29

Progress in Paramagnetic Ionic Liquids

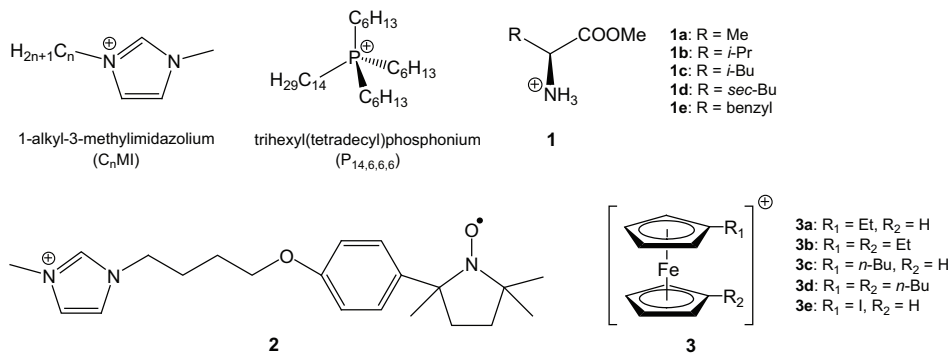Yukihiro Yoshida and Gunzi Saito
Meijo University
Japan

1. Introduction

Ionic liquids are entirely composed of ions as the name implies, and melt below room temperature (RT) or 100 °C. The ionic character means the extraordinary high ion density (i.e., the order of a molarity), and thus results in the negligible vapor pressure (i.e, wide liquid temperature region and negligible flammability) and high ionic conductivity. Such special fascinations attract considerable attention of researchers in many fields, as promising greener alternatives to the volatile molecular solvents for many areas of synthetic, separation, and electrochemical applications (Wasserscheid & Keim, 2000; Dupont et al., 2002; Buzzeo et al., 2004; Armand et al., 2009; Yoshida & Saito, 2010). Although ionic liquids have been known for nearly a century (Walden, 1914; Gabriel & Weiner, 1888), efforts in exploring new and more versatile ionic liquids have only recently been devoted, after the discovery of the first water- and air-stable RT ionic liquids formed with 1-ethyl-3-methylimidazolium (C_2MI; Scheme 1) cation reported by Wilkes and Zaworotko (Wilkes & Zaworotko, 1992), and Cooper and O'Sullivan (Cooper & O'Sullivan, 1992), in 1992. The majority of existing ionic liquids is composed of organic quaternary cations (e.g., 1,3-dialkylimidazolium, *N*-alkylpyridinium, and tetraalkylphosphonium) and inorganic small anions (e.g., BF_4^-, PF_6^-, and $AlCl_4^-$), for which monovalent ions are favorable for stabilizing the liquid state because of the depressed interionic Coulomb interactions. In general, cations are responsible for reducing the melting point, and therefore, low-symmetrical hetero cations with well-delocalized charge and/or long alkyl group(s) have been used.
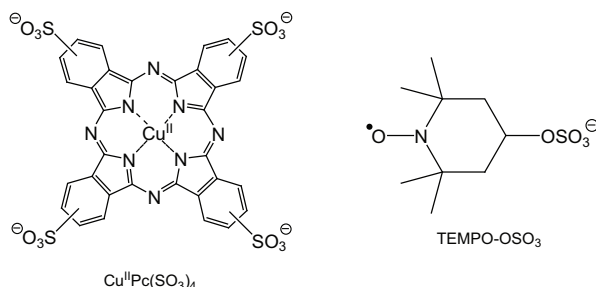
On the other hand, the selection of anions can readily tailor the liquid properties and introduce the desired functionalities. For example, the combination with PF_6 and $(CF_3SO_2)_2N$ (bis(trifluoromethanesulfonyl)amide; Tf_2N) anions gives the hydrophobic ionic liquids (Bonhôte et al., 1996; Suarez et al., 1998), and CH_3COO and $EtOSO_3$ anions stabilize the liquid state even at low temperatures (Wilkes & Zaworotko, 1992; Holbrey et al., 2002; Borra et al., 2007). These properties could find a range of synthetic and separation applications. In relation, $HCOO$ and $(MeO)(R)PO_2$ (R = H, Me, MeO) anions give ionic liquids, which can solubilize cellulose (Fukaya et al., 2006; Fukaya et al., 2008). BF_4, Tf_2N and $(FSO_2)_2N$ anions give ionic liquids with a wide electrochemical window, which opens the applicative way for electrolytes of capacitors, lithium ion batteries, field-effect transistors, and electrodeposition (Bonhôte et al., 1996; Fuller et al., 1997; Sato et al., 2004; Zein El Abedin et al., 2005; Matsumoto et al., 2006; Ono et al., 2009). Highly conducting ionic liquids formed with $N(CN)_2$, $C(CN)_3$, and $B(CN)_4$ anions have served as electrolytes for dye-sensitized solar cells (MacFarlane et al., 2001; Wang et al., 2003; Yoshida et al., 2004; Kawano et al., 2004; Wang et al., 2005; Kuang et al., 2006; Yoshida et al., 2007a; Yoshida et al., 2007b).

Recently, a new class of functional ionic liquids, in which chemically synthesized organic or metal complex ions are largely responsible for the functionality, is starting to attract interest, and some reviews on catalytic, pharmaceutical and energetic properties have been published (Fei et al., 2006; Singh et al., 2006; Hough & Rogers, 2007; Smiglak et al., 2007). Such component ions allow the fine and dual tuning of liquid properties of the resulting ionic liquids, by the chemical modification of both cation and anion. In this review, we focus on developments of the functional ionic liquids, especially composed of magneto-active inorganic and organic ions.

Cations

$H_{2n+1}C_n$ — 1-alkyl-3-methylimidazolium (C_nMI)

trihexyl(tetradecyl)phosphonium ($P_{14,6,6,6}$)

R—COOMe / NH_3 **1**
1a: R = Me
1b: R = i-Pr
1c: R = i-Bu
1d: R = sec-Bu
1e: R = benzyl

2

3
3a: R_1 = Et, R_2 = H
3b: R_1 = R_2 = Et
3c: R_1 = n-Bu, R_2 = H
3d: R_1 = R_2 = n-Bu
3e: R_1 = I, R_2 = H

Anions

$Cu^{II}Pc(SO_3)_4$

TEMPO-OSO_3

Scheme 1. Component ions in this chapter.

2. Magneto-active anions

2.1 Inorganic anions containing iron

In most cases, a certain functionality of anions can be passed to the resulting ionic liquid when the interionic interaction has little impact on the functionality. Magneto-active metal complex anions, such as $Fe^{III}X_4^-$ (X: Cl, Br) (Yoshida et al., 2005a; Yoshida et al., 2005b; Yoshida & Saito, 2006; Del Sesto et al., 2008; Li et al., 2009), $Mn^{II}X_4^{2-}$ (X: Cl, Br) (Del Sesto et al., 2008; Pitula & Mudring, 2010), $Mn^{II}(Tf_2N)_3^-$ (Pitula & Mudring, 2010), $Co^{II}X_4^{2-}$ (X: Cl, NCS, NCSe, N(CN)$_2$) (Del Sesto et al., 2005; Del Sesto et al., 2008; Peppel et al., 2010), $Gd^{III}Cl_6^{3-}$ (Del Sesto et al., 2008), and $Dy^{III}(SCN)_{8-x}(H_2O)_x^{(5-x)-}$ (x: 0–2) (Mallick et al., 2008) anions, have been known to form

paramagnetic RT ionic liquids, by pairing with organic quaternary cations. Paramagnetic ionic liquids, whose magnetic properties were given in the literatures, are listed in Table 1. Many of them can be obtained simply by mixing the halide salt and neutral metal halide; for example, dark brown ionic liquids $[C_nMI][FeCl_4]$ are formed by mixing exactly equimolar crystalline $[C_nMI]Cl$ and $FeCl_3$ under inert atmosphere at RT (Yoshida et al., 2005b). This procedure dispenses with the need for reaction solvent and ion exchange process.

