# Chromic Ionic Liquids

# Yukihiro Yoshida<sup>\*,†</sup> and Hiroshi Kitagawa<sup>†</sup>

†Division of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan

\* yoshiday@ssc.kuchem.kyoto-u.ac.jp (YY)

#### ABSTRACT

One of the most prominent features of ionic liquids (ILs) is the possible introduction of a desired functionality that is originally inherited from the functional group tethered to its component ions, as well as the rational control of liquid properties by selecting the component ions. In this review, we present the development of ILs with chromism, which is attributed to the colorimetric response to certain external stimuli such as temperature, light, electric field, pH, and chemicals, mainly focusing on the molecular design of the component ions.

Keywords: ionic liquid, chromism, valence tautomerism, spin-crossover, isomerization

## 1. Introduction

Ionic liquids (ILs), now refer to liquids composed entirely of ions that are melted below room temperature (RT) or 100 °C,<sup>1-3</sup> form an area of chemistry that rises to prominence over the past three decades. A central driving force behind research into ILs is the primary benefit of the control of chemical and physical properties such as hydrophilicity/hydrophobicity, miscibility, viscosity, and ionic conductivity by judicious design of the structures of component ions.<sup>4–10</sup> This makes ILs potentially useful as "designer solvents". Although the Coulombic attraction between component ions inevitably causes the suppression of fluidity, some factors must exist that lower the lattice energy and thereby reduce the melting points, such as charge delocalization (enthalpic effect), incorporation of long alkyl groups (enthalpic/entropic effect), and introduction of asymmetricity (entropic effect). Even after nearly a century since the first discovery of IL, ethanolammonium nitrate (melting temperature  $(T_m) \sim 52$  °C) in 1888,<sup>11</sup> the key breakthrough remained elusive. However, in the 1970s, ILs began to become more interested from the perspective of electrochemistry; for example, the melting point of chloroaluminate was lowered by adding Lewis acidic AlCl<sub>3</sub> followed by a combination with organic heterocyclic cations, such as pyridinium and imidazolium (Figure 1), which enabled their application as electrolytes for aluminum electrodeposition<sup>12,13</sup> and as reaction media for Lewis acid catalyzed reactions including Friedel-Crafts reactions.<sup>1,14,15</sup> Serious drawbacks of ILs such as their instability against air and water were overcome by the advent of air-stable imidazolium-based ILs formed with acetate (AcO) and tetrafluoroborate (BF<sub>4</sub>) anions by Wilkes and Zaworotko<sup>16</sup> and triflate (CF<sub>3</sub>SO<sub>3</sub>) and mesylate (CH<sub>3</sub>SO<sub>3</sub>) anions by Cooper and O'Sullivan<sup>17</sup> in 1992. Compared with traditional molecular solvents, some of the most fascinating features of ILs are their nonvolatility (i.e., wide liquid temperature region and negligible flammability) and high ionic conductivity, both of which primarily arise from their extraordinarily high ion density, as the name predicts. These properties make ILs environmentally benign alternatives to volatile molecular solvents for many areas of synthetic, separation, and electrochemical applications.

#### \*\*\*\*\*\*\*\*\* Figure 1 \*\*\*\*\*\*\*\*\*

The nascent strategy involves selecting component ions from an unlimited number of possible cation-anion combinations to control the aforementioned liquid properties 2a). For example, hexafluorophosphate  $(PF_6)$ (Figure and bis(trifluoromethanesulfonyl)amide (TFSA; Figure 1) anions introduce hydrophobicity in ILs,18,19 whereas dicyanamide (N(CN)2) and tricyanomethide (C(CN)3) anions afford excellent ion-conduction.<sup>20-22</sup> The second stage of molecular design can be regarded as one directing the introduction of a special functionality in ILs (Figure 2b); a term "taskspecific ionic liquid (TSIL)" was coined by Davis, who defined them as ILs that contain a covalently tethered functional group on either cations or anions to impart a certain functionality to an IL.<sup>23</sup> His group reported the first example of TSIL, in which Nalkylated antifungal drug miconazolium cation (Figure 3a) was combined with PF6 anion.<sup>24</sup> For the ILs formed with functionalized anions, 2,2,6,6-tetramethyl-1piperidinyloxyl (TEMPO) moiety, which represents one of the most studied molecules in the organic radicals, was covalently tethered to a sulfate group (Figure 3b) to afford the first genuine organic paramagnetic ILs.<sup>25</sup>

Presently, numerous efforts are being undertaken to develop ILs with functionalities that can be manipulated by external fields such as temperature, light, electric field, pH, and chemicals (Figure 2c).<sup>26-30</sup> Such stimuli-responsive ILs can be considered to be a liquid version of smart materials (or intelligent materials) that have been the subject of long-term research for practical applications such as sensing tools for analysis and diagnosis (e.g., optoelectronics, catalysis, drug delivery, and sensors).<sup>31,32</sup> In this review, we focus on the development of ILs that show a colorimetric response to the aforementioned external stimuli. "Chromic ILs" have a considerable advantage in that the response to external stimuli can be detected by the naked eye; in other words, such a colorimetric detection can minimize the need for more sophisticated instrumentation. The utilization of chromophores that possibly exhibit isomerization (e.g., cis/trans<sup>33,34</sup> and opening/closing<sup>35-38</sup>) in non-metal moieties or a change in the coordination environment<sup>39-</sup> <sup>41</sup> or spin state (e.g., valence tautomeric  $(VT)^{42-45}$  and spin-crossover  $(SCO)^{46,47}$ equilibria) in metal-complex moieties tethered to one or both of the component ions is analogous to the use of traditional solid- or solution-based chromic materials (Figure 4). A trihexyl(tetradecyl)phosphonium (P<sub>14.6.6.6</sub>; Figure 1) cation, which has sometimes been labeled as a "universal liquifier"<sup>48</sup> to produce ILs, whereas a TFSA anion, which readily provides hydrophobic ILs with excellent thermal and electrochemical durabilities as well as relatively high ionic conductivity, are the most common counterions used to produce ILs. In particular, ILs formed with TFSA open the applicative way for electrolytes in capacitors, lithium-ion batteries, field-effect transistors, and electrodeposition.

