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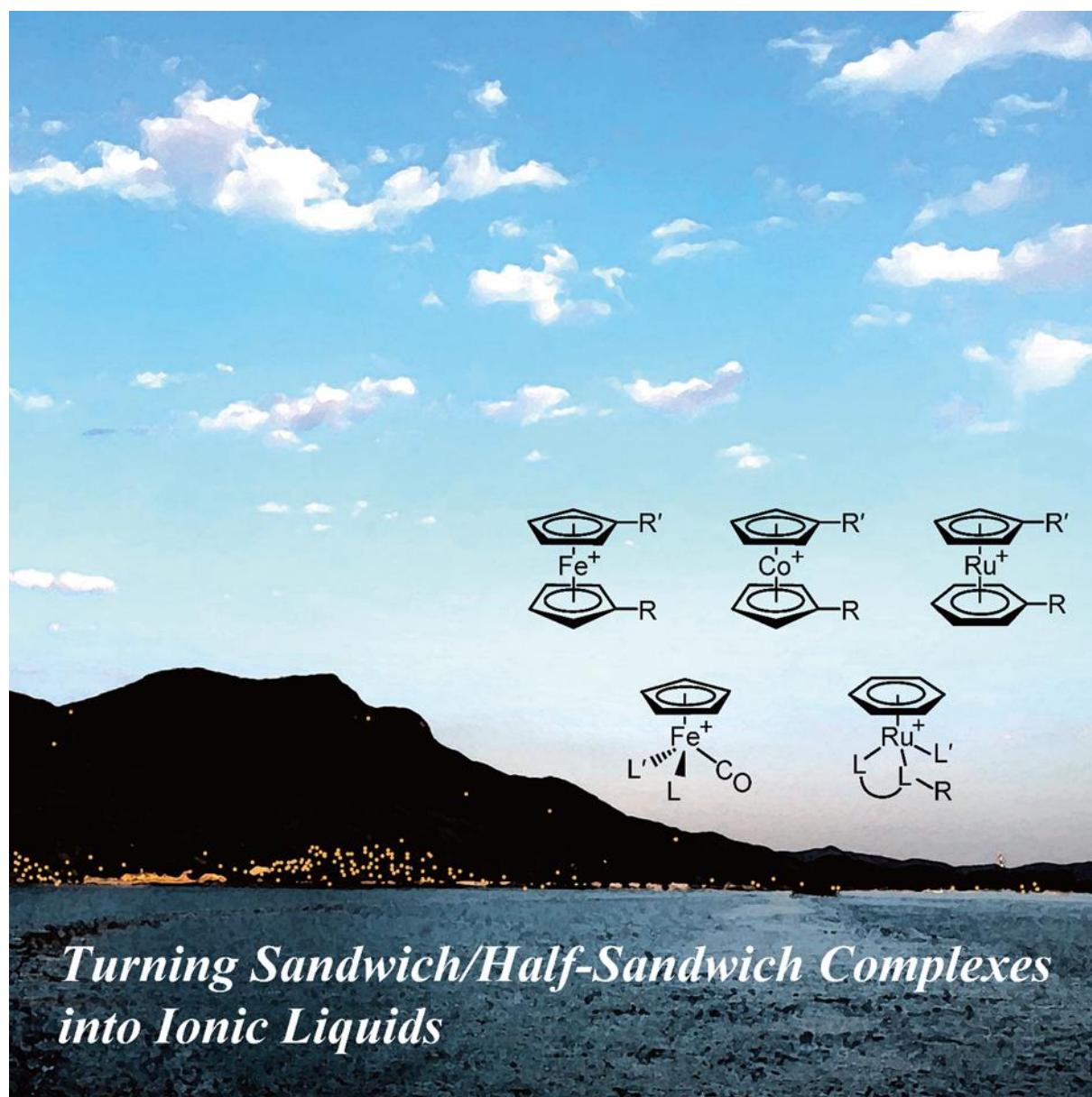
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Organometallic Ionic Liquids Containing Sandwich Complexes: Molecular Design, Physical Properties, and Chemical Reactivities

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Abstract: Ionic liquids (ILs) are salts with low melting points and are useful as electrolytes and solvents. We have developed ILs containing cationic metal complexes, which form a family of functional liquids that exhibit unique physical properties and chemical reactivities originating from metal complexes. Our study explores the liquid chemistry in the field of coordination chemistry, where solid-state chemistry is currently the main focus. This review describes the molecular design, physical properties, and reactivities of organometallic ILs containing sandwich or half-sandwich complexes. This paper mainly covers stimuli-responsive ILs, whose magnetic properties, solvent polarities, colors, or structures change by the application of external fields, such as light, heat, and magnetic fields, or by reaction with coordinating molecules.

1. Introduction

1.1. Objectives and Overview

Recently, extensive studies have been conducted on solid-state properties, such as the electronic, photochemical, and gas absorption properties of solid metal complexes. Although metal complexes generally have high melting points, the idea is that if these functional solids can be liquefied, various functional liquids can be formed, leading to the exploration of liquid-state coordination chemistry. Thus, we have developed ionic liquids (ILs) containing cationic metal complexes. This review describes our research on organometallic ILs containing cationic sandwich or half-sandwich compounds.

ILs have been extensively studied recently, mainly with respect to solvent and electrolyte applications.^[1] Typical ILs comprise quaternary cations and fluorinated anions, such as Tf_2N ($= (\text{CF}_3\text{SO}_2)_2\text{N}^-$) and FSA ($= (\text{FSO}_2)_2\text{N}^-$), and they are characterized by negligible vapor pressure, nonflammability, high ionic conductivity, wide liquid temperature range, etc. Their characteristic miscibility with organic solvents and water makes them suitable solvents for dissolution, separation, and recycling. A major advantage of ILs is that their functions can be

molecularly designed. Accordingly, many functional ILs that exhibit stimuli responses, gas-adsorption properties, catalytic abilities, etc., have been developed.^[1] Although most ILs are organic salts, some metal-containing ILs have been recently developed, and they contain solvated metal ions,^[2] metalate anions,^[3] chelate complexes,^[4] metal salts,^[5] etc., and exhibit interesting physical properties. Onium ILs with organometallic substituents have also been developed.^[6]

We have liquefied various metal complexes by applying the molecular design of ILs. These liquids simultaneously exhibit characteristic properties of ILs and metal complexes, resulting in unique functions that cannot be realized with conventional liquids or solutions.

