Electrochromic and magnetic ionic liquids†

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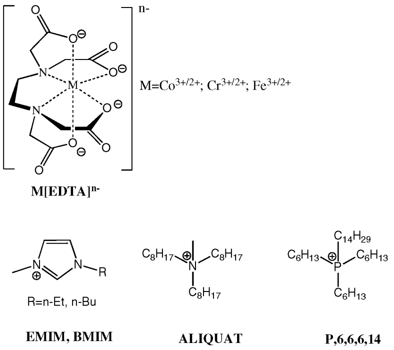
Ionic liquids can be made intrinsically electrochromic and magnetic through the appropriate combination of electrochromic and magnetic anions based on ethylenediaminetetraacetic metal complexes, combined with several organic cations. These novel and highly multi-functional materials encompass the peculiar properties of ionic liquids together with the characteristics of electrochromic and magnetic materials.

New frontiers in materials science have been opened by ionic liquids taking profit from their unique physicochemical properties. Electrochromic materials[1] are the basis of a variety of devices, such as information displays,[2] anti-glare rear view of automobiles,[3] smart windows,[4] *etc.* The fabrication of useful electrochromic devices[5] is dependent on three main components: conducting surfaces, electrochromic compounds and electrolytes. Highly conducting surfaces can be easily achieved in different supports in particular by coating with transparent conducting oxides (TCO).[6] The conducting surfaces are covered by the electrochromic material, consisting of chemicals capable of forming an electrochromic layer due to a strong colour contrast upon oxidation/reduction. Preparation of a high ionic conductive electrolyte[7] is generally the most challenging component of these devices. Ionic liquids (ILs)[8] are known to have some of the properties required for a good electrolyte: high ionic conductivity, large electrochemical windows,[9] excellent thermal and chemical stability and in addition they exhibit a negligible vapour pressure[10] and ability to solubilize organic, inorganic and polymeric materials.[11] Following our strategy to obtain chromogenic materials,[12] we are presenting in this work ionic liquids capable of behaving not only as electrolytes but also as the electrochromic component. Our approach relies on the preparation of ionic liquids possessing anions or cations capable of reversible oxidation/reduction processes involving strong changes in colour, and or their magnetic properties, Scheme 1.

The compounds prepared with these cations and anions encompass the usual conductivity of the ionic liquids together with the change of colour characteristic of an electrochromic material. In addition, according to the metal it is possible to switch reversibly from diamagnetic to paramagnetic states upon oxidation or reduction, defining electrochromic and magnetic ionic liquids.



Scheme 1 Cations and anions used through this work to prepare the ionic liquids.

The novel electrochromic and magnetic ionic liquids have been prepared by a simple combination of cobalt(III), chromium(III) and iron(III) ethylenediaminetetraacetic complexes as anions and the cations 1-ethyl-3-methylimidazolium [EMIM], 1-butyl-3-methylimidazolium [BMIM], 1-octyl-3-methylimidazolium [OMIM], tri-octylmethylammonium [ALIQUAT] and trihexyltetradecylphosphonium [$P_{6,6,6,14}$]. In the case of cobalt EDTA complexes it was possible to develop five RTILs (based on methylimidazolium, ammonium and phosphonium cations) while for chromium and iron EDTA, only the combination with the [EMIM] cation was tested. The synthesis was optimized depending on the reactivity and solubility of selected ions. All the novel ionic liquids were characterized by ^{1}H and ^{13}C NMR (in the case of diamagnetic cobalt(III) compounds) and elemental analysis. For some of them the ionic conductivity, density and magnetic susceptibility were also measured (the details are included as ESI†). An interesting feature of intrinsically electrochromic ionic liquids is the possibility of carrying out cyclic voltammetry or electrolyses, taking profit from the ion conductivity of these compounds. In other words, these ionic liquids behave as the electrolyte and the reversible electrochromic material simultaneously, as shown in Fig. 1.

Attending to cyclic voltammetry analysis (see ESI†, Fig. S1, S4 and S7), it's possible to note that the redox gap between the oxidation and reduction is higher for pure ionic liquids than for Na[Co(EDTA)] in water. One of the possible reasons for this observation is related to the lower diffusion coefficient in the case of ionic liquid systems because of their higher viscosity behaviour. Moreover, the ionic liquids of [Co(EDTA)] anion with the cations [ALIQUAT]$^+$ and [$P_{6,6,6,14}$]$^+$ behave similarly, as described in ESI.†

Liquid electrochromic cells can be easily designed by putting in contact two immiscible RTILs, see Fig. 2. One of the U-tube

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† Electronic supplementary information (ESI) available: Detailed synthesis of electrochromic ionic liquids, physico-chemical properties including their magnetic susceptibility and magnetic moment, and their voltammograms in solution (ethanol) or as bulk materials. See DOI: 10.1039/c0cc03892j

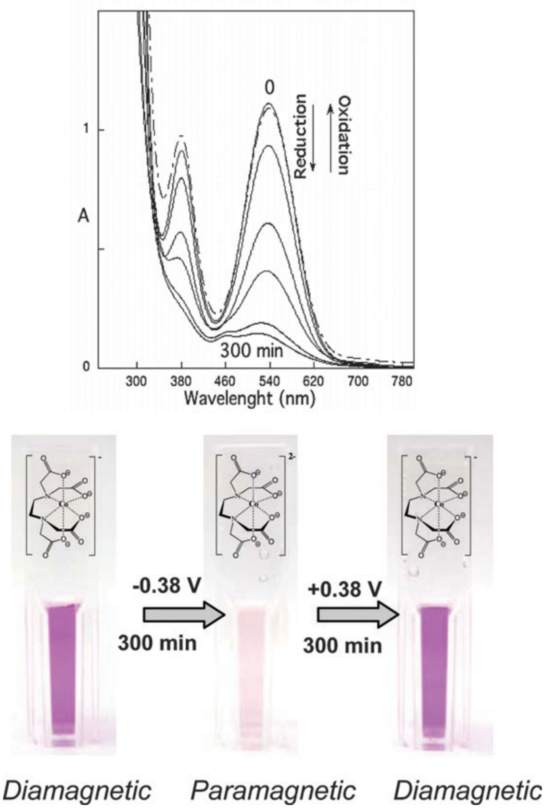

Fig. 1 Full lines—spectral variations of the compound [EMIM][Co(EDTA)] upon reduction at −0.38 V for the following times 0; 33; 83; 117; 225; 300 min. Traced line—after oxidation of the previously reduced solution at +0.38 V after 300 min. The potentials have been selected in order to optimize the chemical stability and time response of the system.