Cation	Anion	T_m (°C)	μ_{eff} $(\mu_B)^c$	References
C$_2$MI (+1)	**Fe^{III}Cl$_4$** (–1)	18	5.83	Yoshida et al., 2005b
C$_4$MI (+1)	**Fe^{III}Cl$_4$** (–1)	–88 (T_g)	5.80	Yoshida & Saito, 2006
C$_6$MI (+1)	**Fe^{III}Cl$_4$** (–1)	–86 (T_g)	5.85	Yoshida & Saito, 2006
C$_8$MI (+1)	**Fe^{III}Cl$_4$** (–1)	–84 (T_g)	5.85	Yoshida & Saito, 2006
C$_{10}$MI (+1)	**Fe^{III}Cl$_4$** (–1)	–81 (T_g)	5.66	Del Sesto et al., 2008
P$_{14,6,6,6}$ (+1)	**Fe^{III}Cl$_4$** (–1)	–71 (T_g)	5.89	Del Sesto et al., 2008
1a (+1)	**Fe^{III}Cl$_4$** (–1)	–48 (T_g)	5.59	Li et al., 2009
1b (+1)	**Fe^{III}Cl$_4$** (–1)	–45 (T_g)	5.56	Li et al., 2009
1d (+1)	**Fe^{III}Cl$_4$** (–1)	–41 (T_g)	5.52	Li et al., 2009
1e (+1)	**Fe^{III}Cl$_4$** (–1)	–31 (T_g)	5.66	Li et al., 2009
C$_4$MI (+1)	**Fe^{III}Br$_4$** (–1)	–83 (T_g)	5.73	Yoshida & Saito, 2006
C$_6$MI (+1)	**Fe^{III}Br$_4$** (–1)	–82 (T_g)	5.75	Yoshida & Saito, 2006
C$_8$MI (+1)	**Fe^{III}Br$_4$** (–1)	–81 (T_g)	5.84	Yoshida & Saito, 2006
P$_{14,6,6,6}$ (+1)	**Mn^{II}Cl$_4$** (–2)	–69 (T_g)	5.81	Del Sesto et al., 2008
C$_4$MI (+1)	**Mn^{II}Br$_4$** (–2)	< RT^b	5.84	Del Sesto et al., 2008
P$_{14,6,6,6}$ (+1)	**Co^{II}Cl$_4$** (–2)	–68 (T_g)	4.45	Del Sesto et al., 2008
P$_{14,6,6,6}$ (+1)	**Co^{II}[N(CN)$_2$]$_4$** (–2)	–70 (T_g)	4.23 ^{d}	Del Sesto et al., 2005
C$_4$MI (+1)	**Co^{II}(NCS)$_4$** (–2)	–61 (T_g)	4.40	Peppel et al., 2010
P$_{14,6,6,6}$ (+1)	**Co^{II}(NCS)$_4$** (–2)	–72 (T_g)	4.06	Del Sesto et al., 2008
P$_{14,6,6,6}$ (+1)	**Gd^{III}Cl$_6$** (–3)	< RT	7.86	Del Sesto et al., 2008
C$_6$MI (+1)	**Dy^{III}(NCS)$_6$(H$_2$O)$_2$** (–3)	–56 (T_g)	10.4	Mallick et al., 2008
C$_6$MI (+1)	**Dy^{III}(NCS)$_7$(H$_2$O)** (–4)	–58 (T_g)	10.6	Mallick et al., 2008
C$_6$MI (+1)	**Dy^{III}(NCS)$_8$** (–5)	–60 (T_g)	10.4	Mallick et al., 2008
C$_4$MI (+1)	**TEMPO-OSO$_3$** (–1)	–27 (T_g)	1.73	Yoshida et al., 2007c
C$_6$MI (+1)	**TEMPO-OSO$_3$** (–1)	–27 (T_g)	1.68	Yoshida et al., 2007c
C$_8$MI (+1)	**TEMPO-OSO$_3$** (–1)	–31 (T_g)	1.61	Yoshida et al., 2007c
P$_{14,6,6,6}$ (+1)	**Co^{II}(DBSQ)$_2$(bpy(COO)$_2$)** (–2)	–11 (T_g)	3.60	Yoshida et al., 2009
2 (+1)	Tf$_2$N (–1)	–37 (T_g)	1.75	Uchida et al., 2009
2 (+1)	BF$_4$ (–1)	–32 (T_g)	1.75	Uchida et al., 2009
2 (+1)	PF$_6$ (–1)	–22 (T_g)	1.69	Uchida et al., 2009
3a (+1)	Tf$_2$N (–1)	3.8	2.33	Inagaki & Mochida, 2010
3b (+1)	Tf$_2$N (–1)	1.0	2.17	Inagaki & Mochida, 2010

^{a} Numbers in parentheses are valences of ions. Bold ions are responsible for the magnetic behavior. T_m: melting temperature, T_g: glass transition temperature, μ_{eff}: effective magnetic moment.
^{b} In a more recent paper (Pitula & Mudring, 2010), T_g = –50 °C and T_m = 44 °C.
^{c} Measured at RT (25–27 °C).
^{d} Private communication from Dr. Del Sesto.

Table 1. Characteristics of paramagnetic RT ionic liquids^a

Effective magnetic moments (μ_{eff}), represented by $g[S(S+1)]^{1/2}\mu_B$, of $[C_nMI][FeCl_4]$ were estimated to be the range of 5.66–$5.89\mu_B$ at 25 °C, which are close to that expected for a paramagnetic $S = 5/2$ high-spin on Fe^{III} ions (spin-only value: $5.92\mu_B$). The temperature dependency simply follows the Curie law in their liquid region, whereas their solid states at low temperatures show the pronounced deviation from the Curie law due to the antiferromagnetic interactions (Figure 1). In particular, $[C_0MI][FeCl_4]$, $[C_2MI][FeCl_4]$, and $[C_2MI][FeBr_4]$ exhibited long-range antiferromagnetic ordering at 9.5, 4.2, and 12.5 K, respectively (Yoshida et al., 2005b; Yoshida & Saito, 2006).
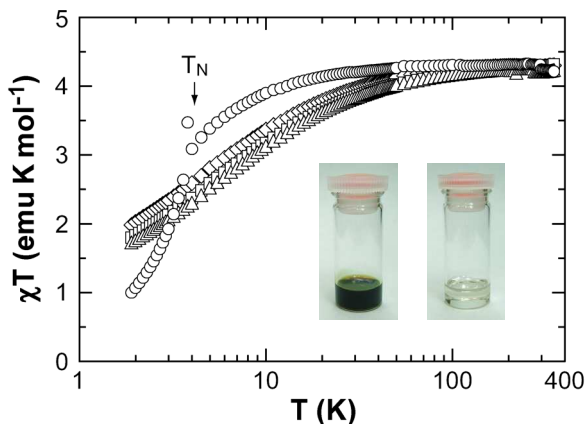
Fig. 1. Temperature dependence of the product of static susceptibility and temperature (χT) for $[C_nMI][FeCl_4]$ in an applied field of 100 Oe on heating process (○: n = 2, Δ: n = 4, □: n = 6, and ◊: n = 8). An arrow indicates the Néel temperature (T_N). The inset is the photographs of $[C_2MI][FeCl_4]$ (left) and $[C_2MI][GaCl_4]$ (right) (Yoshida et al., 2005b).

