Available online at www.sciencedirect.com
ScienceDirect
Current Opinion in Electrochemistry

Review Article
Enantioselective selectors for chiral electrochemistry and electroanalysis: Stereogenic elements and enantioselection performance☆

Serena Arnaboldi, Mirko Magni and Patrizia Romana Mussini*

The ability to select among different electroactive molecules, or among different redox centers on a single molecule, in both analytical and synthetic applications, is a typical asset of electrochemistry, based on fine control of the electrode potential, possibly enhanced by the choice of appropriate electrode surfaces and media. An attractive step further, of great fundamental and applicative interest, is represented by *enantio*selective electrochemistry, implying the ability to discriminate the *enantiomers* of chiral molecules (in electroanalysis), or to selectively activate or achieve a given enantiomer of a chiral molecule controlling the electrode potential (in electrosynthesis). Since the enantiomers of a chiral molecule have identical scalar physico-chemical properties and therefore the same electrochemical behavior except when interacting with some other chiral entity, enantioselective electrochemistry necessarily implies the electron transfer process to take place in asymmetric conditions. This can be achieved by the use of a *chiral electrode surface* or a *chiral medium*. Artificial selectors are particularly interesting on account of the virtually unlimited range of tailored structures possible as well as the possibility to have both enantiomers of a given selector equally available. Among the many approaches so far proposed for this ambitious target along either of the two above ways, outstanding results have been recently obtained, based on the use of "inherently chiral molecular materials" (either as electrode surfaces or as media) in which the same structural element endows the molecule with both its key functional property and with chirality.

Address
Università degli Studi di Milano, Dipartimento di Chimica, Milano, Italy

*Corresponding author: Mussini, Patrizia Romana (patrizia.mussini@unimi.it)

Current Opinion in Electrochemistry 2018, **8**:60–72

This review comes from a themed issue on **Organic and Molecular Electrochemistry**

Edited by **Flavio Maran**

For a complete overview see the Issue and the Editorial

Available online 1 February 2018

https://doi.org/10.1016/j.coelec.2018.01.002

Introduction

The ability to select among different electroactive molecules, or among different redox centers on a single molecule, in both analytical and synthetic applications, is a typical asset of electrochemistry, based on fine control of the electrode potential, possibly enhanced by the choice of appropriate electrode surfaces and media. An attractive step further, of great fundamental and applicative interest, is represented by *enantio*selective electrochemistry, implying the ability to discriminate the *enantiomers* of chiral molecules (in electroanalysis), or to selectively activate or achieve a given enantiomer of a chiral molecule (in electrosynthesis), an issue particularly important in the biological and pharmaceutical fields.

Since the enantiomers of a chiral molecule have identical scalar physico-chemical properties and therefore the same electrochemical behavior except when interacting with chiral entities, resulting in energetically different diastereomeric conditions, enantioselective electrochemistry necessarily implies the electron transfer process to take place in asymmetric conditions, e.g., on a *chiral electrode surface* or in a *chiral medium*.

The task has been defined as one of the most difficult measurements, implying only one separation act, corresponding to a single theoretical plate in chromatographic separations [1].

The many approaches so far proposed for this ambitious target along either of the two above ways will be compared, particularly focusing on a strategy recently

☆ Dedicated to Professor Francesco Sannicolò, an artist in designing intelligent molecules.

resulting in outstanding performance, based on the use of "inherently chiral" molecular materials ([2••], SI.1), either as electrode surfaces [3] or as media [4••].

Looking for an ideal chiral selector: desirable features

A summary of desirable features for an ideal chiral selector is the following one:

- Above all, it should be able to discriminate probe enantiomers in terms of the largest possible peak potential differences, to (analytically) recognize or (preparatively) manage either antipode at its own activation potential. In this respect discrimination in terms of, e.g., current differences appears less useful.
- It should be available in both enantiomer configurations, so that the first activable electron transfer can correspond to the preferred target enantiomer (particularly for preparative purposes).
- It should exhibit a linear dynamic range for currents, possibly with low limit of detection, to complement enantiodiscrimination with quantitative analysis and enantiomeric excess estimation (particularly for analytical purposes).
- It should be of general applicability to many probes and operating protocols/conditions.
- It should have reproducibility in preparation and recognition as well as stability and robustness.
- It should be of easy, fast and low-cost preparation, and/or be required in low quantity, and/or recyclable.

Either natural or artificial chiral selectors can be considered. Actually, many natural ones are currently employed in electroanalysis (e.g., enzymes, antibiotics ...); however, the second alternative looks particularly attractive for many reasons, including the virtually unlimited range of tailored structures possible as well as the possibility to have both enantiomers of a given selector equally available, thus enabling to freely choose the probe enantiomer to be activated first.

In this context, many efforts have been devoted to achieve enantioselective electrochemistry and electroanalysis based either on chiral enantiopure electrodes or in chiral enantiopure media, and with increasing development of artificial selectors.

Chiral electrode strategies

Most efforts have so far concentrated on the *chiral electrode* approach.

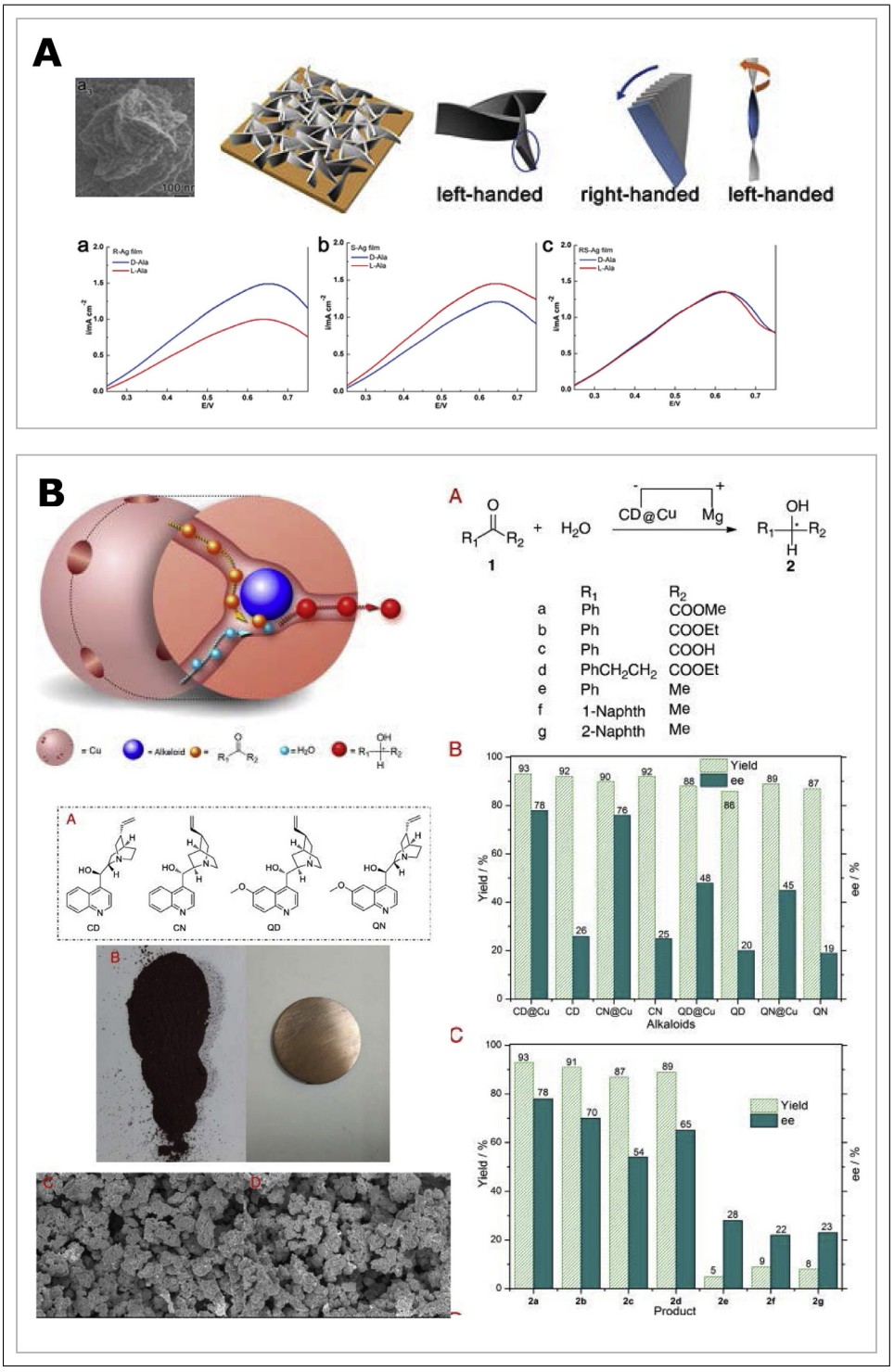
A very wide range of strategies was explored in *analytical experiments*:

a) Chiral metal or metal oxide surfaces, Figure 1 (e.g., [5–14••]; SI.2/A1.a);
b) Mesoporous metals molecularly imprinted with chiral templating molecules, Figure 2 (e.g., [15–17••]; SI.2/A1.b);
c) Electrodes modified with chiral conducting polymers/oligomers, mostly with stereocenters localized in "pendants" attached to the conjugated backbone, or based on monomers including other stereogenic elements (like atropisomeric or helicoidal ones), or grown in asymmetric environments/matrices, or under magnetopolarization, or with chiral counteranions, or with chiral dopants/entrapped chiral selectors, Figure 3 (e.g., [3,18•–30•]; SI.2/A1.c; *detailedly discussed in our concurrent paper* [18•];
d) Electrodes modified with molecularly imprinted polymers (MIP) obtained with chiral templating molecules, Figure 2 (e.g., [1,31–41]; SI.2/A1.d);
e) Electrode surfaces based on inherently chiral single-walled carbon nanotubes (e.g., [42,43••]; SI.2/A1.e);
f) Electrodes modified with adsorbed or covalently grafted chiral molecules, chiral self-assembled monolayers SAMs, or other kinds of non-electroactive thin layers including, or templated with, chiral selectors (e.g., [22••,44–53]; SI.2/A1.f);
g) Electrodes modified by polysaccharide-based selectors, Figure 3 (actually, a large subcategory of the former one; e.g., [54–71]; SI.2/A1.g);
h) Chiral potentiometric electrodes with chiral ionophores incorporated in a membrane (also connected with the former two categories, e.g., [1,72]; SI.2/A1.h);
i) Chiral amperometric biosensors based on enzymes ([1]; SI.2/A1.i);
j) Chiral photoelectrodes, resulting in photocurrent differences (e.g., [23••,73]; SI.2/A1.j);
k) Chiral metal–organic frameworks (e.g., [74•–76•]; SI.2/A1.k);
l) Chiral thin-film transistors, Figure 2 (e.g., [35••, 77,78]; SI.2/A1.l);
m) Complex composites, combining an increasing number of materials including one or more chiral selector(s), a typical recent trend (e.g., [79•–87••]; SI.2/A1.m).

In such approaches the electrochemical transduction of the enantiorecognition event consisted:

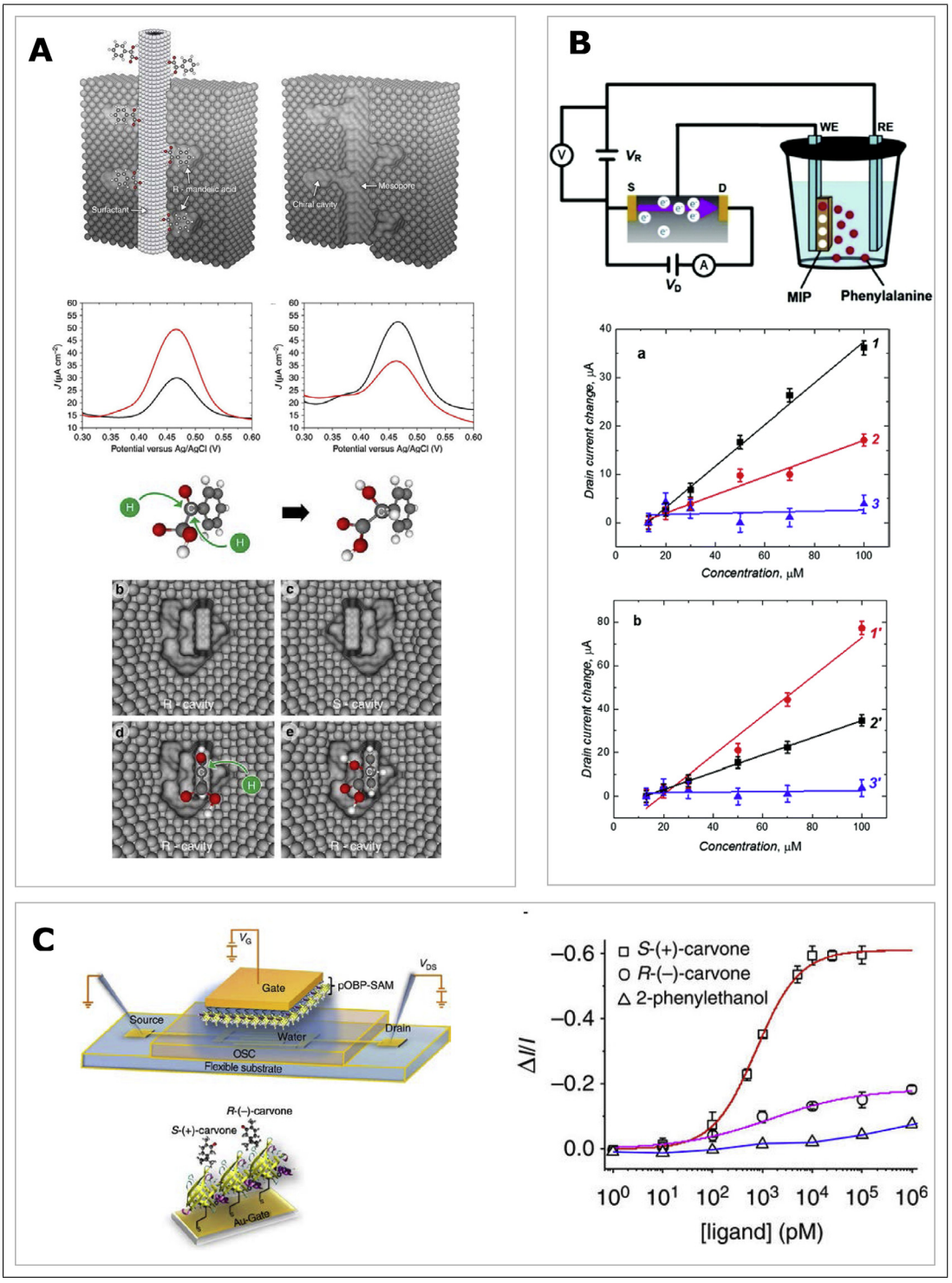
- in most cases, in current differences for the two enantiomers (in voltammetry, amperometry, transistors, photoelectrodes, spin-selective electrochemistry ...);
- in conductivity differences or different electrochemical impedance spectroscopy (EIS) patterns;
- in differences in equilibrium potentials and/or potentials vs. concentration trends in potentiometric mode;

Figure 1



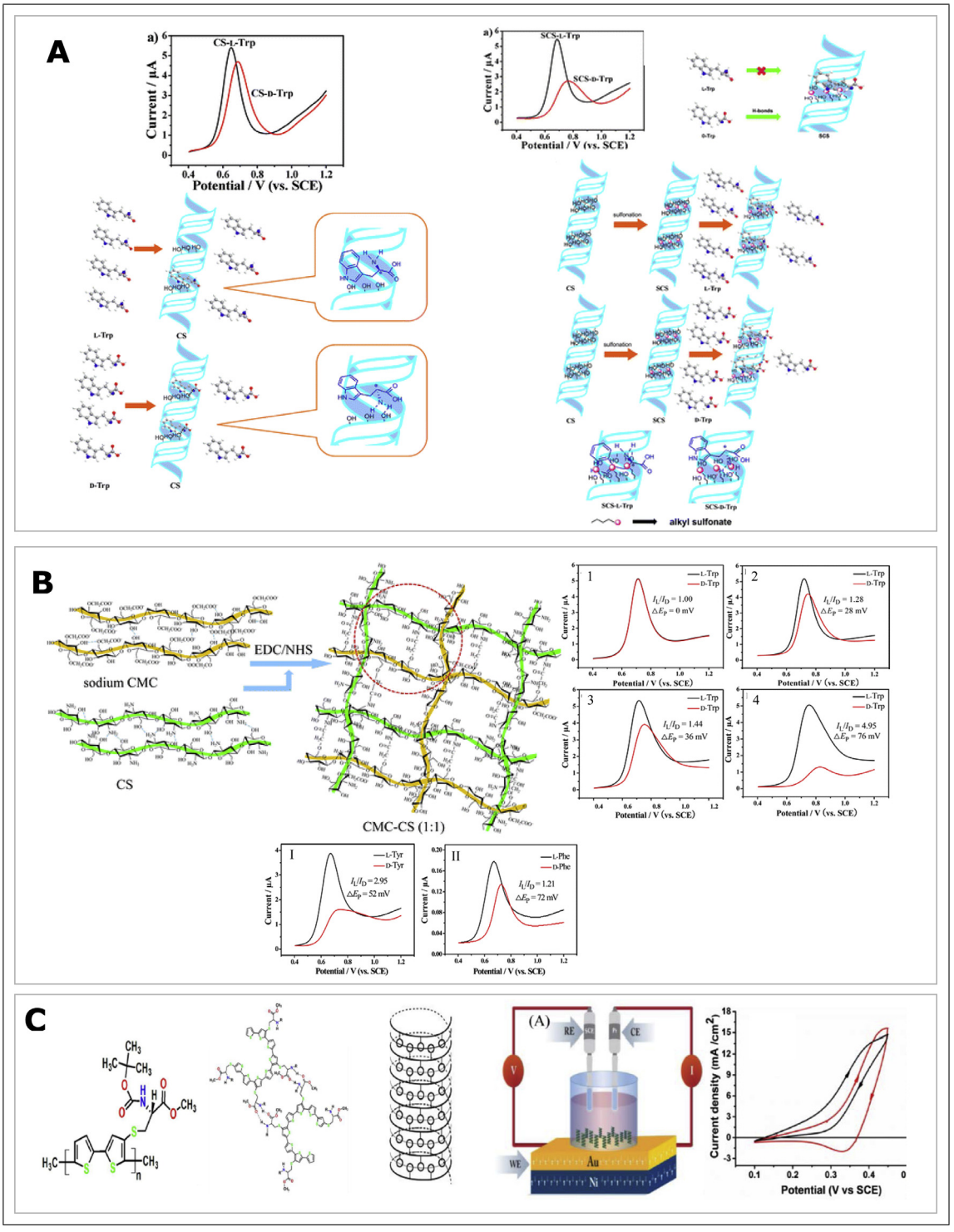
Recent examples of enantioselection on chiral metal surfaces. A. Enantioselective voltammetry of L- and D-alanine (red and blue) on chirally grown Ag surfaces: (a) (*R*)-Ag; (b) (*S*)-Ag; (c) racemate Ag. The SEM photo concerns (*R*)-Ag (adapted with permission from ref. [10••]). B. Chiral electrocatalytic preparative reductions on a copper surface with entrapped alkaloids. Left column (from top to bottom): a process rendering; the tested alkaloids; the composite cathode as a powder and pressed in coin shape; SEM micrographs. Right column: process yields and enantiomeric excesses as a function of alkaloid and substrate (adapted with permission from ref. [14••]).

