Paramagnetic organometallic ionic liquids exhibiting thermochromism based on monomer-dimer equilibrium of cationic half-sandwich complexes

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Paramagntic organometallic ionic liquids exhibiting thermochromism based on monomer–dimer equilibrium of cationic half-sandwich complexes

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Abstract

We synthesized paramagnetic organometallic ionic liquids $[Fe(C_5Me_4Bu)(SC_6H_4R)(CO)\{P(OEt)_3\}][Tf_2N]$ (R = CF_3 (**1**), H (**2**), OMe (**3**)), comprising a cationic half-metallocenium iron-thiolate complex and a bis(trifluoromethanesulfonyl)amide (Tf_2N) anion. These liquids exhibited thermochromism based on the monomer–dimer equilibrium of the cation.

Keywords Ionic liquids; Half-sandwich complexes; Paramagnetic liquids; Thermochromism; Thermal properties

1. Introduction

Room-temperature ionic liquids (ILs) have been studied extensively in terms of their functionalities and applications. ILs are salts with melting points below 100 °C, and they are regarded as designer liquids [1]. Many ILs exhibiting intriguing properties such as fluorescence, photochromic, and electrochromic properties have been synthesized. Several thermochromic ILs have been reported, which are either pure ILs [2,3] or ILs with additives [4].

Recently, various metal-containing ILs have been developed, which exhibit magnetic, electrochemical, photophysical, and other interesting physical properties [5,6]. We previously reported that salts of cationic sandwich or half-sandwich compounds with the bis(trifluoromethanesulfonyl)amide anion (Tf_2N) afford organometallic ILs [7], which is a useful methodology to produce functional ILs. In this paper, we report the preparation and properties of paramagnetic thermochromic ILs based on cationic half-sandwich complexes.

It has been reported that solutions of 17-electron half-sandwich iron-thiolate complexes $[Fe(C_5H_5)(SPh)(CO)(phosphine)]BF_4$ and its derivatives exhibit color changes upon dilution or temperature change [8,9]. Such chromism is attributed to the equilibrium between the blue paramagnetic monomer and the red diamagnetic dimer (Fig. 1). The dimer, formed via a disulfide bond with the concomitant valence change of iron, is predominant at high concentrations or low temperatures [8,9]. To introduce this function into ILs, we synthesized $[Fe(C_5Me_4Bu)(SC_6H_4R)(CO)\{P(OEt)_3\}][Tf_2N]$ (R = H (**1**), CF_3 (**2**), OMe (**3**)) containing iron-thiolate complexes (Fig. 2). The substituents (R) were varied to investigate the effect of electron withdrawing (CF_3) or donating (OMe) substituents on the equilibrium and color.

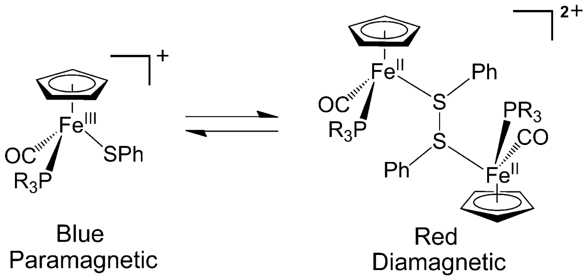

Fig. 1 Monomer–dimer equilibrium of cationic half-sandwich iron-thiolate complex.

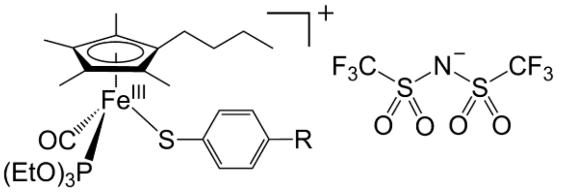

Fig. 2 Chemical formula of thermochromic ILs $[Fe(C_5Me_4Bu)(SC_6H_4R)(CO)\{P(OEt)_3\}][Tf_2N]$ (R = CF_3 (**1**), H (**2**), OMe (**3**)) synthesized in this study. The molecular formula of the monomer is shown.

