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Metalloccenium Ionic Liquids

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Ionic liquids have been prepared from simple metallocenium cations and bis(trifluoromethanesulfonyl)amide anion (TFSA). Their properties were tunable by the choice of metals and substituents; the ferrocenium salts were deep blue paramagnetic liquids, which are readily prepared by a one-step solventless reaction, and the cobaltocenium salts were orange diamagnetic liquids.

Ionic liquids (ILs) are intriguing materials from the viewpoints of fundamental physical chemistry and green chemistry, as well as their technological applications, and their chemistry and physics have attracted special attention.¹ The majority of the ILs thus far investigated have been onium salts, such as alkylimidazolium salts. The conferring of functionality on ILs is an interesting approach toward materials and reaction chemistry.² From this viewpoint, imidazolium ILs with magnetic anions³ and organometallic substituents,⁴ and ILs containing metal complexes,^{2,5} have been developed.

In this study, we employed metallocenium cations as components of ILs with the aim of developing functional liquids.⁶ Metallocenium cations exhibit a variety of chemical functions and physical properties,⁷ the intriguing magnetic properties of metallocenium charge-transfer salts have been well documented.⁸ Thus it was expected that producing ILs from metallocenium cations, or lowering the melting points of the metallocenium salts, might open a route to novel materials chemistry. Here we report for the first time the preparation and properties of metallocenium ILs (Fig. 1), which are characterized by their simple formulae and tunable liquid properties.

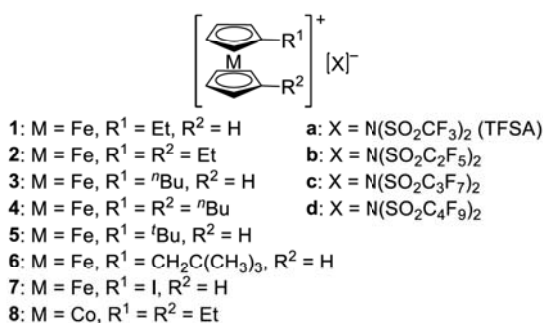


Figure 1. Structural formulae of metallocenium ILs.

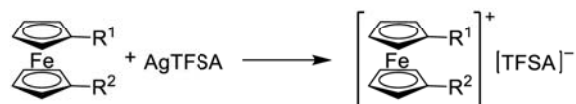
We found that the combination of substituted metallocenium cations (M = Fe and Co) with TFSA and related fluorinated anions afford ILs generally. Figure 2

shows the appearance of the typical metallocenium ILs 1,1'-diethylferrocenium TFSA (**2a**) and 1,1'-diethylcobaltocenium TFSA (**8a**), which are deep blue and orange, respectively. Changing the metal atom leads to the remarkable color change.



Figure 2. Metallocenium ILs; **2a** (M = Fe; left) and **8a** (M = Co; right).

Ferrocenium ILs with low melting points (**1a–4a**, **7a**) were readily prepared by a one-step solventless reaction (Scheme 1); grinding substituted ferrocenes and silver bis(trifluoromethanesulfonyl)amide (AgTFSA) with an agate and mortar for 5 minutes, followed by filtration *via* a syringe filter to remove silver, gave the deep blue ionic liquids in quantitative yield.¹³ Ferrocenium salts with higher melting points were prepared by adding dichloromethane as a solvent to make the filtration process easier. The cobaltocenium ILs (**8a–8d**) were prepared by a metathesis reaction of 1,1'-diethylcobaltocenium hexafluorophosphate with lithium TFSA or other salts.¹³ The ferrocenium ILs were unstable under air, reacting rapidly with oxygen, while the cobaltocenium ILs were stable under air. The decomposition temperature of **8a** was 430 °C, exhibiting high thermal stability comparable to [bmim][TFSA] (dec. at 423 °C).⁹ The ILs were miscible with polar solvents (EtOH, acetone, CH₂Cl₂, etc.) but not with nonpolar solvents (Hexane, Et₂O, Toluene, etc.). Miscibility with water was dependent on the cation substituent.



Scheme 1. Preparation of ferrocenium TFSA.