Among the paramagnetic ionic liquids, $[C_2MI][FeCl_4]$ having a melting point (T_m) of 18 °C has the highest ionic conductivity of 2.0×10^{-2} S cm^{-1} and lowest viscosity of 18 cP at 25 °C (Yoshida et al., 2005b). These values are comparable to those of $[C_2MI][Ga^{III}Cl_4]$ with non-magnetic $Ga^{III}Cl_4$ anion (2.2×10^{-2} S cm^{-1} and 16 cP at 25 °C) (Yoshida et al., 2005b). It appears that the small size and monovalency of both component ions, as well as the charge-delocalized low-symmetrical C_2MI cation, are factors governing the high ion diffusivity. $[C_0MI][FeCl_4]$ containing smaller C_0MI cation is not in liquid state but crystalline solid at RT ($T_m = 103$ °C), and the C_2MI salt with $Fe^{II}Cl_4$ dianion, $[C_2MI]_2[Fe^{II}Cl_4]$, is also in solid state at RT ($T_m = 86$ °C). The crystalline solid $[C_2MI]_2[Fe^{II}Cl_4]$, whose crystal structure was determined by a synchrotron X-ray powder diffraction measurement (Yoshida et al., 2005b), is isostructural to the reported $[C_2MI]_2[Co^{II}Cl_4]$ ($T_m = 100$–102 °C) and $[C_2MI]_2[Ni^{III}Cl_4]$ ($T_m = 92$–93 °C) (Hitchcock et al., 1993). As seen in Figure 2, each C_2MI cation is connected with three $Fe^{II}Cl_4$ dianions through hydrogen bonding type interactions. The shortest distance was found for $C(2)$–$H \cdots Cl$ (3.261 Å), presumably associated with the high acidic character of the 2-hydrogen.

Dual functionalities, namely the paramagnetism and chiral discrimination ability, were recently realized by the combination with the chiral protonated L-amino acid methyl esters (**1**; Scheme 1) (Li et al., 2009). Their RT magnetic moments (5.52–$5.66\mu_B$) are comparable to those of $[C_nMI][FeCl_4]$, and the salt composed of phenylalanine-derivative **1e** shows a
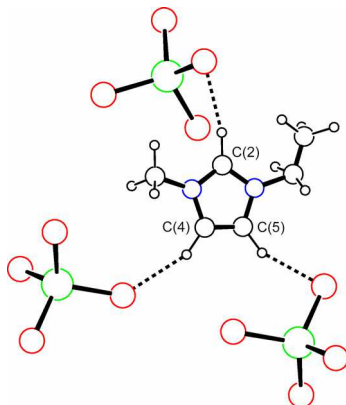
Fig. 2. Interionic contacts between C_2MI cation and $Fe^{II}Cl_4$ dianion in $[C_2MI]_2[FeCl_4]$. Short C–H···Cl contacts are shown by dashed lines. The crystal structure was determined by a synchrotron X-ray powder diffraction measurement (Yoshida et al., 2005b).

positive circular dichromism band at 218 nm with a maximum of 2.4×10^{-2} deg. Luminescence study using several chiral analytes revealed that the salt composed of alanine-derivative **1a** has a chiral discrimination ability. Future works may be to synchronize the dual functionalities, such as chiral extraction and enrichment of chiral compounds by applying the magnetic field.

As seen in Figure 3, the ionic conductivity and viscosity are under the control of the alkyl chain length of C_nMI cations and on the sort of halide of $Fe^{III}X_4$ anions (Yoshida & Saito, 2006). The elongation of alkyl chain results in the increased ion size and interionic van der Waals interactions, both of which modify the ion diffusivity in the unfavorable direction. Replacing the chloride to bromide also results in the significant decrease in ion diffusivity, possibly due to the increased ion size and interionic interactions. The replacement leads to the slight decrease in μ_{eff}, as a consequence of the lower ligand field strength Δ in $FeBr_4$ anion as $\mu_{eff} = \mu_0(1 - 2\lambda/\Delta)$, where μ_0 is the spin-only value and λ is the spin–orbit coupling constant at FeX_4 anions.

Ionic liquids whose magnetic properties extend far beyond that of the existing ones may be those with the pronounced response to the external stimuli and with the pronounced magnetic interactions including long-range magnetic ordering. The former type of ionic liquids will be described later. For the latter, it seems that the combination of magneto-active cations and anions or the use of multinuclear metal complex (metal cluster) ions is effective to enhance the magnetic interactions. Although not strictly an "ionic" liquid, the extreme example may be the successful preparation of superparamagnetic liquid, in which maghemite (γ-Fe_2O_3) nanoparticles with 4 nm in diameter are chemically modified by silyl-containing quaternary cations (Bourlinos et al., 2005). The dark brown liquid may be regarded as a new type of magnetic fluid, namely solvent-free colloidal dispersion of nanoparticles. Magnetorheological fluids, whose rheological behavior can be controlled by the applied magnetic field, were obtained by dispersing 25 wt% micrometer-sized magnetite (Fe_3O_4; < 5 μm) particles in ionic liquids (Guerrero-Sanchez et al., 2007). The use of $[C_4MI][PF_6]$ leads to a colloidal dispersion that is remarkably stable against aggregation over a period of 2 months.
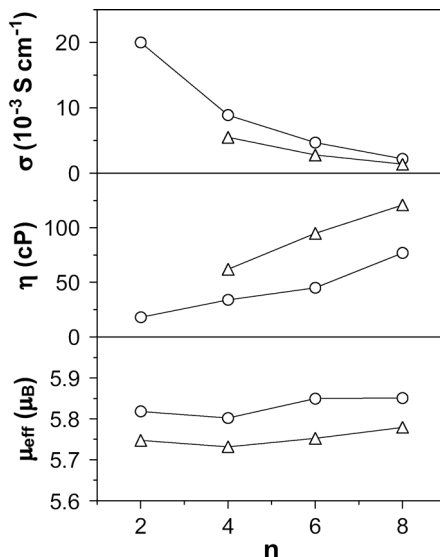
Fig. 3. Dependence of ionic conductivity (σ), viscosity (η), and effective magnetic moment (μ_{eff}) on alkyl chain length in the C_nMI cations for $[C_nMI][FeCl_4]$ ($\circ$) and $[C_nMI][FeBr_4]$ (Δ) salts (Yoshida et al., 2005b; Yoshida & Saito, 2006).

2.2 Inorganic anions containing other transition metals

For the divalent anions such as $Co^{II}Cl_4^{2-}$, twice molar amount of halide salts of exceptionally bulky monocations such as trihexyl(tetradecyl)phosphonium ($P_{14,6,6,6}$; Scheme 1) would be necessary to realize RT ionic liquids such as $[P_{14,6,6,6}]_2[CoCl_4]$ (glass transition T_g = –68 °C) (Del Sesto et al., 2008). Its analogous $[C_2MI]_2[CoCl_4]$ is in solid state at RT, and shows a melting event at 100–102 °C (Hitchcock et al., 1993). Keeping the cation invariant (C_4MI), however, the replacement of chloride of $Co^{II}Cl_4$ dianions (T_m = 62 °C) (Zhong et al., 2007) by bulky bromide (T_m = 45 °C) (Kozlova et al., 2009) and isothiocyanate (T_g = –61 °C) (Peppel et al., 2010) steadily stabilizes the liquid state. Notably, $[C_2MI]_2[Co(NCS)_4]$ (T_g = –62 °C) shows a relatively high ionic conductivity (4.0×10^{-3} S cm^{-1} at 25 °C) and low viscosity (145 cP at 25 °C) despite the divalency of anions (Peppel et al., 2010). Based on the Pearson's HSAB concept, the softness of the ligand NCS, when compared with halides, may relate to the high fluidity as a consequence of the depressed interionic Coulomb interactions with the hard hydrogen atoms of C_nMI cations.