Figure 2



Recent examples of chiral molecular imprinting and of chiral transistor devices. A: Mesoporous Pt imprinted with mandelic acid: DPV tests with L- and D-Dopa (red/black) on (*R*)- or (*S*)-imprinted electrode (right/left); enantioselective reduction of phenylglyoxylic acid to mandelic acid (rendering) (adapted with permission from ref. [17••]). B: A MIP film implemented in a EG-FET applied for L- and D-phenylalanine enantioselective sensing (adapted with permission from ref. [35••]. Published by the Royal Society of Chemistry). C: a capacitance-modulated protein-based transistor: rendering and enantioselective current response to (*S*)- and (*R*)-carvone (adapted with permission from ref. [78]).

Figure 3



Recent examples of enantioselective helicoidal structures. A: DPV of tryptophan enantiomers with chitosan (CS) helices, as such (left) or sulfonated (right) (adapted with permission from ref. [67]. Copyright (2017) American Chemical Society). B: Cooperative effects between CS and carboxymethylcellulose (CMC): DPV patterns for tryptophan enantiomers with 1: no selector; 2: CMC 3: CS; 4: CMC + CS, and DPV patterns for tyrosine and phenylalanine enantiomers with CMC + CS (adapted with permission from ref. [68••], Copyright (2017) American Chemical Society). C: Spin selective electrochemistry through helicoidal molecular film (adapted with permission from ref. [22••]).

- in some voltammetry cases, in differences in peak potentials (particularly with "inherently chiral" selectors, as discussed later);
- sometimes also in peak morphology.

A comparatively much smaller number of studies, most of them very old, is so far available concerning *chiral electrodes applied to asymmetric electrosynthesis*.

According to a recent review [87••] they can be classified into:

(a) non-covalently linked chiral electrode adsorbents, resulting in enantiomeric excesses ranging from small/medium to ~70% in a few cases only, but appearing to be too sensitive to experimental conditions;
(b) chirally modified electrodes, appearing more promising also on account of the smaller selector quantity required; a 93% e.e. in asymmetric oxidation of alkyl aryl sulfides on polymer-coated electrodes has been reported [88].

A detailed casebook is provided in SI/A2. Very recent studies deal with:

- enantioselective hydrogenation on metal-alkaloid hybrid electrode surfaces with water as hydrogen source, resulting in optically active alcohols with 71% e.e. and 93% yield [12,13,14••];
- enantioselective synthesis of mandelic acid (MA) by electroreduction of phenylglyoxylic acid on MA-imprinted chiral mesoporous platinum [17••];
- a striking photoelectrosynthetic application of *photoanodes coated with chiral molecules* [89,90••], resulting in remarkable drop of the overpotential for hydrogen production and elimination of H_2O_2 production. The authors proposed the spin specificity of electrons transferred through chiral molecules to be the origin of a more efficient oxidation process in which oxygen is formed in its triplet ground state. Enhanced hydrogen production is obtained also using *a chiral polymer* respect to an achiral one ([22••]), and when CdSe quantum dots were embedded within the polymer, the current density was doubled.

Chiral media approaches

Respect to the aforementioned chiral electrode strategy, a much smaller number of studies have dealt with electrochemistry or electroanalysis on achiral electrodes, the selector being provided by the medium, either having a chiral selector dissolved into it or being itself endowed with chirality.

A number of early chiral electrosynthesis experiments had been performed using *chiral supporting electrolytes* (SI.2/B1.a), obtaining enantiomeric excesses up to 44% in preparative experiments [91].

More recent analytical works relied on media with dissolved *chiral selectors/receptors/mediators* able to interact with the target molecule forming diastereomeric complexes (SI.2/B1.b; e.g., [92•–95]).

Only a few studies involved *chirality of the medium itself* (SI.2/B2):

- *a chiral diamine cosolvent* in different organic solvents (e.g., [96]) resulted in small enantiomeric excesses (smaller than with chiral supporting electrolytes, which could ensure a more ordered chiral interphase);
- *water/chiral organic liquid interfaces* resulted in differences in enantiomer ion transfers (e.g., [97]);
- *magnetic fields* were employed to induce asymmetry in electropolymerization [18•] or electrodeposition [SI.2/A.1a], and also to produce spin-selective currents (e.g., [22••])];
- *liquid crystals with chiral additives inducing a cholesteric transition* effectively promoted macromolecular asymmetry in electropolymerization (e.g., [98–100••]). Attractively, the resulting polymers can be converted into helical graphite [99,100••]. Notably, years before a cholesteric liquid crystal provided a chiral environment for electrochemical processes at the electrode interphase [101].

Very recently, *inherently chiral ionic liquids (ICILs) and additives* [4••] have resulted in outstanding enantioselection, as discussed further on.

Problems and weaknesses

A problem common to most approaches, even attractive and successful, with only a few exceptions, consists in the difficulty to detect or manage both enantiomers when they are both present (or when it cannot be *a priori* excluded). On one side, sensors approaching full enantioselectivity in current or mass or potentiometric response (i.e., responding 100% to one enantiomer probe and 0% to the other one) can offer outstanding detection and quantification of one molecule antipode even in the presence of the opposite enantiomer, but for the same reason cannot account for the presence and concentration of the antipode (unless two specular sensors be employed concurrently). On the other side, non-fully enantioselective sensors in terms of current, or mass, or conductivity, or potentiometric response (i.e., responding X% to one enantiomer probe and Y% to the other one) could be applied to detection and management of a given enantiomer only provided that the presence of its antipode be *a priori* excluded.

Instead voltammetric peak potential differentiation, which could overcome this limitation (provided that

the two enantiomers be sufficiently separated), is obtained only in a few cases (e.g., significant differences in cyclic voltammetry (CV) potentials besides currents have been recently observed with chitosan-based helicoidal or network structures [67,68••], rationalized in terms of different binding constants [67]), often with too small peak differences and/or suffering from other drawbacks. For example, the elegant and conceptually simple chiral metal surfaces, offering by CV neat differentiation between probe enantiomers, are very difficult to prepare and manage.

Moreover, preparation procedures and/or operating protocols often appear sophisticated and expensive, and/or lacking robustness and/or reproducibility. Furthermore, most of them could hardly be applied to preparative experiments, which could explain the limited number of preparative studies so far available; actually, chiral electrosynthesis, in spite of its perspective importance, appears far from being mature.

The outstanding potential of "inherently chiral" selectors

A weak point possibly connected with modest and/or labile chirality manifestations is that in most of the selectors considered, the chirality source is not intrinsic to the whole selector, but either

- *localized*: in molecular selectors, by one or more stereocenters; in oligo/polymer films, by stereocenters located in external “pendants”; in composite materials, by the stereocenter(s) of the chiral selector(s) included in the hybrid material;

