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Review Article

Electroactive chiral oligo- and polymer layers for electrochemical enantiorecognition[☆]Serena Arnaboldi, Sara Grecchi, Mirko Magni and Patrizia Mussini^{*}

Electronically conducting polymer (ECP) and oligomer films are one of the most popular classes of artificial materials for electrode surface modification and nanostructured electroactive film preparation for use as active layers in advanced sensing electrochemical devices. They can act as both receptors and transducers on account of their electroactivity and easy derivatization in a virtually unlimited structure range, and typically have low cost and easy processability. The tailoring possibilities of ECP films also make them attractive selector candidates to achieve the superior level of molecular recognition represented by *enantioselective* electroanalysis, implying to *discriminate between specular images of a chiral molecule*. This superior recognition level requires to endow them with chirality and to employ them as enantiopure films, which can be made along different strategies, with different implications in terms of enantioselectivity, kind of transduction of the recognition event, specificity vs general applicability, preparation difficulty, robustness, etc. In this context an outstanding tool is provided by the “inherent chirality” strategy.

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Introduction

Electronically conducting polymers (ECPs) as well as oligomers are one of the most popular classes of artificial materials for electrode surface modification and nanostructured electroactive film preparation for use as active

layers in advanced sensing devices, their study being also prompted by molecular electronics [1–5]. They can act as both receptors and transducers on account of their electroactivity and easy derivatization in a virtually unlimited structure range, and typically have low cost and easy processability. The tailoring possibilities of ECP films also make them attractive selector candidates to achieve the superior level of molecular recognition represented by *enantioselective* electroanalysis, implying to *discriminate between specular images of a chiral molecule*. This task requires to make them even more “intelligent”, endowing them with chirality, to be employed as enantiopure selectors so that the recognition event can take place in diastereomeric and therefore electrochemically distinguishable conditions. The different strategies so far adopted will be presented and compared, having different implications in terms of enantioselectivity, transduction of the recognition event, specificity vs general applicability, preparation difficulty, robustness, etc..., particularly focusing on the “inherent chirality” strategy (see SI.1 for definition), recently resulting in outstanding chirality manifestations.

Electronically conducting polymers as active materials for electrochemical sensing devices

Often referred to as “synthetic metals”, on account of combining conventional organic polymer properties with metal-like ones, ECPs offer many advantages like their good electron transfer and transport properties, the commercial availability of many parent monomers, their easy functionalization to tune the material properties (e.g., for catalytic or coordination purposes), the many protocols, most of them low cost, that can be employed to prepare ECP films, either by *in situ* electrodeposition from suitable monomers (which allows to modulate their properties through the operating conditions and to *in situ* monitor their growth by cyclic voltammetry (CV) and electrochemical quartz crystal microbalance (EQCM)) or by chemical synthesis followed by physical techniques (such as drop casting, spin coating, physical vapor deposition, LbL deposition).

Combining electroactivity and virtually unlimited functionalization possibilities, ECPs can concurrently act as receptors and transducers [2,3^{••}]. Transduction can be achieved, e.g., in terms of conductance/impedance, current, potential and/or mass variations. For instance, in ECP-based gas sensors and electronic noses, ECPs

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

undergo easy oxidation/reduction reactions when exposed to redox active chemical agents, such as gases and flavors; the chemically induced conversion of the ECP into the oxidized or reduced state results in significant electrical resistance changes of the material [3**]. In amperometric sensors, ECPs are considered to act as charge transfer mediators and binding agents for the charge transfer process, which is assumed to involve a thin layer at the ECP|solution interface; electron shift through the ECP bulk to the underlying ECP|electrode interface allows to translate the recognition event at the ECP|solution interface into a current flow [3**].

In spite of their already wide exploitation, rationalization of the ECP sensing performance is often hard [6], since, besides considering the molecular properties of ECP monomer unit and probe, one must take into account factors like polydispersivity, roughness and porosity which specifically depend on the film preparation (monomer concentration, medium, potentiostatic vs potentiodynamic conditions, and in the latter case scan rate and cycle number...). The extent of the film layer in which the charge transfer is taking place is also an important issue, as well as the ECP interface with the underlying electrode support [7], and the medium effects (modulating swelling, charge stabilization, proton availability, doping/dedoping processes and so on [3**]). Clues on the film features and on its sensing mechanism can be achieved by many techniques, like EQCM (doping/undoping nature and reversibility [8]), *in situ* spectroelectrochemistry (UV-vis-NIR and ESR for charge state speciation, e.g., radical cation and dication, as a function of potential [9], *in situ* AFT-FTIR [10]), *in situ* conductance [1,11,12] and EIS (for charge transport and charge transfer properties as a function of potential/charge state [13,14] both for characterization purpose, and also, in some cases, for recognition transduction), AFM/STM and profilometry (for morphology and roughness).