Very recently, Pitula and Mudring reported absorption and luminescent properties of a series of manganese(II)-containing ionic liquids $[C_nMI]_2[Mn^{II}X_4]$ (X: Cl, Br) and $[C_nMI][Mn^{II}(Tf_2N)_3]$, though no magnetic data (Pitula & Mudring, 2010). $[C_nMI]_2[MnX_4]$ with a tetrahedral Mn^{II} coordination show a yellow-greenish emission, whereas $[C_nMI][Mn(Tf_2N)_3]$ with an octahedral Mn^{II} coordination show a reddish emission at RT. The colorations derive mainly from the predominant emission band at around 520 nm for the former and at around 590 nm for the latter, both of which are readily assigned to the intramolecular $^4T_1(G) \rightarrow {}^6A_1$ transition on Mn^{II} ions.

Ionic liquids formed with metal complex anions have been used as green solvents for catalysis. For example, $[C_4MI][Co^{III}(CO)_4]$ is active for the catalytic debromination of 2-

bromoketones in the presence of NaOH (Brown et al., 2001), and $[C_4MI][Cr^{VI}ClO_3]$ and $[C_4MI]_2[Mo^{VI}(NCS)_4O_2]$ are active for the catalytic oxidation of alcohol (Noguera et al., 2005).

2.3 Inorganic anions containing rare-earth metals

Only two ionic liquids containing rare-earth metals, $[P_{14,6,6,6}]_3[Gd^{III}Cl_6]$ (Del Sesto et al., 2008) and $[C_6MI]_{5-x}[Dy^{III}(NCS)_{8-x}(H_2O)_x]$ (x: 0–2) (Mallick et al., 2008), have been magnetically-studied, although a series of $[C_4MI]_4[RE(NCS)_{8-x}(H_2O)_x]$ (RE: Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, Yb; x: 1, 2) were prepared and their miscibility and absorption properties were investigated by Nockemann et al. (Nockemann et al., 2006). Magnetic moments of $[C_6MI]_{5-x}[Dy^{III}(NCS)_{8-x}(H_2O)_x]$ were estimated to be 10.4–10.6μ_B at 25 °C, which resemble closely that expected for a paramagnetic high-spin on Dy^{III} ions with f^9 electrons (10.65μ_B). In addition, $[C_6MI]_{5-x}[Dy^{III}(NCS)_{8-x}(H_2O)_x]$ show a yellow emission in the liquid state (Mallick et al., 2008). The coloration derives mainly from the predominant emission band at around 575 nm, which is readily assigned to the intramolecular $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition on Dy^{III} ions. The observed monoexponential intensity decay with a lifetime of 24–48 μs gives evidence of single Dy^{III} species in these ionic liquids.

2.4 Organic and metal complex anions

Davis introduced some complimentary strategies for the synthesis of functional ionic liquids, by the inclusion of functional group (FG) to the cationic skeleton, in his review (Davis, 2004). The called "task-specific ionic liquids" have been synthesized, for example, by *N*-alkylation of alkyl halides covalently linked to FG with appropriate Lewis bases (e.g., imidazole, amine, phosphine, and sulfide; Scheme 2a), accompanied by the anion metathesis to realize ionic liquids. One of other strategies is to use Michael reaction of alkyl vinyl ketones linked to FG with tertiary cations, as in Scheme 2b (Wasserscheid et al., 2003). It is noteworthy that this facile one-pot reaction dispenses with the need for a further anion metathesis step and are free from halide-containing by-product.
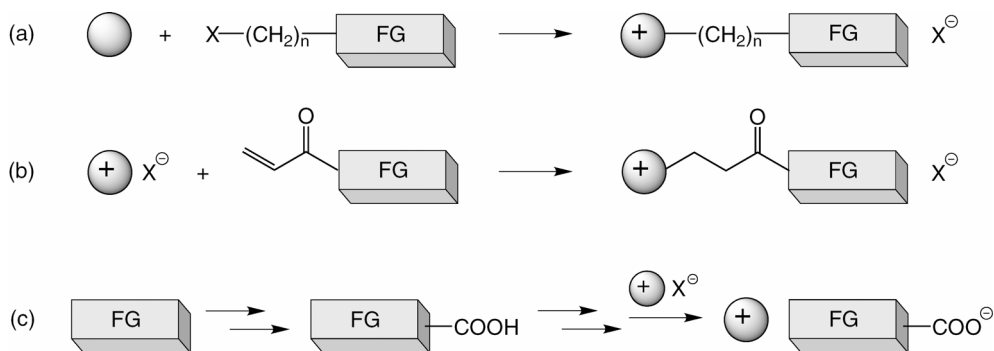
Scheme 2. Schematic synthetic routes of functional ionic liquids by (a) *N*-alkylation reaction (Davis, 2004) and (b) Michael addition reaction (Wasserscheid et al., 2003) to form ionic liquids of functional cations, and (c) the addition of acidic group to form ionic liquids of functional anion. A blank sphere represents a Lewis base such as imidazole, amine, phosphine, and sulfide, while a sphere with a plus sign represents the corresponding cation.

Similarly, functional ionic liquids can be realized by the use of anions, in which an acidic group such as carboxyl and sulfonate is covalently linked to the neutral functional molecule. We note that the molecular makeup, namely a neutral moiety linked to an acidic group, reminds us of amino acids, which offered 20 kinds of ionic liquids formed with C_2MI cation (Fukumoto et al., 2005). The acid form of anions is transformed to the target ionic liquids by combining conventional liquid-forming counter cations as in Scheme 2c. In this approach, the serious obstacle in some cases is the difficulty of the chemical inclusion of the acidic group to the functional molecule. In other words, if the acid form can be realized whatever the synthetic route is used to access, one can anticipate the realization of ionic liquids composed of functional anions with the acidic group. However, such ionic liquids are fraught with drawbacks of their high viscosity, mainly caused by the confined negative charge to the acidic group and the presence of bulky FG.

The $P_{14,6,6,6}$ salt made by combining $Cu^{II}Pc(SO_3)_4^{4-}$ (copper phthalocyanine-tetrasulfonate; Scheme 1) anion, reported by Del Sesto and Wilkes in 2005, may be regarded as the first paramagnetic ionic liquid (T_g = –41 °C) composed of anion with acidic groups (Del Sesto et al., 2005). The highly viscous ionic liquid is anticipated to have an S = 1/2 spin on central Cu^{II} ions, although there is no magnetic evaluation in the paper. However, this is not the synthesis of the component ions but the proper choice of the ions, since commercially available $CuPc(SO_3Na)_4$ was utilized as precursor. Our first step was to design and synthesize the component anions with a special functionality and then combine them with proper counter cations to form ionic liquids. Thus, the nascent strategy has been to search for functional molecules that can chemically introduce the acidic group in the facile synthetic route.