# \*\*\*\*\*\*\*\*\* Figure 4 \*\*\*\*\*\*\*\*\*

#### 2. Thermochromism

Although the gradual color change could be driven by the expansion or shrinkage of the lattice associated with band gap modulation, discontinuous color changes essentially require a phase transition or equilibrium that leads to a distinct change in the electronic state. This feature implies that such a color change facilitates the visual recognition of the electronic state of molecules or metal complexes of interest. The most popular method to intrinsically modify the valence state of metal species is based on thermal treatment to induce phase transition/equilibrium such as VT (Figure 5a) and SCO (Figure 6a) or to release the coordinated solvent molecules. Notably, the magnetic equilibrium has a potential applicability for molecular devices such as information storage and switches.<sup>42–47</sup> The selection criteria for the functional group include functionality working without interionic interactions to inherit to the resulting ILs.

**2.1. Spin equilibrium.** Based on the rational strategy described above, in which a functional molecule bearing an acidic group serves as an anionic component of ILs, cobalt bis(dioxolene) complex dianion with 2,2'-bipyridine ligand bearing two carboxylate groups at the 4,4'-position (Figure 5b) was combined with P14,6,6,6 cation to form IL (glass transition temperature  $(T_g) = 262$  K) in 2009.<sup>49</sup> Such a complex undergoes a VT interconversion between redox isomers, i.e., a low-spin (LS) Co(III) complex with a radical 3,5-di-t-butyl-1,2-semiquinonate monoanion (DBSQ<sup>-</sup>) and a closed-shell 3,5-dit-butyl-1,2-catecholate dianion (DBCat<sup>2-</sup>) ligands and a high-spin (HS) Co(II) complex with two momoanionic DBSQ<sup>-</sup> ligands, mainly driven by either thermal treatment or light irradiation.<sup>42–45</sup> Considering that the VT behavior was observed in the diluted solution (the order of  $10^{-3}$  M),<sup>50,51</sup> it is evident that the intermolecular interaction is not indispensable for triggering the interconversion. In the dark-green IL,  $(P_{14,6,6,6})_2[Co^{II}(DBSQ)_2(bpy(COO)_2)]$  (or  $(P_{14,6,6,6})_2[Co^{III}(DBCat)(DBSQ)(bpy(COO)_2)]$ ), the absorption band ascribed to ligand-to-metal charge transfer (LMCT) from the DBCat<sup>2-</sup> ligand to the central cobalt at 610 nm becomes less intense upon heating from 280 to 320 K, whereas the band at 740 nm ascribed to metal-to-ligand charge transfer (MLCT) from the central cobalt to the DBSQ<sup>-</sup> ligand apparently increases in intensity. This spectral change, although not significant, in the visible region is firm evidence of the occurrence of VT interconversion in the IL at around RT. Although it is difficult to overcome the deep coloration to visually detect color changes, it is fair to say that this IL is the first example exhibiting the thermochromism. Of particular importance is that the magnetic moment, which is estimated to be  $1.40\mu_B$  at 2 K as expected for the S = 1/2unpaired spin (spin-only value:  $1.73\mu_B$ ), shows a pronounced upturn at around 300 K, above which it begins to approach the value expected for an uncorrelated three-spin system with S = 1/2, 1/2, and 3/2 (spin-only value:  $4.58\mu$ B) (Figure 5c).

In 2013, Mochida et al. reported the first IL exhibiting a SCO transition,<sup>52</sup> which arises from the thermodynamic equilibrium between the LS and HS states of central metal ions manipulated reversibly by external stimuli such as temperature and light irradiation.<sup>46,47</sup> The central Fe(III) ion is octahedrally coordinated by a tetradentate Schiff base, *N*,*N*<sup>2</sup>ethylenebis(acetylacetonylideneaminato) (acacen), at the equatorial position and two 1*n*-butylimidazoles at both apical positions (Figure 6b), and the combination with the TFSA anion affords a blue IL, [Fe(acacen)(1-*n*-butylimidazole)<sub>2</sub>](TFSA) ( $T_g = 242$  K). The low-temperature phase is in the LS state (blue-green) at 248 K, above which the IL gradually begins to exhibit the HS state (violet-blue) (Figure 6c). At 310 K, it has a magnetic moment of  $3.06\mu_B$ , which is intermediate between those of ideal LS (S = 1/2;  $1.73\mu_B$ ) and HS (S = 5/2;  $5.92\mu_B$ ) states. In a similar fashion, an IL containing Fe(III) complex trications with a hexadentate Schiff base bearing two cationic imidazole moieties exhibits SCO behavior at approximately 250 K, although little visible color change was observed.<sup>53</sup>

2.2. Coordination environment. Another modification to endow the thermochromism in metal complex-containing ILs is the change in the coordination number of the metal ions. After various ILs containing lanthanoid metal complex ions have been explored by several research groups,<sup>54–56</sup> the U(VI) isothiocyanate complex anion was used to obtain an orange IL by combining it with the 1-n-butyl-3-methylimidazolium (C<sub>4</sub>MI; Figure 1) cation,  $(C_4MI)_3[UO_2(NCS)_5]$  ( $T_g = 228$  K) in 2011.<sup>57</sup> The color is reversibly changed to red upon heating (343 K) possibly because of the equilibrium reaction of the dissociation of an NCS group, that is,  $[UO_2(NCS)_5]^{3-}$  (orange)  $\leftrightarrow [UO_2(NCS)_4]^{2-} + SCN^-$  (red). Similarly, Co(NCS)<sub>2</sub> dissolved in (C<sub>2</sub>MI)(SCN) (C<sub>2</sub>MI: 1-ethyl-3-methylimidazolum; Figure 1),<sup>58</sup> (C<sub>4</sub>MI)(SCN),<sup>58</sup> and (P<sub>14,6,6,6</sub>)(SCN)<sup>59</sup> exhibited thermochromic behavior, making use of the reversible dissociation of SCN groups in [Co(NCS)<sub>6</sub>]<sup>4-</sup>, that is, octahedral  $[Co(NCS)_6]^{4-}$  (pink)  $\leftrightarrow$  tetrahedral  $[Co(NCS)_4]^{2-} + 2SCN^{-}$  (blue), although not strictly genuine ILs. Such thermochromic behavior was also observed in IL containing Ni(II)-isothiocyanate complex tetraanions,  $(C_4MI)_4[Ni(NCS)_6]$  ( $T_m = 337$  K),<sup>60</sup> in which the pale blue turns grass green upon heating to 343 K. Notably, no sign of color change was observed in C<sub>4</sub>MI-based ILs formed with other metal complex anions with Cr, Mn, Fe, Co, Cu, Zn, and Cd, and the authors argued that the increased oscillator strength of Laporte-forbidden transition through vibronic coupling is responsible for the observed thermochromic response in (C<sub>4</sub>MI)<sub>4</sub>[Ni(NCS)<sub>6</sub>].

