds were formed in the NO₃ and PF₆ salts between the ring hydrogen of the cation and the oxygen or fluorine atom in the anion (Fig. S3 in the ESI⁺). The CH···X (X = O or F) distances were shorter than the van der Waals distances by 0.15–0.36 Å. The Tf_2N salts exhibited no such contacts.

The packing arrangements of the salts depended on the alkyl chain length in the cation. In the salts with short alkyl chains ([C3Fc][Tf₂N] and [C4Fc][PF₆]), the anions and cations are packed alternately in the unit cell (Fig. 5a and b). [C4Fc]-[Tf₂N] also exhibited a similar structure.^{7b} In contrast, lamellar structures are formed in the salts with longer alkyl chains $([C6Fc][X] \text{ and } [C10Fc][X]; X = PF_6, NO_3)$ (Fig. 5c-f). In these crystals, the anions and cations are arranged alternately to form layers, which are stacked with their alkyl chains extending outside the layers. The alkyl chains are in contact with each other between the layers and there are no direct π - π interactions between the cations. The interlayer distances in [C10Fc][X] are longer than those in [C6Fc][X] as a result of the longer alkyl chains. In the salts, except for [C10Fc][NO₃], the C_5 axes of the ferrocenium moieties are aligned parallel to the stacking direction of the layers. The difference between the packing patterns of the long chain and short chain salts, giving different lattice entropies, accounts for the observed different tendencies of the phase change entropies. A similar phenomenon has been observed in cobaltocenium salts.²⁴ Although the crystal structures of the Tf₂N salts with long alkyl chains were not determined, it is likely that the Tf₂N salts with $n \ge 8$ form lamellar structures, considering the tendency of the phase transition entropies in Fig. 4.

Magnetic properties of [C4Fc][Tf₂N]

The Tf₂N salts are paramagnetic ionic liquids containing magnetically anisotropic paramagnetic cations. We investigated the effects of magnetic fields on their crystallization. A remarkable effect was found in $[C4Fc][Tf_2N]$, which we reported previously in a communication^{7b} and briefly describe here. As shown in Fig. 6 (open circles), when the liquid was cooled



Fig. 6 Temperature dependence of the magnetic susceptibilities of [C4Fc]-[Tf₂N] in the form of a χ *T*-*T* plot. The data measured under 0.5 T are shown by open circles, and those for a sample crystallized under a perpendicular field of 0.59 T are shown by filled circles (heating run).

under a magnetic field (0.5-2 T), the magnetic susceptibility suddenly increased upon solidification at 26 °C, and, when heated, the value decreased again to the liquid value at 36 °C upon melting. The magnetic field affected the susceptibility increase, which increased with increasing field strength, but not the phase transition temperature.^{7b} A similar magnetic response was also found in a ferrocenium ionic liquid [Fe- $(C_5H_4Et)_2$ [Tf₂N],^{7d} albeit with less reproducibility and controllability. We ascribe this phenomenon to magnetic orientation, and detailed investigations of the phenomenon are described below. To confirm the magnetic orientation of the field-cooled sample, we first measured the anisotropy of the magnetic susceptibility. A liquid sample of [C4Fc][Tf₂N] was crystallized under a magnetic field of 0.59 T, and the magnetic susceptibility (χT value) of this sample measured under a perpendicular field was 0.63 emu K mol⁻¹ (Fig. 6, filled circles), which was smaller than that in the liquid state, whereas the value measured under the parallel field increased. This result directly demonstrates that the orientation of the crystal is controlled by the direction of the magnetic field.

The magnetic susceptibility of $[C4Fc][Tf_2N]$ solidified under a field of 0.8 T was 1.36 emu K mol⁻¹ when measured under a parallel field,^{7b} whereas the value for a fully oriented sample is calculated to be 1.73 emu K mol⁻¹, using $\chi T = [g^2S(S + 1)]/8$, where $g_{\parallel} = 4.3$ (*vide infra*) and S = 1/2. Assuming that there are only two components in the sample, a fully oriented fraction and a non-oriented isotropic fraction, the ratio of the former fraction was calculated to be 0.61 from the susceptibility values.