In 2007, our own group reported the first metal-free paramagnetic ionic liquids, by the inclusion of a sulfate group to a neutral 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) radical moiety (Scheme 1) (Yoshida et al., 2007c). Whereas the C_2MI salt is reddish crystalline solid with T_m = 57 °C, the salts with n = 4, 6, and 8 are reddish highly viscous liquids (> 400 cP even at 70 °C; see the inset of Figure 4). As mentioned above, the confined
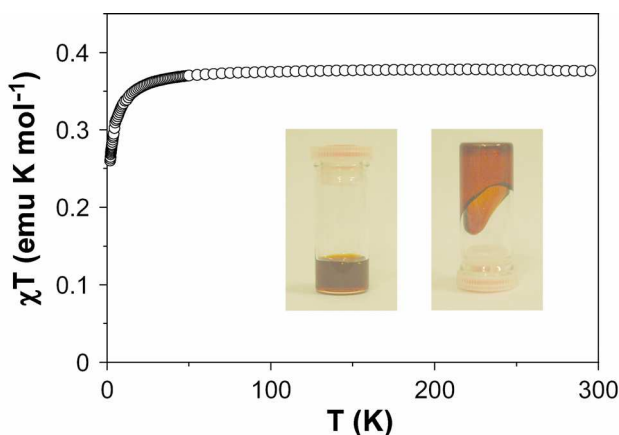

Fig. 4. Temperature dependence of the product of static susceptibility and temperature (χT) for [C_4MI][TEMPO-OSO_3] in an applied field of 1 kOe on heating process. The inset is the photographs of [C_4MI][TEMPO-OSO_3] (Yoshida et al., 2007c).

negative charge on a sulfate group, which leads to the significant interionic Coulomb interactions, would be a factor governing the high viscosity. These ionic liquids show Curie-like behavior in their liquid region. The RT magnetic moments were estimated as values in the range of 1.61–1.72μ_B (Figure 4), which resemble closely that expected for a paramagnetic $S = 1/2$ spin (spin-only value: 1.73μ_B) on nitroxyl radical.

Our strategy, that introduces the acidic group to functional molecules to form functional ionic liquids, can be used to access the next stage of ionic liquids, namely the liquids that can modify the physical properties by applying external stimuli, e.g., temperature, pressure, electric field, and light irradiation. The selection criteria for the functional molecules includes that the functionality can work without having interionic interactions and even at high temperature (at least RT), and also that the molecules can introduce the acidic group in the facile synthetic route. We chose to utilize the cobalt bis(dioxolene) complex as FG, which has been known to exhibit the valence tautomerism (VT) by the intramolecular interconvert between low-spin Co^{III} ($S = 0$) system with a radical 3,5-di-*tert*-butyl-1,2-semiquinonate monoanion (DBSQ$^{\bullet-}$) and a closed-shell 3,5-di-*tert*-butyl-1,2-catecholate dianion (DBCat^{2-}) ligands and high-spin Co^{II} ($S = 3/2$) system with two DBSQ$^{\bullet-}$ ligands (Scheme 3) (Pierpont, 2001). Such phase equilibrium has potential applicability for molecular devices such as information storage and switches, and could be driven by either temperature change or light irradiation. Considering the fact that the VT behavior has been observed in the diluted solution (Pierpont, 2001), it appears that the intermolecular interaction is not indispensable for the appearance of the equilibrium.

We combined the cobalt bis(dioxolene) unit with 2,2'-bipyridine (bpy) having two carboxylate groups at 4-positions, to realize an ionic liquid showing valence-tautomeric behavior. The dark green liquid [P$_{14,6,6,6}$]$_2$[Co^{II}(DBSQ)$_2$(bpy(COO)$_2$)] is highly viscous (> 10^3 cP) and shows a glass transition at –11 °C (Yoshida et al., 2009). The ionic conductivity is determined to be 1.0 × 10^{-6} S cm^{-1} at 27 °C and follows the Arrhenius law with an activation energy of 0.625 eV in the whole measured temperature range (27–77 °C). The RT σ value is much lower than that of [P$_{14,6,6,6}$]Cl (8.9 × 10^{-6} S cm^{-1} at 27 °C) apparently due to the bulky dianions.
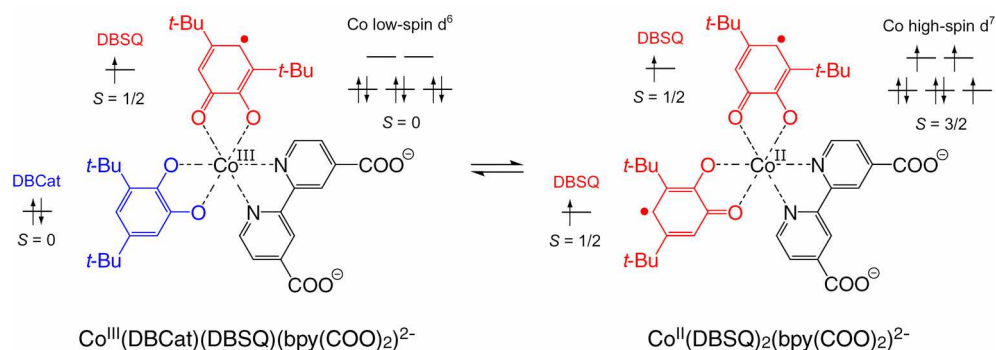
Scheme 3. Valence tautomeric bistability of cobalt bis(dioxolene) complex (Pierpont, 2001; Yoshida et al., 2009).

Figure 5a shows the electronic absorption spectrum at –173 °C, which is reminiscent of that of crystalline solid Co^{III}(DBCat)(DBSQ)(bpy) (Pierpont, 2001). At low temperatures, an absorption band characteristic of a ligand to metal charge transfer (LMCT) from DBCat ligand to central cobalt was observed at around 610 nm. As the temperature increases from 7

to 47 °C, the intensity of the 610 nm band apparently decreases whereas a band at around 740 nm increases in intensity (Figure 5b). Since the 740 nm band is associated with a metal to ligand charge transfer (MLCT) from the central cobalt to DBSQ ligand, this spectral change indicates that the present salt exhibits a VT equilibrium in the liquid state at around RT. The presence of isosbestic point (ca. 670 nm) would confirm two different species in equilibrium. As expected, a low-energy band (ca. 2400 nm), which is ascribed to mixed valence intervalence charge transfer from the DBCat to DBSQ ligands (ligand-to-ligand charge transfer; LLCT), gradually decreases in intensity with increasing temperature (Figure 5c).

The μ_{eff} value at 2 K (1.40μ_B) falls into the range of values expected for the S = 1/2 unpaired spin (spin-only value: 1.73μ_B). With increasing temperature, it exhibits a gradual increase up to ca. 10 °C through the glass transition. As seen in Figure 6, there is an upturn of μ_{eff} above 10 °C, which then begins to approach the value expected for an uncorrelated three-spin system with S = 1/2, 1/2, and 3/2 (spin-only value: 4.58μ_B) without magnetic saturation. Such temperature dependency is rather different from that of polycrystalline VT complex Co(DBSQ)$_2$(bpy) (Pierpont, 2001), but reminds us of that of the colloidal suspension of nanoparticles composed of VT coordination polymer Co^{II}(DBSQ)$_2$(bix), where bix is 1,4-bis(imidazol-1-ylmethyl)benzene (Imaz et al., 2008). It should be noted that the observed VT behavior has little impact on the ion diffusivity, since no anomaly was observed for ion conduction in this temperature region.
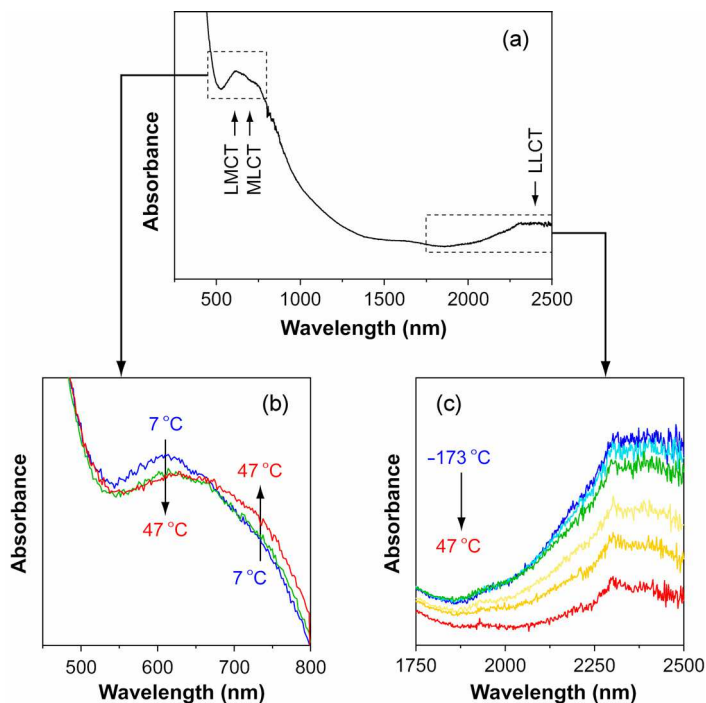