Changes in coordination mode also allow to envisage ILs in feasible applications such as thermochromic sensors. For example,  $(C_4MI)_2NiCl_4$  ( $T_m = 329 \text{ K}^{61}$ ) dissolved in hydroxy-functionalized ILs,  $(HOC_nMI)X$  ( $X = BF_4$  or PF\_6; see Figure 1 for  $HOC_nMI$ ),<sup>62– <sup>64</sup> undergoes a structural transformation by thermal treatment, that is, octahedral {NiCl<sub>3</sub>[( $HOC_nMI$ )X]<sub>3</sub>}<sup>-</sup> + Cl<sup>-</sup> (yellow/green)  $\leftrightarrow$  tetrahedral NiCl<sub>4</sub><sup>2-</sup> + 3( $HOC_nMI$ )X (blue), because of the coordination of a hydroxy group in  $HOC_nMI$  cations at low temperatures. In an Eu(III)-based IL, one of the four  $\beta$ -diketonate chelators that can act as bidentate ligands to give an octa-coordinated Eu(III) complex monoanion forms a bridge between the Eu(III) center and the P<sub>14,6,6,6</sub> cation upon heating to 80 °C (Figure 7a).<sup>65</sup> It is likely that the presence of an electron-withdrawing heptafluoropropyl group</sup> attached to the diketone skeleton is responsible for this transformation, which results in a change in color from light yellow to deep red because of the weakened complexation strength. Another recent development is the observation of thermochromic behavior caused by a dimer to monomer transformation of half-sandwich Fe(III) complex monocations through the cleavage of an intermolecular S–S bond upon heating (Figure 7b).<sup>66</sup> Thermochromic response induced by the change in the oligomerization ratio has also been observed in square-planar Rh(I) complex monocations with four *n*-butylisocyanide groups (blue purple at -100 °C to orange at 100 °C)<sup>67</sup> and square-planar Pt(II) complex monocations, [Pt(CN)<sub>2</sub>L]<sup>-</sup>, with a bidentate heterocyclic ligand such as 2-(*p*-tolyl)pyridine (as HL),<sup>68</sup> benzo[*h*]quinoline (as HL),<sup>69</sup> and 1-methyl-3-phenyl-1*H*-imidazolium (as H<sub>2</sub>L).<sup>69</sup> The ILs, (C<sub>n</sub>MI)[Pt(CN)<sub>2</sub>L] (*n* = 2 or 4), undergo transformation from monomers in the glass state to dimers in the liquid state.

## \*\*\*\*\*\*\*\*\* Figure 7 \*\*\*\*\*\*\*\*\*

It is important to note that thermochromism making use of the dissociation of coordinated solvent molecules by heating, that is, the change in coordination number, is also classified as vapo- or solvatochromism (see Section 6.1). Therefore, such thermochromic ILs have the potential to exhibit a colorimetric response to multiple external stimuli, i.e., *multichromism*. A good example is that two water molecules that occupy the axial positions of octahedrally coordinated Co(II) complex dianions with two bidentate salicylate (sal) ligands are released upon standing under vacuum or heating of the IL, (P<sub>4,4,4,4</sub>)<sub>2</sub>[Co(sal)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (Figure 7c; see Figure 1 for P<sub>4,4,4,4</sub>).<sup>70</sup> The transformation results in a reversible color change between magenta in the dihydrate (or octahedral coordination) form at RT and deep blue in the anhydrate (or square-planar coordination) form at 50 °C. Notably, the water molecules preferentially coordinate to the Co(II) ions according to the equilibrium constant for the binding of several solvents (water, methanol, and ethanol), which makes it a viable candidate for applications such as moisture detection and water-alcohol separation. A heteroleptic Ni(II) complex monocation, which is coordinated by bidentate acetylacetate (acac) and N,N,N',N'-tetraalkylethylenediamine bearing a methoxypropyl group (Figure 7d), gives a light-blue solid when combined with TFSA anion.<sup>71</sup> It enters a supercooled liquid state after heating above  $T_{\rm m} = 353$  K. At RT, the Ni(II) ion occupies a square pyramidal environment with intramolecular ether coordination (closed form), whereas the Ni(II)...O coordination bond is cleaved to form a square-planar geometry (open form) upon heating. The intramolecular coordination equilibrium leads to a color change from blue (243 K) to red (373 K) accompanied by a

marked change in the magnetic moment associated with the spin equilibrium between the LS and HS states. The solvatochromic response of the IL is given in Section 6.1.

#### 3. Photochromism

Photo-responsive materials have now emerged into the maturity of industrial applications as photonic devices as optical memories, color switches, and actuators.<sup>72–75</sup> The prominent advantages of using light as a trigger are that the stimulus can be remotely controlled and can convert only a desired part in a clean and non-invasive manner. Photo-responsive ILs are the current subject of relatively extensive research, although most of the experiments have been conducted in diluted solutions, and the color change is less significant. To date, most existing photochromic ILs involve functional moieties with the capacity to show *cis/trans* photoisomerization, such as azobenzene,<sup>34</sup> stilbene,<sup>33</sup> and cinnamate.<sup>76</sup> However, a serious obstacle for isomerization in ILs is the difficulty of structural reorientation under dense conditions,<sup>35–38</sup> and therefore, most of the photoisomerization behavior of ILs has been investigated in diluted conditions such as in solvents, inactive ILs, and polymer matrices. Another apparent drawback of the dense conditions is the limited visual detection of photochromism due to the anticipated deep coloration.