Most ECPs in the literature are based on thiophene, pyrrole, and aniline scaffolds. Thiophene materials, both as such or as composite film components, are currently the preferred option for sensor applications, on account of the variety of possible functionalizations easily achievable and of their chemical and mechanical stability and high electrical conductivity. Thiophene-based polymer or oligomer films have been employed in sensing devices for a wide probe variety, ranging from ions, to molecules, to biological compounds, up to electronic noses and tongues [5]. Oligomers can be preferred over long-chain systems on account of their ability to deposit as crystalline grains, resulting in high conductivity and porosity [5]. Examples of popular thiophene monomers for ECP deposition are 2,2'-bithiophene, 3-methylthiophene, and 3,4-ethylenedioxythiophene (EDOT), affording electrooxidation at much milder potentials [15], as such or functionalized.

Endowing ECPs with chirality: concepts and strategies

The tailoring possibilities of ECPs also make them attractive selector candidates to achieve the superior level of molecular recognition represented by *enantioselective* electroanalysis, implying to *discriminate between specular images of a chiral molecule*. Since enantiomers have identical scalar physico-chemical properties and therefore also share the same electrochemical reactivity, they can only be discriminated having the electron transfer process taking place in an enantiopure chiral environment. With a ECP-based sensor, this implies to use an enantiopure chiral electronically conducting polymer (CECP) as the active film.

Many CEC polymers/copolymers/oligomers have been so far developed, mostly including, again, thiophene, pyrrole, and aniline derivatives (especially considering the last two decades) [16–20, SI.2/A]. Chirality can be introduced:

- starting from chiral monomers*, either bearing pendants with one or more stereocenters (for example, in 3 or 3,4-thiophene position(s) or in 3- or 1-pyrrole position) [e.g., 16,17, SI.2/B]; or including other stereogenic elements, like paracyclophane, spiro-, atropisomeric or helical structures [e.g., 18,19, SI.2/C];
- especially in the aniline case, performing electropolymerization in the presence of *chiral counter anions* (in most cases (+) or (–)-camphorsulfonate (CSA[–]) [e.g., 16,21,22, SI.2/D];
- by molecular imprinting of an achiral ECP with a *chiral template*, [e.g., 2,5,23, SI.2/E];
- performing the (electro)polymerization of an achiral monomer in *cholesterised liquid crystals* [24,25,26**, SI.2/F];
- performing (electro)polymerization under magnetopolarization [27, SI.2/G];
- by the presence of templating scaffolds or other chirality inducers, like *inter alia* chiral biopolymers, saccharides, aminoacids [28–30, SI.2/F1-F7]; metal ions can cooperate to chiral macroassemblies [31, SI.2/F8].

In many of the above cases chirality entirely originates from a helix-like “secondary” structure (to borrow a typical protein definition) induced by external conditions on an ECP constituted of achiral monomers. However, the formation of such a chiral secondary structure is also very important in the case of ECPs constituted by monomers with stereogenic centers in attached substituents; in this case it can remarkably depend on the polymerization regioregularity (thus becoming a requirement for significant macroscopic chirality effects); moreover, changing the experimental conditions such as pH, solvent, temperature, charge..., can dramatically affect the overall chirality manifestations, resulting in conformational change from a he-

lix structure to a random coil one, e.g., [16, SI.2/B]. Such effects can be followed by circular dichroism (CD) spectroscopy, enabling to study CECP chirality as a function of the macromolecule conformation, and also, when coupled with electrochemistry, as a function of potential/charge state. A very stable secondary structure can instead result from monomers including other stereogenic elements, as discussed more in detail later on.

Chiral electronically conducting polymers CECPs: enantioselective performance

Only several of the many CECPs reported in the literature have been so far tested as chiral electrodes.

Pyrrole-based CECPs

A pyrrole monomer [32] with a substituent including a β -D-glucose unit at the N atom, showed **facile electropolymerization** in the presence of (–) camphorsulfonate (CSA^-) anions, while the same process was **inhibited** by (+)- CSA^- ones; moreover the corresponding polypyrrole film showed **significant differences in oxidation/reduction currents** in the presence of the two antipode anions; the latter effect was also observed for films electropolymerized from pyrrole monomers with a lactate group either on the N atom or in 3-pyrrole position as substituent [33,34], which observation prompted testing the electrodes for the **electroselective reduction** of prochiral ketones, with significant enantiomeric excesses [35]. Again, in the presence of (+)- or (–)- CSA^- electropolymerization of pyrrole monomers with *N*-substituents ending with chiral groups took place with **different degrees of chiral anion doping**, and the resulting films showed **different conductivities** [36,37]. Chemically synthesized polypyrroles bearing in position 3 a substituent with a chiral ester of either (*R*)- or (*S*)-menthol, or Boc-alaninol, or 1-phenylethanol, exhibited chiral discrimination in terms of **electrical resistance and mass changes** between enantiomers of chiral probes like **limonene, carvone, 2-butanol** [38]. Electrodes functionalized by electropolymerization of (6*S*,7*R*,10*R*)-2,2,7-trimethyl-10-isopropyl-1-azaspiro[5.5]undecane-1-yloxy precursors containing a pyrrole side chain resulted in **significantly different peak currents** for (*R*)-(+)- and (*S*)-(–)-1-phenylethanol oxidation [39]. **Electrocatalytic hydrogenation** of α -ketoester compounds (methyl benzoylformate and butyl benzoylformate) to **preferentially** (*R*)-methyl mandelate and (*R*)-butyl mandelate was reported using Pd electrodes modified with poly(*N*-substituted pyrrole) film with L-(+)-lactic acid substituents [40].

