Supporting Information

Magneto-Electrochromic Ionic Liquids

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Experimental Section

All glassware was oven dried and cooled in a desiccator prior to use. Following chemicals were purchased from Aldrich and were used as supplied: Sodium Ethylenediaminetetraacetate (Na_2EDTA), Cobalt(III) chloride, Chromium (III) chloride, Iron(III) chloride hexahydrate, acetonitrile, acetic acid and sodium acetate anhydrous.
The ILs 1-ethyl-3-methyl imidazolium bromide [EMIM]Br, 1-butyl-3-methyl imidazolium chloride [BMIM]Cl, 1-octyl-3-methyl imidazolium chloride [OMIM]Cl were prepared according to the reported procedures.[1],[2] The ILs trihexyltetradecylphosphonium chloride $[P_{6,6,6,14}]Cl$ and trioctylmethylammonium chloride [ALIQUAT] Cl were purchased from Aldrich and Cytec Inc. respectively.
^1H and ^{13}C NMR spectra in D_2O or MeOD were recorded on a Bruker AMX400 spectrometer. Chemical shifts are reported downfield in parts per million (ppm) from a tetramethylsilane reference. Elemental analysis (C, H, N analyzer) of each synthesized ionic liquid was performed by the Laboratório de Análises at REQUIMTE.
Optical Spectroscopic Measurements: Absorption spectra were recorded on a Cary 100 Bio UV-Vis spectrophotometer.
Electrochemical Measurements: Cyclic voltammetry was performed in a conventional three-electrode cell under argon atmosphere at 21°C using a potentiostat-galvanostat Model 20 Autolab, from Eco-Chemie Inc. The collection of data was controlled by the GPES Version 4.9 Eco Chemie B.V. Software (Utrecht, The Netherlands). The working electrode was a glassy carbon microelectrode, auxiliary electrode was a platinum wire and the reference electrode was an Ag/AgCl (1 mol dm^{-3} NaCl) as reference electrode (BAS). Electrolysis was made in a configuration identical to the cyclic voltametry, using a platinium net working electrode.
Density Measurements were determined by using a micropicnometer.
Conductivity Measurements were performed using a Conductimeter Basic 30 Crison.
pH Measurements were determined using a PH/ion Meter PHM 240.
Magnetic Moment and Magnetic susceptibility were determined by using a Balance
The water and halogen content for each ionic liquid was measured using Karl-Fischer and potentiometry titration respectively.

General Synthesis of electrochromic ionic liquids (ILs)

The starting compounds of sodium metal EDTA complexes were synthesized according to reported procedures. [3] Using the experimental protocol was possible to prepare and purify the solids Na[Co(EDTA)], Na[Fe(EDTA) and Na[Cr(EDTA)] respectively.

The selected salt (3 g of each: [EMIM]Br, [BMIM]Cl, [OMIM]Cl, [ALIQUAT]Cl and [$P_{6,6,6,14}$]Cl) was dissolved in ethanol (10-25 mL) and then the correspondent sodium metal [Cobalt(III); Chromium(III) or Iron(III)] EDTA complex (1.2 equiv) in water (25-50 mL) was added to the ethanol solution. The resulted mixture was stirred at room temperature for 24 h. The ethanol and water solvents were removed under vacuum. Then, the correspondent residue was redissolved in acetone or dichloromethane in order to check the possible precipitation of inorganic salts or starting materials. The final compound was purified and completely dried under vacuum overnight. All the final and pure electrochromic ionic liquids were characterized by ^{1}H and ^{13}C NMR (only for diamagnetic cobalt(III) complexes), elemental analysis, water content and halogen content (less than 1000 and 50 ppm respectively for all the ILs).