1.2. Development of Organometallic Ionic Liquids

Sandwich and half-sandwich complexes form important families of organometallic compounds. Among sandwich complexes, the material science of ferrocene ($[\text{FeCp}_2]$, $\text{Cp} = \text{C}_5\text{H}_5$) and its derivatives has been extensively studied in terms of their electrochemical and magnetic properties.^[7] Apart from ferrocene, there are dozens of sandwich complexes, including those with arene ligands and metal ions other than iron. The half-sandwich complexes are of interest mainly because of their reactivity, as they are particularly useful as catalysts for organic reactions.

Before starting the research on ILs, we were investigating the solid-state electronic properties of ferrocene derivatives. Charge-transfer salts of cationic ferrocene derivatives and planar π -conjugated anions (Figure 1a) are interesting because of their solid-state properties.^[7,8] Although most of them decompose at high temperatures without melting, we observed that a few of them melt without decomposition. Thereafter, we had an idea that if their melting points could be lowered, various functional fluids could be realized. Metallocenium cations appeared suitable for ILs, considering their spherical molecular shape, charge delocalization, and tendency to exhibit molecular motion in crystals. In addition, some ferrocene derivatives, such as alkylferrocenes, have low melting points, and some of them are liquid at room temperature. Thus, following the molecular design of conventional ILs, the introduction of an alkyl group into a cationic sandwich complex and the use of a fluorinated anion successfully yielded a series of organometallic ILs (Figure 1b).

The concept of our research as described in this review is shown in Figure 2. The first step of the research was to establish the molecular design of ILs from sandwich complexes while evaluating their thermal properties (Section 2). In addition, the cation species were extended to half-sandwich complexes. In the second step, we developed various stimuli-responsive ILs, focusing on physical properties (Section 3) and chemical

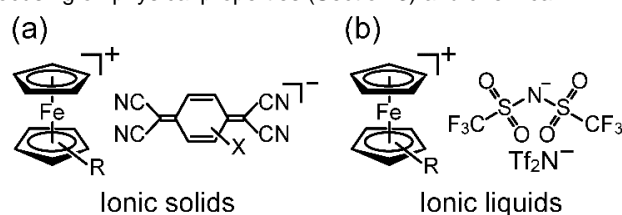


Figure 1. Ionic solids (charge-transfer salts) and ILs containing cationic ferrocene derivatives

Prof. Tomoyuki Mochida has been a Professor of inorganic chemistry at Kobe University, Japan, since 2007, where he is also a member of the Research Center for Membrane and Film Technology. He graduated from the University of Tokyo in 1990 and joined the Institute for Molecular Science as a research associate in 1994. He received his Ph.D. from the University of Tokyo in 1995. In 1997, he moved to Toho University as a lecturer and became an associate professor in 2003. From 1997 to 2000, he was engaged in a JST-PREST project. His current research interests are the development of functional ILs, ionic plastic crystals, and soft matter containing metal complexes.



Research Concepts of Organometallic ILs

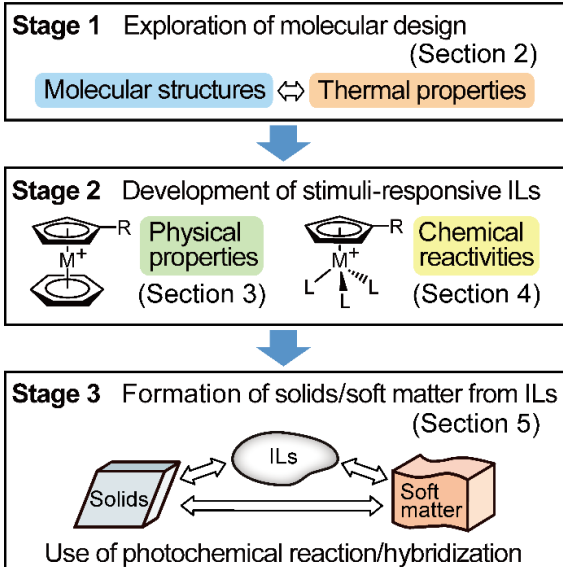


Figure 2. Research concepts of organometallic ILs. The corresponding sections in this account are indicated in the chart.

reactivities (Section 4). The third step involved the construction of functional solids, such as coordination polymers (CPs) and soft matter from ILs via photochemical reactions (Section 5).

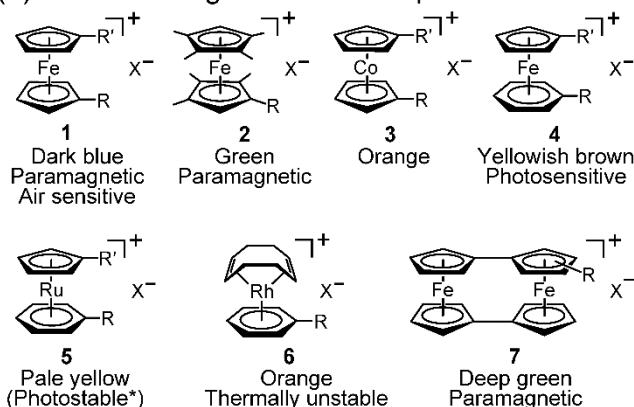
2. Design and Synthesis of Organometallic Ionic Liquids

2.1. Synthesized Ionic Liquids

Following the aforementioned molecular design, the introduction of alkyl substituents into a cationic complex and the use of the Tf_2N^- anion produced the desired ILs. Representative ILs containing cationic sandwich or half-sandwich complexes are described below (Figure 3).