Fig. 5. (a) Electronic absorption spectrum of [P$_{14,6,6,6}$]$_2$[Co(DBSQ)$_2$(bpy(COO)$_2$)] at −173 °C. Temperature dependence of the spectra (b) in the high-energy region (7, 27, 47 °C) and (c) in the low-energy region (−173, −73, −13, 7, 27, 47 °C) (Yoshida et al., 2009).

The use of chelate complex anions is preferred due to a huge variety of chemically tunable organic ligands, which allow the fine tuning of ligand π orbital levels and thus charge transfer between the central metal and ligands. The modification of electronic structures exerts a drastic effect on physical properties such as magnetic (e.g., spin and charge states, and spin polarization) and emission (e.g., lifetime, emission energy, and quantum efficiency) properties. We would note that the "bidentate ligand ionic liquid" $[P_{14,6,6,6}]_2[bpy(COO)_2]$ is a useful tool to synthesize ionic liquids containing chelate complex anions, in a combinatorial fashion, especially Fe[II], Mn[II], Ru[II], and Ir[III] metal complexes. Such functional ionic liquids can be envisaged to become a grown area because of the enormous accumulated knowledge of complex chemistry from both fundamental and practical aspects.
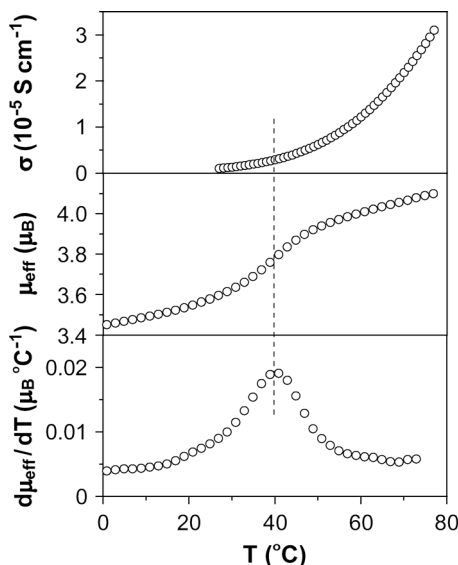

Fig. 6. Temperature dependence of ionic conductivity (σ), effective magnetic moment (μ_{eff}), and its derivative $d\mu_{eff}/dT$ of $[P_{14,6,6,6}]_2[Co(DBSQ)_2(bpy(COO)_2)]$. A vertical dotted line indicates the equilibrium temperature (Yoshida et al., 2009).

3. Magneto-active cations

Metal-free paramagnetic ionic liquids, in which a chiral pyrrolidin-1-yloxyl (PROXYL) radical moiety is included in the component cation (**2**; Scheme 1), were reported by Tamura and his coworkers in 2009 (Uchida et al., 2009). It is apparent that this approach falls into the category as in Scheme 2a. The RT magnetic moments were estimated to be 1.69–1.75μ_B as expected from a paramagnetic $S = 1/2$ spin on nitroxyl radical. Notably, the Tf$_2$N salt is more fluidic (7.2 × 10^{-4} S cm^{-1} and 84 cP at 70 °C) than [C$_n$MI][TEMPO-OSO$_3$] (2.0 × 10^{-4} S cm^{-1} and 568 cP at 70 °C for n = 4), presumably associated with the well-delocalized charge on the Tf$_2$N anions.

In a more recent study, Inagaki and Mochida reported a series of paramagnetic ionic liquids by making use of a new breed of component cations (**3**; Scheme 1) (Inagaki & Mochida, 2010). In the ferrocenium cations, negatively-charged cyclopentadienyl rings would inhibit

the attractive Coulomb interactions between the positively-charged central iron and counter anions. Moreover, it seems that the thermal motion of the substituents as well as the low symmetry in the cations stabilizes the liquid state, since the pristine ferrocenium ($R_1 = R_2 =$ H) and methyl-substituted ferrocenium ($R_1 =$ Me, $R_2 =$ H or $R_1 = R_2 =$ Me) cations give salts with T_m higher than 100 °C. Among the ferrocenium-based ionic liquids, the salt combining **3a** with Tf$_2$N anion ($T_m =$ 24.5 °C) is highly fluidic (26.6 cP at 25 °C). The RT magnetic moments of the salts combining **3b** and **3d** with Tf$_2$N were estimated to be 2.33μ_B and 2.17μ_B, respectively, which lie in the range of typical ferrocenium salts (Kahn, 1993).

4. Conclusion

In this review, the known range of paramagnetic ionic liquids has been discussed concerning the choice and chemical synthesis of magneto-active ions. The selection of small-sized and monovalence C$_2$MI cation and Fe^{III}Cl$_4$ anion gives the most fluidic paramagnetic [C$_2$MI][Fe^{III}Cl$_4$]. Metal complex anion containing soft pseudo-halides gives relatively fluidic ionic liquids [C$_n$MI]$_2$[Co^{II}(NCS)$_4$] despite the divalency of the anion. By the chemical inclusion of acidic group to the neutral magneto-active molecules, metal-free paramagnetic ionic liquids [C$_n$MI][TEMPO-OSO$_3$] and a valence-tautomeric ionic liquid [P$_{14,6,6,6}$]$_2$[Co^{II}(DBSQ)$_2$(bpy(COO)$_2$)] have been realized. Imidazolium cation covalently linked to PROXYL radical moiety, also gives a new type of metal-free paramagnetic ionic liquids.

Ionic liquids whose functionality is inherited from the component ions will increasingly come to be attracting attentions, because of a vast number of the potential functional molecules that can introduce the acidic group and develop their functionality without having interionic interactions. The development of smart ionic liquids whose external-field-responsivity extends far beyond that of existing ones has also been an active area of research are also anticipated to be strong growth in the field of ionic liquids. Future works are also to develop a special functionality for each ion and then combine them to realize ionic liquids having cooperative functionalities.