2. Experimental

2.1. General

$[Fe(C_5R_5)(CO)_2I]$ (C_5R_5 = C_5Me_4Bu, C_5H_5) was prepared by applying a method described in the literature [10]. Silver bis(trifluoromethanesulfonyl)amide was also synthesized according to a literature method [11]. Other compounds were obtained from commercially available sources. All manipulations were performed using the Schlenk technique or in a globe box under a nitrogen atmosphere. ^{1}H NMR spectra were recorded on a JEOL JNM-ECL-400 spectrometer. UV-Vis absorption spectra were recorded using an Ocean Optics HR2000 CG-UV-NIR spectrometer with a Mikropack DH2000 light source and equipped with a Lincam #1002L thermostatically controlled stage. The liquid samples were sandwiched between two quarts plates, and the sample thickness varied slightly upon changing temperature. Magnetic susceptibilities were measured using a Quantum Design MPMS-XL7 SQUID susceptometer over the temperature range 2–350 K, with a sweeping rate of 2 K min^{-1} under an applied field of 1 T. The samples were held in an aluminum capsule. DSC measurements were performed using a TA Instruments Q100 differential scanning calorimeter at a heating rate of 10 K min^{-1}. TG measurements were performed using a Rigaku TG8120 system under a nitrogen atmosphere, at a scanning rate of 1 K min^{-1}.

2.2. Preparation of [Fe(C_5Me_4Bu)(CO){P(OEt)$_3$}(SC_6H_4R)] (R = CF_3, H, OMe)

These compounds were prepared applying the methods reported in the literature [9]. For compounds with R = H, an anhydrous THF solution of [Fe(C_5Me_4Bu)$(CO)_2$I] (3.76 g, 10.4 mmol, crude) was allowed to react with silver tetrafluoroborate (2.15 g, 11.0 mmol) under a nitrogen atmosphere. After stirring the reaction mixture for 3 h, the solvent was removed under reduced pressure at room temperature. The residue was dissolved in dichloromethane, and the solution was filtered through a short Celite plug. Benzenethiol (1.1 mL, 11 mmol) was added to the solution and stirred for 3 h. The reaction mixture was then washed with aqueous Na_2CO_3 and water, and dried over magnesium sulfate; then, the solvent was removed by evaporation. The crude product was purified over a short alumina column (hexane:diethyl ether = 9:1), and the solvent was subsequently removed by evaporation at room temperature. Next, the residue was dissolved in toluene, to which triethylphosphate (2.1 mL, 10.4 mmol) was added under a nitrogen atmosphere. Then, the reaction mixture was refluxed for 3 h at 125 °C. After cooling the reaction mixture to room temperature, the solvent was removed by evaporation. The crude product was purified successively on a column of silica gel (hexane and hexane:diethyl ether = 9:1) and alumina (hexane and hexane:Et_2O = 8:2). Following this, the solvent was removed by evaporation, and the residue was dried under vacuum. Dark-red oil, yield 1.69 g, 81%. δ = 0.904 (t, 3H, J = 6.6 Hz), 1.228 (t, 9H, J = 7.2 Hz), 1.28–1.33 (m, 4H), 1.689, 1.704, 1.710 (s, 12H), 2.202 (t, 2H, J = 7.4 Hz), 3.95–3.99 (m, 6H), 6.831 (t, 1H, J = 7.2 Hz), 6.981 (t, 2H, J = 7.6 Hz), 7.472 (d, 2H, J = 8.4 Hz). Compound with R = OMe: dark-red oil, yield 1.71 g, 75%. ^{1}H