The magnetic orientation was further investigated using ESR spectroscopy. In the ESR spectra of an oriented polycrystalline sample crystallized under 0.8 T, a sharp, symmetrical peak was observed below -233 °C for a parallel orientation of the magnetic fields for crystallization and ESR measurements (Fig. S4a in the ESI⁺). In contrast, asymmetric peaks typical of a non-oriented material were observed for the sample crystallized without magnetic fields (Fig. S4b in the ESI⁺). Furthermore, a clear angular dependence was observed in the ESR spectra of the oriented sample recorded at -269.4 °C, as shown in Fig. 7. An upfield shift and broadening of the peak were observed with increasing angle (θ) between the magnetic fields for the measurement and crystallization. The g_{\parallel} component along the C_5 axis of the cation is observed for $\theta = 0^\circ$, and the g_{\perp} component appears with sample rotation. The small residual peak of the g_{\parallel} component observed even for θ = 90° is a non-oriented fraction. Thus, the spectrum for each rotation angle contains the angular-dependent component of the oriented fraction and the angular-independent component of the isotropic fraction (Fig. S5 in the ESI⁺). The g-values obtained by fitting the angular dependence (Fig. 7, inset) were g_{\parallel} = 4.3, g_{\perp} = 1.7, and g_{av} = 2.84, which are comparable to the typical values for ferrocenium salts such as [Fe(C₅Me₅)₂][PF₆] $(g_{\parallel} = 4.43, g_{\perp} = 1.35, g_{av.} = 2.78)$ and $[Fe(C_5Me_4H)_2][BF_4]$ $(g_{\parallel} = 4.11, g_{\perp} = 1.42, g_{av} = 2.64)$.²⁵ The average *g*-value calculated from the χT value in the liquid state (0.78 emu K mol⁻¹) was 2.87, which is in good agreement with the analysis. The linewidths



Fig. 7 Angular dependence of ESR spectra recorded at intervals of 10°. Inset shows the angular dependences of *g*-value at -269.4 °C, measured on a sample of **[C4Fc]**[Tf₂N] crystallized under a magnetic field of 0.8 T. θ is defined as the angle between the magnetic fields used for crystallization and ESR measurements.

and intensities of the g_{\parallel} and g_{\perp} peaks were obtained by fitting the spectra, and then the peak areas of the angle-dependent and -independent components were calculated from the simulated spectra for $\theta = 0^{\circ}$ and $\theta = 90^{\circ}$, respectively. The ratio of the former component, which corresponds to the ratio of the oriented fraction, was 0.6. The value is again in good agreement with that estimated from the magnetic susceptibility data (0.61) as shown above.

Mechanism of magnetic orientation in [C4Fc][Tf₂N]

To investigate the mechanism of the magnetic-field effect, the direction of the magnetic orientation was examined using powder X-ray diffraction (XRD) measurements. A liquid sample of [C4Fc][Tf₂N] was placed on a glass plate and crystallized under the magnetic field (0.36 T) of a neodymium magnet placed below the plate. The XRD patterns showed a significant increase in the intensity of the peaks at $2\theta = 13^{\circ}$, 14.5° , and 23° for the out-of-plane measurement compared with that of an unoriented sample (Fig. S6 in the ESI[†]), but the crystal structure was unchanged by the magnetic field. The peak at $2\theta = 14.5^{\circ}$ was indexed as (200), which shows that the *a*-axis, along which the C_5 axis of the cation is oriented, is oriented along the magnetic field, in agreement with the magnetic anisotropy of the crystal.7b In repeated experiments on the oriented samples, differences were observed in the relative peak intensities; this results from an in-plane distribution of the growth direction. The crystal growth pattern on the surface accompanying the radial distribution was visually observable under a polarized optical microscope.^{7b}

The effect of the sample shape on the magnetic response was also investigated. For liquid samples in fine tubes (inner diameter 0.2 mm) or in the form of thin layers (thickness