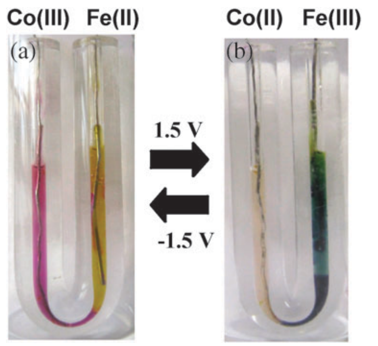

Fig. 2 A liquid electrochromic cell can be designed in a glass U tube containing two immiscible ionic liquids. (a) Left: [ALIQUAT][Co(EDTA)]; right: ferrocene (0.8 M) dissolved in [ALIQUAT][DCA] (DCA = dicyanamide). (b) Upon reduction and simultaneous oxidation of the cobalt and iron respectively. The system is reversible and the initial state is obtained upon changing the signal of the applied potential.

sides is filled with the intrinsically electrochromic RTIL [ALIQUAT][Co(EDTA)] while the other with the conventional RTIL, [ALIQUAT][DCA] (DCA = dicyanamide), where ferrocene was dissolved (0.8 M). Reduction of the cobalt ionic liquid leads to a pale pink solution and at the same time ferrocene is oxidized to the blue ferricinium. On reversing the potential (−1.5 V) the system goes back to the initial state.

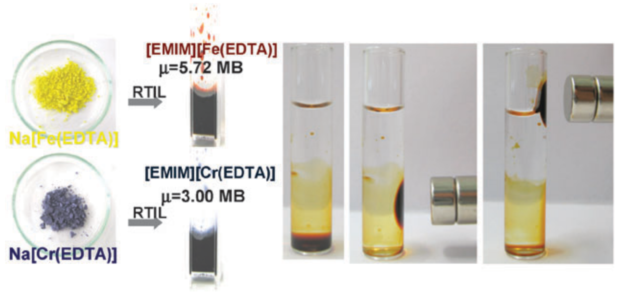

Fig. 3 Development of novel Magnetic Room Temperature Ionic Liquids based on the combination of 1-ethyl-3-imidazolium cation and iron(III) and chromium(III) EDTA complexes anions. For comparison purposes Na[Fe(EDTA)] and Na[Cr(EDTA)] exhibit, respectively, 3.53 MB and 2.91 MB. Right side: effect of a Neodymium (NdFeB) magnet on the RTIL [EMIM][Fe(EDTA)] in *n*-heptane.

In addition to its electrochromic behaviour, the [Co(EDTA)] ionic liquids can switch reversibly from diamagnetic to paramagnetic upon reduction/oxidation, defining magnetic and electrochromic ionic liquids. Depending on the *n*-alkyl group (*n*-ethyl to *n*-octyl) attached to position 3 of 1-methylimidazolium cation it is possible to tune some relevant properties of novel electrochromic RTILs such as density, viscosity, ion conductivity, water solubility and redox electrochromic behaviour (see Table S1 of ESI†), extending the possible applications of these systems.

Other paramagnetic ionic liquids were synthesized using chromium(III) and iron(III) EDTA compounds, Fig. 3. They have not been extensively studied from the point of view of their electrochromic properties due to the poor colour contrast upon switching. However they can find applications as paramagnetic ionic liquids, such as contrast agent for Magnetic Resonance Image (MRI)[13] and flow batteries systems.[14] Magnetic Resonance Image (MRI)[15] is a powerful method for obtaining images of the body in thin slices. However, extensive application of MRI for medical diagnostics is limited by the selection of paramagnetic contrast agents (lanthanides and transition metals) due to their toxicity.[16] Recent investigations[17] have been focused on the development of stable paramagnetic ion complexes. The complexation of a paramagnetic ion with an organic ligand may create a thermodynamically and kinetically stable compound which is much less toxic.[18] On this line, the novel magnetic RTILs based on chromium(III) and iron(III) EDTA complexes can be alternative, robust and efficient MRI contrast agents for many diagnostic applications. Depending on the appropriate combination with organic cations it is possible at the same time to reduce the toxicity problem and allow a long-term paramagnetic complex stability and magnetic moment.

One interesting feature of these compounds is that, differently from the common magnetic fluids, which should be dissolved and stabilized in an appropriate solvent, they are intrinsically liquids. The other potential application, redox flow batteries, offers a very attractive alternative to energy storage with some advantages over conventional rechargeable batteries.[19]

The energy of these batteries is stored in liquid electrolytes (tanks), which can be pumped through an electrochemical cell.[20] The advantages of the ionic liquids based on chromium and iron EDTA complexes compared with the conventional redox flow batteries, such as those based on vanadium[21] and zinc–cerium[22] systems, are their higher concentration of the electro-active species and the lack of a solvent to play the role of the electrolyte. It is worth of note that this potential application as redox flow batteries is dependent on the adequate selection of a reversible or quasi-reversible behaviour of the electrochromic metal complex.

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