NMR (400 MHz, $CDCl_3$, TMS): δ = 0.906 (t, 3H, *J* = 6.8 Hz), 1.230 (t, 9H, *J* = 7.0 Hz), 1.322 (m, 4H), 1.678, 1.694 (s, 12H), 2.180 (t, 2H, *J* = 7.4 Hz), 3.726 (s, 3H), 3.975 (m, 6H), 6.596 (t, 2H, *J* = 8.4 Hz), 7.33–7.41 (m, 2H, *J* = 8.4 Hz). Compound with R = CF_3: dark-red oil, yield 1.73 g, 81%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.908 (t, 3H, *J* = 6.6 Hz), 1.235 (t, 9H, *J* = 7.0 Hz), 1.32–1.39 (m, 4H), 1.688, 1.701, 1.709 (s, 12H), 2.197 (t, 2H, *J* = 7.0 Hz), 3.89–4.02 (m, 6H), 7.192 (d, 2H, *J* = 8.4 Hz), 7.527 (d, 2H, *J* = 8.4 Hz).

2.3. $[Fe(C_5Me_4Bu)(CO)\{P(OEt)_3\}(SC_6H_4R)][Tf_2N]$ (1: R = CF_3; 2: R = H; 3: R = OMe)

All manipulations were performed in a glove box under a nitrogen atmosphere, and all solvents were degassed prior to use. For the preparation of **1b**, an ether solution of $[(C_5Me_4Bu)Fe(CO)\{P(OEt)_3\}(SC_6H_5)]$ (545.8 mg, 1.017 mmol) was allowed to react with silver bis(trifluoromethanesulfonyl)amide (271.3 mg, 0.6992 mmol), and the reaction mixture was stirred for 30 min in the dark. Then, the solution was filtered off to remove any precipitated silver. The solvent was removed under reduced pressure. Next, the residue was dissolved in a small amount of CH_2Cl_2, to which excess hexane was added and stirred. The suspension was left to stand for 30 min, after which the supernatant was removed. This washing process was repeated three times to remove excess $[Fe(C_5Me_4Bu)(CO)\{P(OEt)_3\}(SC_6H_5)]$. To remove any trace of hexane, the residue was further washed with pentane by following the same procedure, and the residue was dried under vacuum at 60 °C for one day. This procedure gave **2** in an almost quantitative yield. Dark-purple liquid. Calcd. for $C_{28}H_{41}F_6FeNO_8PS_3$: C, 41.18; H, 5.06; N, 1.72%. Found: C, 41.22; H, 5.20; N, 1.60%. **1** and **3** were synthesized by the same method. **1**: dark-blue liquid. Calcd. for $C_{29}H_{40}F_9FeNO_8PS_3$: C, 39.37; H, 4.56; N, 1.58%. Found: C, 39.77%; H, 4.70; N, 1.54%. **3**: black liquid. Calcd. for $C_{29}H_{43}F_6FeNO_9PS_3$: C, 41.14; H, 5.12; N, 1.65%. Found: C, 40.74; H, 4.94; N, 1.95%.

3. Results and discussion

Salts **1**–**3** were synthesized by the reaction of neutral precursor complexes and silver Tf_2N. These salts were viscous, air-sensitive liquids. Differential scanning calorimetry measurements revealed that these liquids do not crystallize upon cooling and exhibit glass transition at T_g = 240, 225, and 229 K, respectively. The thermal decomposition temperatures of these ILs determined by thermogravimetric analyses under a nitrogen atmosphere (−3 wt%; heating rate: 1 K min^{-1}) were 405, 406, and 414 K, respectively.

These salts exhibited thermochromism based on the monomer-dimer equilibrium. Photographs of **1**–**3** at 353 K and 233 K are shown in Fig. 3. The color of **1** changed from purple to pale purple upon cooling, whereas **2** showed a color change from dark purple to bluish purple. Thermochromism of **3** was less prominent, with a color change from dark gray to gray. The color changes were reversible within this temperature range. These results demonstrate that the colors can be tuned by changing the substituents, though the thermochromism was less prominent as compared with other thermochromic ionic liquids [3].