or

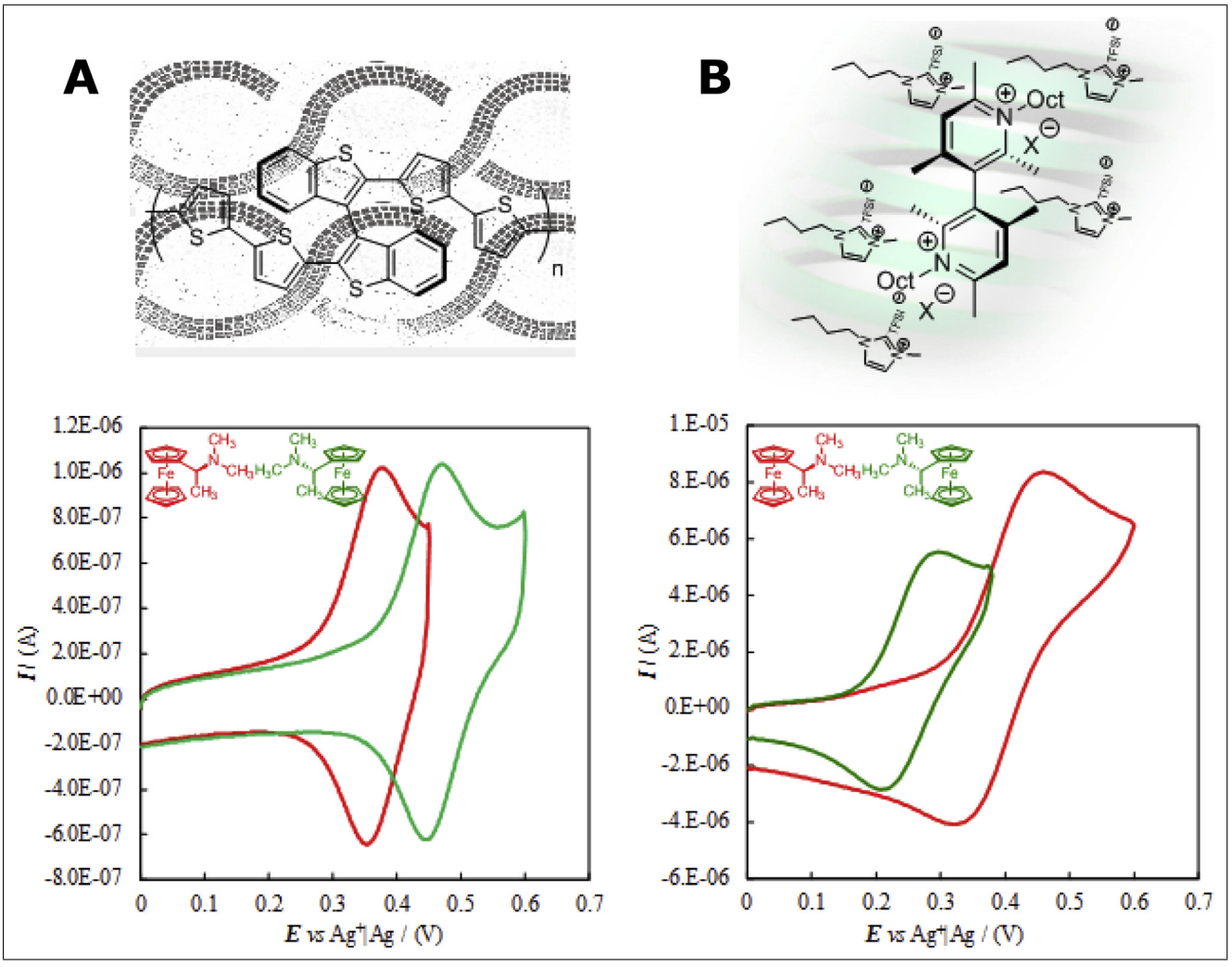
- *external*: from external molecular templating agents in molecularly imprinted materials or in conducting polymers with chiral counterions or from a chiral electropolymerization medium, for asymmetrically grown films.

In this context, a breakthrough can come exploiting the "inherent chirality" strategy, according to which *the stereogenic element responsible for chirality coincides with the functional group responsible for the molecular material specific property* (that is, following F. Sannicolò’s definition, SI.1). This concept can be effectively implemented as a stable tailored torsion in the main molecular scaffold (responsible of the key functional properties). In the case of chiral conducting polymers [18•] such molecular design strategy implies a stable torsion in monomeric units regioregularly propagating into very stable foldamers, unlike, e.g., helicoidal "secondary" structures of achiral conjugated systems induced by chiral electropolymerization media or by weak interactions involving chiral pendants on the achiral main chain (which can be easily overcome by solvent, pH and/or temperature changes) [17••,102]. Such stable torsion can be induced by insertion in the selector backbone of stereogenic elements like helicoidal conjugated systems (like [103]) or atropisomeric ones (i.e., with sterically hindered rotation between two moieties) systems with C_2 symmetry (e.g., [2••,3,26–29,46,47,95,104]). In both cases of course the monomer torsional energy barrier must be very high, not to be overcome in the temperature range of interest, so that the selector be available in two stable antipodes; moreover, regioregularity in the selector backbone design is a key issue to maximize chirality manifestations.

Reconsidering the above overviewed approaches, atropisomeric systems have been successfully employed to induce liquid crystals cholesterization, achieving effective media to obtain "secondary" chiral structures in achiral polymers ([98–100••]). Furthermore, importantly, metal surfaces grown with a helicoidal pattern resulted in significant differences between CV patterns of chiral probe antipodes [5–8]; and significant differences in potential trends with enantiomer concentrations were obtained with different kinds of selectors based on binaphthyl atropisomeric elements [26,46,47].

The potential of the "inherent chirality" strategy for electrochemical enantioselection proved to be outstanding when Sannicolò et al. developed inherently chiral electrodes of impressive chirality manifestations [3,27–29] obtained by easy and fast oxidative (electro)oligomerization of the enantiopure antipodes of the inherently chiral BT_2T_4 monomer [105] (Figure 4A). The monomer design implies a very high torsional angle and energy barrier, granting atropisomerism and a strong 3D character, while not entirely hampering conjugation; it ensures high electroactivity as well as regioregularity in oligomerization on account of the two homotopic terminal positions. The oligomer films retain the (*R*) or (*S*) configuration of the starting monomer antipode and include a significant amount of cyclic terms (e.g., dimers, trimers, tetramers [27,106], providing attractive cavities of different diameters with heteroatoms for potential host/guest effects). Such enantiopure films showed outstanding chiroptical properties, such as circularly polarized luminescence and sharp specular circular dichroism signals, reversibly modulated by electrochemistry (chirality and electroactivity both originating from the molecular backbone). Tested as chiral electrode surfaces in CV experiments, they resulted in significant peak potential differences for the probe enantiomers, specular inverting the selector configuration, besides a linear dynamic range on peak currents; this appeared to hold for very different chiral probes and operating conditions (solvent, electrode support) [3,28,29]. Similar results were also obtained starting from a different, all-thiophene atropisomeric monomer with two pairs of homotopic terminals [30•] confirming the validity of the inherent chirality concept. Extending such studies

Figure 4



Examples of enantiomer peak separation obtained for a model ferrocenyl probe on screen-printed electrodes in achiral ionic liquid medium (A) on an electrodeposited inherently chiral enantiopure BT_2T_4 oligomer film or (B) adding inherently chiral bicollidinium double salts.

to inherently chiral films based on other stereogenic elements is very important.

More recently, the same strategy proved its effectiveness also implemented as medium rather than as electrode surface. Considering that increasing order at the electrode|solution interphase should enhance enantioselectivity manifestations, it is surprising that, to our knowledge, no attempts have been made so far with chiral ionic liquids (CILs).

Ionic liquids, organic salts with low melting points, are increasingly popular media on account of many peculiar advantageous properties respect to volatile organic solvents (low vapor pressure, chemical and thermal stability, high solvating ability, non-flammability …) [107,108].

They are even more attractive for electrochemical processes (and already popular, e.g., for batteries and electrodepositions), acting as both solvent and supporting electrolyte, and especially featuring an extremely well-ordered structure at the interface with a charged electrode, expanding for many layers, like a semisolid crystal [109••–112], even in the presence of significant water traces [113••,114•], and modulated by other species possibly present at the interface [115]. Sometimes, they even border with liquid crystals [116•]. They also provide valuable components for electrochemical biosensors [117]. With CILs, already available in many structures (a well-organized overview up to 2012 is available in [118,119]), such a high degree of supramolecular organization can induce significant chirality transfer from the medium to the dissolved species. And, analogously to the electrode case,

this attitude could be maximized by the "inherent chirality" strategy, that is, working in ICILs.

To implement inherent chirality in ionic liquids, that are usually based on a heteroaromatic cation with at least one long alkyl chain (to lower the melting point), Sannicolò et al. proposed to start from *bi*heteroaromatic scaffolds, like bipyridine or bibenzimidazole ones [4••,120], bearing several alkyl substituents placed in such a way to result in strong reciprocal sterical hindrance and therefore high torsion between the two rings, being nearly perpendicular; this results in low reactivity and a very large potential window, as well as in the existence as two stable enantiomers. By dialkylation such inherently chiral scaffolds can be converted into the corresponding double salts. With at least one suitably long alkyl chain and a suitable anion such as bistrifilimidate, the melting point can be lowered below room temperature; thus, two ICILs have been very recently obtained as enantiopure antipodes, starting from bicollidine, a very convenient scaffold on account of its low-cost synthesis and possibility to be separated into enantiomers by fractional crystallization, without expensive chiral HPLC [4••]. Their enantioselectivity was tested as low-concentration additives in achiral commercial ionic liquids on screen-printed electrodes, with chiral probes already used for inherently chiral electrode tests; large, specular enantiomer peak potential differences were observed (Figure 4B). Attractively, the same behavior as chiral additives was also shown by family terms solid at room temperature, of faster and easier synthesis. The peak potential separation appears to regularly increase with inherently chiral salt concentration and to be modulated by the nature of the bulk ionic liquid. As a possible explanation, it was proposed that in the peculiar highly ordered electrode–ionic liquid interface the inherently chiral additives might induce a local chiral organization, analogously to the nematic/cholesteric transition in liquid crystals. Moreover, even if bulk complexation was excluded by NMR experiments (which could be expected, since the additives are not specifically tailored to complex the chiral probes, and appear to work with different probes), local specific interactions between chiral additive and chiral probe at the electrode|solution interface cannot be excluded. Application to preparative experiments is the next frontier; in the meanwhile, preliminary tests of electrooligomerization of BT_2T_4 chiral monomer on achiral electrodes using inherently chiral bibenzimidazolium additives pointed to significant differences according to the additive/monomer enantiomer combinations [120].