PANI-based CECPs

PANI electrodeposited with (1*S*)-(+)-10-camphorsulfonic acid (CSA) dopant exhibited **chirality and specular CD** for opposite doping CSA configurations (on Au nanoparticles/colloids) [41–43]; the same material also showed **enantioselectivity toward phenylalanine enantiomers** (a peak in differential pulse voltammetry

(DPV) for a given antipode on a given film enantiomer and vice versa [44]; different quartz crystal microbalance responses [45]; significant differences in ΔE vs $\log c$ potentiometric response [46]) and **alanine enantiomers** (in terms of different open circuit potential (OCP) [47,48]) and **enantioselection ability** in binding the herbicide dinoseb enantiomers [49]. Much more recently, **increasing conductivity** was observed with increasing CSA mole fraction, inducing a predominantly one-handed helix in the backbone [21]. Also, chiral polyaniline electrodes prepared by the magnetoelectropolymerization showed **current differences** for L-ascorbic acid (L-AA) and D-isoascorbic acid (D-AA) [27], specular upon inverting the magnetic field direction [50,51].

Moreover, a gas sensor was recently presented, consisting in a PANI superhelical microfiber, showing **enantioselective response to chiral 2-aminohexane antipodes in terms of different resistance changes**, specular upon inverting the helical configuration [22] (Figure 1).

