Anion effect on the redox properties of copper ions in ionic liquids and deep eutectic solvents

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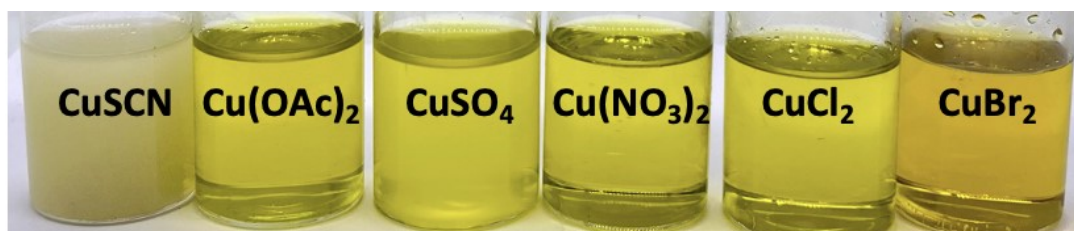*School of Chemistry, University of Leicester, Leicester, LE1 7RH, UK*

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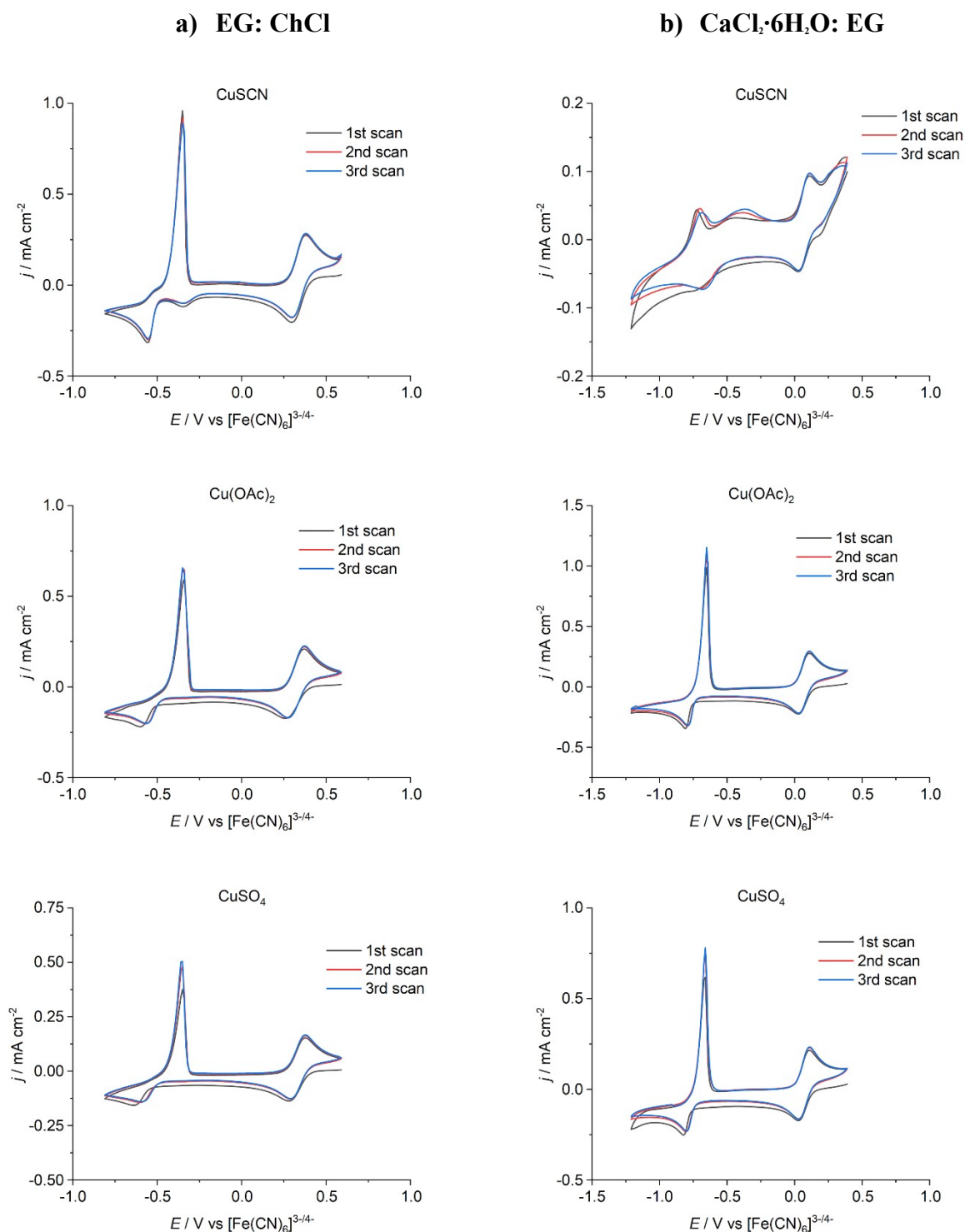**Supplementary Information**

a)

b)