Conclusions

A wide variety of chiral surfaces and chiral media have been developed and tested to achieve enantioselective electrochemistry, with different enantioselectivity degrees and transduction modes in analytical experiments, including, e.g., enantiomer differences in currents (the most common occurrence), potentiometric response, conductance and/or EIS patterns, mass variations, photocurrents... as well as significant enantiomeric excesses in preparative experiments. High to full specificity for a single enantiomer can be reached by the use of very specifically tailored selectors, like, e.g., in several MIP or enzyme sensor cases. However, in nearly all cases the kind of response is unsuitable to enable recognition of the (*R*)- or (*S*)-probe enantiomer configuration (alone or in mixture) by a single selector.

In this frame, a valuable asset appears to be provided by inherently chiral selectors, resulting in the observation of significant potential differences between probe enantiomers, working either on inherently chiral electrodes or on achiral electrodes in inherently chiral media. Importantly, this feature appears to be of general character (testing different kinds of probes and selectors) and requires in most cases only small amounts of inherently chiral selector (thin chiral films, low-concentration chiral additives). Of course, the newly available attractive palette of inherently chiral tools must be supported by detailed studies about the discrimination mechanism, as well as fully exploited by exploring a wider range of selector/probe combinations, as well as applications of preparative character and in advanced electrochemistry devices.

Acknowledgments

The Authors' inherent chirality work is currently financially supported by Fondazione Cariplo and Regione Lombardia (2016-0923 RST - Avviso congiunto FC-RL Sottomisura B) rafforzamento (Enhancing VINCE (Versatile INherently Chiral Electrochemistry)). The Authors are also grateful to Professor F. Sannicolò for kindly revising the manuscript draft as well as for precious discussions, particularly acknowledging his contribution to the formulation of SI.1.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.coelec.2018.01.002.

References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- • Paper of special interest.
- •• Paper of outstanding interest.

1. Trojanowicz M: **Enantioselective electrochemical sensors and biosensors: a mini-review**. *Electrochem. Commun.* 2014, **38**:47–52 and references therein cited.

2. •• Pasini D, Nitti A: **Recent advances in sensing using atropoisomeric molecular receptors**. *Chirality* 2016, **28**:116–123.

This paper provides a very useful discussion as well as review of atropisomeric selectors for enantioselective analysis, from a molecular designer point of view.

3. Sannicolò F, Arnaboldi S, Benincori T, Bonometti V, Cirilli R, Dunsch L, Kutner W, Longhi G, Mussini PR, Panigati M, Pierini M, Rizzo S: **Potential-driven chirality manifestations and impressive enantioselectivity by inherently chiral electroactive organic films**. *Angew. Chem. Int. Ed.* 2014, **53**:2623–2627.

4. •• Rizzo S, Arnaboldi S, Mihali V, Cirilli R, Forni A, Gennaro A, Isse AA, Pierini M, Mussini PR, Sannicolò F: **Inherently chiral ionic-liquid media: effective chiral electroanalysis on achiral electrodes**. *Angew. Chem. Int. Ed.* 2017, **56**:2079–2082.

A proof-of-concept paper concerning the outstanding performance of the inherent chirality strategy applied to ionic liquid media and related additives/supporting electrolytes.

5. Ahmadi A, Attard G, Feliu J, Rodes A: **Surface reactivity at "chiral" platinum surfaces**. *Langmuir* 1999, **15**:2420–2424.

6. Attard GA: **Electrochemical studies of enantioselectivity at chiral metal surfaces**. *J. Phys. Chem. B* 2001, **105**:3158–3167.

7. Hazzazi OA, Attard GA, Wells PB: **Molecular recognition in adsorption and electrooxidation at chiral platinum surfaces**. *J. Mol. Catal. A: Chem.* 2004, **216**:247–255.

8. Hazzazi OA, Harris CA, Wells PB, Attard GA: **Electrooxidation of d- and l-glucose at well-defined chiral bimetallic electrodes**. *Top. Catal.* 2011, **54**:1392–1402.

9. Mogi I, Morimoto R, Aogaki R, Watanabe K: **Surface chirality induced by rotational electrodeposition in magnetic fields**. *Sci. Rep. UK* 2013, **3**:2574.

10. •• Ma L, Cao Y, Duan Y, Han L, Che S: **Silver films with hierarchical chirality**. *Angew. Chem. Int. Ed.* 2017, **56**:8657–8662.

The paper reports a strategy for chiral molecule-induced formation of chiral silver films on a copper substrate through a redox reaction. The resulting three levels of chirality are described.

11. Switzer JA, Kothari HM, Poizot P, Nakanishi S, Bohannan EW: **Enantiospecific electrodeposition of a chiral catalyst**. *Nature* 2003, **425**:490–493.

12. Yang H, Chi D, Sun Q, Sun W, Wang H, Lu J: **Entrapment of alkaloids within silver: from enantioselective hydrogenation to chiral recognition**. *Chem. Commun.* 2014, **50**:8868–8870.

13. Yang H-P, Wang H, Lu J-X: **Alkaloid-induced asymmetric hydrogenation on a Cu nanoparticle cathode by electrochemical conditions**. *Electrochem. Commun.* 2015, **55**:18–21.

14. •• Yang H-P, Fen Q, Wang H, Lu J-X: **Copper encapsulated alkaloids composite: an effective heterogeneous catalyst for electrocatalytic asymmetric hydrogenation**. *Electrochem. Commun.* 2016, **71**:38–42.

An heterogenenous composite catalyst obtained encapsulating commercially purchased alkaloids within metallic Cu nanoparticles was synthesized and then compacted into coin-shape cathode for electrocatalytic asymmetric hydrogenation of aromatic ketones.

15. Wattanakit C, Saint Come YB, Lapeyre Bopp V, Philippe A, Heim M, Yadnum S, Nokbin S, Warakulwit C, Limtrakul J, Kuhn A: **Enantioselective recognition at mesoporous chiral metal surfaces**. *Nat. Commun* 2014 4325/1–4325/8.

16. Yutthalekha T, Warakulwit C, Limtrakul J, Kuhn A: **Enantioselective recognition of DOPA by mesoporous platinum imprinted with mandelic acid**. *Electroanalysis* 2015, **27**:2209–2213.

17. •• Yutthalekha T, Wattanakit C, Lapeyre V, Nokbin S, Warakulwit C, Limtrakul J, Kuhn A: **Asymmetric synthesis using chiral-encoded metal**. *Nat. Commun.* 2016, **7**:12678.

The paper deals with chiral-encoded mesoporous metal electrodes, obtained by the electrochemical reduction of Pt salts in the presence of a liquid crystal phase and the chiral template molecule. Such electrodes were profitably employed in the asymmetric synthesis of mandelic acid by electro-reduction of prochiral phenylglyoxylic acid.

18. • Arnaboldi S, Grecchi S, Magni M, Mussini PR: **Electroactive chiral oligo-and polymer layers for electrochemical entiorecognition**. *Curr. Opin. Electrochem.* 2018, **7**:188–199.

19. • Dong L, Zhang L, Duan X, Mo D, Xu J, Zhu X: **Synthesis and characterization of chiral PEDOT enantiomers bearing chiral moieties in side chains: chiral recognition and its mechanism using electrochemical sensing technology**. *RSC Adv.* 2016, **6**:11536–11545.

In this work a pair of chiral PEDOT derivatives were employed as chiral recognition materials for fabricating chiral sensors and then discriminating between DOPA enantiomers. The mechanism of the stereospecific interaction between the DOPA enantiomers and chiral polymer was discussed specifically.

20. •• Dong L, Zhang Y, Duan X, Zhu X, Sun H, Xu J: **Chiral PEDOT-based enantioselective electrode modification material for chiral electrochemical sensing: mechanism and model of chiral recognition**. *Anal. Chem.* 2017, **89**:9695–9702.

With a 2′-functionalized chiral PEDOT derivative neat DPV current differences (and possibly in some cases, even small potential differences) are observed for DOPA, tryptophane and propranolol, with good specularity in the response upon inverting the polymer configuration; a mechanism of chiral recognition is also proposed, based on hydrogen bonding and a 3-point interaction model.

21. Mondal PC, Kantor-Uriel N, Mathew SP, Tassinari F, Fontanesi C, Naaman R: **Chiral conductive polymers as spin filters**. *Adv. Mater.* 2015, **27**:1924–1927.

22. •• Mondal PC, Fontanesi C, Waldeck DH, Naaman R: **Spin-dependent transport through chiral molecules studied by spin-dependent electrochemistry**. *Acc. Chem. Res.* 2016, **449**:2560–2568.

Spin-dependent electrochemistry measurements were described and used to probe the spin-dependent charge transport properties of nonmagnetic chiral conductive polymers and biomolecules. Moreover photoelectrochemical experiments in which light is used to affect the spin selective electron transport through the chiral molecules were carried out.

23. •• Tassinari F, Banerjee-Ghosh K, Parenti F, Kiran V, Mucci A, Naaman R: **Enhanced hydrogen production with chiral conductive polymer-based electrodes**. *J. Phys. Chem. C* 2017, **121**:15777–15783.

In the present study anodes coated with chiral conductive polymer are used. The hydrogen production from water is enhanced, and the threshold voltage is reduced, as compared with anodes coated with achiral polymer.

24. Borazjani M, Mehdinia A, Jabbari AJ: **Betamethasone-based chiral electrochemical sensor coupled to chemometric methods for determination of mandelic acid enantiomers**. *J. Mol. Recognit.* 2017. https://doi.org/10.1002/jmr.26.