5. References

Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H. & Scrosati, B. (2009). Ionic-liquid materials for the electrochemical challenges of the future. *Nat. Mat.*, 8, 621–629

Bonhôte, P.; Dias, A. –P.; Armand, M.; Papageorgiou, N.; Kalyanasundaram, K. & Grätzel, M. (1996). Hydrophobic, highly conductive ambient-temperature molten salts. *Inorg. Chem.*, 35, 1168–1178

Borra, E. F.; Seddiki, O.; Angel, R.; Eisenstein, D.; Hickson, P.; Seddon, K. R. & Worden, S. P. (2007). Deposition of metal films on an ionic liquid as a basis for a lunar telescope. *Nature*, 447, 979–981

Bourlinos, A. B.; Herrera, R.; Chalkias, N.; Jiang, D. D.; Zhang, Q.; Archer, L. A. & Giannelis, E. P. (2005). Surface-functionalized nanoparticles with liquid-like behavior. *Adv. Mater.*, 17, 234–237

Brown, R. J. C.; Dyson, P. J.; Ellis, D. J. & Welton, T. (2001). 1-Butyl-3-methylimidazolium cobalt tetracarbonyl [bmim][Co(CO)$_4$]: a catalytically active organometallic ionic liquid. *Chem. Commun.*, 1862–1863

Buzzeo, M. C.; Evans, R. G. & Compton, R. G. (2004). Non-haloaluminate room-temperature ionic liquids in electrochemistry –a review. *ChemPhysChem*, 5, 1106–1120

Cooper, E. I. & O'Sullivan, E. J. M. (1992). New, stable, ambient-temperature molten salts. *Proc. –Electrochem. Soc.*, 92-16, 386–396

Davis, Jr., J. H. (2004). Task-specific ionic liquids. *Chem. Lett.*, 33, 1072–1077

Del Sesto, R. E.; Corley, C.; Robertson, A. & Wilkes, J. S. (2005). Tetraalkylphosphonium-based ionic liquids. *J. Organomet. Chem.*, 690, 2536–2542

Del Sesto, R. E.; McCleskey, T. M.; Burrell, A. K.; Baker, G. A.; Thompson, J. D.; Scott, B. L.; Wilkes, J. S. & Williams, P. (2008). Structure and magnetic behavior of transition metal based ionic liquids. *Chem. Commun.*, 447–449

Dupont, J.; de Souza, R. F. & Suarez, P. A. Z. (2002). Ionic liquid (molten salt) phase organometallic catalysis. *Chem. Rev.*, 102, 3667–3692

Fei, Z.; Geldbach, T. J.; Zhao, D. & Dyson, P. J. (2006). From dysfunction to bis-function: on the design and applications of functionalised ionic liquids. *Chem. Eur. J.*, 12, 2122–2130

Fukaya, Y.; Sugimoto, A. & Ohno, H. (2006). Superior solubility of polysaccharides in low viscosity, polar, and halogen-free 1,3-dialkylimidazolium formates. *Biomacromolecules*, 7, 3295–3297

Fukaya, Y.; Hayashi, K.; Wada, M. & Ohno, H. (2008). Cellulose dissolution with polar ionic liquids under mild conditions: required factors for anions. *Green Chem.*, 10, 44–46

Fukumoto, K.; Yoshizawa, M. & Ohno, H. (2005). Room temperature ionic liquids from 20 natural amino acids. *J. Am. Chem. Soc.*, 127, 2398–2399

Fuller, J.; Carlin, R. T. & Osteryoung, R. A. (1997). The room temperature ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate: electrochemical couples and physical properties. *J. Electrochem. Soc.*, 144, 3881–3886

Gabriel, S. & Weiner, J. (1888). Ueber einige Abkömmlinge des Propylamins. *Ber.*, 21, 2669–2679

Guerrero-Sanchez, C.; Lara-Ceniceros, T.; Jimenez-Regalado, E.; Raşa, M. & Schubert, U. S. (2007). Magnetorheological fluids based on ionic liquids. *Adv. Mater.*, 19, 1740–1747

Hitchcock, P. B.; Seddon, K. R. & Welton, T. (1993). Hydrogen-bond acceptor abilities of tetrachlorometalate(II) complexes in ionic liquids. *J. Chem. Soc., Dalton Trans.*, 2639–2643

Holbrey, J. D.; Reichert, W. M.; Swatloski, R. P.; Broker, G. A.; Pitner, W. R.; Seddon, K. R. & Rogers, R. D. (2002). Efficient, halide free synthesis of new, low cost ionic liquids: 1,3-dialkylimidazolium salts containing methyl- and ethyl-sulfate anions. *Green Chem.*, 4, 407–413

Hough, W. L. & Rogers, R. D. (2007). Ionic liquids then and now: from solvents to materials to active pharmaceutical ingredients. *Bull. Chem. Soc. Jpn.*, 80, 2262–2269

Imaz, I.; Maspoch, D.; Rodríguez-Blanco, C.; Pérez-Falcón, J. M.; Campo, J. & Ruiz-Molina, D. (2008). Valence-tautomeric metal–organic nanoparticles. *Angew. Chem. Int. Ed.*, 47, 1857–1860

Inagaki, T. & Mochida, T. (2010). Metallocenium ionic liquids. *Chem. Lett.*, 39, 572–573

Kahn, O. (1993). *Molecular Magnetism*, Wiley-VCH, New York

Kawano, R.; Matsui, H.; Matsuyama, C.; Sato, A.; Susan, M. A. B. H.; Tanabe, N. & Watanabe, M. (2004). High performance dye-sensitized solar cells using ionic liquids as their electrolytes. *J. Photochem. Photobiol. A*, 164, 87–92

Kozlova, S. A.; Verevkin, S. P.; Heintz, A.; Peppel, T. & Köckerling, M. (2009). Paramagnetic ionic liquid 1-butyl-3-methylimidazolium tetrabromidocobaltate(II): activity coefficients at infinite dilution of organic solutes and crystal structure. *J. Chem. Eng. Data*, 54, 1524–1528

Kuang, D.; Wang, P.; Ito, S.; Zakeeruddin, S. M. & Grätzel, M. (2006). Stable mesoscopic dye-sensitized solar cells based on tetracyanoborate ionic liquid electrolyte. *J. Am. Chem. Soc.*, 128, 7732–7733

Li, M.; De Rooy, S. L.; Bwambok, D. K.; El-Zahab, B.; DiTusa, J. F. & Warner, I. M. (2009). Magnetic chiral ionic liquids derived from amino acids. *Chem. Commun.*, 6922–6924

MacFarlane, D. R.; Golding, J.; Forsyth, S.; Forsyth, M. & Deacon, G. B. (2001). Low viscosity ionic liquids based on organic salts of the dicyanamide anion. *Chem. Commun.*, 1430–1431

Mallick, B.; Balke, B.; Felser, C. & Mudring, A.-V. (2008). Dysprosium room-temperature ionic liquids with strong luminescence and response to magnetic fields. *Angew. Chem. Int. Ed.*, 47, 7635–7638

Matsumoto, H.; Sakaebe, H.; Tatsumi, K.; Kikuta, M.; Ishiko, E. & Kono, M. (2006). Fast cycling of Li/LiCoO$_2$ cell with low-viscosity ionic liquids based on bis(fluorosulfonyl)imide [FSI]$^-$. *J. Power Sources*, 160, 1308–1313

Nockemann, P.; Thijs, B.; Postelmans, N.; Van Hecke, K.; Van Meervelt, L. & Binnemans, K. (2006). Anionic rare-earth thiocyanate complexes as building blocks for low-melting metal-containing ionic liquids. *J. Am. Chem. Soc.*, 128, 13658–13659

Noguera, G.; Mostany, J.; Agrifoglio, G. & Dorta, R. (2005). Room temperature liquid salts of Cr and Mo as self-supported oxidants. *Adv. Synth. Catal.*, 347, 231–234

Ono, S.; Miwa, K.; Seki, S. & Takeya, J. (2009). A comparative study of organic single-crystal transistors gated with various ionic-liquid electrolytes. *Appl. Phys. Lett.*, 94, 063301/1–3

Peppel, T.; Köckerling, M.; Geppert-Rybczyńska, M.; Ralys, R. V.; Lehmann, J. K.; Verevkin, S. P. & Heintz, A. (2010). Low-viscosity paramagnetic ionic liquids with doubly charged [Co(NCS)$_4$]$^{2-}$ ions. *Angew. Chem. Int. Ed.*, in press