Ferrocenium ILs **1** are highly air-sensitive, dark-blue paramagnetic liquids (Figure 4, left),^[9] whereas their octamethyl derivatives **2** are green, air-stable, and paramagnetic liquids.^[10] Cobaltocenium ILs **3** are orange, diamagnetic liquids (Figure 4, middle), which are air-stable and thermally more robust than ferrocenium ILs. ILs containing Cp-arene complexes are air-stable, diamagnetic liquids; Fe-containing ILs **4** are yellowish-brown liquids (Figure 4, right), which are sensitive to visible light,^[9a] whereas Ru-containing ILs **5** are colorless to pale-yellow liquids, which are photostable.^[11] However, introduction of coordinating substituents into ILs **5** makes them photoreactive, which is a versatile feature to design photoreactive ILs (Section 5). Rh-containing ILs **6** are orange diamagnetic liquids, and they are thermodynamically unstable because they gradually transform into an anion-coordinated complex.^[12] Dinuclear ILs **7** are deep-green, mixed-valence liquids whose melting points are close to room temperature despite their high molecular weight.^[13] ILs containing half-sandwich complexes, such as ILs **8–10**, are generally highly viscous, colored liquids.^[14] These ILs

(a) ILs containing sandwich complexes



(b) ILs containing half-sandwich complexes

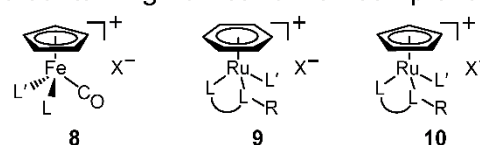


Figure 3. Organometallic ILs containing (a) sandwich or (b) half-sandwich complexes (R, R': alkyl group, L–L': bidentate ligand, L': monodentate ligand, X: anion, typically Tf_2N^-). ILs **5** are photostable in the absence of coordinating substituents or molecules.

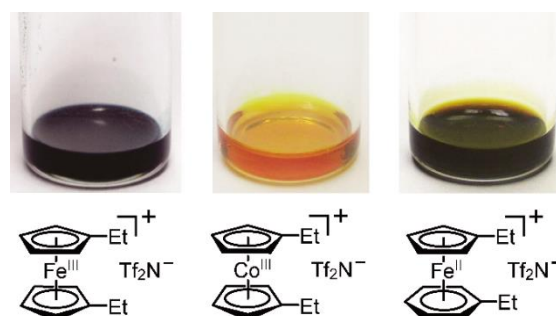


Figure 4. Images of some typical ILs containing sandwich complexes.

tend to be somewhat susceptible to oxygen, light, heat, or some solvents because of their high reactivity.

Anions other than Tf_2N^- , such as FSA and $\text{B}(\text{CN})_4^-$, can also be used, but Tf_2N^- is the most effective for lowering melting points. The molecular motion, microstructure, and electronic states of some of these ILs have been studied by theoretical calculations, terahertz spectroscopy, and NMR spectroscopy.^[15]

2.2. Synthesis

This section summarizes the synthesis of typical organometallic ILs, some of which are air- or photosensitive.

Alkylferrocenium salts: We first synthesized alkylferrocenium ILs **1** with the Tf_2N^- anion, which are highly air-

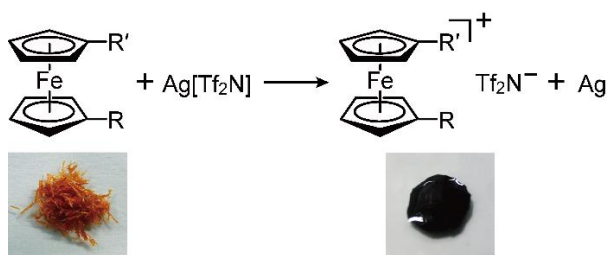


Figure 5. Preparation scheme for ferrocenium ILs. Images of compounds with $R' = I$ and $R = H$ are shown below.

sensitive. These ILs are rapidly synthesized quantitatively in a single step by grinding neutral alkylferrocenes (liquid or solid) and solid $AgTf_2N$, using an agate mortar under an inert atmosphere (Figure 5). In this reaction, the silver ion acted as an oxidant, and the resulting silver deposit could be easily removed by syringe filtration. This solvent-free method was devised to simplify the synthetic procedure and avoid possible contamination from solvents.^[9] Indeed, many experiments were performed to isolate the desired ILs before we noticed that they were highly sensitive to oxygen. In contrast, solid ferrocenium salts are sufficiently air-stable. Since the air sensitivity of these ILs prevented a detailed study of their physical properties, we further synthesized air-stable octamethyl derivatives **2**, which allowed detailed magnetic studies and led to the discovery of a magnetic orientation phenomenon, as shown in Section 3.

Other salts: Many air-stable organometallic ILs are synthesized via PF_6 salts, which are typically solid and can be purified by recrystallization or washing with appropriate solvents. The PF_6 salts are then converted into the desired ILs by anion exchange, either with an ion-exchange resin or by solvent extraction after the addition of the desired anion. A frequently encountered problem is the difficulty of purification; these ILs are generally purified by a combination of solvent extraction, charcoal treatment, and column chromatography, and certain ILs can be purified by recrystallization at low temperatures, but these methods are not always effective. In addition, certain complexes are stable in the crystalline state but considerably less stable in the liquid state, becoming susceptible to oxygen, moisture, light, or heat. Actually, we abandoned the isolation of several organometallic ILs because of purification problems.

2.3. Correlation between Molecular Structures and Thermal Properties

ILs containing cationic sandwich complexes generally exhibit significantly higher viscosities and higher melting points or glass transition temperatures than typical imidazolium ILs. Therefore, appropriate substituents are required to obtain room-temperature ILs, as discussed below.

