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Metallocenium Ionic Liquids

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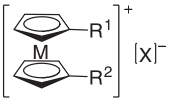
Ionic liquids have been prepared from simple metallocenium cations and bis(trifluoromethanesulfonyl)amide anion (TFSA). Their properties were tunable by the choice of metals and substituents; the ferrocenium salts were deep-blue paramagnetic liquids, which are readily prepared by a one-step solventless 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 anions[3] 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 (Figure 1), which are characterized by their simple formulae and tunable liquid properties.

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 bis(trifluoromethanesulfonyl)amide (**2a**) and 1,1′-diethylcobaltocenium bis(trifluoromethanesulfonyl)amide (**8a**), which are deep blue and orange, respectively. Changing the metal atom leads to the remarkable color change.



1: M = Fe, R^1 = Et, R^2 = H
2: M = Fe, R^1 = R^2 = Et
3: M = Fe, R^1 = *n*-Bu, R^2 = H
4: M = Fe, R^1 = R^2 = *n*-Bu
5: M = Fe, R^1 = *t*-Bu, R^2 = H
6: M = Fe, R^1 = $CH_2C(CH_3)_3$, R^2 = H
7: M = Fe, R^1 = I, R^2 = H
8: M = Co, R^1 = R^2 = Et

a: X = $N(SO_2CF_3)_2$ (TFSA)
b: X = $N(SO_2C_2F_5)_2$
c: X = $N(SO_2C_3F_7)_2$
d: X = $N(SO_2C_4F_9)_2$

Figure 1. Structural formulae of metallocenium ILs.

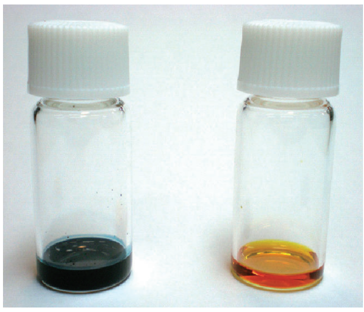
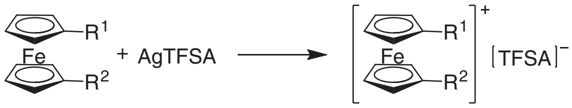


Figure 2. Metallocenium ILs: **2a** (M = Fe, left) and **8a** (M = Co, right).



Scheme 1. Preparation of ferrocenium bis(trifluoromethanesulfonyl)amide.

Ferrocenium ILs with low melting points (**1a**–**4a**, and **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 min, 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 LiTFSA 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, CH_2Cl_2, etc.) but not with nonpolar solvents (hexane, Et_2O, toluene, etc.). Miscibility with water was dependent on the cation substituent.

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 bis(trifluoromethanesulfonyl)amide (**7a**) was 33 °C; the introduction of a simple substituent to ferrocenium

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

ILs	T_m /°C	T_g /°C	$\eta_{25\,°C}$ /mPa s	$T_{m(precursor)}$[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_2Fc][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. 10. [d] Ref. 11.

bis(trifluoromethanesulfonyl)amide (mp: 131.5 °C) resulted in a remarkable decrease in the melting point. Comparison of **2a** (M = Fe, mp: 3.8 °C) and **8a** (M = Co, mp: 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 $–CF_2–$ 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).

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 **7a** (mp: 33 °C), which exhibits a lower milting 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),[12] but the values increased with increasing substituent length in both the cation and the anion. In particular, elongation of the $–CF_2–$ 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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