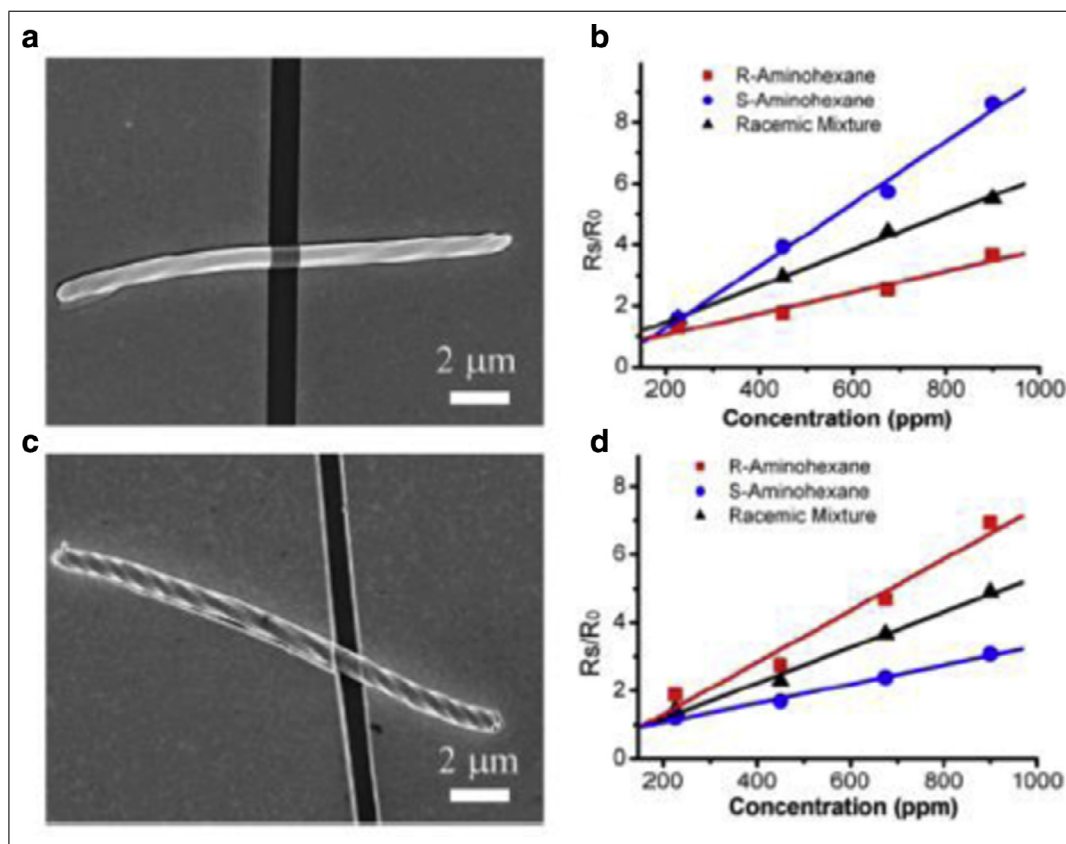
Thiophene-based CECPs

Small differences in redox cycles were observed with (+)- or (–)- CSA^- for a polythiophene with a chiral pendant in 3-thiophene position [52]. CECP obtained from thiophene monomers substituted in 3-position with chiral pendants showed **different doping/dedoping degrees** as a function of the stereocenter configuration [53,54]. Instead, more recently, no enantioselection was observed (in terms of electroactive material CV pattern) testing with alanine and leucine amino acid enantiomers (as methyl esters) polythiophenes with leucine-based chiral pendants [55]. Recently, a series of works with 2'-functionalized chiral PEDOT derivatives resulted in increasing enantioselectivity achievements: from **small differences in CV and/or pulsed voltammetry patterns** for DOPA enantiomers [56,57] to more significant **DPV and SWV current differences** for the same probe [58*] to neat **DPV current differences** (and possibly in some cases, even small potential differences) for **DOPA, tryptophan and propranolol**, with good specularity in the response upon inverting the polymer configuration [59**]; a mechanism of chiral recognition was also proposed, based on hydrogen bonding and a three-point interaction model (Figure 2) [58*,59**].

A thiophene-based electroactive oligomer with stereocenters in attached pendants was employed as active material to prepare a **sensitivity enhanced field-effect chiral sensor** [60].

Quite recently, poly{[methyl *N*-(tert-butoxycarbonyl)-*S*-3-thienyl-L-cysteinate]-cothiophene} (PCT-L) resulted in **current differences** for *R* or *S* chiral *N,N*-dimethyl-1-ferrocenyl-ethylamine, besides being studied as **spin filter** [61]; moreover, it gave significantly different CV responses with an achiral ferrocene probe by invert-

Figure 1



Resistance changes with concentration of 2-aminohexane (as racemate or *R*- or *S*-antipode) of a left-handed (first row) or right-handed (second row) PANI-CSA helical microfiber tested as gas sensor. Reprinted with permission from [22]. Copyright (2017) American Chemical Society.

ing the direction of an external applied magnetic field [62**]. Spin-selectivity studies were also carried out by the same group by injecting spin polarized electrons into non thiophene-based helicene monolayer films [63*]. The same group also reported significant enhancement of hydrogen production from water using anodes coated with a chiral poly(flourene-co-chiral thiophene) conducting polymer (further enhanced in case of embedded CdSe quantum dots within the polymer) (Figure 3) [64**]. This effect, also obtained with other chiral films, has been explained by the spin-selective transport through the chiral layer, inducing relative spin alignment in the oxidized radicals [65].

Recent performance of thiophene-based films including atropisomeric scaffolds will be specifically discussed further on.