In most cases, a cationic headgroup such as imidazolium and ammonium is covalently tethered to the azo chromophore, which has a *trans* configuration in the as-prepared ILs. Ultraviolet (UV) irradiation induces isomerization to the *cis* configuration, which isomerically returns to the *trans* form by subsequent heating (including standing at RT) or visible-light irradiation. Generally, the *cis* form undergoes a melting event at a lower temperature than the counterpart *trans* form mainly because of the entropic effect.<sup>77–79</sup>

**3.1.** *Cis/trans* isomerization. In 2009, Branco and Pino applied methyl orange monoanions involving an azobenzene chromophore in the preparation of unprecedented photochromic ILs.<sup>80</sup> Although the sodium salt has a melting point higher than 300 °C, the combination with several organic cations gives orange ILs at RT. Flash light irradiation of the thin films induces *trans-cis* isomerization (Figure 8a) accompanied by the disappearance of an absorption band at 420 nm (probably  $\pi$ - $\pi$ \* transition). The introduction of a phenyl azo group to an imidazolium-based cation (Figure 8b) gives an IL by combining with the bis(pentafluoroethanesulfonyl)amide (PFSA; Figure 1) anion ( $T_m = 306$  K but is a supercooled liquid at RT after melting).<sup>81</sup> The thin film shows a small but discernible change in the absorption spectra upon visible-light irradiation (wavelength: 436 nm), that is, the weakened  $\pi$ - $\pi$ \* band at 350 nm is accompanied by a concurrent increase in the n- $\pi$ \* band at 460 nm. In both cases,<sup>80,81</sup> back *cis-trans* 

isomerization readily occurs at RT. The azobenzene moiety covalently tethered to a cationic ternary ammonium group (Figure 8c) affords an orange IL when combined with the TFSA anion ( $T_g$  or  $T_m$ : < -60 °C).<sup>82</sup> The colorimetric *trans-cis* isomerization is initiated by irradiation with UV light, as evidenced by the disappearance of the  $\pi$ - $\pi$ \* band (ca. 360 nm) and the concurrent appearance of the n- $\pi^*$  band (ca. 450 nm). The red *cis* isomer can be easily transformed to the yellow (or orange) trans isomer by either visiblelight irradiation or gentle heating (ca. 60 °C), and the isomerization reaction can be reversibly modulated using alternative irradiation with UV and visible light. Notably, Br salt, obtained as a yellow solid ( $T_m = 87$  °C), exhibits photo-induced transformation between the yellow crystalline *trans* isomer and the red liquid *cis* isomer in a reversible manner, in contrast to the irreversible transformation from the liquid cis isomer to the solid trans isomer observed in stilbene-containing ILs.77,78 The photolique faction leads to a marked increase in RT ionic conductivity ( $4.2 \times 10^{-10}$  to  $1.2 \times 10^{-7}$  S cm<sup>-1</sup>) associated with the increased ion diffusivity in the liquid state. The presence of long alkyl chains, which can facilitate structural reorientation under neat conditions, may be a part of the reason for the reversible photoisomerization and photoliquefaction.

#### \*\*\*\*\*\*\*\*\* Figure 8 \*\*\*\*\*\*\*\*\*

As mentioned above, serious intermolecular interactions inhibit structural isomerization because of the significant restriction in molecular motion, and therefore, many research groups have investigated the photoisomerization behavior of azo group-containing ILs dissolved in organic solvents<sup>83–85</sup> or an ordinary IL.<sup>86</sup> Photoisomerization of stilbene-containing ILs has also been investigated in acetonitrile solution,<sup>77,78</sup> although the back reaction from the nonfluorescent liquid *cis* form to the fluorescent solid *trans* form can be initiated by UV irradiation, as mentioned above. Several observations of *cis/trans* isomerization of cinnamate-containing ILs have been made in diluted solutions,<sup>87,88</sup> whereas the photoisomerization of ILs containing imidazolium cations covalently linked to a *p*-hydroxycinnamate moiety ( $T_m = 83 \text{ °C}$  for n = 1 and 54 °C for n = 4; Figure 8d) was observed in the thin films.<sup>79</sup> UV irradiation of the films at their melting temperatures produced a photostationary state involving a mixture of ca. 45% of the *trans* form, ca. 30% of the *cis* form, and ca. 25% of the photooxidation product.

**3.2. Opening/closing isomerization.** Recently, ILs exhibiting photochromism based on ring-opening/closing isomerization were prepared by combining *N*-octylated spiropyran cations (Figure 9a) with bis(fluorosulfonyl)amide (FSA; Figure 1) ( $T_g = -10.5$  °C) and TFSA ( $T_g = -8.4$  °C) anions.<sup>89</sup> UV irradiation induces isomerization from the yellow

nonplanar spiropyran (closed) form to the purple planar merocyanine (open) form, which is associated with bond cleavage of the spiropyran ring. Although the low conversion ratio (ca. 25%) is due to competition with the thermal back reaction, the colorimetric response is an excellent feature that is less significant in most azo group-containing ILs. The cyclization of merocyanine is initiated by visible-light irradiation, and the isomerization reaction occurs in a reversible manner. Similar photochromic behavior was observed in the ionogel matrix.<sup>90</sup> Another popular chromophore that undergoes a reversible ringopening/closing photoisomerization is diarylethene,<sup>35,36</sup> which can be regarded as a stilbene derivative and exhibits a bule-shifted absorption band in the closed form with reduced  $\pi$ -conjugation. After the initial work aimed at developing ILs using diarylethenebased cations (all salts have  $T_{\rm m} > 100$  °C),<sup>91</sup> diarylethene involving two anionic 2thiophenecarboxylates as aryl moieties (Figure 9b) was utilized to build ILs by combining them with methyltri(*n*-octyl)ammonium (N<sub>8,8,8,1</sub>;  $T_g \sim 0$  °C) and P<sub>14,6,6,6</sub> ( $T_g \sim -34.8$  °C) cations.<sup>92</sup> Transparent thin films of each open form exhibit purple and pink colors, respectively, by UV irradiation, and visible-light irradiation of the closed forms readily induces back isomerization to produce the original open forms.