0.5 µm), no magnetic orientations were observed, even under 7 T. Magnetic orientation was also inhibited by adding quartz wool to the liquid.^{7b} In these circumstances, the orientation of the crystal growth may be affected largely by the surface rather than by the external fields. These results indicate that magnetic orientation is a bulk property, and that the phenomenon is not attributable to the orientation of independent molecules, but is more likely to be a result of orientation of the crystal nucleus or crystal growth direction during crystallization. This seems to be consistent with the less controllable response in a ferrocenium ionic liquid, $[Fe(C_5H_4Et)_2][Tf_2N]$, with a much lower viscosity than the present salt,^{7d} because the slower crystallization of high-viscosity liquids may lead to better magnetic-field orientation. There might be a critical size of crystal nucleus for magnetic orientation, and further investigations may be needed to explore its microscopic mechanism. The above results unfortunately suggest that fabrication of thin-layer magnetic memory devices based on this mechanism is unfeasible.

Magnetic properties of [C5'Fc][Tf₂N] and [C12Fc][Tf₂N]

In contrast to $[C4Fc][Tf_2N]$, no significant magnetic orientation was observed in $[C5'Fc][Tf_2N]$ and $[C12Fc][Tf_2N]$. The magnetic susceptibility of $[C5'Fc][Tf_2N]$ increased by only 0.05 emu K mol⁻¹ (0.73 emu K mol⁻¹) upon crystallization at -16 °C under 2 T (Fig. S7 in the ESI†) and, with heating, the value returned to the liquid value at 57 °C. Although the crystal structure is unknown, the negligible magnetic change can probably be ascribed to the small magnetic anisotropy of the crystal, if any.

When $[C12Fc][Tf_2N]$ was cooled from the liquid phase, it crystallized into a disordered phase at 25 °C, which further exhibited a phase transition in the solid state at around 7 °C. The temperature dependences of the magnetic susceptibility upon cooling under 0.5 T, 1 T, and 7 T are shown in Fig. 8. Repeated experiments showed that this salt exhibited small, random changes of the χT values at the phase transitions, but



Fig. 8 Temperature dependences of magnetic susceptibilities of $[C12Fc][Tf_2N]$ in the form of $\chi T - T$ plots, measured under 0.1 T (dotted line), 1 T (solid line), and 7 T (broken line) in the cooling processes.

the direction of the change was random, indicating that no orientation is caused by the magnetic fields. The χT value in the liquid state was 0.76 emu K mol⁻¹, which increased or decreased by less than 0.05 emu K mol⁻¹ upon crystallization, and the value further increased or decreased by about 0.1 emu K mol⁻¹ at the solid phase transition temperature. The absence of magnetic orientation in this salt is probably correlated with the rotational motion of the ferrocenium moiety, probably present in the disordered phase, which reduces the magnetic anisotropy of the crystal. The larger change in susceptibility observed at the solid phase transition is ascribed to the increased magnetic anisotropy of the crystal caused by ordering of the cation. In the solid phase transition, the orientations of the cations are fixed according to the crystal lattice; hence they are not affected by magnetic fields.

These results show that not all ferrocenium ionic liquids show a magnetic orientation effect, despite the magnetic anisotropy of the molecule, and that the phenomenon is instead related to the crystal properties. The orientation mechanism is therefore significantly different from the well-known magnetic orientation of diamagnetic liquid crystal molecules. The magnetic-field alignments of materials upon solidification have attracted much interest,²⁶ and magnetic susceptibility changes coupled with liquid-solid transformations have also been observed in several molecular materials such as paramagnetic ionic liquids^{4,27} and a solid composed of radical dimers.²⁸ The magnetic orientation of metallomesogens coupled with a phase transition to a liquid crystalline phase is an interesting phenomenon.²⁹ In [C4Fc][Tf₂N], the magnetic orientation occurs near room temperature with hysteresis and with a large susceptibility change, the degree of which can be controlled by the strength of the applied field. These are unique magnetic switching properties not seen in other materials.