[EMIM][Co(EDTA)] was obtained as a violet viscous liquid, 88%.
^{1}H NMR (400 MHz, D_2O, 25°C): 1.29 (3 H,t, J=7.5 Hz), 2.39 (4H, m), 3.32 (2H, s), 3.35 (2H, s), 3.48 (4H, s), 4.12 (2H, m), 4.29 (3H, s), 7.26 (2H, d), 7.64 (1H, s).
^{13}C NMR (100 MHz, D_2O, 25°C): 15.2, 37.0, 39.5, 52.1, 57.7, 59.3, 123.0, 124.2, 137.0, 173.1.Elemental Analysis calcd (%) for C16H23CoN4O8.2H_2O (494.34): C, 38.87; H, 5.51; N, 11.33; found: C 38.42, H 5.27, N 11.28.
[BMIM][Co(EDTA)] was obtained as a violet viscous liquid, 84%.
^{1}H NMR (400 MHz, D_2O, 25°C): 0.91 (3 H,t, J=7.5 Hz), 1.31 (2H, m), 1.74 (2H, m), 2.40 (4H, m), 3.28 (4 H, s), 3.33 (2H, s), 3.37 (2H, s), 4.04 (2H, t, J= 7.3 Hz), 4.37 (3H, s), 7.48 (2H, d), 8.02 (1H, s).
^{13}C NMR (100 MHz, D_2O, 25°C): 13.8, 20.7, 33.5, 44.8, 51.8, 55.2, 57.8, 59.0, 123.3, 124.1, 137.2. Elemental Analysis calcd (%) for C18H27CoN4O8.2H_2O (522.14): C, 41.39; H, 5.98; N, 10.73; found: C 41.21, H 5.63, N 10.58.
[OMIM][Co(EDTA)] was obtained as a violet viscous liquid, 78%.
^{1}H NMR (400 MHz, MeOD, 25°C): 0.86 (3 H,t, J=7.6 Hz), 1.32 (4H, m), 1.38 (4H, m), 1.58 (2H, m), 1.91 (2 H, m), 2.46 (4H, m), 3.30 (2H, s), 3.37 (2H, s), 3.43 (4H, s), 3.83 (2H, m), 4.09 (2H, t, J= 7.2 Hz), 7.91 (2H, d), 8.23 (1H, s).
^{13}C NMR (100 MHz, MeOD, 25°C): 14.3, 22.6, 27.7, 29.5, 30.8, 32.3, 44.8, 52.7, 54.5, 58.3, 59.8, 123.4, 125.1, 138.3, 173.7. Elemental Analysis calcd (%) for C22H35CoN4O8.H_2O (560.48): C, 47.14; H, 6.65; N, 10.00; found: C 47.03, H 6.71, N 10.06.
[$P_{6,6,6,14}$][Co(EDTA)] was obtained as a pale violet liquid, 91%
^{1}H NMR (400 MHz, MeOD, 25°C): 0.91 (12H, t, J=7.3 Hz), 1.36 (40H, m), 1.83 (8H, m), 2.49 (4H, m), 3.32 (2H, s), 3.35 (2H, s), 3.41 (4H, s), 3.81 (8H, m).
^{13}C NMR (100 MHz, MeOD, 25°C): 14.3, 19.8, 22.5, 23.9, 29.3, 31.5, 31.9, 32.8, 52.5, 57.8, 60.3, 174.0. Elemental Analysis calcd (%) for C42H80CoN2O8P (831.0): C, 60.70; H, 9.70; N, 3.37; found: C 60.24, H 9.53, N 3.31.
[ALIQUAT][Co(EDTA)] was obtained as a blue- violet liquid, 93%
^{1}H NMR (400 MHz, MeOD, 25°C): 0.88 (9H, t, J=7.4 Hz), 1.27 (30H, m), 1.79 (6H, m), 2.52 (4H, m), 3.27 (6H, s), 3.35 (2H, s), 3.38 (2H, s), 3.41 (3H, s), 3.47 (4H, s).
^{13}C NMR (100 MHz, MeOD, 25°C): 14.1, 21.2, 22.9, 25.7, 29.4, 30.9, 50.1, 53.1, 56.7, 57.5, 61.8, 173.9. Elemental Analysis calcd (%) for C35H66CoN3O8 (715.85): C, 58.72; H, 9.29; N, 5.87; found: C 58.39, H 9.22, N 5.79.
[EMIM][Cr(EDTA)] was obtained as a blue-gray viscous liquid, 85%.
Elemental Analysis calcd (%) for C16H23CrN4O8.2H_2O (487.40): C, 39.43; H, 5.58; N, 11.49; found: C 39.31, H 5.44, N 11.45.
[EMIM][Fe(EDTA)] was obtained as a dark red viscous liquid, 90%.

Elemental Analysis calcd (%) for C16H23FeN4O8.2H_2O (491.25): C, 39.12; H, 5.54; N, 11.40; found: C 39.02, H 5.43, N 11.37.

The Figures 1 and 2 show the cyclic voltametry of Na[Co(EDTA)] in water acetate buffer (pH 4) comparing with pure IL [EMIM][Co(EDTA)] (Fig. S1) and the spectral modifications during the reduction-oxidation process of Na[Co(EDTA)] in water acetate buffer (pH 4) (Fig. S2).

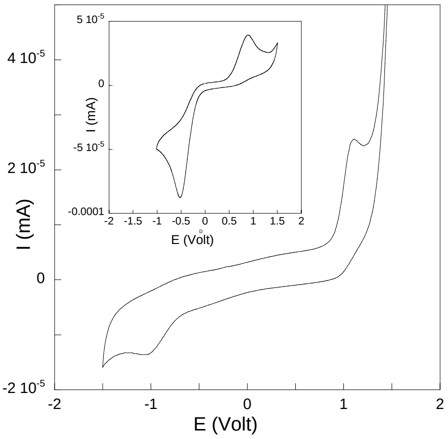

Fig. S1. Cyclic Voltametry of pure ionic liquid [EMIM][Co(EDTA)] 50 mV/s. Inset-the same for Na[Co(EDTA)] 10^{-3} M in water at pH=4.0 (acetate buffer) 50 mV/s, (versus Ag/AgCl).