The temperature dependence of the UV-Vis spectra of **1**–**3** measured between 228 K and 333 K are shown in Fig. 4. Each salt showed two peaks at around 520 nm and 600–700 nm. With decreasing temperature, the intensity of the peak at 520 nm increased for each IL, concomitant with the decrease of absorption intensities at lower energy region. This change can be attributed to the increase in the dimer ratio at low temperatures [8]. However, the small degree of spectral change suggests that the degree of equilibrium shift is small, which is consistent with the less prominent thermochromism in the present liquids. The absorption maximum of the band at around 520 nm was almost the same for **1**–**3**, whereas the broad absorption peak in the low-energy region exhibited a significant redshift in the order of **1** (620 nm), **2** (660 nm), and **3** (710 nm). It seems reasonable that an electron-donating substituent causes a redshift of the low-energy band due to the higher π-orbital of the benzenethiolato ligand and vice versa. The less prominent thermochromism in **3** is ascribed to its dark color resulting from the large absorption band in the visible region. The area of the low-energy absorption band changed in the order **1** < **2** < **3**, whereas the relative height of the dimer-related peak at around 520 nm changed in the order **1** > **2** > **3**. The low-energy band is related to monomer absorption [8]; hence, this feature suggests that the monomer ratio followed the order **1** < **2** < **3**. The spectrum of each salt was temperature-independent below T_g (spectra not shown), which is consistent with the freezing of the equilibrium below T_g.

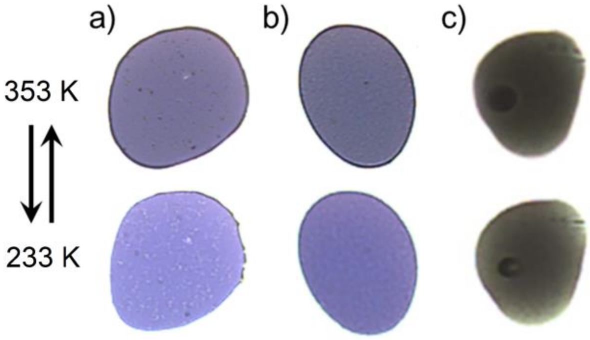

Fig. 3 Photographs of (a) **1**, (b) **2**, and (c) **3** at 353 K (upper) and 233 K (lower).

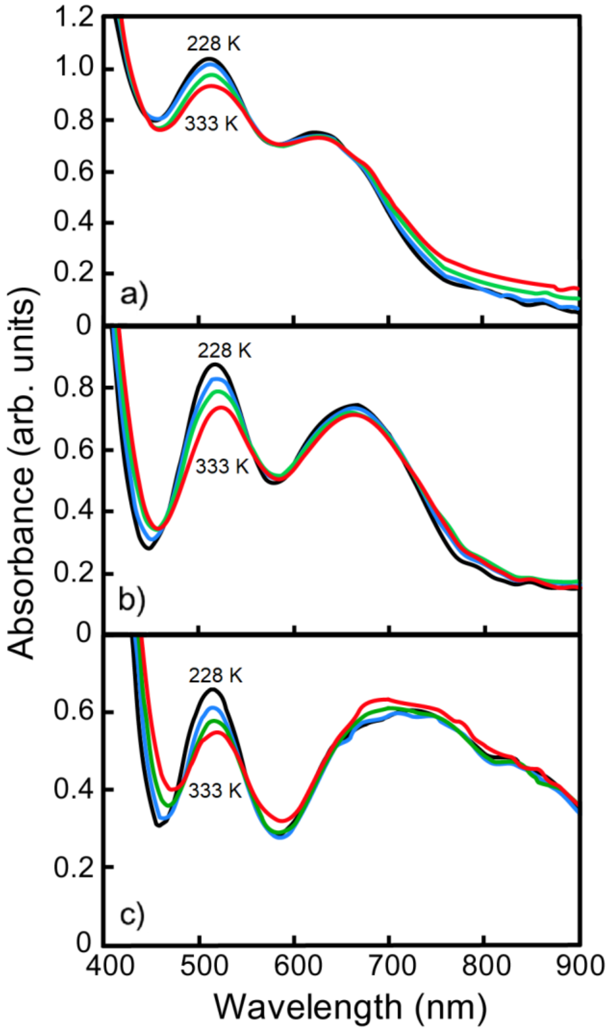

Fig. 4. Temperature dependence of the UV-Vis spectra of (a) **1**, (b) **2**, and (c) **3**, recorded at 333 K (red), 298 K (blue), 263 K (green), and 228 K (black).