3. Conclusion

A series of alkyloctamethylferrocenium salts with Tf_2N , PF_6 , and NO₃ anions ($[Fe(C_5Me_4C_nH_{2n+1})(C_5Me_4H)][X]$) were prepared. Investigation of their thermal properties, phase transition behaviors, and crystal structures revealed the following. The Tf₂N salts are ionic liquids that are stable under air. The alkyl chain length dependences of the melting points are similar to those observed for ionic liquids of alkylimidazolium salts. Most of the salts exhibit phase transitions in the solid state. In the salts with short alkyl chains, the sum of the phase change entropies is nearly constant, whereas the salts with longer alkyl chains display an entropy increase with elongation of the alkyl chain. Crystal structure determinations revealed that the short chain salts exhibit alternate stacking of cations and anions, whereas the long chain salts form lamellar structures, where the alkyl chains are aligned between the layers. The effect of magnetic fields on crystallization of the Tf₂N salts was investigated in detail. The magnetic orientation phenomenon in the salt with n = 4 upon crystallization originates from the magnetic anisotropy of the crystal structure, which is

Experimental

General

Octamethylformylferrocene³⁰ and silver bis(trifluoromethylsulfonyl)amide (AgTf₂N)³¹ were synthesized according to literature methods. The preparations of butyloctamethylferrocene and its Tf₂N salt ([C4Fc][Tf₂N]) were reported previously.^{7b} Other reagents and solvents were commercially available. ¹H NMR spectra were recorded using a JEOL JNM-ECL-400 spectrometer. Elemental analyses were performed using a Yanaco CHN MT5 analyzer. DSC measurements were performed using a TA Instrument Q100 calorimeter in the temperature range -180 to 210 °C at a rate of 10 °C min⁻¹. The viscosities of the liquids were measured under an N2 atmosphere using a Toki Sangyo TV-22 viscometer with a $3^{\circ} \times R7.7$ cone rotor, in the temperature range 14-36 °C. XRD data for the powder samples were recorded on a Rigaku SmartLab diffractometer using Cu K α radiation (λ = 1.54056 Å). ESR spectra were recorded on an X-band JEOL TE-260 spectrometer in the temperature range -269.4 to -233 °C. For the ESR measurements, a powder sample of [C4Fc][Tf₂N] was loaded into a quartz tube, which was sealed under nitrogen, and the sample was heated to melt it. The field-oriented samples were prepared by cooling the sample to crystallize under the magnetic field of the ESR magnet (0.8 T). The non-oriented samples were obtained by the same procedure, without applying magnetic fields.

Preparation of propyloctamethylferrocene

(a) 1-Hydroxypropyloctamethylferrocene. All the manipulations were carried out under a nitrogen atmosphere. Ethyl bromide (1.0 mL, 12.8 mmol) was added dropwise to a stirred mixture of magnesium turnings (0.330 g, 13.6 mmol) and ether (15 mL), and the solution was stirred until most of the magnesium dissolved. The Grignard reagent thus prepared was added slowly to a solution of octamethylformylferrocene (0.30 g, 1.0 mmol) in dry THF (20 mL) cooled at -78 °C, and the solution was stirred for 30 min. The reaction mixture was quenched at -78 °C with saturated NH₄Cl solution (20 mL) and extracted with ether. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography (silica, CH_2Cl_2). The product was obtained as a yellow solid (0.324 g, 99.9% yield). ¹H NMR (400 MHz, CDCl₃, TMS): δ = 0.89 (t, 3H, J = 7.6 Hz), 1.69–1.89 (m, 26H), 2.33 (s, 2H), 3.55 (s, 1H), 4.28 (t, 1H, J = 7.0 Hz). (b) Propyloctamethylferrocene. A solution of BH₃·SMe₂ (6.3 mmol) in THF (3.0 mL, 2 m solution) was added to a stirred solution of 1-hydroxypropyloctamethylferrocene (0.320 g, 0.90 mmol) in THF (15 mL). After refluxing the solution for 1 h, the reaction was quenched with aqueous NH₄Cl (20 mL), and the solution was extracted with CH₂Cl₂. The organic layer was dried over magnesium sulfate and

concentrated under reduced pressure. The crude product was purified by column chromatography (alumina, pentane). The product was obtained as a yellow oil (0.253 g, yield 82.8%). ¹H NMR (400 MHz, CDCl₃, TMS): δ = 0.90 (t, 3H, *J* = 7.6 Hz), 1.29 (q, 4H, *J* = 7.5 Hz), 1.65–1.73 (br, 24H), 2.17 (t, 2H, *J* = 7.4 Hz), 3.21 (s, 1H).