## \*\*\*\*\*\*\*\*\* Figure 9 \*\*\*\*\*\*\*\*\*

Recently, it was reported that a yellow IL composed of the Ru(II) cyclopentadienylarene sandwich complex monocation and FSA anion ( $T_g = -60 \text{ °C}$ )<sup>93</sup> is sensitive to UV irradiation.<sup>94</sup> The optical absorption below 450 nm becomes more pronounced, possibly because of the dissociation of the arene ligand followed by the oligomerization of the cations (Figure 9c). It is intuitively reasonable that this transformation leads to a decrease in the ionic conductivity ( $4.0 \times 10^{-4}$  to  $3.7 \times 10^{-5}$  S cm<sup>-1</sup> at 25 °C) and an increase in viscosity ( $9.2 \times 10^2$  to  $5.3 \times 10^3$  mPa s at 25 °C).

Apparently, photochromic ILs have become increasingly important as potential systems, which have scarcely been investigated. The difficulty in initiating isomerization in a solid may be partly overcome by the impregnation of the photochromic IL or its solution into porous materials with inorganic compounds (e.g., zeolite and mesoporous silica), organic-inorganic hybrid compounds (e.g., metal-organic frameworks (MOFs)), and organic compounds (e.g., covalent organic frameworks (COFs)). In particular, MOFs are a promising platform for developing such photo-responsive solids, because numerous combinations of metal nodes and organic linkers allow control of their pore chemistry (i.e., cationic/anionic, Lewis acidic/basic, and hydrophilicity/hydrophobicity) and structures (size and dimension).<sup>95–99</sup> The incorporation of ILs into MOFs is emerging as

a topic of research primarily because of their ion-conducting properties inherited from pristine ILs,<sup>100–104</sup> and MOFs built from closed-shell metal ions such as Al(III), Zn(II), and Zr(IV) can serve as colorless solid reservoirs for diluted photo-responsive ILs.

#### 4. Electrochromism

Because of their fluidity, ILs can act not only as electrochromes but also as electrolytes in electrochromic display devices, which dispense with the problem of strict closure or packaging for preventing the evaporation of volatile solvents. Electrochromic materials with tunable light absorption, reflection, or transmission are currently being pursued for various applications such as smart displays and windows, especially in recent years with memory or energy-saving functions that maintain their colored states even after switching off the applied potentials.<sup>105–107</sup> While many existing electrochromic ILs exploit the redox reaction of viologen (or dimethyl-4,4'-bipyridinium dication; Figure 10a)<sup>108–118</sup> because of their prominent electrochromic contrast, stability, and turnover, metal ions in metal complexes (e.g., Co(II)/Co(III) in a chelate metal complex)<sup>119</sup> and metal oxides (V(III)/V(IV)/V(V) in VO<sub>3</sub>)<sup>120</sup> have also been utilized as redox sources for electrochromism.

#### \*\*\*\*\*\*\*\* Figure 10 \*\*\*\*\*\*\*\*\*

Co(edta)-based (edta: ethylenediaminetetraacetate) ILs formed with C<sub>2</sub>MI, P<sub>14,6,6,6</sub>, and N<sub>8,8,8,1</sub> cations are the first electrochromic ILs, which were reported by Branco and Pina in 2011. In these ILs, the Co(III) ion occupies an octahedral environment with the hexadentate edta ligand (Figure 10b).<sup>119</sup> An application of a constant potential of -0.38 V (vs. Ag/AgCl) leads to the reduction of Co(III) (violet) to Co(II) (pale pink) accompanied by a weakened d-d absorption band at approximately 540 nm. The corresponding oxidation occurs in a reversible manner by applying a potential of 0.38 V. The same group reported (C<sub>2</sub>MI)VO<sub>3</sub> with  $T_g = -52.5$  °C, which displays a sequential reduction, V(V) (yellow)  $\rightarrow$  V(IV) (blue)  $\rightarrow$  V(III) (green) in acetate buffer solution.<sup>120</sup>

Viologen chromophores have been extensively investigated as redox indicators in biological studies because of their stepwise reduction from dications (colorless) to radical monocations (blue) to eventually neutral quinoids (colorless).<sup>105–107</sup> Coloration of the middle redox state, i.e., radical monocations, is caused by the intramolecular electronic transition in the  $\pi$ -conjugated plane, and therefore, the chemical modification of alkyl groups attached to the pyridine nitrogen leads to color change of the radical monocation state.<sup>121</sup> It was first utilized as components of electrochromic ILs in 2013.<sup>108</sup> The viologen

dication with the trioctylphosphonium headgroup (Figure 10c) is combined with halides to produce a yellow liquid with  $T_g = -57$  °C. The colorless ionogel film embedded with the IL turns blue by the reduction from dicationic to radical cationic species at -0.84 V (vs. Ag/AgCl). When the potential is further swept in the negative direction, it undergoes a further reduction from the radical cation (blue) to neutral quinoid (colorless) at -1.21 V.

#### 5. Acidichromism

Efforts have been devoted to develop pH-responsive materials, as exemplified by litmus paper, over past decades largely because the most promising carriers for controlled and targeted drug delivery heavily rely on the pH difference between normal and pathological (e.g., tumor) tissue environments.<sup>122–124</sup> To date, intramolecular bond alternations in  $\pi$ -conjugated molecules such as azo dyes (e.g., methyl red and methyl orange; Figures 11a and 11b)<sup>125,126</sup> and phthalein dyes (e.g., fluorescein; Figure 11c)<sup>127–131</sup> have been widely utilized to provide component anions in acidichromic ILs. It is worth noting that this liquefication may overcome the only apparent drawback of the limited solubility of most dyes. Because such acidichromic ILs display a color change upon exposure to solvents or vapors with different pH values, acidichromism appears to constitute a specific subclass of vapo- and solvatochromisms (see Section 6).