Figure S1: Photos of the different copper salts in: a) EG: ChCl, and b) $CaCl_2 \cdot 6H_2O$: EG. The copper salt concentration was 0.02 mol dm^{-3}.

a) EG: ChCl　　　　　　　　　　**b) CaCl₂·6H₂O: EG**

Figure S2: Cyclic voltammograms of the different copper salts (each 0.02 mol dm⁻³) in: a) EG: ChCl, and b) CaCl₂·6H₂O: EG at a 0.5 mm diameter Pt-disc, referenced to the $[Fe(CN)_6]^{3-/4-}$ redox couple, with a scan rate of 20 mV s⁻¹. Temperature = 20 °C. Presented data is the full set of scans for each system measured.

a) EG: ChCl **b) CaCl₂·6H₂O: EG**
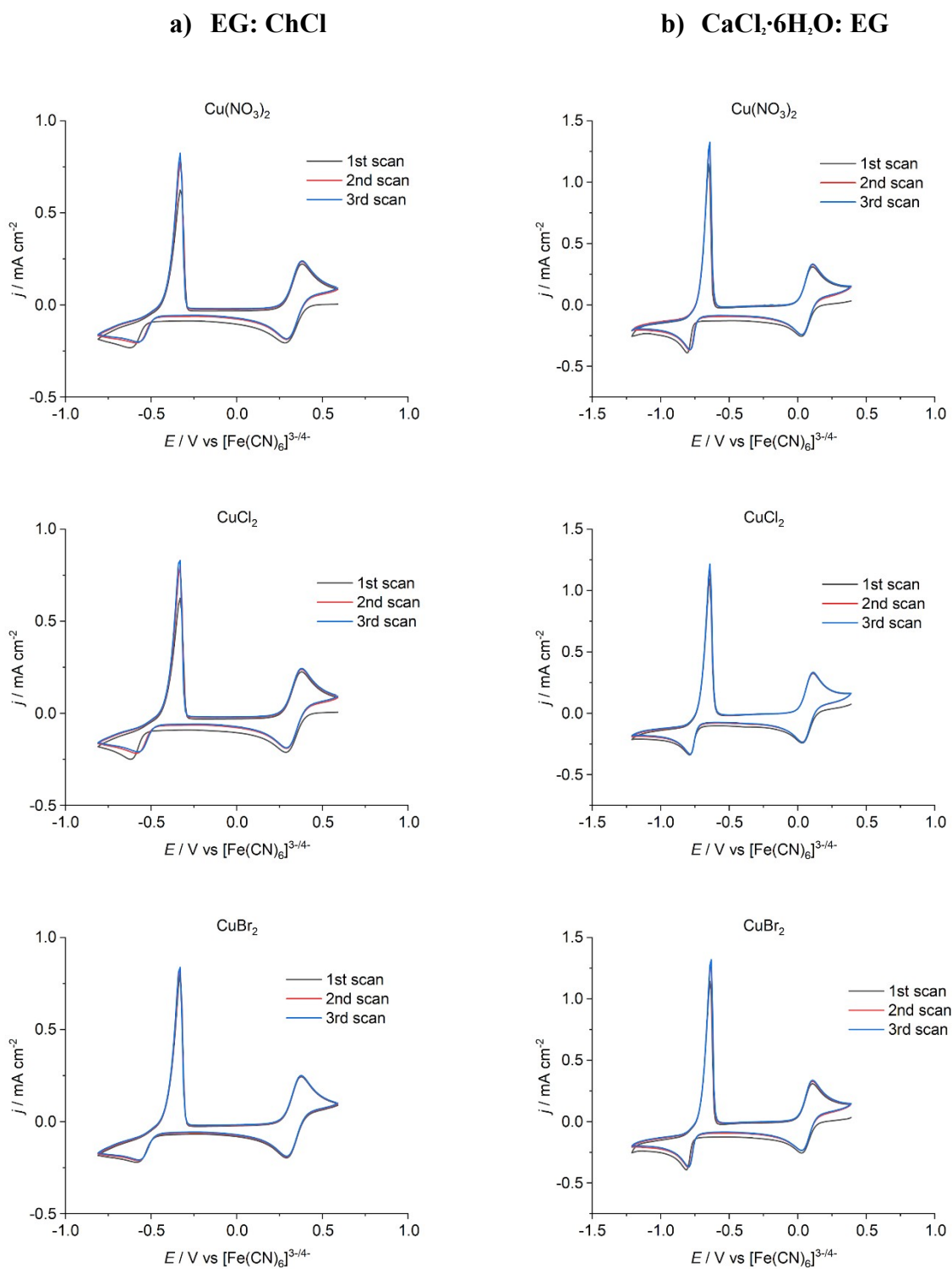
