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Potential-Driven Chirality Manifestations and Impressive Enantioselectivity by Inherently Chiral Electroactive Films

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Dedicated to the memory of Professor Lothar Dunsch, IFW Dresden

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Molecular materials coupling electroactivity with enantioselective recognition capability are an attractive objective in materials research. The usual strategy, hinging on attaching chiral pendants to an electroactive polyconjugated backbone, generally results in modest chirality manifestations. We have thus designed electroactive chiral polyheterocycles, where chirality is not external to the electroactive backbone, but inherent to it, resulting from a tailored torsion produced by the presence of atropisomeric, conjugatively active biheteroaromatic scaffolds. The coincidence of the stereogenic element with the whole electroactive backbone affords by electrooligomerization enantiopure electroactive films of impressive chiroptical activity, which can be finely and reversibly tuned by the electric potential, since injection of positive charges results in decrease of the atropisomeric scaffold angle to favour delocalization, as revealed by CD spectroelectrochemistry, suggesting us the image of a "breathing chirality". To test the enantioselective recognition ability of the new inherently chiral conducting films we have developed an efficient protocol in ionic liquid affording preparation of very reproducible electrode surfaces by electrooxidation of the enantiopure monomers on screen printed electrode supports. The resulting specular *R* and *S* electrodes have been tested with (*R*)-(+)- and *S*-(-)-*N,N*-dimethyl-1-ferrocenylethylamine specular probes. The response is highly and reproducibly enantioselective (with ~100 mV separation between *R* and *S* probes with single enantiomers and even more with the racemate), specular for *R* vs *S* surfaces with respect to *S* and *R* probes, and reversible in repeated alternating sequences of *S* and *R* probe sensing on a single electrode.^[1]

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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. Chemie* **2014**, *53*, 2623-2627.