25. Dong L, Lu B, Duan X, Xu J, Hu D, Zhang K, Zhu X, Sun H, Ming S, Wang Z, Zhen S: **Novel chiral PEDOTs for selective recognition of 3,4-dihydroxyphenylalanine enantiomers: synthesis and characterization**. *J. Polym. Sci. A1* 2015, **53**:2238–2251.

26. Kang S, Cha I, Han JG, Song C: **Electroactive polymer sensors for chiral amines based on optically active 1,1′-binaphthyls**. *Mater. Express* 2013, **3**:119–126.

27. Sannicolò F, Mussini PR, Benincori T, Cirilli R, Abbate S, Arnaboldi S, Casolo S, Castiglioni E, Longhi G, Martinazzo R, Panigati M, Pappini M, Quartapelle Procopio E, Rizzo S: **Inherently chiral macrocyclic oligothiophenes: easily accessible electrosensitive cavities with outstanding enantioselection performances**. *Chem. Eur. J.* 2014, **20**:15261–15634.

28. Arnaboldi S, Benincori T, Cirilli R, Kutner W, Magni M, Mussini PR, Noworyta K, Sannicolò F: **Inherently chiral electrodes: the tool for chiral voltammetry**. *Chem. Sci.* 2015, **6**:1706–1711.

29. Arnaboldi S, Benincori T, Cirilli R, Grecchi S, Santagostini L, Sannicolò F, Mussini PR: **Inherently chiral thiophene-based electrodes at work: a screening of enantioselection ability toward a series of pharmaceutically relevant phenolic or catecholic amino acids, amino esters, and amine**. *Anal. Bioanal. Chem.* 2016:7243–7254.

30. • Sannicolò F, Mussini PR, Benincori T, Martinazzo R, Arnaboldi S, Appoloni G, Panigati M, Quartapelle Procopio E, Marino V, Cirilli R, Casolo S, Kutner W, Noworyta K, Pietrzyk-Le A, Iskierko Z, Bartold K: **Inherently chiral spider-like oligothiophenes**. *Chem. Eur. J.* 2016, **22**:10839–10847.

Introducing a second example of inherently chiral monomer and related electrodeposited films, of comparable performance with respect to the first case introduced in Angew. Chem. 2014, thus confirming the validity of the inherent chirality strategy.

31. Sharma PS, Pietrzyk-Le A, D'Souza F, Kutner W: **Electrochemically synthesized polymers in molecular imprinting for chemical sensing**. *Anal. Bioanal. Chem.* 2012, **402**:3177–3204 and references therein cited.

32. Tiwari MP, Prasad A: **Molecularly imprinted polymer based enantioselective sensing devices: a review**. *Anal. Chim. Acta* 2015, **853**:1–18 and references therein cited.

33. Suriyanarayanan S, Mandal S, Ramanujam K, Nicholls IA: **Electrochemically synthesized molecularly imprinted polythiophene nanostructures as recognition elements for an aspirin-chemosensor**. *Sens. Actuators B* 2017, **253**:428–436.

34. Saksena K, Shrivastava A, Kant R: **Chiral analysis of ascorbic acid in bovine serum using ultrathin molecular imprinted polyaniline/graphite electrode**. *J. Electroanal. Chem.* 2017, **795**:103–109.

35. •• Iskierko Z, Checinska A, Sharma PS, Golebiewska K, Noworyta K, Borowicz P, Fronc K, Bandi V, D'Souza F, Kutner W: **Molecularly imprinted polymer based extended-gate field-effect transistor chemosensors for phenylalanine enantioselective sensing**. *J. Mater. Chem. C* 2017, **5**:969–977.

In this work extended-gate field-effect transistors served as transducers. The EG-FET gates were coated by electropolymerization with D- or (L-Phe)-templated MIP films to result in complete chemosensors. These chemosensors rapidly and selectively responded to D- and L-Phe enantiomer analytes.

36. Gu J, Dai H, Kong Y, Tao Y, Chu H, Tong Z: **Chiral electrochemical recognition of cysteine enantiomers with molecularly imprinted overoxidized polypyrrole-Au nanoparticles**. *Synth. Met.* 2016, **222**:137–143.

37. Iacob B-C, Bodoki E, Farcau C, Barbu-Tudoran L, Oprean R: **Study of the molecular recognition mechanism of an ultrathin MIP film-based chiral electrochemical sensor**. *Electrochim. Acta* 2016, **217**:195–202.

38. Gutierrez-Climente R, Gomez-Caballero A, Unceta N, Aranzazu GM, Barrio RJ: **A new potentiometric sensor based on chiral imprinted nanoparticles for the discrimination of the enantiomers of the antidepressant citalopram**. *Electrochim. Acta* 2016, **196**:496–504.

39. • Huynh T-P, Wojnarowicz A, Kelm A, Woznicki P, Borowicz P, Majka A, D'Souza F, Kutner W: **Chemosensor for selective determination of 2,4,6-trinitrophenol using a custom designed imprinted polymer recognition unit cross-linked to a fluorophore transducer**. *ACS Sens.* 2016, **1**:636–639.

A good example of molecularly imprinted polymer selective and sensitive to the target trinitrophenol analyte in solution. The limit of detection reaches a level of subnanogram per dm^3 of trinitrophenol concentration and the procedure is readily extendable for selective determination of other nitroaromatic explosives.

40. Iacob BC, Bodoki E, Florea A, Bodoki AE, Oprean R: **Simultaneous enantiospecific recognition of several β-blocker enantiomers using molecularly imprinted polymer-based electrochemical sensor**. *Anal. Chem.* 2015, **87**:2755–2763.

41. Pandey I, Jha SS: **Molecularly imprinted polyaniline-ferrocene-sulfonic acid-carbon dots modified pencil graphite electrodes for chiral selective sensing of d-ascorbic acid and l-ascorbic acid: a clinical biomarker for preeclampsia**. *Electrochim. Acta* 2015, **182**:917–928.

42. Chen L, Liu S, Chang F, Xie X, Zhu Z: **A gold nanoparticles-enhanced carbon nanotubes electrochemical chiral sensor**. *Electroanalysis* 2017, **29**:955–959.

43. •• Zhu H, Chang F, Zhu Z: **The fabrication of carbon nanotubes array-based electrochemical chiral sensor by electrosynthesis**. *Talanta* 2017, **166**:70–74.

A new strategy to fabricate vertically aligned SWCNTs array-based electrochemical chiral sensor was presented in combination with DOPA as a model molecule. The highly ordered standing of SWCNTs and the application of square wave voltammetry amplified the intrinsic chirality of chiral NTs.

44. Yang F, Kong N, Conlan XA, Wang H, Barrow CJ, Yan F, Guo J, Yang W: **Electrochemical evidences of chiral molecule recognition using l/d-cysteine modified gold electrodes**. *Electrochim. Acta* 2017, **237**:22–28.

45. Afkhami A, Kafrashi F, Ahmadi M, Madrakian T: **A new chiral electrochemical sensor for the enantioselective recognition of naproxen enantiomers using l-cysteine self-assembled over gold nanoparticles on a gold electrode**. *RSC Adv.* 2015, **5**:58609–58615.

46. Qian P, Matsuda M, Miyashita T: **Chiral molecular recognition in polymer Langmuir–Blodgett films containing axially chiral binaphthyl groups**. *J. Am. Chem. Soc.* 1993, **115**:5624–5628.

47. Piao M-H, Hwang J, Won M-S, Hyun MH, Shim Y-B: **A solid state polymer-coated electrode containing a chiral crown ether derivative for enantioselective detection of phenylglycine methyl ester isomer**. *Electroanalysis* 2008, **20**:1293.

48. Cichelli J, Zharov I: **Chiral permselectivity in surface-modified nanoporous opal films**. *J. Am. Chem. Soc.* 2006, **128**:8130–8131.

49. Yu Y, Liu W, Ma J, Tao Y, Qin Y, Kong Y: **An efficient chiral sensing platform based on graphene quantum dot-tartaric acid hybrids**. *RSC Adv.* 2016, **6**:84127–84132.

50. Gou H, He J, Mo Z, Wei X, Hu R, Rere, Wang Y, Guo R: **A highly effective electrochemical chiral sensor of tryptophan enantiomers based on covalently functionalize reduced graphene oxide with l-lysine**. *J. Electrochem. Soc.* 2016, **163**:B272−B279.

51. Kasinathan B, Zawawi RM, Lim HN: **Voltammetric studies and characterizations of biocompatible graphene/collagen nanocomposite-modified glassy carbon electrode towards enantio-recognition of chiral molecules**. *J. Appl. Electrochem.* 2015, **45**:1085−1099.

52. Xuan C, Xia Q, Xu J, Wang Q, Lin X, Fu Y: **A biosensing interface based on Au@BSA nanocomposite for chiral recognition of propranolol**. *Anal. Methods* 2016, **8**:3564−3569.

53. Naaman R, Waldeck DH: **Spintronics and chirality: spin selectivity in electron transport through chiral molecules**. *Annu. Rev. Phys. Chem.* 2015, **66**:263–281.

54. Bao L, Dai J, Yang L, Ma J, Tao Y, Deng L, Kong Y: **Electrochemical recognition of tyrosine enantiomers based on chiral ligand exchange with sodium alginate as the chiral selector**. *J. Electrochem. Soc.* 2015, **162**:H486–H491.