The melting points of the metallocenium salts are summarized in Table 1. The metallocenium salts with ethyl and longer substituents were all ILs, while unsubstituted

ferrocene, methylferrocene, and 1,1'-dimethylferrocene did not give ILs; the melting points of their TFSA salts were higher than 100 °C. The melting points of salts with branched alkyl substituents (**5a** and **6a**) were much higher than those with linear substituents, in accordance with the smaller degree of motional freedom. Among the ILs in Table 1, it is notable that the melting point of iodoferrocenium TFSA (**7a**) was 33 °C; the introduction of a simple substituent to ferrocenium TFSA (m.p. = 131.5 °C) resulted in a remarkable decrease in the melting point. Comparison of **2a** (M = Fe; m.p. = 3.8 °C) and **8a** (M = Co; m.p. = 14.2 °C) shows the effect of the different metal ions; the higher melting point of the latter is probably ascribable to its smaller molecular volume. Comparison of **8a–8d** indicates that the melting points are nearly independent of the length of the $-\text{CF}_2-$ chain in the anion. This contrasts with the effect of the cation substituents as noted above. The use of TFSA-type anions is essential for obtaining metallocenium ILs, in view of the high melting point of 1,1'-diethylcobaltocenium hexafluorophosphate (150.1 °C).

Table 1. Melting points^[a], glass transition temperatures^[a], and viscosities of metallocenium salts.

ILs	T_m [°C]	T_g [°C]	$\eta_{25\text{ °C}}$ [mPa s]	$T_{m(\text{precursor})}$ ^[b] [°C]
1a	24.5	–	26.6	–1.3
2a	3.8	–	45.0	–36.2
3a	–	–80.7	112.3	7.4
4a	1.0	–87.4	94.3	–18.4
5a	79.7	–		9.4
6a	60.0	–		9.1
7a	33.1	–58.5		44.8
8a	14.52	–	57.3	
8b	6.3	–	107.5	
8c	14.5	–84.2	182.6	
8d	6.1	–64.1	386.7	
Non-ILs				
[Fch][TFSA]	131.5			174.6 ^[c]
[MeFc][TFSA]	104.5			38.8 ^[d]
[Me ₂ fc][TFSA]	104.1			38.4 ^[c]

[a] Determined by means of differential scanning calorimetry with a scan rate of 10 K min^{–1} (Ref. 13). [b] Melting points of neutral ferrocene derivatives. [c] Ref. 11. [d] Ref. 12.

The melting points of the precursors of the salts—i.e., the neutral ferrocene derivatives—are also included in Table 1. It was found that precursors with lower melting points tend to give ILs with lower melting points; melting points of ferrocenium ILs with linear substituents (**1a**, **2a** and **4a**) are higher than those of their precursors by about 30 K. An exception was iodoferrocenium TFSA (**7a**; m.p. 33 °C), which exhibits a lower melting point than iodoferrocene (44.8 °C). In metallocenium ILs, the properties of the neutral precursors and the ILs can be compared without changing the molecular framework, which may provide important information on fundamental aspects of ILs.

Viscosities were measured at 25 °C for some of the salts (Table 1). The viscosities of TFSA salts with ethyl groups (**1a**, **2a**, and **8a**) were comparable to those of typical imidazolium ILs such as [ethylmethylimidazolium][TFSA] (36.5 mPa s) and [butylmethylimidazolium][TFSA] (50.5 mPa s),¹⁰ but the values increased with increasing substituent length in both the cation and the anion. In particular, elongation of the $-\text{CF}_2-$ chain in the anion resulted in a remarkable increase in viscosity (**8a–8d**). Furthermore, a reasonable correlation was found between viscosity and the thermal behavior of the salts (Table 1). Upon cooling, the ILs exhibited either (i) crystallization (**1a**, **2a**, **8a** and **8b**), (ii) glass transition (**3a**), or (iii) either of these depending on the cooling conditions (**4a**, **8c** and **8d**); the ILs with high viscosities (> 90 mPa s) exhibited glass transitions, while less viscous ILs (< 60 mPa s) exhibited only crystallization.