Alkyl-chain length: The relationship between alkyl-chain length and melting point in metallocenium ILs is similar to that observed for typical onium ILs.^[16] Although their melting points are high because of their bulkiness and high molecular weights, the introduction of an ethyl or long substituent is usually sufficient to produce salts with melting points below 100°C. Figure 6a shows the melting points of alkylferrocenium ILs **2** as

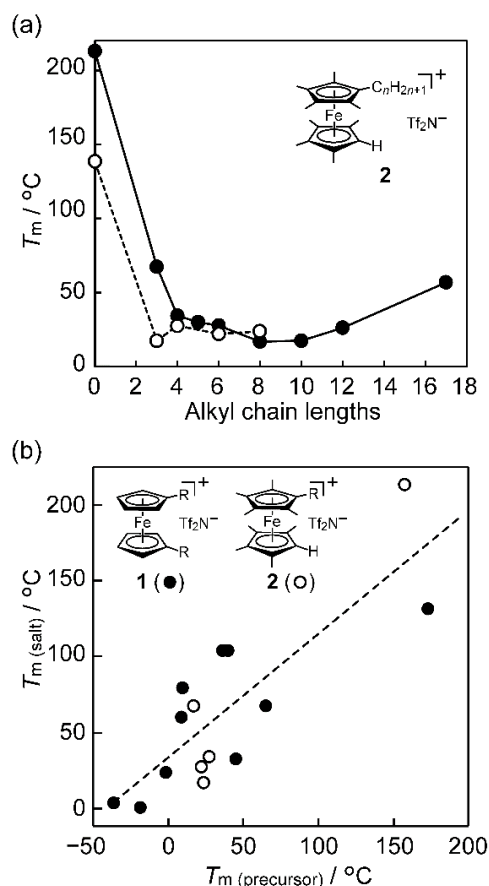


Figure 6. (a) Melting points of alkyloctamethylferrocenium ILs **2** ($X = Tf_2N$) plotted as a function of alkyl-chain length (\bullet), including that of octamethylferrocenium salt ($n = 0$). The values for alkyloctamethylferrocenes (\circ) are also plotted. (b) Correlation between the melting points of alkylferrocene derivatives and their Tf_2N salts, including ILs **1** (\bullet), **2** (\circ), and related high-melting-point compounds.

a function of carbon number in the substituent, which exhibits minima ($\sim 17^\circ C$) at carbon numbers in the range of 8–10.^[10a] Their melting points are comparable to those of corresponding alkyloctamethylferrocenes, as shown in Figure 6a. Ferrocenium ILs **1** have lower melting points than ILs **2** owing to their smaller cation volume. The melting points of ILs **1** and **2** are plotted in Figure 6b against those of their precursors (alkylferrocenes and alkyloctamethylferrocenes), which shows roughly a linear correlation.^[9,10a] The introduction of polar substituents such as ether, carbonyl, and cyano groups resulted in high melting points and high viscosities, as expected.^[11]

In contrast, salts of unsubstituted or monomethyl sandwich complexes do not produce ILs; instead of melting, most of them undergo a phase transition into an ionic plastic crystal (IPC) phase at high temperatures owing to the nearly spherical shape of the cations, as shown in Figure 7.^[17] This tendency is common to salts with Tf_2N , FSA, and $B(CN)_4$ anions, although a planar $C(CN)_3$ anion is an exception, the salts of which melt without exhibiting a plastic phase. Noteworthy, metallocenium salts produce ILs and IPCs depending on the substituent length.

Chiral substituents: Branched alkyl substituents are known to reduce the crystallinity of molecular materials; however, a few studies have investigated the origin. We observed that branched substituents were effective in lowering the melting point of metallocenium salts.^[18] The racemic mixtures of the stereoisomers of **5a** with a branched chiral substituent (Figure 8a; X = PF₆, FSA, or Tf₂N) are considerably less easy to crystallize, compared with isomer **5b** with a linear substituent. Furthermore, for PF₆ salts, the melting point of chiral salt **5a** (T_m = 71 °C, S-isomer) was comparable with that of the linear chain salt, **5b**, whereas that of the corresponding racemic mixture of **5a** was lower (T_m = 42 °C). The lower melting point of the racemic mixture, which was a conglomerate (a mixture of chiral crystals) in this case, is ascribed to the effect of mixing entropy. In these ILs, branched substituents increase the viscosity, compared with linear substituents. NMR spectroscopic studies have shown that this tendency correlates with the motion of the alkyl substituents.^[15d] Similarly, in the PF₆ and CF₃BF₃ salts of **5c**, the racemate has a lower melting point than the chiral salt, where these salts formed a conglomerate and racemic compound, respectively.^[19] Racemates more often form racemic compounds rather than conglomerates, and the melting point may increase or decrease in the case of racemic compounds.

Cation shape: Cation shape and substituent positions also affect the melting points. For the PF₆ salts of **5d** and **5e** with three substituents at the 1,2,3- or 1,3,5- positions of the arene ring (Figure 8b; R = OC_nH_{2n+1}, n = 6, 12, 18), the latter isomer has significantly lower melting points than the former.^[20] Crystal structure analysis suggested that the higher melting point of the 1,2,3-isomer was due to the layered structure formed by the interaction between the alkyl chains, although there was no clear tendency observed for FSA salts. This tendency of PF₆ salts appears reasonable since 1,2,3-trisubstituted benzenes frequently form organized structures, such as liquid crystals. These were investigated for the design of photoreactive ILs, as described in the last section.