The other alkyloctamethylferrocenes were prepared in a similar manner, and *trans*-1-pentenyloctamethylferrocene was obtained by dehydration of 1-hydroxypentyloctamethylferrocene (see ESI[†]).

Preparation of Tf₂N salts

 $[C3Fc][Tf_2N]$. In the dark, AgTf_2N (0.232 g, 0.60 mmol) was added to a solution of propyloctamethylferrocene (0.200 g, 0.59 mmol) in CH₂Cl₂ (10 mL). After stirring the solution for a few minutes, the mixture was filtered via a syringe equipped with a membrane filter to remove silver deposits and unreacted AgTf₂N. Removal of the solvent from the filtrate under reduced pressure gave the product as a dark-green solid (0.336 g, 92% yield), which was recrystallized from ethanol/ hexane. Dark-green plate crystals. Anal. Calcd (%) for C₂₃H₃₂F₆FeNO₄S₂ (620.47): C, 44.52; H, 5.20; N, 2.26. Found: C, 44.58; H, 5.23; N, 2.32. The other Tf₂N salts were prepared in a similar manner. For the purification of [C10Fc][Tf2N] and [C12Fc][Tf₂N], they were dissolved in methanol and washed repeatedly with hexane to remove impurities. The solvents were evaporated under reduced pressure, and the residue was dried under vacuum at 80 °C for one day. [C5Fc][Tf2N]. Darkgreen oil, 99% yield. Anal. Calcd (%) for C25H36F6FeNS2O4 (648.53): C, 46.30; H, 5.60; N, 2.16. Found: C, 46.51; H, 5.74; N, 2.13. [C5'Fc][Tf₂N]. Dark-green powder, 79% yield. Anal. Calcd (%) for C₂₅H₃₄F₆FeNO₄S₂ (646.51): C, 46.44; H, 5.30; N, 2.17. Found: C, 46.54; H, 5.39; N, 2.26. [C6Fc][Tf₂N]. Dark-green oil, 95% yield. Anal. Calcd (%) for C₂₆H₃₈F₆FeNO₄S₂ (662.55): C, 47.13; H, 5.78; N, 2.11. Found: C, 47.27; H, 5.87; N, 2.13. [C8Fc][Tf₂N]. Dark-green oil, 98% yield. Anal. Calcd (%) for C₂₈H₄₂F₆FeNO₄S₂ (690.60): C, 48.70; H, 6.13; N, 2.03. Found: C, 48.52; H, 6.18; N, 2.13. [C10Fc][Tf₂N]. Dark-green oil, 68.3% yield (total yield from octamethylferrocene). Anal. Calcd (%) for C₃₀H₄₆F₆FeNO₄S₂ (718.66): C, 50.14; H, 6.45; N, 1.95. Found: C, 49.91; H, 6.55; N, 2.02. [C12Fc][Tf₂N]. Dark-green solid, 92% yield. Anal. Calcd (%) for C32H50F6FeNO4S2 (746.71): C, 51.47; H, 6.75; N, 1.88. Found: C, 51.44; H, 6.58; N, 1.98. [C17Fc][Tf₂N]. Dark-green solid, 38.3% yield (total yield from octamethylferrocene). Anal. Calcd (%) for C37H60F6FeNO4S2 (816.84): C, 54.40; H, 7.40; N, 1.71. Found: C, 54.18; H, 7.46; N, 1.96.