Figure S2 (cont.): Cyclic voltammograms of the different copper salts (each 0.02 mol dm^{-3}) in: a) EG: ChCl, and b) CaCl₂·6H₂O: EG at a 0.5 mm diameter Pt-disc, referenced to the [Fe(CN)₆]$^{3-/4-}$ redox couple, with a scan rate of 20 mV s^{-1}. Temperature = 20 °C. Presented data is the full set of scans for each system measured.
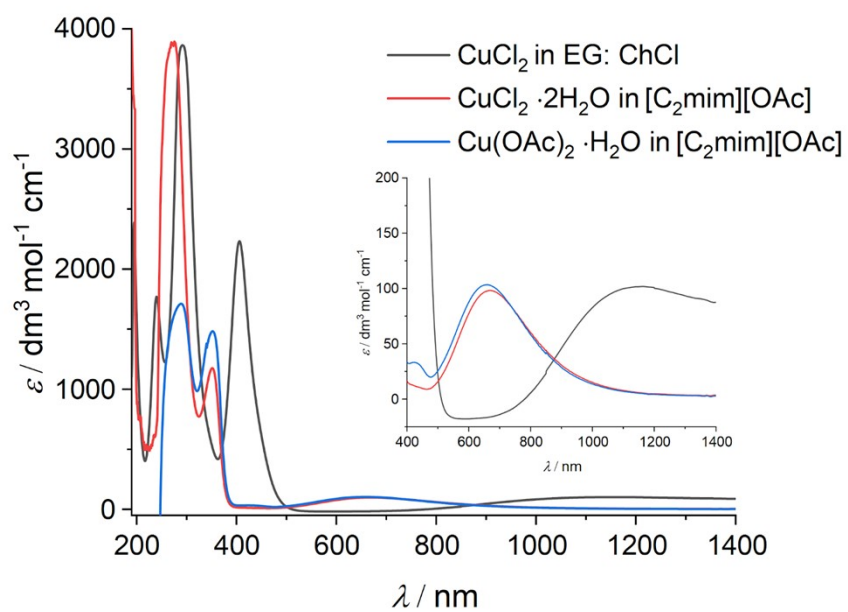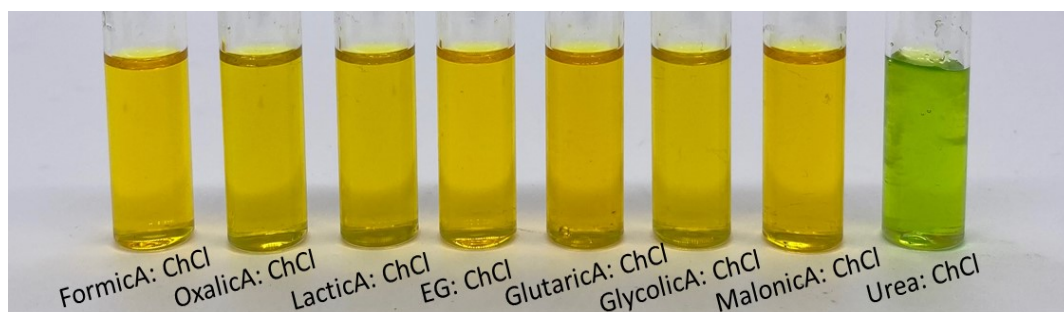
Figure S3: UV-vis spectra of copper(II) chloride dihydrate and copper(II) acetate hydrate in [C$_2$mim][OAc], with spectrum of copper(II) chloride dihydrate in EG: ChCl for comparison. Inset are the expanded d-d transitions.
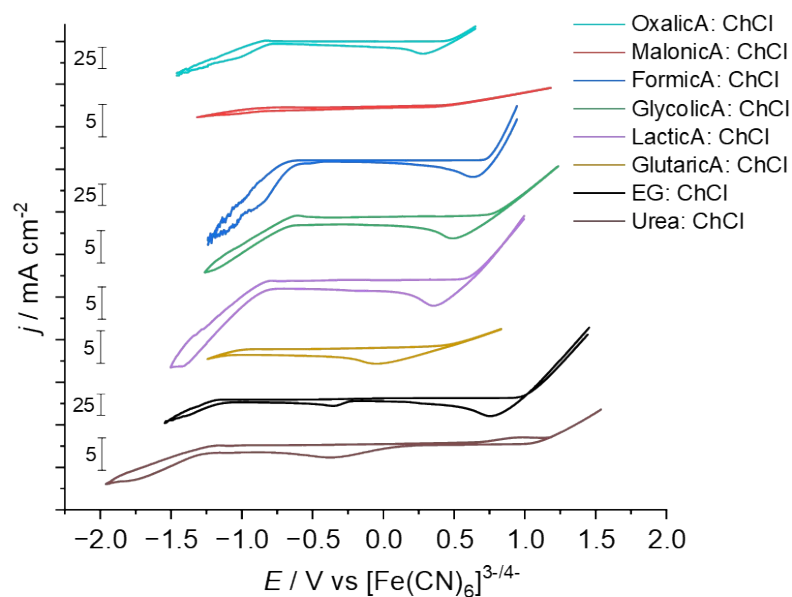
a)