The ferrocenium ILs were paramagnetic liquids; the magnetic susceptibilities (χT values) of **2a** and **4a** at around room temperature were 0.68 and 0.59 emu K mol^{–1}, respectively, which are typical for ferrocenium salts.⁸ In contrast, the cobaltocenium salts were diamagnetic liquids.

In conclusion, we have shown that metallocenes with various substituents, anions, and metal ions afford metal-containing functional ILs which are distinguished by the absence of an onium framework, simple preparation methods, and tunable liquid properties such as color, magnetism, and melting point. The strategy presented here may be extended to other highly functional metallocenes, which might be a promising approach toward the development of various functional liquids.

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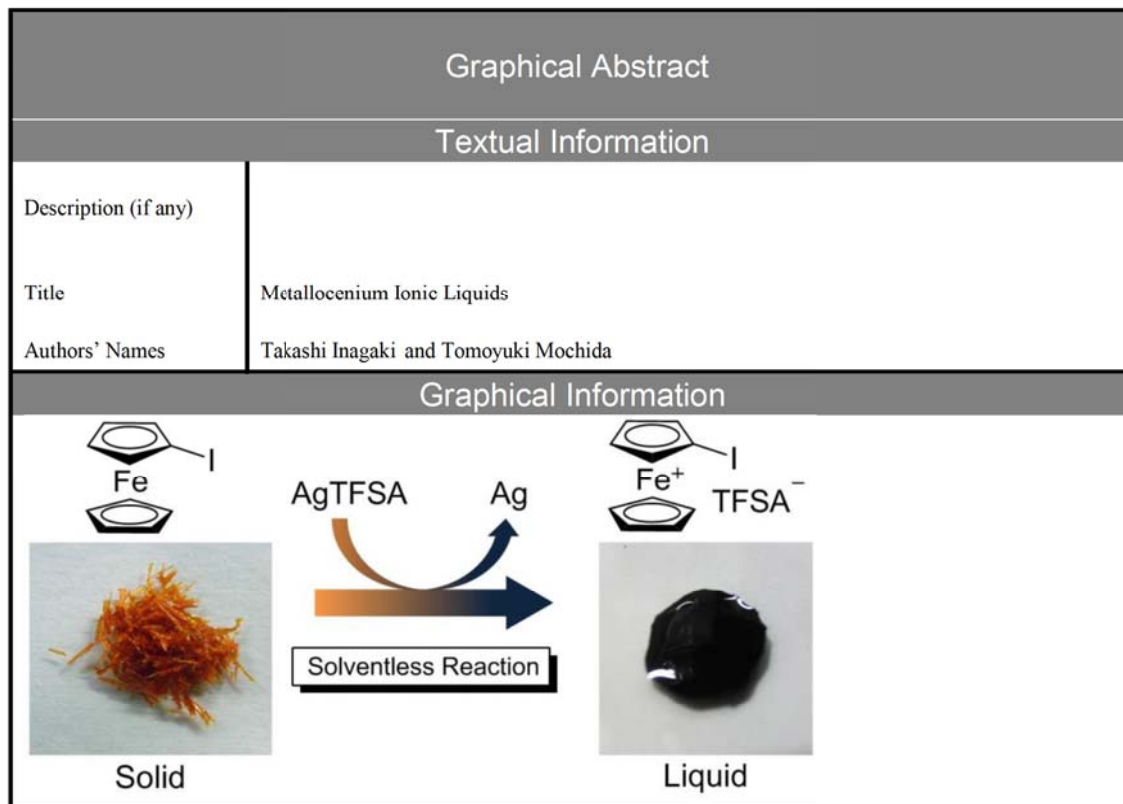
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NOTE The diagram is acceptable in a colored form. Publication of the colored G.A. is free of charge. For publication, electronic data of the colored G.A. should be submitted. Preferred data format is EPS, PS, CDX, PPT, and TIFF. If the data of your G.A. is "bit-mapped image" data (not "vector data"), note that its print-resolution should be 300 dpi.