55. Ou J, Zhu Y, Kong Y, Ma J: **Graphene quantum dots/β-cyclodextrin nanocomposites: a novel electrochemical chiral interface for tryptophan isomer recognition**. *Electrochem. Commun.* 2015, **60**:60–63.

56. Han C, Hou X, Zhang H, Guo W, Li H, Jiang L: **Enantioselective recognition in biomimetic single artificial nanochannels**. *J. Am. Chem. Soc.* 2011, **133**:7644–7647.

57. Dong S, Bi Q, Qiao C, Sun Y, Zhang X, Lu X, Zhao L: **Electrochemical sensor for discrimination tyrosine enantiomers using graphene quantum dots and β-cyclodextrins composites**. *Talanta* 2017, **173**(173):94−100.

58. Xiao Q, Lu S, Huang C, Su W, Zhou S, Sheng J, Huang S: **An electrochemical chiral sensor based on amino-functionalized graphene quantum dots/β-cyclodextrin modified glassy carbon electrode for enantioselective detection of tryptophan isomers**. *J. Iranian Chem. Soc.* 2017, **14**:1957–1970.

59. Zor E, Morales-Narvaez E, Alpaydin S, Bingol H, Ersoz M, Merkoci A: **Graphene-based hybrid for enantioselective sensing applications**. *Biosens. Bioelectron.* 2017, **87**:410−416.

60. Ates S, Zor E, Akin I, Bingol H, Alpaydin S, Akgemci EG: **Discriminative sensing of DOPA enantiomers by cyclodextrin anchored graphene nanohybrids**. *Anal. Chim. Acta* 2017, **970**:30−37.

61. Xiao Q, Lu S, Huang C, Su W, Huang S: **Novel N-doped carbon dots/β-cyclodextrin nanocomposites for enantioselective recognition of tryptophan enantiomers**. *Sensors* 2016, **16**:1–16.

62. Wang N, Chang PR, Zheng P, Ma X: **Carbon nanotube-cyclodextrin adducts for electrochemical recognition of tartaric acid**. *Diam. Relat. Mater.* 2015, **55**:117–122.

63. Xie G, Tian W, Wen L, Xiao K, Zhang Z, Liu Q, Hou G, Li P, Tian Y, Jiang L: **Chiral recognition of l-tryptophan with beta-cyclodextrin-modified biomimetic single nanochannel**. *Chem. Commun.* 2015, **1**:3135–3138.

64. Zor E, Bingol H, Ramanaviciene A, Ramanavicius A, Ersoz M: **An electrochemical and computational study for discrimination of d- and l-cystine by reduced graphene oxide/β-cyclodextrin**. *Analyst* 2015, **140**:313–321.

65. Wang Q, Lin X, Guo D, Xu J, Xuan C, Chen C, Fu Y: **A novel chiral electrochemiluminescence sensor that can discriminate proline enantiomers**. *RSC Adv.* 2015, **5**:94338–94343.

66. Bi Q, Dong S, Sun Y, Lu X, Zhao L: **An electrochemical sensor based on cellulose nanocrystal for the enantioselective discrimination of chiral amino acids**. *Anal. Biochem.* 2016, **508**:50–57.

67. Gu X, Tao Y, Pan Y, Deng L, Bao L, Kong Y: **DNA-inspired electrochemical recognition of tryptophan isomers by electrodeposited chitosan and sulfonated chitosan**. *Anal. Chem.* 2015, **87**:9481–9486.

68. •• Bao L, Chen X, Yang B, Tao Y, Kong Y: **Construction of electrochemical chiral interfaces with integrated polysaccharides via amidation**. *ACS Appl. Mater. Interfaces* 2016, **8**:21710–21720.

The paper presents the synthesis of chiral interfaces by amidation of chitosan and sodium carboxymethylcellulose and shows how this combination results in the amplification of chiral recognition (with respect to single components) in term of current differences for antipodes of three different probes.

69. Li Z, Mo Z, Meng S, Gao H, Niu X, Guo R, Wei T: **The construction of electrochemical chiral interfaces using hydroxypropyl chitosan**. *RSC Adv.* 2017, **7**:8542–8549.

70. Yu L-Y, Liu Q, Wu X-W, Jiang X-Y, Yu J-G, Chen X-Q: **Chiral electrochemical recognition of tryptophan enantiomers at a multi-walled carbon nanotube-chitosan composite modified glassy carbon electrode**. *RSC Adv.* 2015, **5**:98020–98025.

71. Ou J, Tao Y, Xue J, Kong Y, Dai J, Deng L: **Electrochemical enantiorecognition of tryptophan enantiomers based on graphene quantum dots-chitosan composite film**. *Electrochem. Commun.* 2015, **67**(57):5–9.

72. Kaniewska M, Sikora T, Kataky R, Trojanowicz M: **Enantioselectivity of potentiometric sensors with application of different mechanisms of chiral discrimination**. *J. Biochem. Biophys. Methods* 2008, **70**:1261–1267.

73. Shi H, Chen C, Tang B, Zhao G: **Photoelectrochemical enantioselective recognition of amino acid enantiomers on (001) facet TiO_2 surface**. *Electrochim. Acta* 2014, **146**:359–364.

74. • Kuang R, Zheng L, Chi Y, Shi J, Chen X, Zhang C: **Highly efficient electrochemical recognition quantification of amine enantiomers based on a guest-free homochiral MOF**. *RSC Adv.* 2017, **7**:11701–11706.

α-methylbenzylamine enantiomer result in neatly different DPV currents on a easily synthesized guest-free homochiral MOF.

75. • Deng C-H, Li T, Chen J-H, Ma J-G, Cheng P: **The electrochemical discrimination of pinene enantiomers by a cyclodextrin metal–organic framework**. *Dalton Trans.* 2017, **46**:6830–6834.

The α- and β-pinene enantiomers give neatly different responses with a cyclodextrin metal–organic framework (CD-MOF) as an electrochemical chiral sensor.

76. • Tao Y, Gu X, Yang B, Deng L, Bao L, Kong Y, Chu F, Qin Y: **Electrochemical enantioselective recognition in a highly ordered self-assembly framework**. *Anal. Chem.* 2017, **89**:1900–1906.

A simple and effective chiral sensing device based on a highly ordered self-assembly framework of Cu(II)-modified β-cyclodextrin and chitosan was here described. Its chiral discrimination ability was tested for tryptophan enantiomers.

77. Torsi L, Farinola GM, Marinelli F, Tanese MC, Omar OH, Valli L, Babudri F, Palmisano F, Zambonin PG, Naso F: **A sensitivity-enhanced field-effect chiral sensor**. *Nat. Mater.* 2008, **7**:412–417.

78. Mulla MY, Tuccori E, Magliulo M, Lattanzi G, Palazzo G, Persaud K, Torsi L: **Capacitance-modulated transistor detects odorant binding protein chiral interactions**. *Nat. Commun.* 2015, **6**:6010.

79. • Shi X, Wang Y, Peng C, Zhang Z, Chen J, Zhou X, Jiang H: **Enantiorecognition of tyrosine based on a novel magnetic electrochemical chiral sensor**. *Electrochim. Acta* 2017, **241**:386–394.

A novel magnetic electrochemical chiral sensor resulting in significantly different peak potentials for tyrosine enantiomers, besides different peak currents.

80. • Lin X, Zhu S, Wang Q, Xia Q, Ran P, Fu Y: **Chiral recognition of penicillamine enantiomers using hemoglobin and gold nanoparticles functionalized graphite-like carbon nitride nanosheets via electrochemiluminescence**. *Colloid Surf. B* 2017, **148**:371–376.

Resulting in significantly different ECL vs. potential characteristics for the penicillamine enantiomers; pH and time effects also investigated.

81. He Z, Zuyu, Zang S, Liu Y, He Y, Lei H: **A multi-walled carbon nanotubes-poly(l-lysine) modified enantioselective immunosensor for ofloxacin by using multi-enzyme-labeled gold nanoflower as signal enhancer**. *Biosens. Bioelectron.* 2015, **73**:85–92.

82. Pandey I, Kant R: **Electrochemical impedance based chiral analysis of anti-ascorbutic drug: l-ascorbic acid and d-ascorbic acid using C-dots decorated conductive polymer nano-composite electrode**. *Biosens. Bioelectron.* 2015, **77**:715–724.

83. Wang L, Gong W, Wang F, Yu Z, Chen Z: **Efficient bienzyme nanocomposite film for chiral recognition of l-tryptophan, l-phenylalanine and l-tyrosine**. *Anal. Methods* 2016, **8**:3481–3487.

84. Xia Q, Huang Y, Lin X, Zhu S, Fu Y: **Highly sensitive d-alanine electrochemical biosensor based on functionalized multi-walled carbon nanotubes and d-amino acid oxidase**. *Biochem. Eng. J.* 2016, **113**:1–6.

85. • Ding S, Cao S, Zhu A, Shi G: **Wettability switching of electrode for signal amplification: conversion of conformational change of stimuli-responsive polymer into enhanced electrochemical chiral analysis**. *Anal. Chem.* 2016, **88**:12219–12226.

An interesting detailed investigation on the sensing platform conformational changes connected with saccharide probe sensing; EIS different responses to the enantiomer of a saccharide series.