\*\*\*\*\*\*\*\* Figure 11 \*\*\*\*\*\*\*\*\*

**5.1. Azo dyes.** ILs containing a tethered azo group in either cations or anions are promising candidates for photo-responsive ILs, as shown in Section 3.1. The first potential pH-responsive ILs were reported by Deng et al. in 2011, in which the methyl red monoanion (Figure 11a) was combined with C<sub>4</sub>MI ( $T_g = -10 \text{ °C}$ ), C<sub>6</sub>MI ( $T_g = -3 \text{ °C}$ ), and *n*-butylpyridinium ( $T_g$  or  $T_m$ : no data).<sup>125</sup> In acidic aqueous solutions, these red ILs displayed a pH-responsive behavior accompanied by a color change from red (pH = 1) to yellow (pH = 7). The combination of methyl orange monoanion (Figure 11b) and heterocyclic monocations yielded orange solid salts with  $T_m > 100 \text{ °C}$ ; however, a follow-up study revealed that the C<sub>4</sub>MI salt ( $T_m = 189 \text{ °C}^{125}$  or 180 °C<sup>126</sup>) embedded in poly(methyl methacrylate) (PMMA)-based ionogel clearly displays acidichromic behavior in a HCl aqueous solution in the concentration range of  $10^{-4}$  to  $10^{-1}$  M.<sup>126</sup>

**5.2. Phthalein dyes.** Another popular family of promising chromophores that are capable of indicating pH over a wide range is phthalein dyes, which have also been applied to the synthesis of acidichromic ILs. The orange viscous IL composed of fluorescein monoanion (Figure 11c) and  $P_{14,6,6,6}$  cation forms a nanodroplet suspension in water, and therefore,

dispenses with the need for a specialized hydrophobic matrix/substrate for immobilization.<sup>127</sup> While the sodium salt exhibits little color change with pH, the  $P_{14,6,6,6}$  salt significantly changes its color from light green at pH = 2.2 to red at pH = 8.4. Colorimetric response of ILs formed with monoanionic fluoresceins bearing a long alkyl chain has recently been observed in poly(vinyl chloride) (PVC)-based membranes.<sup>130,131</sup> A naphtholphthalein-containing IL was prepared using the  $P_{14,6,6,6}$  cation, although the conversion efficiency of the metathesis reaction was low (ca. 40%).<sup>129</sup> The PVC-based membrane embedded with the purple IL becomes transparent when the pH decreases. Although no chemical characterizations such as composition and thermal properties was provided in the paper, ILs produced by combining 12 types of anionic dyes (both azo and phthalein dyes) with  $P_{14,6,6,6}$  cations exhibit distinctive colorimetric responses to pH changes in various matrices such as cotton threads and alumina thin-layer chromatography plates.<sup>128</sup>

In the same year when ref. 125 was published, a P<sub>14,6,6,6</sub>-based IL ( $T_g = -13.5$  °C) was prepared by combining with pyranine (8-hydroxy-1,3,6-pyrenetrisulfonate; Figure 11d) trianion,<sup>48</sup> which is a well-known fluorescent pH indicator and is often used in biological studies of living cells and phospholipids.<sup>132</sup> The brown IL changes its emission color between blue and green when the thin film is exposed to amine vapors with different p $K_a$ ; from 9.25 (NH<sub>3</sub>) to 10.93 (Et<sub>2</sub>NH). Such sensitive detection of vapor or liquid amines is of considerable scientific and technological interest because they cause serious toxicological effects but are common pollutants in industrial and agricultural effluents due to their diverse applications.<sup>133–135</sup>

#### 6. Vapo- and Solvatochromisms

Finally, we introduce chromic ILs that change their color upon exposure to vapor or liquid phase while maintaining a constant pH. Generally, vapo- or solvatochromism arises mainly from the changes in the electronic state of chromophores depending on the Lewis basicity of the coordinated solvent molecules<sup>39–41</sup> and the polarity of the surrounding media.<sup>136–138</sup>

**6.1. Coordination environment.** In 2012, Mochida et al. reported an IL containing heteroleptic square-planar Cu(II) complex monocations with bidentate acac and  $N,N,N^{\circ},N^{\circ}$ -tetraalkylethylenediamine ligands ( $T_{\rm g} = -49$  °C) (Figure 12a).<sup>139</sup> The corresponding Ni(II)-based IL ( $T_{\rm g} = -58$  °C), which is less stable in air and has a spin state depending on the coordination environment, is unfavorable for vapo- and solvatochromic probes for the coordination of solvent molecules. In the Cu(II)-based IL, the d-d transition energy decreases proportionally to the Lewis basicity (Gutmann's donor

number; DN<sup>140–142</sup>) of vapors ranging from acetonitrile (DN = 14.1; purple) to pyridine (DN = 33.1; green). This IL also acts as a colorimetric sensor for ammonia vapor, with color variation from dark purple to green. Heteroleptic Cu(II) complex monocations with N,N,N',N'-tetraalkylethylenediamine ligand bearing a methoxyalkyl group (Figure 12b) were applied as components of solvatochromic ILs instead of vapochromic ILs,<sup>143</sup> because their deep coloration is fraught with the drawbacks of the difficulty in visual detection of vapochromism. An IL with n = 3 ( $T_m = 44$  °C) exhibits little solvatochromic response in the low DN region, in contrast to its nickel counterpart,<sup>71</sup> because of the ether oxygen coordination to Cu(II) (see Figure 7d). In contrast, the Cu(II)-based IL with n = 4 ( $T_m = 50$  °C but vitrifies at  $T_g = -46$  °C after melting) displays a well-defined color change depending on DN over the entire experimental range, from dichloromethane (DN = 0; reddish violet) to pyridine (DN = 33.1; green).

# \*\*\*\*\*\*\*\*\* Figure 12 \*\*\*\*\*\*\*\*\*

**6.2. Polarity.** 4-(2,4,6-Triphenylpyridin-1-ium-1-yl)phenolate derivatives, which were adopted after thorough research by Dimroth and Reichardt,<sup>136–138</sup> are among the most popular dyes used in solvatochromic measurements owing to their high dipole moment. Because of their zwitterionic nature, the coloration in relation to the transition energy depends largely on the polarity of the solvents. Such a chromic response is sometimes termed "halosolvatochromism" because these derivatives exhibit a color change depending on the ionic strength (or polarity) without any chemical change. In ref. 144, the protonation of two dyes designated  $E_T(30)$  and  $E_T(33)$  (Figure 12c) allows the formation of a beige ionic solid with the TFSA anion. Although no thermal evaluation was presented in the paper, the ionogel films obtained by the sol-gel process of tetramethoxysilane displayed a remarkable response to amine vapor. Reflecting the higher acidity of protonated  $E_T(33)$  (p $K_a = 4.78$ ) than that of protonated  $E_T(30)$  (p $K_a = 8.65$ ), the  $E_T(33)$ -containing ionogel shows a colorimetric response to amine vapor with a wider p $K_b$  (Figure 12d).