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Supporting Information

General. Alkylferrocenes were purchased from TCI or Sigma-Aldrich. Lithium bis(trifluoromethanesulfonyl)amide (abbreviated as LiTFSA) was purchased from Wako Chemical Co. Iodoferrocene^[1] and silver bis(trifluoromethanesulfonyl)amide^[2] (abbreviated as AgTFSA) were prepared according to the literature methods. 1,1'-Diethylcobaltocenium hexafluorophosphate was purchased from Sigma-Aldrich and used after recrystallization from ethanol. Elemental analysis was performed by using Yanaco CHN corder MT5. Melting points and glass transition points were determined using TA Instrument Q100 Differential scanning calorimeter. DSC traces of [1,1'-diethylferrocenium][TFSA] (**2a**) are shown in Figure S1 as a typical example. Viscosities were measured using a Toki Sangyo TV-22 viscometer with a 3°×R7.7 cone rotor. Thermogravimetric analysis was performed using Rigaku Thermo Plus TG8120. Manipulations of ferrocenium ILs were carried out in a glove box under a nitrogen atmosphere.

Preparation of ferrocenium salts. All manipulations were carried out in a glove box under a nitrogen atmosphere. *n*-Butylferrocenium TFSA (**3a**) was prepared in a solventless reaction: *n*-butylferrocene (0.256 g, 1.05 mmol) and AgTFSA (0.414 g, 1.07 mmol) were mixed on an agate mortar and ground for 5 minutes. The mixture turned deep blue immediately, and elemental silver was deposited. The mixture was then filtered via a syringe equipped with a membrane filter to remove silver deposits and unreacted AgTFSA. This procedure gave the desired product quantitatively as a deep blue liquid. Calcd. for C₁₆H₁₈F₆FeNO₄S₂: C, 36.79; H, 3.47; N, 2.68%. Found: C, 36.72; H, 3.69; N, 2.82%.

Other salts (**1a**, **2a**, **4a** and **7a**) were prepared by similar methods. **1a**: Calcd. for C₁₄H₁₄F₆FeNO₄S₂: C, 34.02; H, 2.86; N, 2.83%. Found: C, 34.46; H, 2.88; N, 2.88%. **2a**: Calcd. for C₁₆H₁₈F₆FeNO₄S₂: C, 36.79; H, 3.47; N, 2.68%. Found: C, 36.73; H, 3.52; N, 2.67%. **4a**: Calcd. for C₂₀H₂₆F₆FeNO₄S₂: C, 39.14; H, 4.38; N, 2.54%. Found: C, 38.90; H, 4.50; N, 2.52%. **7a**: Calcd. for C₂₄H₁₈F₁₂Fe₂I₂N₂O₈S₄ (= [Fe(C₅H₄I)(C₅H₅)]⁺[TFSA]⁻ + 1/2 O₂): C, 23.70; H, 1.49; N, 2.30%. Found: C, 23.91; H, 1.61; N, 2.58%. Due to the extreme sensitivity of **7a** to oxygen, inevitable exposure to air during elemental analysis produced an oxygen adduct.^[3]

n-Butylferrocenium TFSA (**5a**) was prepared using a solvent to make filtration easier. To a CH₂Cl₂ solution (10 mL) of *n*-butylferrocene (0.223 g, 0.922 mmol) was added AgTFSA (0.367 g, 0.947 mmol) with stirring. The solution turned deep blue immediately, and elemental silver was deposited. After stirring for 30 min, the solution was filtered via a syringe equipped with a membrane filter, and then washed with water and dried over MgSO₄. After evaporation of the solvent, the product was recrystallized from a mixture of EtOH and a small amount of hexene at -50°C. This procedure gave the desired product as deep blue crystals (0.229 g, 47.7%). Calcd. for C₁₆H₁₈F₆FeNO₄S₂: C, 36.79; H, 3.47; N, 2.68%. Found: C, 36.56; H, 3.50; N, 2.74%.