These salts were paramagnetic ILs, as demonstrated by magnetic susceptibility measurements (Fig. 5). The χT values of **1**–**3** at 300 K were 0.35, 0.36, and 0.47 emu K mol^{-1}, respectively, and they decreased slightly with decreasing temperature. The magnetic moment of the paramagnetic monomer of iron-thiolate complexes is considered to be ~0.65 emu K mol^{-1} [9,12]. The value is similar to that of the ferrocenium cation and larger than the spin-only value (0.375 emu K mol^{-1}) due to orbital contribution [13]. Thus, the magnetic susceptibility values of **1**–**3** indicate that roughly 50% (**1**, **2**) and 30% (**3**) of the cations are dimerized at room temperature. The magnetic susceptibility values follow the order **1** < **2** < **3** over the entire temperature range. This trend indicates that the monomer ratio increases in the same order, which is consistent with the UV-vis spectra, and is ascribed to stabilization of the 17-electron monomer species by an electron-donating substituent. Concerning the temperature dependence, the decrease in susceptibility in the liquid state with decreasing temperature is consistent with the increase in the dimer ratio above T_g. The weak temperature dependence suggests that the degree of equilibrium shift is small, which accounts for the small change in the UV-vis spectra. However, no significant change was observed in the temperature dependence of susceptibility at T_g. The decrease in the magnetic moment below T_g is probably ascribed to antiferromagnetic intermolecular interactions and depopulation of the spin-orbit state [13].

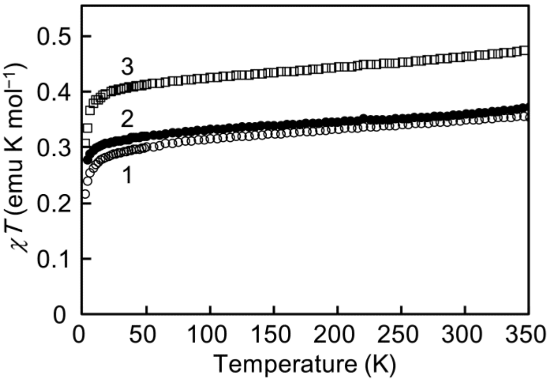

Fig. 5. Temperature dependence of the magnetic susceptibilities of **1** (○), **2** (●), and **3** (□), represented in the form of χT–T plots.

4. Conclusion

We synthesized paramagnetic ILs containing cationic half sandwich complexes, which exhibit thermochromism based on monomer-dimer equilibrium of the cation. This study demonstrates that chemical reactivities of organometallic complexes can be used as the mechanism of thermochromic ILs. The use of reactive organometallic complexes as a component of ILs is a promising approach for producing multifunctional liquids.

Acknowledgment

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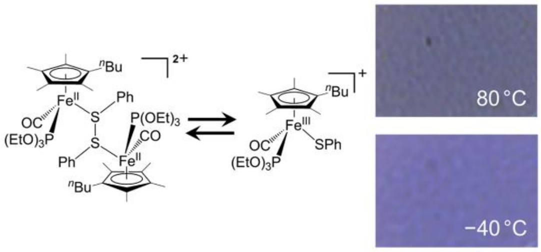
Graphical abstract



Highlights

- Ionic liquids containing cationic half-sandwich iron-thiolate complexes were synthesized.

- The ionic liquids exhibited paramagnetic behavior with a slight temperature dependence of the magnetic moment.

- The ionic liquids exhibit thermochromism based on the monomer–dimer equilibrium of the cation.