7. Unexplored chromic ILs. According to an IUPAC technical report published in 2001,<sup>145</sup> one of the chromic ILs that evidently is yet to be well established is one that shows mechanochromic behavior, which is known to induce a color change by the application of mechanical forces such as rubbing, crushing, pressing, shearing, or smearing. In an initial report by Angell and Abkemeier in 1973, a distinct pressure-induced spectral change was observed for Ni(II) ions dissolved in binary IL,  $\alpha$ -picolinium

chloride/ethanolammonium chloride, derived from the transformation from tetrahedral NiCl<sub>4</sub><sup>2–</sup> to octahedral NiCl<sub>6</sub><sup>4–</sup>.<sup>146</sup> It was shown in ref. 59 that the transformation temperature between  $[Co(NCS)_4]^{2-} + 2SCN^- \leftrightarrow [Co(NCS)_6]^{4-}$  (Section 2.2) accompanied by a color change in IL,  $(P_{14,6,6,6})(SCN)$ , steadily increases with increasing applied hydrostatic pressure. Despite the non-stoichiometric composition, this behavior may provide an important clue for exploring mechanochromic (or piezochromic) ILs.

8. Multichromic ILs. Another function that has been hardly explored in ILs is multichromism; the term multichromism in this review is used to describe that two or more independent stimuli induce a color change to produce an identical or similar species. We should have in mind that acidichromism, which occurs upon adsorption of acidic or basic chemicals, can be regarded as a particular subclass of vapo- and solvatochromisms. As described above, ILs containing square-planar Co(II) complex dianions<sup>70</sup> and Ni(II) complex monocations<sup>71</sup> exhibit both thermo- and solvato- (or vapo-) chromic responses. While the former IL shows a reversible transformation between octahedral hydrated and square-planar dehydrated forms regardless of the type of external stimuli (Figure 7c), it is likely that, in the latter IL, the thermal treatment and exposure to solvents lead to different coordination environments (five or six coordination; Figure 13a). Although it has not yet been investigated, ILs that undergo the VT or SCO equilibria upon thermal treatment have the potential to exhibit multichromic behavior, because such equilibria could be driven not only by thermal treatment but also by other external stimuli such as light-irradiation<sup>42–47</sup> and pressure application<sup>147,148</sup> in the solid state. In addition, some VT complexes are known to show marked solvatochromism in solution<sup>149</sup> because the solvent polarity significantly affects the stability of the redox isomers with different charge distributions (or polarities) in the complex.

# \*\*\*\*\*\*\*\*\* Figure 13 \*\*\*\*\*\*\*\*\*

**9. Dual-mode chromic ILs.** Finally, we introduce a more complex but more sophisticated control strategy of colorimetric response, called *dual-mode chromism*, in which two consecutive independent stimuli can be used to regulate the chromic behavior. An illustrative example is the pH-dependent photochromic response in spiropyran/merocyanine,<sup>150,151</sup> in which the formation of colored species upon addition of acid to spiropyran was observed prior to the discovery of its well-established photoisomerization.<sup>152</sup> In this case, the final state, protonated *E*-merocyanine (MCH<sup>+</sup>), which is inaccessible to each stimulus independently, is essentially identical regardless of

the order of photo-irradiation and acidification (Figure 13b). We note that the photochemical quantum yield of *E*-merocyanine in the protonated form (*Z*-MCH<sup>+</sup>  $\rightarrow$  MCH<sup>+</sup>;  $\Phi_{365nm} = 0.92$ ) is much higher than that in the non-protonated form (SP  $\rightarrow$  MC;  $\Phi_{300nm} = 0.07$ ).<sup>150,151</sup>

Interestingly, there are still some types of unexplored dual-mode chromisms; for example, the combination of electro- and acidichromisms seems to be achieved by utilizing proton-coupled electron transfer (PCET) processes, which play a vital role in biological energy transduction and artificial energy-related systems such as fuel cells and chemical sensors.<sup>153–155</sup> Alhough less explored for color changes, ions containing moieties that can facilitate the PCET reaction may be promising candidates for components of diverse multichromic ILs because the PCET process is ubiquitous throughout chemistry and biology. In particular, PCETs, including a redox process of metal ions, are ideally suited for exploring dual-mode chromic ILs given that the metal complexes have been utilized for various chromic responses, as shown in this review, because their color change largely depends on the electronic state. The metal dithiolate complexes (M = Ni, Pd, and Pt) shown in Figure 13c, in which two pyrazine moieties are included in the  $\pi$ -conjugated system as Lewis basic sites, can exhibit a recombination of  $\pi$ -bonds by varying the protonated state.<sup>156–160</sup> The possible multiple states associated with the multiredox and stepwise protonation/deprotonation reactions may allow fine tuning of coloration by adjusting the applied potential and pH.

Of particular importance is that, in some cases, the application of only several external stimuli in the correct order can facilitate the running of the logic response and the unlocking of molecular locks. For example, a diarylethene containing hydroxybenzene group provides a closed form by UV irradiation (*writing*), as shown in Figure 13d.<sup>161,162</sup> While it can be reversibly transformed to the open form upon visible-light irradiation (*reading*), application of an electrochemical potential results in the PCET-type interconversion between benzenoid and quinoid forms. Because the oxidized closed form remains unchanged even with visible-light irradiation, it is safe to say that the information is safeguarded by the electrooxidation process. The reduced closed form produced by the electroreduction of the oxidized closed form can be readily converted to the parent open form by visible-light irradiation (*erasing*).