Preparation of PF₆ salts

[*C4Fc*][*PF*₆]. In the dark, a solution of AgPF₆ (51 mg, 0.20 mmol) in acetone (5 mL) was added to a solution of butyloctamethylferrocene (55 mg, 0.16 mmol) in acetone (10 mL). After stirring the solution for a few minutes, the mixture was filtered *via* a syringe equipped with a membrane filter to remove silver deposits and unreacted AgPF₆. Removal of the solvent from the filtrate under reduced pressure gave a solid, which was dissolved in CH₂Cl₂ (10 mL) and washed with water. After drying the organic phase over magnesium sulfate, removal of the solvent gave the product as a dark-green solid (57 mg, 74% yield), which was recrystallized from ethanol (-50 °C). Green plate crystals. Anal. Calcd (%) for C₂₂H₃₄FeF₆P (499.31): C, 52.62; H, 6.72. Found: C, 52.92; H, 6.86. The other PF₆ salts were prepared in a similar manner to that described above. *[C6Fc][PF₆]*. Green plate crystals, 93% yield. Anal. Calcd (%) for C₂₄H₃₈FeF₆P (527.37): C, 54.66; H, 7.26. Found: C, 54.45; H, 7.26. *[C10Fc][PF₆]*. Green plate crystals, 63.3% yield. To remove impurities, the product was dissolved in methanol and washed repeatedly with hexane. Anal. Calcd (%) for C₂₈H₄₆FeF₆P (583.47): C, 57.67; H, 7.95. Found: C, 57.35; H, 7.79.

Preparation of NO₃ salts

[C6Fc][NO₃]. In the dark, a solution of AgNO₃ (32 mg, 0.18 mmol) in water (2 mL) was added to a solution of hexyloctamethylferrocene (50 mg, 0.13 mmol) in acetone (2 mL) under stirring. After stirring for a few minutes, silver deposits and unreacted AgNO3 were removed by filtration. The solvent was evaporated under reduced pressure, and the residue was dissolved in CH₂Cl₂ (50 mL) and washed with water (50 mL). The organic layer was dried over magnesium sulfate, and evaporation of the solvent under reduced pressure gave the product as a green powder in 85% yield; it was recrystallized from acetone-ether-pentane (1:30:70). Green plate crystals. Anal. Calcd (%) for $C_{24}H_{36}FeNO_3$ (444.22): C, 64.86; H, 8.62; N, 3.15. Found: C, 64.52; H, 8.62; N, 3.24. The other nitrate salts were prepared in a similar manner. [C10Fc][NO3]. Green powder, 48% yield from octamethylferrocene. To remove impurities, the product was dissolved in methanol and washed repeatedly with hexane. The solvent was evaporated under reduced pressure, and the residue was dried under vacuum at 80 °C for one day. Anal. Calcd (%) for $C_{28}H_{46}FeNO_3$ (500.51): C, 67.19; H, 9.26; N, 2.80. Found: C, 66.01; H, 9.07; N, 2.74. Recrystallization from acetone-ether-pentane (1:30:70) gave a small amount of single crystals.

Magnetic measurements

Magnetic measurements were carried out using a Quantum Design MPMS-XL7 SQUID susceptometer; 30-60 mg of samples were loaded in a quartz tube and used for the measurements. Samples of [C4Fc][Tf₂N] in confined spaces were prepared as follows. A glass capillary (inner diameter 0.2 mm, outer diameter 0.3-0.4 mm) was filled with a liquid sample of [C4Fc][Tf₂N] (11 mg), and cut into lengths of 5 mm. The short capillary-tubes were aligned and loaded into a quartz tube for SQUID measurements. To prepare thin-layer samples of thickness 25 µm, a liquid sample of [C4Fc][Tf₂N] was loaded into a quartz sample-tube, in which 200 sheets of spacers and separators prepared from copper TEM grids (diameter 3 mm, thickness 25 µm) were alternately carefully immersed. The magnetic susceptibility data were corrected for the diamagnetic contribution so that the χT values became constant in the high-temperature region. The data for [C4Fc]- $[Tf_2N]$ and $[C5'Fc][Tf_2N]$ were further corrected for a very small amount of ferromagnetic impurities $(3 \times 10^{-5} \text{ emu})$ from the magnetization curve.