Pierpont, C. G. (2001). Studies on charge distribution and valence tautomerism in transition metal complexes of catecholate and semiquinonate ligands. *Coord. Chem. Rev.*, 216-217, 99–125

Pitula, S. & Mudring, A.-V. (2010). Synthesis, structure, and physico-optical properties of manganate(II)-based ionic liquids. *Chem. Eur. J.*, 16, 3355–3365

Sato, T.; Masuda, G. & Takagi, K. (2004). Electrochemical properties of novel ionic liquids for electric double layer capacitor applications. *Electrochim. Acta*, 49, 3603–3611

Singh, R. P.; Verma, R. D.; Meshri, D. T. & Shreeve, J. M. (2006). Energetic nitrogen-rich salts and ionic liquids. *Angew. Chem. Int. Ed.*, 45, 3584–3601

Smiglak, M.; Metlen, A. & Rogers, R. D. (2007). The second evolution of ionic liquids: from solvents and separations to advancedmaterials –energetic examples from the ionic liquid cookbook. *Acc. Chem. Res.*, 40, 1182–1192

Suarez, P. A. Z.; Einloft, S.; Dullius, J. E. L.; de Souza, R. F. & Dupont, J. (1998). Synthesis and physical-chemical properties of ionic liquids based on 1-n-butyl-3-methylimidazolium cation. *J. Chim. Phys.*, 95, 1626–1639

Uchida, Y.; Oki, S.; Tamura, R.; Sakaguchi, T.; Suzuki, K.; Ishibashi, K. & Yamauchi, J. (2009). Electric, electrochemical and magnetic properties of novel ionic liquid nitroxides, and their use as an EPR spin probe. *J. Mater. Chem.*, 19, 6877–6881

Yoshida, Y.; Muroi, K.; Otsuka, A.; Saito, G.; Takahashi, M. & Yoko, T. (2004). 1-Ethyl-3-methylimidazolium based ionic liquids containing cyano groups: synthesis, characterization and crystal structure. *Inorg. Chem.*, 43, 1458–1462

Yoshida, Y.; Fujii, J.; Muroi, K.; Otsuka, A.; Saito, G.; Takahashi, M. & Yoko, T. (2005a). Highly conducting ionic liquids based on 1-ethyl-3-methylimidazolium cation. *Synth. Met.*, 153, 421–424

Yoshida, Y.; Otsuka, A.; Saito, G.; Natsume, S.; Nishibori, E.; Takata, M.; Sakata, M.; Takahashi, M. & Yoko, T. (2005b). Conducting and magnetic properties of 1-ethyl-3-methylimidazolium (EMI) salts containing paramagnetic irons: liquid [EMI][$Fe^{III}Cl_4$] and solid [EMI]$_2$[$Fe^{II}Cl_4$]. *Bull. Chem. Soc. Jpn.*, 78, 1921–1928

Yoshida, Y. & Saito, G. (2006). Influence of structural variations in 1-alkyl-3-methylimidazolium cation and tetrahalogenoferrate(III) anion on physical properties of the paramagnetic ionic liquids. *J. Mater. Chem.*, 16, 1254–1262

Yoshida, Y.; Baba, O. & Saito, G. (2007a). Ionic liquids based on dicyanamide anion: influence of structural variations in cationic structures on ionic conductivity. *J. Phys. Chem. B*, 111, 4742–4749

Yoshida, Y.; Baba, O.; Larriba, C. & Saito, G. (2007b). Imidazolium-based ionic liquids formed with dicyanamide anion: influence of cationic structure on ionic conductivity. *J. Phys. Chem. B*, 111, 12204–12210

Yoshida, Y.; Tanaka, H. & Saito, G. (2007c). Organic paramagnetic ionic liquids based on anion containing 2,2,6,6-tetramethyl-1-piperidinyloxy radical moiety. *Chem. Lett.*, 36, 1096–1097

Yoshida, Y.; Tanaka, H.; Saito, G.; Ouahab, L.; Yoshida, H. & Sato, N. (2009). Valence-tautomeric ionic liquid composed of cobalt bis(dioxolene) complex dianion. *Inorg. Chem.*, 48, 9989–9991

Yoshida, Y. & Saito, G. (2010). Design of functional ionic liquids using magneto- and luminescent-active anions. *Phys. Chem. Chem. Phys.*, 12, 1675–1684

Walden, P. (1914). Ueber die Molekulargrösse und elektrische Leitfähigkeit einiger geschmolzenen Salze. *Bull. Acad. Imper. Sci. (St. Petersburg)*, 8, 405–422

Wang, P.; Zakeeruddin, S. M.; Moser, J.-E. & Grätzel, M. (2003). A new ionic liquid electrolyte enhances the conversion efficiency of dye-sensitized solar cells. *J. Phys. Chem. B*, 107, 13280–13285

Wang, P.; Wenger, B.; Humphry-Baker, R.; Moser, J.-E.; Teuscher, J.; Kantlehner, W.; Mezger, J.; Stoyanov, E. V.; Zakeeruddin, S. M. & Grätzel, M. (2005). Charge separation and efficient light energy conversion in sensitized mesoscopic solar cells based on binary ionic liquids. *J. Am. Chem. Soc.*, 127, 6850–6856

Wasserscheid, P. & Keim, W. (2000). Ionic liquids –new "solutions" for transition metal catalysis. *Angew Chem. Int. Ed.*, 39, 3772–3789

Wasserscheid, P.; Drießen-Hölscher, B.; van Hal, R.; Steffens, H. C. & Zimmermann, J. (2003). New, functionalised ionic liquids from Michael-type reactions –a chance for combinatorial ionic liquid development. *Chem. Commun.*, 2038–2039

Wilkes, J. S. & Zaworotko, M. J. (1992). Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids. *J. Chem. Soc., Chem. Commun.*, 965–966

Zein El Abedin, S.; Moustafa, E. M.; Hempelmann, R.; Natter, H. & Endres, F. (2005). Additive free electrodeposition of nanocrystalline aluminium in a water and air stable ionic liquid. *Electrochem. Commun.*, 7, 1111–1116

Zhong, C.; Sasaki, T.; Jimbo-Kobayashi, A.; Fujiwara, E.; Kobayashi, A.; Tada, M. & Iwasawa, Y. (2007). Syntheses, structures, and properties of a series of metal ion-containing dialkylimidazolium ionic liquids. *Bull. Chem. Soc. Jpn.*, 80, 2365–2374
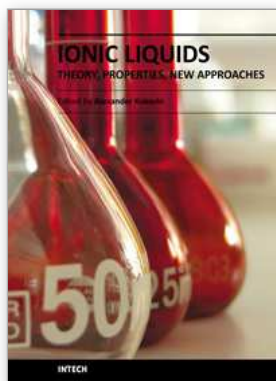
Ionic Liquids: Theory, Properties, New Approaches

Edited by Prof. Alexander Kokorin

Ionic Liquids (ILs) are one of the most interesting and rapidly developing areas of modern physical chemistry, technologies and engineering. This book, consisting of 29 chapters gathered in 4 sections, reviews in detail and compiles information about some important physical-chemical properties of ILs and new practical approaches. This is the first book of a series of forthcoming publications on this field by this publisher. The first volume covers some aspects of synthesis, isolation, production, modification, the analysis methods and modeling to reveal the structures and properties of some room temperature ILs, as well as their new possible applications. The book will be of help to chemists, physicists, biologists, technologists and other experts in a variety of disciplines, both academic and industrial, as well as to students and PhD students. It may help to promote the progress in ILs development also.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

INTECH

open science | open minds