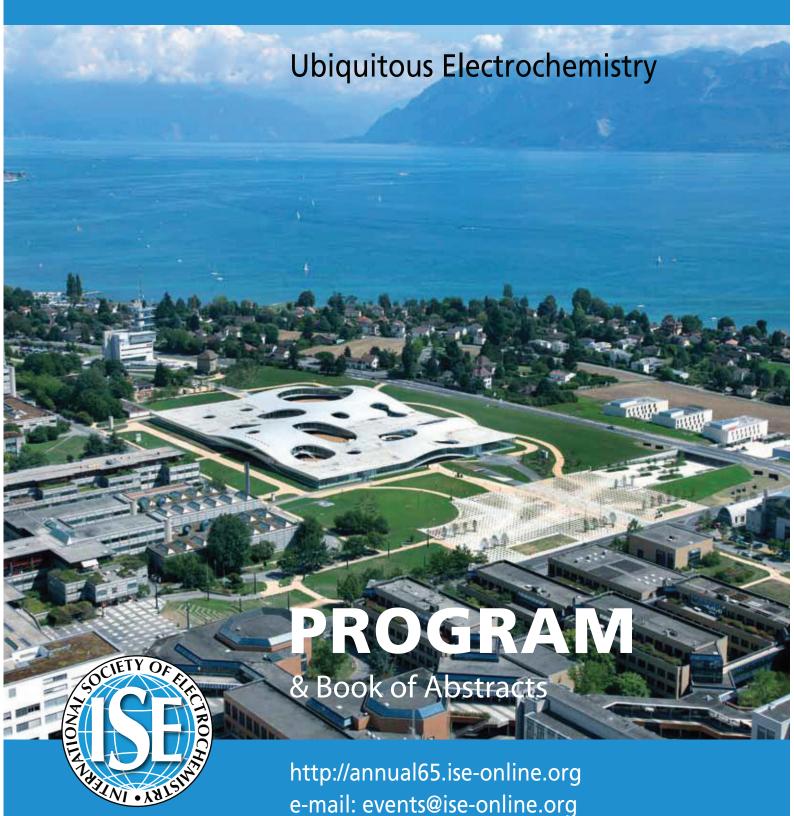
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Electrochemistry of Inherently Chiral Thiophene-Based Materials in Achiral and Chiral Ionic Liquids

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Recently, ionic liquids have been frequently proposed as convenient substitutes for VOCs-supporting electrolyte systems in a variety of electrochemical processes. In particular, recent studies show that they are very good electrodeposition media for inorganic and organic conducting films, on account of their peculiar features.

In this frame, our ongoing studies on redox properties and electrooligomerization of inherently chiral thiophene-based molecular materials^[1] provide a particularly significant and attractive test for both achiral and chiral ionic liquids as reaction media. 1) Achiral ionic liquids as electrodeposition media for the preparation of inherently chiral electrode surfaces of outstanding reproducibility and enantioselectivity. In our above cited research only a slight discrimination of chiral enantiomeric probes could be observed on films electrodeposited in a traditional 3-electrode minicell from traditional VOCs-supporting electrolyte systems, in spite of an outstanding chiroptical activity of the materials (CD spectroelectrochemistry). This was associated with (a) insufficient reproducibility in the deposited films arising from insufficient reproducibility in the cell geometry and solution concentration, and (b) from insufficient regularity and compactness of the deposited films. The problem was completely solved turning to screen printed supports in combination with an ionic liquid medium (BMIM+ PF₆-). granting the desired reproducibility together with the possibility to perform the electrodeposition from a small drop (20 microliter and less) of monomer solution, resulting in electrodeposited electrode surfaces of outstanding reproducibility, stability and enantiorecognition performances.

2) Electrochemical tests on chiral monomers and electrodeposited oligomer films in chiral ionic liquid (CILs). A step further consists in evaluating the reactivity of our chiral monomers and electrodeposited oligomer films, both as racemic and enantiopure, in chiral ionic liquids, both racemic and enantiopure, focusing on reciprocal recognition manifestations, applying electrochemical techniques such as CV, EIS and EQCM. For this aim we are considering both commercially available CILs and a new series of CILs currently under development in our laboratories, based on the same innovative inherent chirality approach as the oligomers to be tested.

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[1] F. Sannicolò, S. Arnaboldi, T. Benincori, V. Bonometti, R. Cirilli, L. Dunsch, W. Kutner, G. Longhi, P.R. Mussini, M. Panigati, M. Pierini, S. Rizzo, *Angew. Chem. Int. Ed.* **2014**, 53, 2623-2627.