86. Wu L, Zhao C, Ren J, Qu X: **Label-free electrochemiluminescent enantioselective sensor for distinguishing between chiral metallosupramolecular complexes**. *Chem. Eur. J.* 2014, **20**:11675–11679.

87. •• Fushigami T, Inagi S: **Stereochemistry of organic electrode processes**: *Organic Electrochemistry*. Edited by Hammerich O, Speiser B. 5th ed.. Boca Raton: CRC Press; 2016:1489–1491.

An authoritative, clear review on chiral electrodes and media applied to asymmetric electrosynthesis, critically discussed and classified according to the different approaches.

88. Komori T, Nonaka T: **Electroorganic reactions on organic electrodes. 6. Electrochemical asymmetric oxidation of unsymmetric sulfides to the corresponding chiral sulfoxides on poly(amino acid)-coated electrodes**. *J. Am. Chem. Soc.* 1984, **106**:2656–2659.

89. Mtangi W, Kiran V, Fontanesi C, Naaman R: **Role of the electron spin polarization in water splitting**. *J. Phys. Chem. Lett.* 2015, **6**:4916–4922.

90. •• Mtangi W, Tassinari F, Vankayala K, Vargas Jentzsch A, Adelizzi B, Palmans ARA, Fontanesi C, Meijer EW, Naaman R: **Control of electrons' spin eliminates hydrogen peroxide formation during water splitting**. *J. Am. Chem. Soc.* 2017, **139**:2794–2798.

Spin selectivity, obtained by coating anodes with chiral organic semiconductors from helically aggregated dyes as sensititizers, results in enhancement of water splitting process as well as hydrogen peroxide formation suppression.

91. Maekawa H, Itoh K, Goda S, Nishiguchi I: **Enantioselective electrochemical oxidation of enol acetates using a chiral supporting electrolyte**. *Chirality* 2003, **15**:95–100.

92. • Challier L, Miranda-Castro R, Barbe B, Fave C, Limoges B, Peyrin E, Ravelet C, Fiore E, Labbé P, Coche-Guérente L, Ennifar E, Bec G, Dumas P, Mavré F, Noël V: **Multianalytical study of the binding between a small chiral molecule and a DNA aptamer: evidence for asymmetric steric effect upon 3′- versus 5′-end sequence modification**. *Anal. Chem.* 2016, **88**:11963–11971.
An advanced multitechnique investigation on the enantiospecific binding mechanism involving small chiral molecules with aptamers.

93. Mirri G, Bull SD, Horton PN, James TD, Male L, Tucker JHR: **Electrochemical method for the determination of enantiomeric excess of Binol using redox-active boronic acids as chiral sensors**. *J. Am. Chem. Soc.* 2010, **132**:8903–8905.

94. Mulas A, Willener Y, Carr-Smith J, Joly KM, Male L, Moody CJ, Horswell SL, Nguyen HV, Tucker JH, James HR: **The effect of central and planar chirality on the electrochemical and chiral sensing properties of ferrocenyl urea H-bonding receptors**. *Dalton Trans.* 2015, **44**:7268–7275.

95. Abbott AP, Barker GW, Davies DL, Griffiths GA, Walter AJ, Kočovsky P: **Electrochemical recognition of chiral species using quaternary ammonium binaphthyl salts**. *Anal. Chem.* 2002, **74**:4002–4006.

96. Seebach D, Oei HA: **Mechanism of electrochemical pinacolization. First asymmetric electrosynthesis in a chiral medium**. *Angew. Chem.* 1975, **87**:629–630.

97. Mirceski V, Quentel F, L'Her M: **Chiral recognition based on the kinetics of ion transfers across liquid/liquid interface**. *Electrochem. Commun.* 2009, **11**:1262–1264.

98. Matsushita S, Akagi K: **Synthesis of conjugated polymers in chiral nematic liquid crystal fields**. *Isr. J. Chem.* 2011, **51**:1075–1095 (a review).

99. Matsushita S, Yan B, Yamamoto S, Jeong YS, Akagi K: **Helical carbon and graphite films prepared from helical poly(3,4-ethylenedioxythiophene) films synthesized by electrochemical polymerization in chiral nematic liquid crystals**. *Angew. Chem. Int. Ed.* 2014, **53**:1659–1663.

100. •• Yan B, Matsushita S, Akagi K: **An advanced method for preparation of helical carbon and graphitic films using a carbonization substrate**. *Chem. Mater.* 2016, **28**:8781–8791.
The paper reports an attractive way to obtain helical graphite films with large domains of left- and right-handed spiral morphologies, starting from an helical PEDOT films (as carbonization precursors) electrochemically grown by an asymmetric reaction solution containing the chiral nematic liquid crystal, the monomer and an electrolyte.

101. Mariani RD, Abruna HD: **Stereoselective processes at electrodes modified with a cholesteric liquid crystal**. *J. Electrochem. Soc.* 1989, **136**:113–119.

102. Kane-Maguire LAP, Wallace GG: **Chiral conducting polymers**. *Chem. Soc. Rev.* 2010, **39**:2545–2576.

103. Rajca A, Miyasaka M, Pink M, Wang H, Rajca S: **Helically annelated and cross-conjugated oligothiophenes: asymmetric synthesis, resolution, and characterization of a carbon–sulfur [7]helicene**. *J. Am. Chem. Soc.* 2004, **46**:15211–15222.

104. Pu L: **Novel chiral conjugated macromolecules for potential electrical and optical applications**. *Macromol. Rapid Commun.* 2000, **21**:795–809 *(with 75 refs., particularly focusing on binaphthyl stereogenic elements)*.

105. Sannicolò F, Rizzo S, Benincori T, Kutner W, Noworyta K, Sobczak JW, Bonometti V, Falciola L, Mussini PR, Pierini M: **An effective multipurpose building block for 3D electropolymerization: 2,2′-bis(2,2′-bithiophene-5-yl)-3,3′-bithianaphthene**. *Electrochim. Acta* 2010, **55**:8352–8364.

106. Quartapelle Procopio E, Benincori T, Appoloni G, Mussini PR, Arnaboldi S, Carbonera C, Cirilli R, Cominetti A, Longo L, Martinazzo R, Panigati M, Pò R: **A family of solution-processable macrocyclic and open-chain oligothiophenes with atropoisomeric scaffolds: structural and electronic features for potential energy applications**. *New J. Chem.* 2017, **41**:10009–10019.

107. Freemantle M (Ed): *An Introduction to Ionic Liquids*. RSC Publishing; 2010.

108. Jain R, Jadon N, Singh K: **Review—new generation electrode materials for sensitive detection**. *J. Electrochem. Soc.* 2016, **163**:H159–H170.

109. •• Ma K, Jarosova R, Swain GM, Blanchard GJ: **Charge-induced long-range order in a room-temperature ionic liquid**. *Langmuir* 2016, **32**:9507–9512.
Experimentally obtained fundamental information about the peculiar ionic liquid structure at the interface with a charged electrode.

110. Bazant MZ, Storey BD, Kornishev AA: **Double layer in ionic liquids. Overscreening versus crowding**. *Phys. Rev. Lett.*, vol 106 2011 046102/1–046102/4.

111. Perkin S, Crowhurst L, Niedermeyer H, Welton T, Smith AM, Goswami NN: **Self-assembly in the electrical double layer of ionic liquids**. *Chem. Commun.* 2011, **47**:6572–6754.

112. Ivaništšev V, Kirchner K, Fedorov MV: **Restructuring of the electrical double layer in ionic liquids upon charging**. *J. Phys. Condens. Mater.*, vol 27 2015 102101/1-102101/5.

113. •• Cui ALahiri, Carstens T, Borisenko N, Pulletikurthi G, Kuhl C, Endres F: **Influence of water on the electrified ionic liquid/solid interface: a direct observation of the transition from a multilayered structure to a double-layer structure**. *J. Phys. Chem. C* 2016, **120**:9341–9349.
About peculiar ionic liquid structure at the interface with a charged electrode, particularly in the presence of water traces.

114. • Zhong T, Yan J, Li M, Chen L, Ma B: **The electric double layer in an ionic liquid incorporated with water molecules: atomic force microscopy force curve study**. *ChemElectroChem* 2016, **3**:2221–2226.
Also on the same important topic of [113].

115. Ivaništšev V, O'Connor S, Fedorov MV: **Poly(a)morphic portrait of the electrical double layer in ionic liquids**. *Electrochem. Commun.* 2014, **48**:61–64.

116. • Fernandez AA, Kouwer PHJ: **Key developments in ionic liquid crystals**. *Int. J. Mol. Sci.*, vol 17 2016 731/1–731/31.
Discussing an attractive class combining ionic liquid and liquid crystal properties.

117. Wang X, Hao J: **Recent advances in ionic liquid-based electrochemical biosensors**. *Sci. Bull.* 2016, **61**:1281–1295.

118. Payagala T, Armstrong DW: **Chiral ionic liquids: a compendium of syntheses and applications (2005–2012)**. *Chirality* 2012, **24**:17–53 (and literature cited).

119. Ding J, Armstrong DW: **Chiral ionic liquids. Synthesis and applications**. *Chirality* 2005, **17**:281–292 (and literature cited).

120. Arnaboldi S, Cirilli R, Forni A, Gennaro A, Isse AA, Mihali V, Mussini PR, Pierini M, Rizzo S, Sannicolò F: **Electrochemistry and chirality in bibenzimidazole systems**. *Electrochim. Acta* 2015, **179**:250–262.