Other salts (**6a**, ferrocenium TFSA, methylferrocenium TFSA, and 1,1'-dimethylferrocenium TFSA) were prepared by similar methods. **6a**: Calcd. for $C_{17}H_{20}F_6FeNO_4S_2$: C, 38.07; H, 3.76; N, 2.61%. Found: C, 38.34; H, 4.01; N, 2.70%. Ferrocenium TFSA: Calcd. for $C_{12}H_{10}F_6FeNO_4S_2$: C, 30.71; H, 2.15; N, 2.98%. Found: C, 30.51; H, 2.18; N, 3.00%. Methylferrocenium TFSA: Calcd. for $C_{13}H_{12}F_6FeNO_4S_2$: C, 32.52; H, 2.52; N, 2.92%. Found: C, 32.74; H, 2.58; N, 3.14%. 1,1'-Dimethylferrocenium TFSA: Calcd. for $C_{14}H_{14}F_6FeNO_4S_2$: C, 34.02; H, 2.86; N, 2.83%. Found: C, 33.91; H, 2.85; N, 2.94%.

Preparation of cobaltocenium salts. 1,1'-Diethylcobaltocenium TFSA (**8a**) was prepared by metathesis: to a hot aqueous solution (50 mL) of 1,1'-diethylcobaltocenium hexafluorophosphate (0.326 g, 0.837 mmol) was added an aqueous solution (2 mL) of LiTFSA (0.510 g, 1.78 mmol) with stirring, and the solution was allowed to cool to room temperature. The mixture was extracted with CH_2Cl_2 , washed with water, and dried over $MgSO_4$. After evaporation of the solvent, the desired product was obtained as a yellow oil, which was dried under vacuum for 1 day at 80°C. Calcd. for $C_{16}H_{18}CoF_6NO_4S_2$: C, 36.58; H, 3.45; N, 2.67%. Found: C, 36.60; H, 3.48; N, 2.72%.

Other cobaltocenium salts (**8b–8d**) were prepared by similar methods. **8b**: Calcd. for $C_{18}H_{18}F_{10}FeNO_4S_2$: C, 34.57; H, 2.90; N, 2.24%. Found: C, 34.46; H, 3.09; N, 2.41%. **8c**: Calcd. for $C_{20}H_{18}CoF_{14}FeNO_4S_2$: C, 33.13; H, 2.51; N, 1.94%. Found: C, 33.33; H, 2.75; N, 2.09%. **8d**: Calcd. for $C_{22}H_{18}F_{18}FeNO_4S_2$: C, 32.01; H, 2.20; N, 1.70%. Found: C, 31.83; H, 2.51; N, 1.89%.

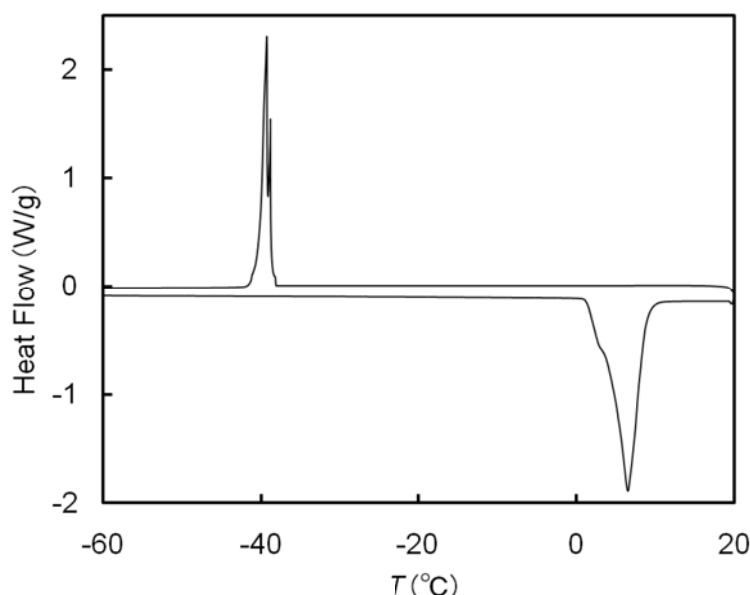


Figure S1. DSC traces of [1,1'-diethylferrocenium][TFSA] (**2a**).

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