CECPs based on other monomers

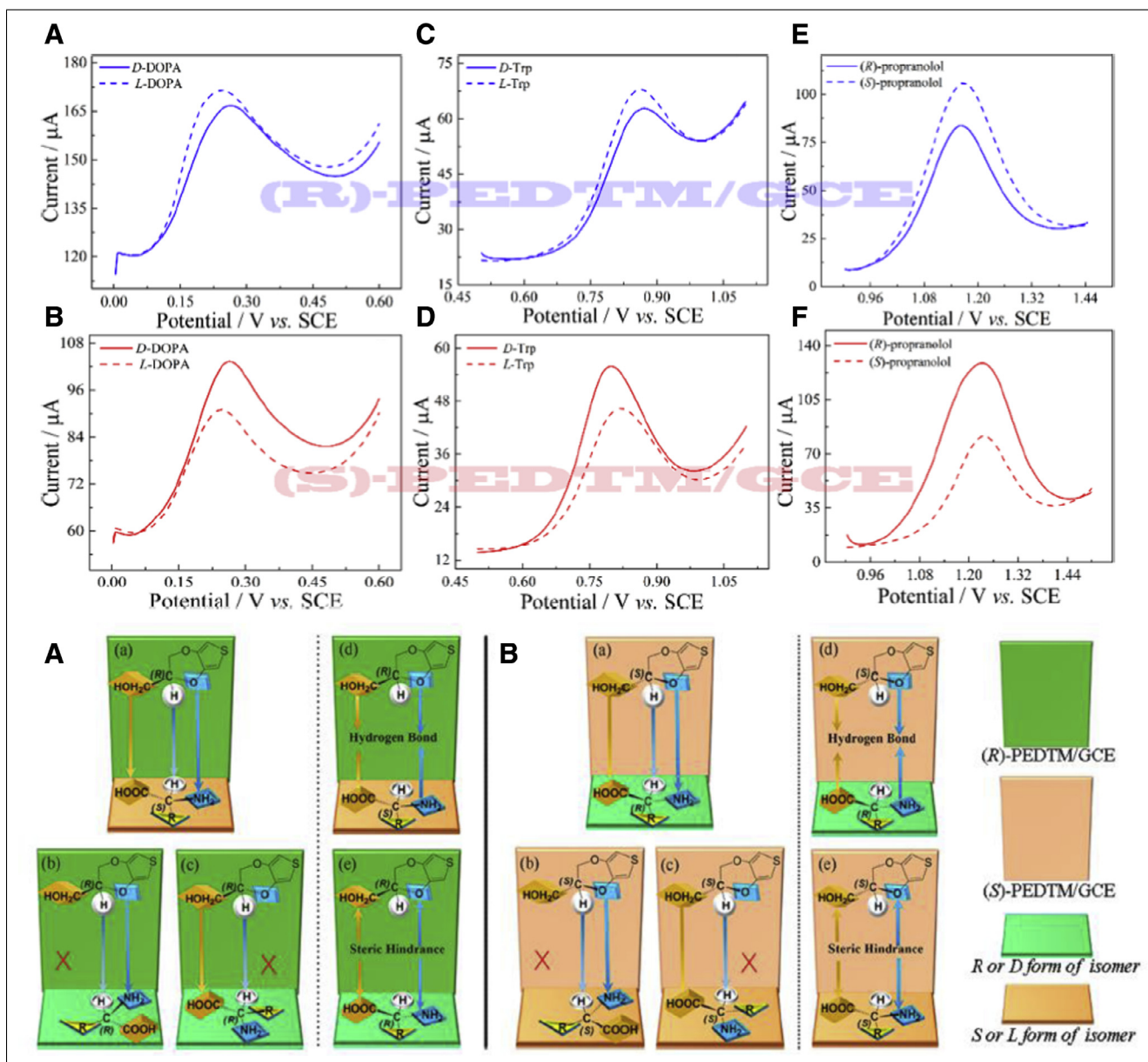
Only a few cases concern other monomers. Electrooxidation of fluorenylmethoxycarbonyl amino acids gave chiral films exhibiting slightly different CV patterns and rest potential trends with CSA enantiomers, and slight

enantiomeric excesses in racemate amine solutions involved in enantiopure film reduction [66]. [Ru(4-methyl-4'-vinyl-2,2'-bipyridine)₃]²⁺ polymer showed an enantioselectivity degree in K₃[Co(ox)₃] photoelectrochemical reduction [67]. A carbazole-based, cross-linked biotinylated conducting polymer showed significant current differences for L- and D-norepinephrines [68].

CECP by molecularly imprinting with chiral templates

In the last years, frequent are the examples of chiral sensors based on conducting polymers or oligomers (especially pyrrole and thiophene-based) as component of chiral MIPs (an approach reviewed in [2,23,69]). According to the general MIP concept, similar to enzyme chemosensors, such chiral imprinted materials selectively respond, in terms, e.g., of current or mass variation, to the templating molecule, in this case a chiral molecule antipode. Among recent examples, a MIP prepared from a terthiophene monomer and templating molecule (–)-ephedrine showed neat differences (although not full selectivity) between QCM responses to the ephedrine enantiomers [70]. A potentiometric chiral sensor for L-phenylalanine based on cross-linked polymethylacrylic