b)

Figure S4: Photos of copper(II) chloride in: a) five different imidazolium-based ILs, and b) in eight DESs formed with different HBDs. The copper(II) chloride concentration was 0.02 mol dm^{-3}.

Figure S5: Voltammograms of the eight pure DESs measured at a Pt-disc working electrode, at a scan rate of 20 mV s^{-1}. CVs are referenced to the $[Fe(CN)_6]^{3-/4-}$ redox couple. Temperature = 20 °C. CVs are offset for clarity.

Table S1: Absorbance maxima for the different copper salts dissolved in EG: ChCl and $CaCl_2 \cdot 6H_2O$: EG. Absorbance maxima present as shoulders or broad peaks are estimated and shown in italics.

Salt	Absorbance / nm (EG: ChCl)			Absorbance / nm ($CaCl_2 \cdot 6H_2O$: EG)		
Acetate	238.8	291.6	405.4	*ca. 232*	277.4	389.4
Bromide	239.6	291.2	406.2	*ca. 235*	280.4	390.4
Chloride	239.8	291.8	406.4	*ca. 235*	280.4	391.0
Nitrate	*ca. 239*	291.6	406.4	–	279.2	390.2
Sulfate	239.2	291.2	406.0	*ca. 234*	279.0	389.4
Thiocyanate	–	269.8	406.4	–	263.8	391.4

Table S2: Absorbance maxima for copper(II) chloride in different ionic liquids. Absorbance maxima present as shoulders or broad peaks are estimated and shown in italics.

Solvent	Absorbance / nm		
[C$_2$mim][OAc]	–	*ca. 275.5*	351.5
[C$_2$mim][BF$_4$]	*ca. 249*	285	402.6
[C$_6$mim][Cl]	–	290	407.5
[C$_4$mim][DCN]	–	*ca. 290*	369
[C$_4$mim][HSO$_4$]	*ca. 289*	*ca. 304*	482
[C$_2$mim][SCN]	–	*ca. 274*	399

Table S3: Absorbance maxima for copper(II) chloride in ChCl-based DESs with different HBDs, presented in order of relative acidity. Absorbance maxima present as shoulders or broad peaks are estimated and shown in italics.

HBD	Absorbance / nm		
Oxalic acid dihydrate	–	287	403
Malonic acid	–	291.2	405
Malic acid	*ca. 244*	291	404.8
Mandelic acid	–	291.6	407.2
Formic acid	242	291	405
Glycolic acid	239.2	290.4	405
Lactic acid	243.2	290.8	404.8
Glutaric acid	240.6	291.4	405.2
Ethylene glycol	239.8	291.8	406.4
Urea	*ca. 241*	274.5	401.5