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ELECTROCHEMISTRY OF, AND ELECTROANALYSIS IN, CHIRAL AND INHERENTLY CHIRAL IONIC LIQUID MEDIA

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Ionic liquids ILs are attractive media for electrochemistry and electroanalysis, since, in addition to other useful properties, they provide both solvent and supporting electrolyte; moreover, they feature an extremely well defined structure at the interphase with a charged electrode, resembling a semisolid crystal or a bulk liquid crystal, extending for many layers, also standing in the presence of water traces, and possibly tunable by *in-situ* present additives. For this reason *chiral* ionic liquids CILs are surprisingly still nearly unexplored by electrochemists, in spite of appearing quite attractive, since they could transmit chiral information more effectively than chiral organic solvents or chiral supporting electrolytes.[1] In this context we have recently started a detailed investigation of (a) *bio-based chiral* ionic liquids and (b) *inherently chiral* ionic liquids ICILs, investigating both their physico-chemical and electrochemical features and their performance as media for chiral electroanalysis experiments. Our bio-based CILs feature cations with a building block of natural origin, including one or more localized stereocentres, from which their chirality arises (as in most so far available CILs) [2]. Instead in our ICILs chirality is intrinsic of the whole biheteroaromatic cation, which features a high torsional angle between two equal moieties, with a related energy barrier too high to be overcome at room temperature, so that the ICIL can be obtained in two stable enantiopure antipodes. Actually, while interesting but (at least so far) small are the chirality effects observed working in our bio-based CILs with localized stereocentres [2], large peak potential differences have been observed for the enantiomers of very different chiral probes in CV experiments in an enantiopure bulk ICIL. Very conveniently, impressive enantiodiscrimination is observed even using ICILs (or other related inherently chiral molecular salts, solid at room *T* but of easier synthesis) as low-concentration chiral additives in common achiral ionic liquids ILs [2]. Furthermore, similar impressive performances have also been observed dissolving in an achiral IL a thiahelicene-based additive, also inherently chiral, but uncharged and based on a different stereogenic element, *i.e.* a *helical* scaffold.

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References

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- [2] M. Longhi, S. Arnaboldi, E. Husanu, S. Grecchi, I.F. Buzzi, R. Cirilli, S. Rizzo, C. Chiappe, P.R. Mussini, L. Guazzelli, *Electrochim. Acta* 298 (2019) 194-209.