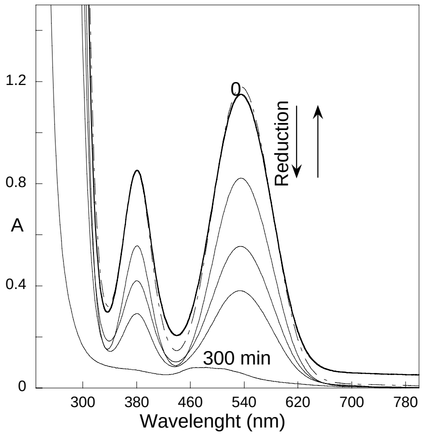

Fig.S2. Spectral modifications involving a cycle of reduction-oxidation of the compound Na[Co(EDTA)] in water at pH=4.0, acetate buffer.

The electrolysis study of [EMIM][Co(EDTA)] is presented in the article (Figure 1) and a similar behavior was observed in the case of [BMIM][Co(EDTA)] and [OMIM][Co(EDTA)].

Figures 3 and 4 show the electrolysis study and cyclic voltammetry of pure RTIL [ALIQUAT][Co(EDTA)].

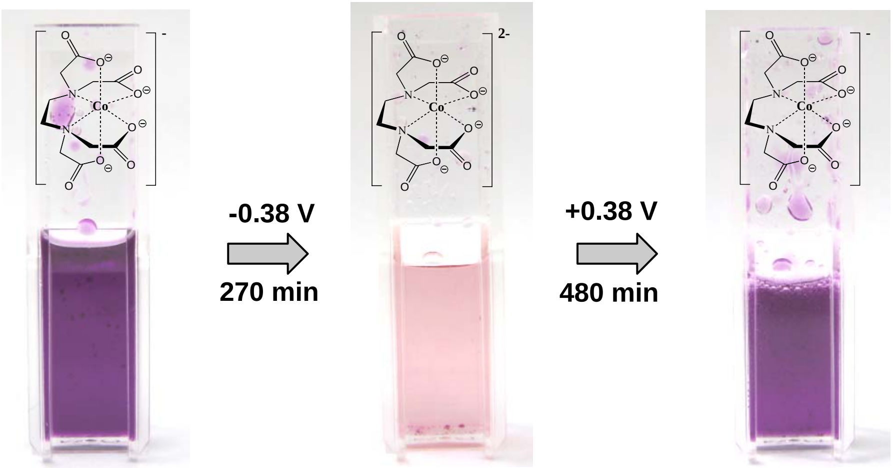

Fig. S3. Electrochromic behavior of the ionic liquid [ALIQUAT][Co(EDTA)]

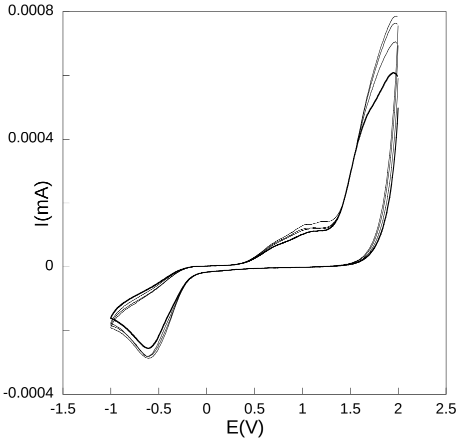

Fig. S4. Cyclic voltammetry of pure [ALIQUAT][Co(EDTA)], 50 mV/s. $E_{\text{reduction}}$ = -0.62 V; $E_{\text{oxidation}} \approx 1$V (versus Ag/AgCl)

Figures 5 to 7 show the electrochemical study of pure RTIL [P6,6,6,14][Co(EDTA)] in particular the spectral variations during the reduction-oxidation process, electrolysis process and cyclic voltammetry respectively.

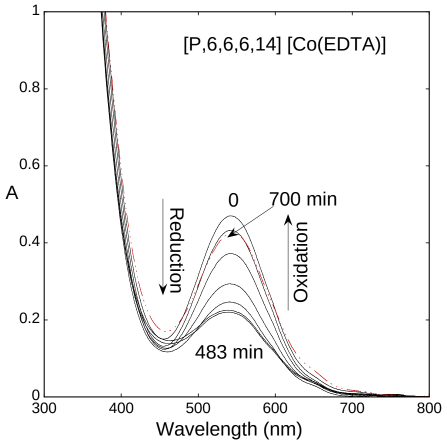

Figure S5. (Full lines) - Spectral variations of the compound [P,6,6,6,14][Co(EDTA)] upon reduction at -0.38 V for the following times 0; 33; 100; 200; 283; 433, 483 min.: (Traced line)-after oxidation of the previously reduced solution at +0.38V after 700 min.