Furthermore, the effect of cation symmetry on ILs **4** was investigated.^[9] The Cp-substituted isomer, [Fe(C₅H₅R)(C₆H₆)]Tf₂N, has a higher melting point than the arene-substituted isomer, [Fe(Cp)(C₆H₅R)]Tf₂N, and the corresponding monosubstituted ferrocenium salt, [Fe(C₅H₄R)(Cp)] Tf₂N. ILs **6** with a cyclooctadiene ligand exhibit higher melting points than ILs **4**.

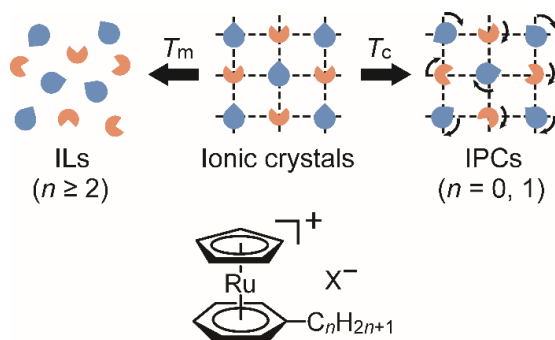


Figure 7. Schematic illustrations of ILs, ionic crystals, and ionic plastic crystals (IPCs). The structure of Cp-arene complexes is shown as an example.

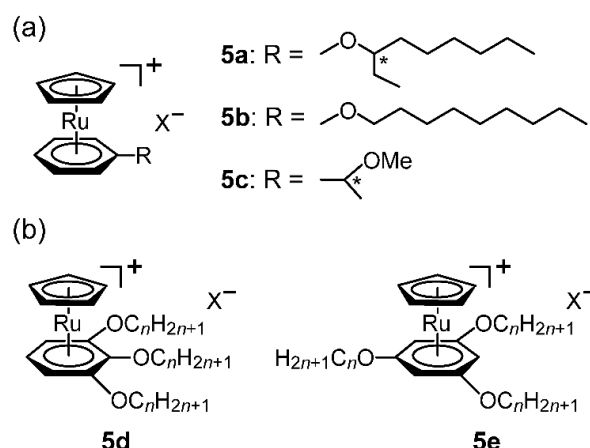


Figure 8. Ru-containing ILs **5a–e** used to study substituent effects.

The melting points of ILs containing half-sandwich complexes are dominated by the bulkiness of the ligands. The melting points of ILs with small ligands, such as ILs **8**,^[14a] can be low, but those of ILs with \square -conjugated bidentate ligands, such as ILs **9** and **10**,^[14b] are generally high, limiting their use as ILs. Although salts that do not readily crystallize can be used as liquids above their glass transition temperature, they are generally highly viscous.

3. Ionic Liquids Containing Sandwich Complexes: Physical Properties

ILs containing sandwich complexes exhibit unique physical phenomena based on their magnetic and electronic properties. Selected topics of magnetic and solvent properties are discussed below.

3.1. Magnetic Orientation of Ferrocenium Ionic Liquids

Dozens of magnetic ILs containing paramagnetic ions have been recently reported, and their applications have been investigated.^[3a,21] Ferrocenium ILs are also paramagnetic liquids, but they differ from conventional magnetic ILs **1** and **2** in that the cations exhibit uniaxial magnetic anisotropy. Although the effect of magnetic fields on liquid solidification is usually negligible, certain ferrocenium ILs exhibit a significant effect because of this feature.

IL **2a** is a green paramagnetic liquid with a melting point near room temperature (Figure 9a, inset).^[22] Although its magnetic susceptibility is almost unchanged upon crystallization when cooled under a weak magnetic field (< 0.1 T), the application of strong magnetic fields significantly increases its magnetic susceptibility upon crystallization at 27 °C. After heating, the value returns to the liquid value at T_m = 34 °C, indicating hysteresis. The increase in magnetic susceptibility is attributed to the crystal orientation induced by the magnetic field during crystallization. The oriented structures are visually

observed using a polarized optical microscope (Figure 9b). The degree of orientation and magnetic susceptibility in the crystal phase increase with an increase in the magnetic field before attaining saturation at ~ 2 T. The mechanism is that, since the cations are aligned in the same direction in the crystal of **2a**, the alignment of the magnetically anisotropic crystal is induced by the magnetic field during in situ crystal growth. Most other ferrocenium-based ILs do not exhibit the magnetic orientation effect owing to their magnetically isotropic crystal structures. A few ferrocenium ILs **1** exhibit the same phenomenon, but the crystal orientation is less controllable because of rapid crystallization owing to their low viscosity.^[9a]

The present IL is a unique magnetic fluid in which the orientation and magnetic susceptibility of the crystalline phase can be controlled by the magnetic field, exhibiting a magnetic memory effect with thermal hysteresis. Although many studies have been conducted on the magnetic field effect on the solidification of liquids, the phenomenon is exceptional, and the mechanism may be applied to the electromagnetic control of dielectric functions or ionic conductivities. Furthermore, ferrocenium ILs are redox active ILs, and this feature may be applicable to redox-active devices.

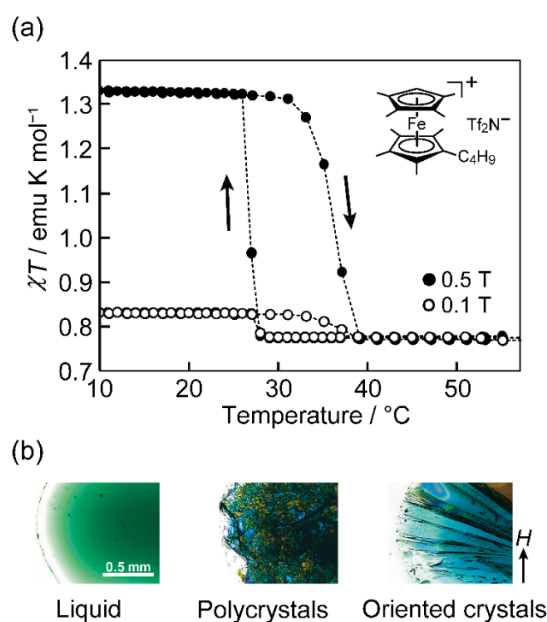


Figure 9. (a) Temperature dependence of the magnetic susceptibility of **2a**. Data measured at 0.1 and 0.5 T are indicated by black and white circles, respectively. (b) Polarized optical microscopy images of **2a** on a glass plate at room temperature: sample in the liquid state (left), crystallized without a magnetic field (middle), and crystallized at 0.6 T (right).