Figure 2



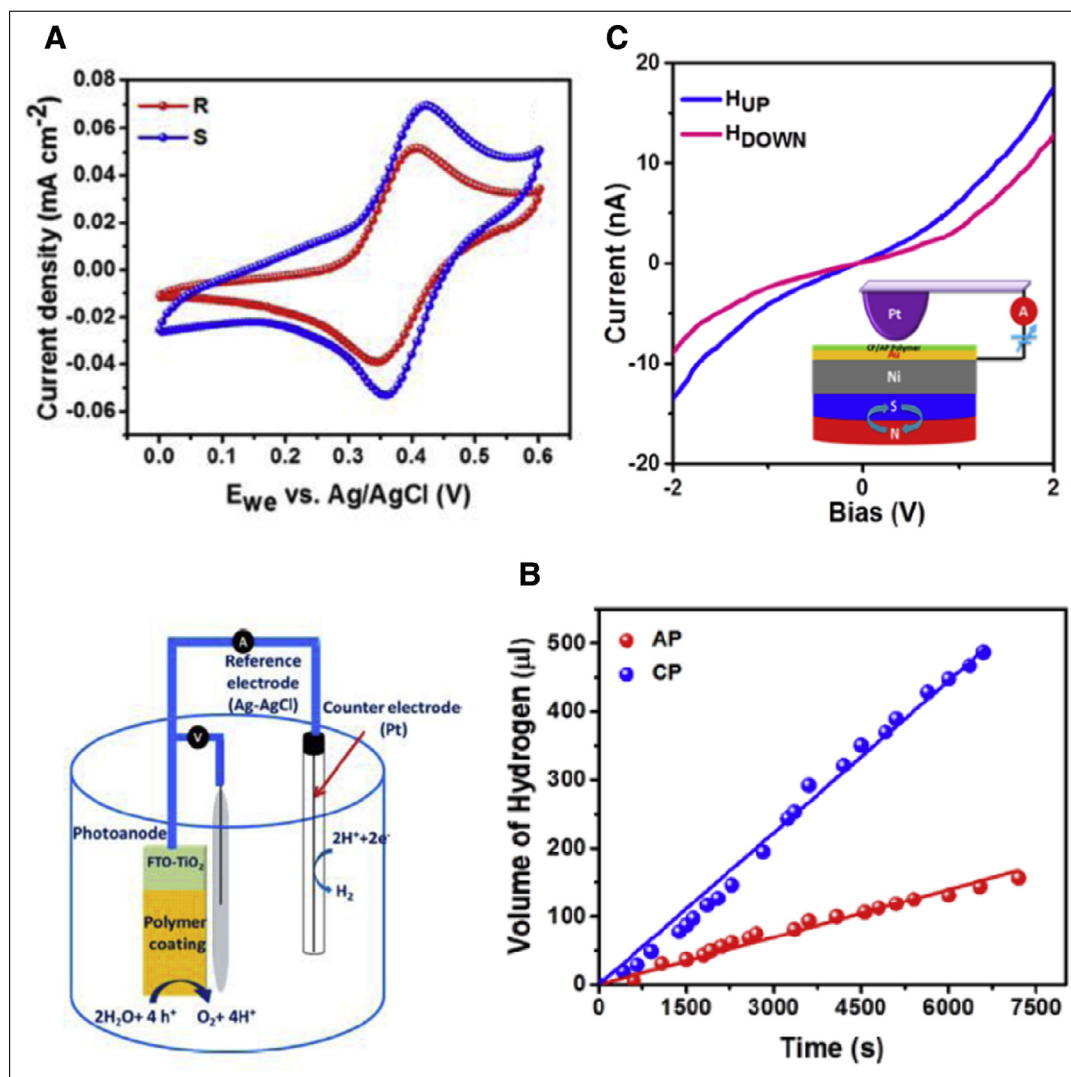
DPV discrimination of the enantiomers of three different chiral probes (DOPA, tryptophan, propranolol) achieved on enantiopure films of a 2'-functionalized chiral PEDOT derivative, and proposed rationalization in terms of "three-point interaction" or "pseudo two-point interaction" models. Reprinted with permission from [59]. Copyright (2017) American Chemical Society.

acid-polycarbazole hybrid molecularly imprinted polymer displayed a very low selectivity constant for the D-phenylalanine enantiomer [71]. Polypyrrole films with L-cysteine imprinting, obtained from pyrrole monomers attached through thiol terminals to Au nanoparticles on GC, gave significant current differences for L- vs D-cysteine enantiomers [72]. A L-ascorbic acid imprinted (polyaniline-ferrocenylsulfonic acid) pencil graphite electrode showed high enantioselectivity since practically no

current was observed for the D-ascorbic acid enantiomer ([73°], differently from [74]; a similar former study [75]). High enantioselectivity was also observed with a polypyrrole film molecularly imprinted with L-aspartic acid [76].

Very recently, a thiophene-based molecularly imprinted copolymer was exploited as the recognition unit in an **extended-gate field-effect transistor chemosensor** for phenylalanine, resulting in neat enantiomer current dif-

Figure 3



Top left: cyclic voltammety patterns for the enantiomers of a model ferrocenyl chiral probe on a chiral poly(fluorene-co-chiral thiophene) CP layer self-assembled on Au. Top right: polarization curves under magnetopolarization for CP on Au/Ni. Bottom: photoelectrochemical cell setup and hydrogen production by photoanode coated with CP or with an achiral polymer AP. Reprinted with permission from [64••]. Copyright (2017) American Chemical Society.

ferences, specular upon inverting the template configuration, besides having a low detection limit and good selectivity respect to other aminoacids [77••].

Molecularly imprinted polypyrrole was also applied in **electromodulated columns** for enantioselective recognition of tryptophan [78], glutamic acid [79] and other aminoacids [80].

A **composite chiral sensor material** based on overoxidized polypyrrole incorporating bethamethasone (providing the chiral selector) resulted in current differences and a slight potential shift for mandelic acid enantiomers;

chemometrics was applied for simultaneous enantiomer determination [81].

Global considerations on the CECP performance

In most approaches discussed in the former paragraphs the electrochemical enantioselectivity target appeared to have been only partially achieved.

High to complete specificity for a single enantiomer can be reached in some cases, by the use of very specifically tailored selectors (implying however no general applicability), like, e.g., in MIP cases.