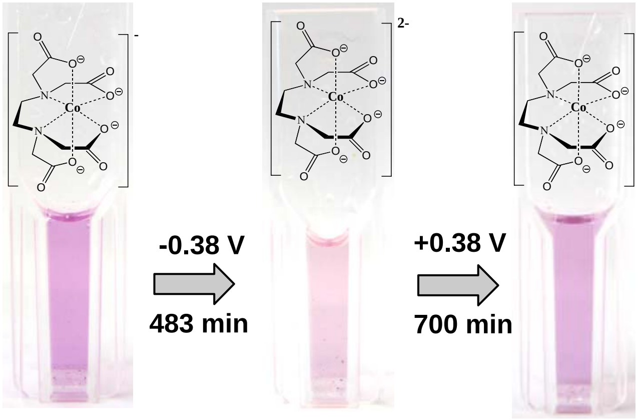

Fig. S6. Electrochromic behavior of the ionic liquid [P,6,6,6,14][Co(EDTA)]

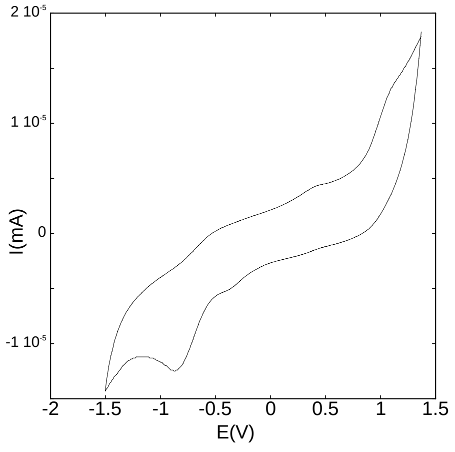

Fig. S7. Cyclic voltametry of the ionic liquid [$P_{6,6,6,14}$][Co(EDTA)] 100 mV/s. $E_{\text{reduction}}$ = -0.88 V; $E_{\text{oxidation}} \approx$1.1V (versus Ag/AgCl).

In Table 1 is presented some physico-chemical properties of electrochromic ionic liquids in particular their density, ionic conductivity and magnetic moment values.

Table 1- Some Physico-chemical properties of novel electrochromic ionic liquids.

RTILs [a]	Density[b] (g.mL^{-1})	Ionic Condutivity[c] (mS.cm^{-1})	Magnetic Moment (MB)[d]	Water Solubility
EMIM[Co^{III}(EDTA)]	1.46	-	0 (Co(III)) 3.72 (Co(II))	Soluble
EMIM[Co^{III}(EDTA)] pH4	-	4.63	-	-
Aliquat[Co^{III}(EDTA)]	1.12	38.00	0	Insoluble
Aliquat[Co^{III}(EDTA)] pH4	-	1.47	-	-
[$P_{6,6,6,14}$][Co^{III} (EDTA)]	1.19	-	0	Insoluble
[$P_{6,6,6,14}$][Co^{III} (EDTA)] pH4	-	2.04	-	-
Na[Co^{III} (EDTA)]	-	-	0 (Co(III)) 3.93 (Co(II))	Soluble
Na[Co^{III} (EDTA)] pH4	-	1.71	-	-
EMIM[Fe^{III} (EDTA)]	1.53	-	5.72	Soluble
EMIM[Fe^{III} (EDTA)] pH4	-	14.83	-	-
Na[Fe^{III} (EDTA)]	-	-	3.53	Soluble
Na[Fe^{III} (EDTA)] pH4	-	1.68	-	-
EMIM[Cr^{III} (EDTA)]	1.35	-	3.00	Soluble
EMIM[Cr^{III} (EDTA)] pH4	-	4.82	-	-
Na[Cr^{III} (EDTA)]	-	-	2.91	Soluble
Na[Cr^{III} (EDTA)] pH4	-	1.05	-	-

[a] Room Temperature Ionic Liquids (RTILs) tested as pure or in acetate buffer at pH 4. For comparison is indicated the starting sodium compounds with Cobalt, Chromium and Iron respectively. [b] Density values (g.cm^{-1}) at 25ºC of different RTILs. [c] Ionic Conductivity (mS.cm^{-1}) at 25ºC of ionic liquids in acetate buffer at pH 4 and in the case of RTIL Aliquat[Co^{III}(EDTA)] as pure. For comparison were presented the values of correspondent sodium salts in acetate buffer at pH 4. [d] Magnetic Moment (MB) of RTILs as pure and correspondent sodium salts as solids. In the case of cobalt compounds is presented the values for Cobalt(II) (diamagnetic) and Cobalt (III) (paramagnetic).