3.2. Temperature Dependent Solvent Polarity of Mixed-Valence Ionic Liquids

Dinuclear complexes comprising two ferrocene units, such as biferrocene^[23] and biferrocenylene,^[24] are of interest in terms of electron transfer and mixed valency. To investigate the effect of mixed valency on solvent properties, we synthesized dark-green mixed-valence ILs **7a** and **7b**, and their positional isomers

containing cationic biferrocenylene derivatives.^[13] Their melting points were close to room temperature (25 °C–39 °C), and they maintained the liquid state above their glass transition temperatures after melting (T_g , –66 °C to –45 °C).

The solvent polarity of ILs is important because it reflects their solvent properties, such as solubilizing power and miscibility with other solvents.^[25] E_T^N values and Kamlet–Taft parameters are representative solvent polarity parameters and have been evaluated for ILs using solvatochromic dyes.^[26] The E_T^N values for the mixed-valence ILs (0.67–0.76) are comparable to those for common imidazolium ILs, with higher values for **7a** than those for **7b**, correlating with substituent polarity. The values are larger than those for mononuclear ILs **2** and **3**, correlating with the higher polarization of the dinuclear moiety.

Notably, the E_T^N of **7a** exhibited a remarkable temperature dependence (Figure 10b). In contrast, only a slight linear increase was observed for **7b** and mononuclear ILs **2**, which is attributable to increased intermolecular interactions at low temperatures, as frequently observed for onium-based ILs.^[27] The Kamlet–Taft parameters of **7a** also significantly varied with temperature. This temperature dependence is probably due to changes in the valence state; increase of the contribution of the more stable form of the two resonance structures (Figure 10a, top one) at low temperatures due to less thermal vibrational excitation may result in a more localized charge distribution with a higher polarity. In addition, the temperature-dependent solvent polarity resulted in a thermochromic shift in the intervalence charge-resonance absorption band. Electron transfer in mixed-valence ILs is intriguing in terms of liquid properties, and furthermore, the feature would be useful for electronic applications.

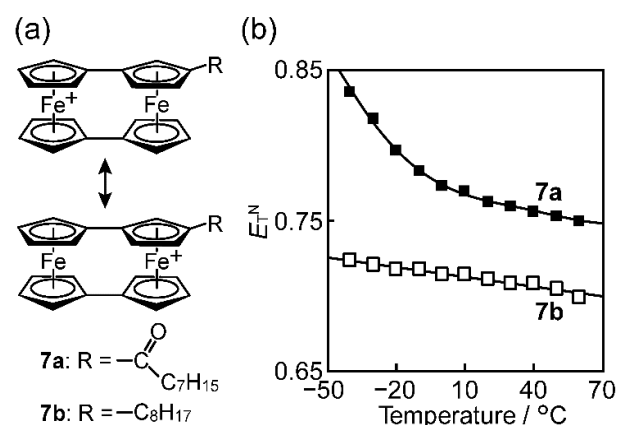


Figure 10. (a) Resonance structures of cations in ILs **7a** and **7b**. (b) Temperature dependence of the solvent polarity parameter, E_T^N , of the dinuclear ILs.

4. Ionic Liquids Containing Half-Sandwich Complexes: Chemical Reactivities

Reactive ILs containing half-sandwich complexes were designed to harness the diverse reactivities of the complexes. As a result,

in situ transformation between ILs with different physical and chemical properties has been realized, which are based on thermodynamic aspects and also rely on the nonvolatility of ILs.

4.1. In Situ Ligand Exchange

CpFe dicarbonyl complexes are versatile reactive and catalytic species.^[28] ILs containing this moiety were prepared, which transform into different ILs via in situ ligand-exchange reactions.^[14a] The exposure of red IL **8a** ($T_m = 17^\circ\text{C}$) to dimethylsulfide vapor at 40°C for 6 h causes a nearly quantitative ligand exchange to afford a reddish-orange viscous solid, **8a'** ($T_m = 65^\circ\text{C}$) (Figure 11a, top). Conversion into other ILs can be similarly achieved by exposure to coordinating molecules, such as pyridine and NH_3 , and the subsequent vacuum removal of excess ligands. The conversion depends on the relative coordination ability of the ligands and the yields were sometimes low owing to decomposition.

Half-sandwich arene-Ru complexes with chelating ligands can be used as homogeneous catalysts.^[29] Red IL **9a** containing an arene-Ru complex was prepared, which undergoes ligand exchange toward more thermally stable ILs **9a'** and **9a''** (Figure 11a, bottom).^[30] These ILs exhibited high catalytic activity for solvent-free alcohol oxidation, and the products were easily separated, but unfortunately, the complexes gradually decomposed during the reaction. ILs with various *N,N*-bidentate ligands were also prepared, but the situation was similar.^[14b] Further studies on organometallic catalytic ILs may lead to homogeneous and even heterogeneous liquid catalysts.

ILs **10a** and its analogues containing half-sandwich CpRu complexes enable quantitative interconversion between ILs with different colors, physical properties, and reactivity via in situ ligand exchange (Figure 11a, right).^[31] ILs **10a** and **10a'** with SMe_2 and dimethyl sulfoxide (DMSO) as auxiliary ligands are red-brown and orange liquids, respectively, and the exchange between them occurs by the addition of excess ligands. The exposure of these liquids to CO results in conversion into **10a''**, which is a yellow liquid, and the reverse reaction occurs via photoreaction. The CO release ability of the IL upon UV photoirradiation may be useful for catalytic reactions and

biomedical applications.