In other cases, enantioselectivity manifestations appear weak or labile. But, above all, in nearly all cases discussed, the kind of response (e.g., in terms of current or conductance differences or potential vs concentration trends) appears unsuitable for purposes of recognition and quantification by a single selector of either (*R*)- or (*S*)-probe enantiomer in mixture, or when the presence of both enantiomers cannot be *a priori* ruled out.

A weak point of the former approaches could be that in most cases the stereogenic elements are either stereocenters localized in pendants external to the main material backbone and/or a “secondary” chiral structure easily lost as a function of operating conditions, as above discussed, or a chiral shape derived from external templating agents.

“Inherent chirality”, a winning strategy

In this context a powerful tool is provided by electroactive heterocycle-based oligomer films endowed with “inherent” chirality (that is, following F. Sannicolò’s definition [82,83^{••}, SI.1], originating from the same element responsible for the key functional property, here electroactivity) on account of the presence of atropisomeric (i.e., with hindered rotation) or helicoidal elements in the main conjugated backbone, resulting in a regular torsion with an energy barrier far too high to be overcome in the working operating conditions.

Such approach to electroactive oligomers and polymers of “robust” chirality had been already exploited, e.g., with binaphthyl elements [18] (very popular in chiral catalysis), or helical elements [19], often with conjugation partially impaired by ring connectivity, but hardly for application to electrochemical enantiodiscrimination. An exception was a recent study concerning chiral phenylethylamines behavior on films obtained from thiophene-based monomers including a binol or a binaphthyl crown-ether atropisomeric scaffold [84]. In the binol cases, specific acid/base interactions between amine and binol hydroxy groups were revealed by (i) a decrease in film conductivity, (ii) a decrease in the film oxidation current with concurrent formation of a smaller peak at less negative potentials; (iii) in potentiometric mode and in one case, a significant difference in potential vs concentration trends for the two probe enantiomers, justified in terms of enantio-recognition ability of the atropisomeric scaffold. Similar potential/concentration trends for the same probe/receptor couple, but with binol implemented in a Langmuir–Blodgett film, were reported before, also with a proposed interpretation [85].

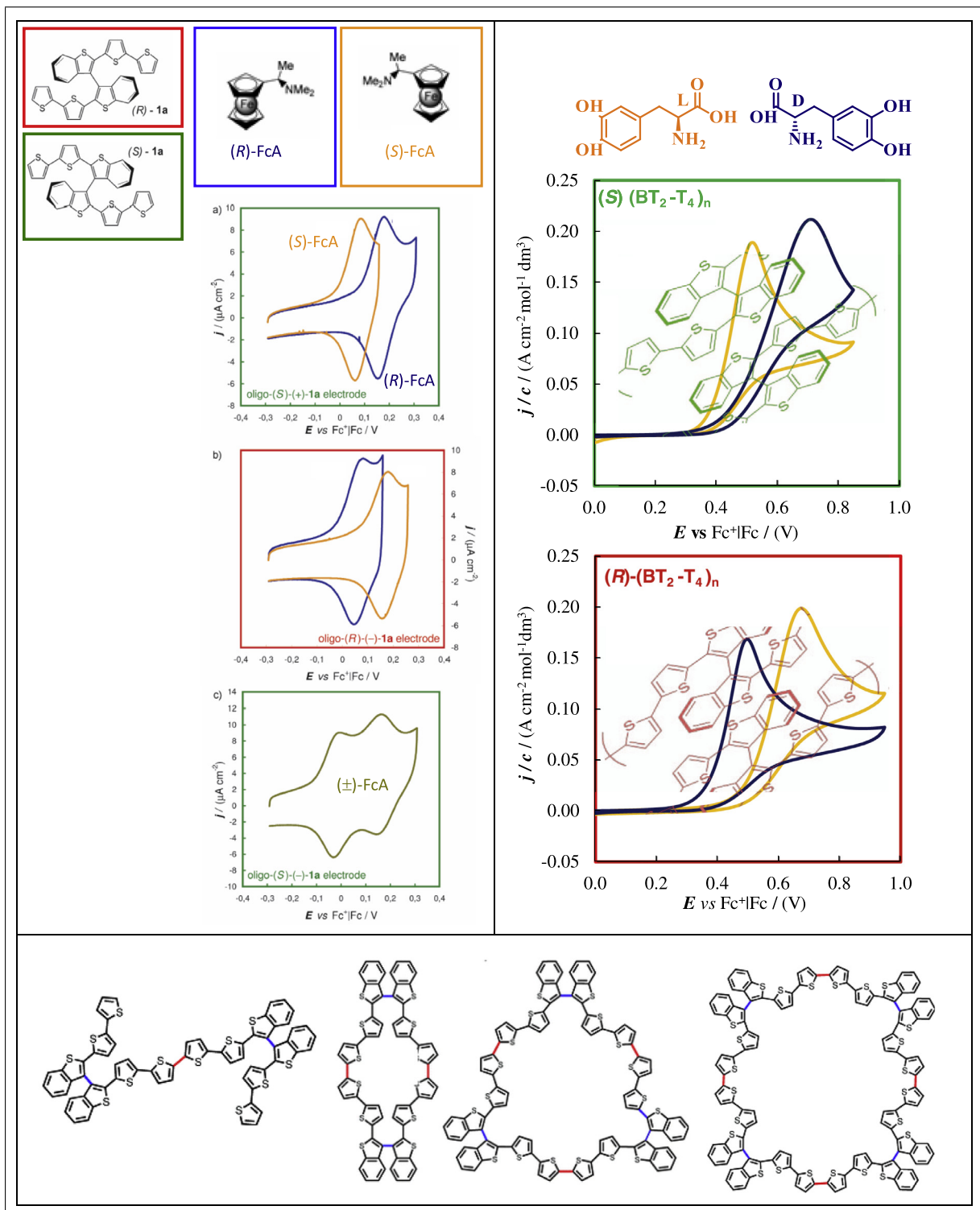
Recently, outstanding chirality manifestations and enantioselectivity in electrochemistry experiments were observed by Sannicolò *et al.* with enantiopure electrodes prepared from the thiophene-based starting monomer BT₂T₄ (Figure 4). BT₂T₄, of affordable synthesis, can be discussed as a model, being endowed with a bundle of