X-ray structure determination

Single crystals for X-ray structure determination were obtained by recrystallization. $[C3Fc][Tf_2N]$ was recrystallized from ethanol at -14 °C, and $[C4Fc][PF_6]$, $[C6Fc][PF_6]$, and [C10Fc]- $[PF_6]$ from ethanol at -50 °C. $[C6Fc][NO_3]$ and $[C10Fc][NO_3]$ were obtained by slow diffusion of ether/pentane into acetone

Table 3 Crystallographic parameters for [C3Fc][Tf₂N], [C4Fc][PF₆], [C6Fc][PF₆], [C6Fc][NO₃], [C10Fc][PF₆], and [C10Fc][NO₃]

	$[C3Fc][Tf_2N]$	[C4Fc][PF ₆]	[C6Fc][PF ₆]	[C6Fc][NO ₃]	[C10Fc][PF ₆]	[C10Fc][NO ₃]
Empirical formula	C ₂₃ H ₃₂ F ₆ FeNO ₄ S ₂	C ₂₂ H ₃₄ F ₆ FeP	C ₂₄ H ₃₈ F ₆ FeP	C24H38FeNO3	C ₂₈ H ₄₆ F ₆ FeP	C ₂₈ H ₄₆ F ₆ FeP
Formula weight	620.49	499.31	527.36	444.40	583.47	500.51
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	C2/c (No. 15)	<i>P</i> 1̄ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	<i>P</i> 1̄ (No. 2)
a/Å	16.389(3)	12.6489(14)	16.0571(16)	17.982(5)	19.6648(18)	8.0742(13)
b/Å	18.944(3)	13.2409(15)	8.9074(9)	8.762(2)	8.7837(8)	9.8377(16)
c/Å	19.262(3)	13.8307(16)	17.6910(18)	17.319(5)	17.5494(16)	17.596(3)
$\alpha / ^{\circ}$		91.767(2)	. ,			90.473(2)
$\beta/^{\circ}$	113.192(2)	91.233(2)	96.246(2)	115.567(4)	102.498(2)	92.713(3)
γ/°		94.617(2)				97.649(3)
Volume/Å ³	5497.1(16)	2307.1(5)	2515.3(4)	2461.6(11)	2959.5(5)	1385.5(4)
Ζ	8	4	4	4	4	2
$d_{\rm calcd}/{\rm g~cm^{-3}}$	1.499	1.438	1.393	1.199	1.310	1.201
μ/mm^{-1}	0.771	0.777	0.717	0.635	0.616	0.572
Reflections collected	14 381	12 027	12 924	11 578	15 520	6926
Independent reflections	5195	8005	4741	4324	5600	4763
F(000)	2568	1044	1108	956	1236	542
Parameters	343	595	298	271	334	307
$R_1^a, WR_2^b (I > 2\sigma(I))$	0.0390, 0.1087	0.0400, 0.1055	0.0641, 0.1901	0.0584, 0.1196	0.0392, 0.1061	0.0349, 0.1051
R_1^{a} , w R_2^{b} (all data)	0.0447, 0.1135	0.0511, 0.1133	0.0772, 0.2038	0.0808, 0.1296	0.0546, 0.1175	0.0403, 0.1083
Goodness-of-fit on F^2	1.068	1.040	1.050	0.972	1.032	1.091

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|. {}^{b}WR_{2} = [\Sigma W (F_{o}^{2} - F_{c}^{2})^{2}/\Sigma W (F_{o}^{2})^{2}]^{1/2}.$

solutions (acetone–ether–pentane = 1:30:70). XRD data were collected with a Bruker Smart1000 CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å) at –100 °C (cooling rate: 1 °C min⁻¹). The structures were solved by direct methods and refined using SHELXTL.³² The crystallographic data are listed in Table 3. The crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. 900446 ([C3Fc][Tf₂N]), 900447 ([C4Fc][PF₆]), 900448 ([C6Fc][PF₆]), 900449 ([C6Fc][NO₃]), 900450 ([C10Fc][PF₆]), and 900451 ([C10Fc][NO₃]).

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