4.2. Isomerization and Dimerization

Linkage isomerization is a fundamental reaction of metal complexes.^[32] To investigate linkage isomerization in the IL state, an IL containing a thiocyanate complex (Figure 11b) was prepared. The IL, obtained as a 7:3 mixture of linkage isomers **9b** and **9b'**, is a dark-brown liquid with extremely high viscosity.^[33] UV irradiation induced isomerization from the *N*- to the *S*-isomer; the photoisomerization of Ru-SCN complexes was unprecedented. Thermal isomerization occurred in the same direction but was accompanied by decomposition. The *N*- and *S*-isomers were brown and orange liquids, respectively, and their UV-visible absorption bands exhibited a small solvatochromic absorption shift in organic solvents, with different trends for each isomer. This observation indicates that the solvent properties of ILs can be controlled based on isomerization.

The half-sandwich iron thiolate complex exhibits dimerization via the formation of S-S bonds in solution.^[34] ILs containing this cation are air-sensitive and are equilibrium mixtures of a paramagnetic monomer and diamagnetic dimer (Figure 11c).^[35] IL **8b** ($\text{R} = \text{CF}_3$) changes from pale purple to purple upon heating from -40°C to 80°C , exhibiting thermochromism based on a temperature-dependent equilibrium shift. The color and monomer ratio (70%–50%) vary with substituents. This study demonstrated that an equilibrium of metal complexes is a useful mechanism for thermally controlling the physical properties of ILs. In addition, compared with the thermochromism of metal complexes in organic solvents,^[36] the nonvolatility of ILs is advantageous for applications.

5. Formation of Coordination Polymers from Ionic Liquids

Coordination polymers (CPs) are metal complexes in which the metal ions are linked by multidentate ligands.^[37] We have

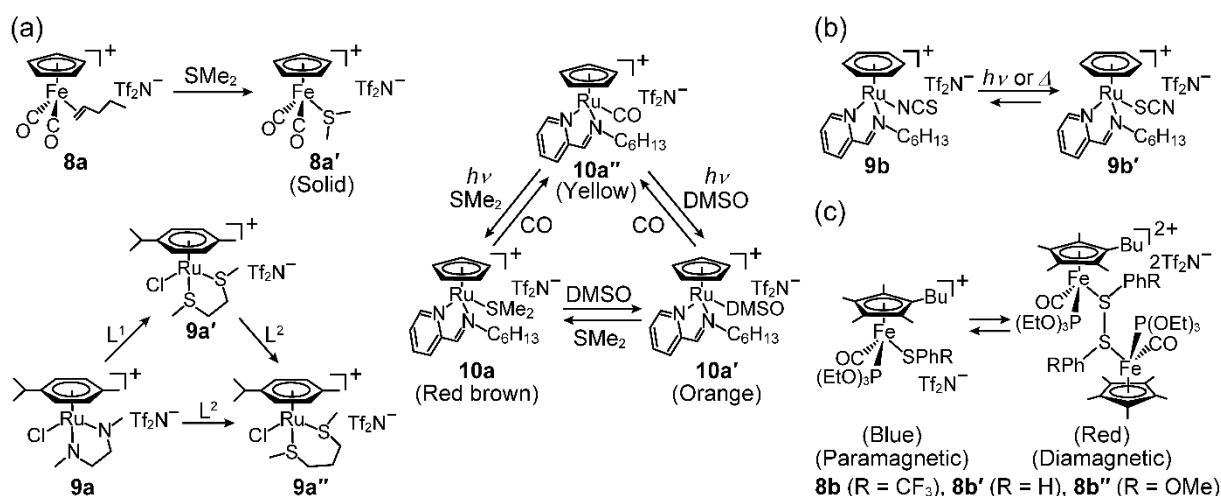


Figure 11. Reactivity of ILs containing half-sandwich complexes. (a) Ligand-exchange reactions, (b) linkage isomerization, and (c) dimerization equilibria.

developed ILs that transform into amorphous CPs upon photoirradiation, which is a novel method of CP formation. The mechanism was designed based on the typical photochemical reactivity of sandwich CpRu arene complexes through a photodissociation of the arene ligand in coordinating solvents, as shown in Figure 12a.^[38] By extending this methodology, stimuli-responsive soft matter can be also formed,^[39,40] but we will focus on the formation of CPs here.

5.1. Reversible Formation of Amorphous Coordination Polymers

IL **5f** (Figure 12b) is a pale-yellow liquid with three coordinating substituents. When this liquid is sandwiched in a quartz plate and irradiated with UV light, it gradually hardens to transform into a film of yellow amorphous CP in ~ 5 h.^[41] In this reaction, the photoirradiation of a benzene ring and coordination of three cyano groups occur, resulting in a three-dimensional bridged structure. The conversion rate is ~80%, with some undissociated cations incorporated in the CP. The resulting CP is elastic and becomes brittle below the glass transition temperature ($T_g = 10^\circ\text{C}$). A reverse reaction occurs upon heating the CP at 130°C for 1 min, completely transforming back into the original IL. This feature is advantageous for reuse, contrasting with conventional photocurable resins, whose reaction is irreversible. Furthermore, the ionic conductivity of the material reversibly changes with this transformation, which is a versatile feature for electronic applications.^[42] The IL was designed considering the substituent effects in CpRu complexes.^[20, 43] Although the material requires a long photoirradiation time, it can be reduced by further modification, such as the addition of bridging molecules.^[44]

Noteworthy, the IL–CP transformation involves the cleavage and formation of intra and intermolecular bonds (a drastic change in bonding modes), not achievable with organic molecules. This phenomenon exploits the reactivity of organometallic compounds and the flexibility of coordination bonds. These materials are novel types of photopolymers and may be applicable in soft electronic devices.