# **10. Conclusion and Outlook**

Chromic ILs constitute a specific subclass of stimuli-responsive ILs, which are now recognized as state-of-the-art smart materials because of their excellent deformability and non-volatility. Most chromic ILs have been designed and synthesized by the introduction

of functional groups in one or both component ions based on the enormous accumulated knowledge of organic, organometallic, and coordination chemistry. Owing to the higher degree of orientational freedom, it is most likely that functional groups that have been exploited for solid- or solution-based chromic materials are promising for the exploration of the desired chromic ILs. A serious obstacle for synthesizing chromic ILs might be the difficulty of liquefaction, because most of functional groups addressed in this review include a heterocyclic ring, which leads to the increased melting temperature due to the intermolecular  $\pi$ - $\pi$  interactions. Nonetheless, the utilization of ionized nanostructures (e.g., nanoparticles, nanowires, nanotubes, and nanosheets, although not strictly "ionic")<sup>163–167</sup> or multinuclear complex ions<sup>168–170</sup> may provide more advanced chromic ILs that are not yet found, brought about by their promising intra-unit spin or charge interactions.

It will be necessary to quantify the colorimetric response such as sensitivity, coloration efficiency, reversibility, and repeatability, in addition to characteristics of the external field (e.g., temperature, wavelength of irradiated light, potential, pH, and polarity), to provide systematic evaluation of the chromic behavior. Such a quantitative evaluation must facilitate not only rational exploration of chromic ILs but also more rigorous comparison with those of solid- or solution-based chromic materials. We hope that this review, which covers the molecular design and colorimetric response to external stimuli in chromic ILs, will stimulate further research to explore new and more versatile chromic ILs that surpass the existing chromic ILs.

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Figure 1.Molecular structures of the typical cations and anions in this review; (a)imidazoliumcations,(b)phosphoniumcations,and(c)bis(perfluoroalkanesulfonyl)amide anions.



**Figure 2.** Schematic structures of (a) conventional, (b) functional (or task-specific), and (c) stimuli-responsive ILs (FG: functional group).



**Figure 3.** Molecular structures of (a) *N*-alkylated antifungal drug miconazolium cation<sup>24</sup> and (b) TEMPO-OSO<sub>3</sub> anion (TEMPO: 2,2,6,6-tetramethyl-1-piperidinyloxyl),<sup>25</sup> where functional groups are depicted in green.



Figure 4. Classification of chromic responses.



**Figure 5.** (a) Valence tautomerism (VT) in cobalt dioxolene (Cat: catecholate, SQ: semiquinone), (b) VT interconversion in a cobalt bis(dioxolene) complex dianion bearing two carboxylate groups, and (c) temperature dependence of the effective magnetic moment ( $\mu_{eff}$ ) of [P<sub>14,6,6,6</sub>]<sub>2</sub>[Co(DBSQ)<sub>2</sub>(bpy(COO)<sub>2</sub>)] (or (P<sub>14,6,6,6</sub>)<sub>2</sub>[Co<sup>III</sup>(DBCat)(DBSQ)(bpy(COO)<sub>2</sub>)]).<sup>49</sup>



**Figure 6.** (a) Spin-crossover (SCO) equilibrium in Fe(III), (b) molecular structure of the  $[Fe(acacen)(1-n-butylimidazole)]^+$  complex monocation, and (c) temperature dependence of  $\mu_{eff}$  of [Fe(acacen)(1-n-butylimidazole)]X (upper: X = TFSA (liquid at RT), lower: X = PF<sub>6</sub> (solid at RT)). Reproduced from ref. 52. Copyright 2013 The Royal Society of Chemistry.



**Figure 7.** Thermal equilibria (a) between discrete ionic and bridged neutral forms in ref. 65 (C<sub>6</sub> and C<sub>14</sub> represent the C<sub>6</sub>H<sub>13</sub> and C<sub>14</sub>H<sub>29</sub> groups, respectively; R, R': *t*-Bu or C<sub>3</sub>F<sub>7</sub> group), (b) between dimeric and monomeric forms in ref. 66 (R = CF<sub>3</sub>, H, or OMe), (c) between hydrated and dehydrated forms in ref. 70, and (d) between closed and open forms associated with intramolecular ether coordination in ref. 71.



**Figure 8.** (a) *Cis/trans* isomerization of the methyl orange monoanion,<sup>80</sup> (b) molecular structure of the imidazolium cation bearing a phenyl azo group,<sup>81</sup> (c) molecular structure of the ammonium cation bearing an azo benzene moiety,<sup>82</sup> and (d) *cis/trans* isomerization of the imidazolium cation bearing a methyl cinnamate moiety.<sup>79</sup>



**Figure 9.** Opening/closing isomerizations in (a) spiropyran (closed)/merocyanine (open)-based monocation<sup>89</sup> and (b) diarylethene-based dianion<sup>92</sup> and (c) the transformation between the monomer and oligomer in a cyclopentadienyl-arene Ru(II) complex monocation.<sup>94</sup>



**Figure 10.** Redox equilibria of (a) viologen and (b) the Co(ethylenediaminetetraacetate) anion<sup>119</sup> and (c) molecular structure of viologen bearing a cationic trioctylphosphonium moiety.<sup>108</sup>



**Figure 11.** Protonation equilibria in (a) methyl red,<sup>125</sup> (b) methyl orange,<sup>125</sup> (c) fluorescein,<sup>127</sup> and (d) pyranine.<sup>48</sup>



**Figure 12.** (a) Coordination equilibrium in ref. 139 (X: solvent molecule), (b) molecular structure of heteroleptic Cu(II) complex monocation in ref. 143, (c) molecular structures of  $E_T(30)$  (R = Ph) and  $E_T(33)$  (R = Cl), and (d) deprotonation of  $E_T(33)$ -based cation in ref. 144 (X: Lewis base).







**Figure 13.** (a) Intramolecular ether or solvent coordination to heteroleptic Ni(II) complex monocation,<sup>71</sup> (b)  $2 \times 2$  square scheme of pH-dependent photoisomerization in spiropyran/merocyanine,<sup>150,151</sup> (c)  $3 \times 3$  square scheme of the pH-dependent redox reaction in nickel dithiolate complex,<sup>156–160</sup> and (d) schematic representation of the dual-mode switching behavior in diarylethene.<sup>161,162</sup>