5.2. Formation of Porous Amorphous Coordination Polymers

Based on the same mechanism, we developed ILs **5g**, which produce porous amorphous CPs upon photoirradiation (Figure 12c).^[45] After UV photoirradiation, the liquid turned into a yellow powder of amorphous CPs in 30 min. In this reaction, the photodissociation of the arene ligand and anion coordination occurred, resulting in a randomly bridged porous structure. The dissociated arene ligands were readily removed by heating under a vacuum or during washing. The reaction time was considerably shorter than that for the aforementioned ILs because the bridging reaction occurred between the cation and anion. The generated solid exhibited nitrogen gas adsorption by the micropores, with a Brunauer–Emmett–Teller (BET) specific surface area of approximately $120\text{ m}^2\text{ g}^{-1}$, practically independent of the substituent in the cation. Although the adsorption was an order smaller than those of typical porous CPs, hydrogen and carbon dioxide adsorption were observed. Although the photoreaction is irreversible, the original ILs can be regenerated upon heating the CP in the presence of arene ligands.

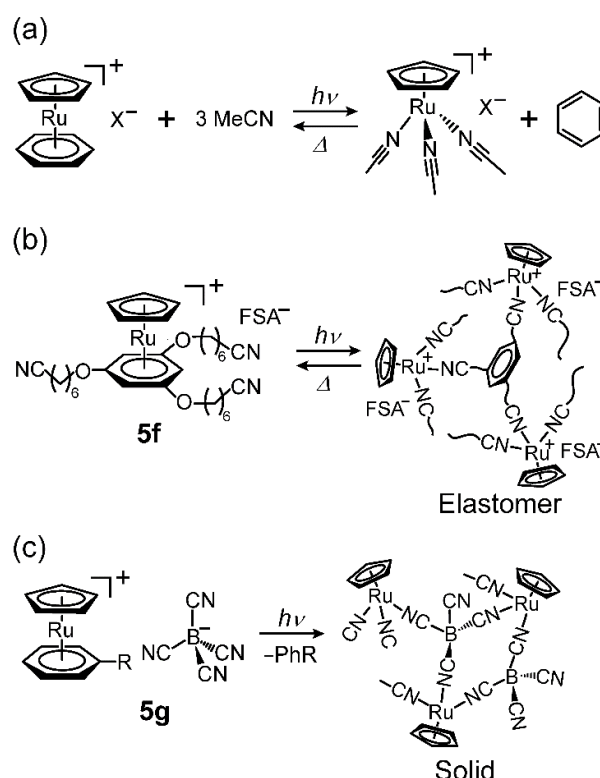


Figure 12. (a) Photoreaction and thermal reaction of a sandwich CpRu complex in acetonitrile.^[38] (b) Reversible transformation between IL **5f** and an amorphous CP. (c) Formation of porous amorphous CPs through the photoirradiation of ILs **5f**. In b and c, the figures on the right show the schematics of the partial structure of the CPs.

The photogenerated amorphous structure inherently has a low gas-adsorption ability and low selectivity, compared with crystalline CPs. However, its compositional and structural flexibility may be advantageous for developing additional functions, such as catalytic activities. Furthermore, the in situ formation method of CPs represents a new methodology for CP synthesis. This approach can expand the science of CPs and is versatile for applications.

6. Summary and Outlook

This review presented the materials design and functions of organometallic ILs containing cationic sandwich or half-sandwich complexes. Based on the methodology of IL fabrication with cationic metal complexes, we prepared many liquid metal complexes with unique physical properties and chemical reactivities, responding to external stimuli, such as light, heat, and materials. These features are distinct from those of conventional liquids, solutions, or solids of metal complexes.

The science of organometallic ILs is the interdisciplinary science of those of metal complexes and ILs. The study contributes to the expansion of materials and concepts in IL science, and it explores the novel liquid chemistry area in coordination chemistry, where solid chemistry is the main focus. In addition, several novel reactions of metal complexes have

been discovered through these studies. Furthermore, organometallic ILs bridge the materials chemistry of liquids and solids; not only solid–liquid phase transitions but also chemical transformations between them have been demonstrated.

Although the current studies are limited to basic studies, the extension of this approach to a wide range of materials and applications will contribute to advances in materials science. First, the use of diverse metal complexes may lead to new phenomena, and as an approach to this, we are synthesizing ILs that contain other types of cations, including organometallic and chelate complexes.^[46] Second, the development of hybrid and composite materials using stimuli-responsive organometallic ILs is promising. For example, we are preparing photoreactive polymerized ILs (polyILs),^[39] photoresponsive gels containing ILs,^[40] and IL-containing CPs.^[47] Third, the research on the application of organometallic ILs for electronic devices and liquid catalysts may have high potential.

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Keywords: Keywords: ionic liquids, sandwich complexes, metallocenes, materials science, coordination polymers

References

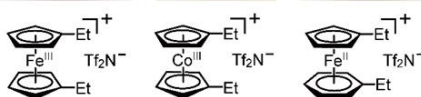
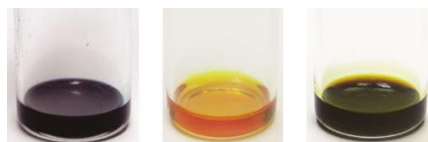
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Table of Contents

The Chemical Record PERSONAL ACCOUNT

This review describes the molecular design, synthesis, physical properties, and reactivities of organometallic ionic liquids containing sandwich or half-sandwich complexes. The major topics covered are stimuli-responsive ionic liquids, whose physical properties, chemical properties, and structures change by the application of external stimuli.



Magnetic Liquids, Photoreactive Liquids, Stimuli-Responsive Liquids, etc.

*Prof. Dr. T. Mochida**

Organometallic Ionic Liquids Containing Sandwich Complexes: Molecular Design, Physical Properties, and Chemical Reactivities