interrelated important properties for the electrochemical enantioselection task [82,86]. It consists of two identical moieties with an atropisomeric bibenzothiophene core, corresponding to a ~70° torsional angle and a torsional energy barrier far too high to be overcome in the operating condition range. As a consequence, it exists in two stable enantiomers that can be separated by chiral HPLC and stored. At the same time, a certain conjugation degree is maintained between the two moieties of the main backbone, which is the source of both molecular chirality and electroactivity, strictly reciprocally related.

The monomer has good charge transfer and charge transport properties as well as **very high oligomerization ability** on account of its intrinsic 3D character, and actually in racemic form it had been exploited by Kutner *et al.* as an outstanding comonomer to obtain fast and regular formation of MIPs for piezogravimetric sensors in the case of functional monomers with lower oligomerization ability [87–89], resulting in materials with excellent mechanical properties and retaining the functional properties of the less reactive comonomer. Moreover, importantly, such oligomerization is **intrinsically regioregular**, on account of the molecule *C*₂ symmetry (only two homotopic thiophene terminals are available). This enables to fully transfer chirality from the monomer to the corresponding electroactive film obtained by chemical or electrochemical oxidation, which fully retains the monomer (*R*) or (*S*) configuration. Antipode films exhibit neat and specular CD signals, reversibly modulated by charge/discharge cycles [82,90], pointing to powerful and stable “macromolecular” chirality: actually, in this case a very strong “secondary” helicoidal chiral structure originates as a consequence of the very regular sequence of atropisomeric bibenzothiophene cores of the same configuration along the backbone. A further valuable feature is that oligo-BT₂T₄ films include a significant amount of cyclic oligomers besides linear terms [91], that is, a collection of potentially coordinating heteroatom-rich cavities of different dimensions (in particular, cyclic dimers, trimers, tetramers were isolated and studied separately, providing with their multiple hexathiophene chains nice cases of equivalent, possibly reciprocally through-space interacting, reversible redox centers [91,92[•]]).

Besides attractive chiroptical properties such as the above electrochemically modulated CD [82,90] as well as circularly polarized luminescence [91], oligo-BT₂T₄ films showed remarkable enantioselection ability. Working with a commercial chiral ferrocenyl probe, significant potential differences were observed in enantiomer peak potentials besides a linear dynamic range in enantiomer peak currents (a desired combination aiming to enantiomeric excess evaluation) in different conditions: working in ionic liquid with oligo-BT₂T₄ films electrodeposited on screen printed electrodes in the same medium [82], or with films drop-casted from a single kind of

Figure 4



Top: cyclic voltammety characteristics (left) for the enantiomers or the racemate of a model chiral ferrocenyl probe, in ionic liquid, on Au screen printed electrode coated with oligomer films electrodeposited from (S) -(BT₂-T₄) (green) or (R) -(BT₂-T₄) (red) (adapted with permission from [82]); (right) for DOPA enantiomers (4 mM in H₂O + NaCl 0.1 M) on GC coated with oligomer films electrodeposited from the same monomers in acetonitrile (36 cycles, 200 mV s⁻¹ growth scan rate). Bottom: a gallery of open and closed oligo-(BT₂-T₄)_n terms (adapted from [92*] by permission of The Royal Society of Chemistry (RSC) on behalf of the Centre National de la Recherche Scientifique (CNRS) and the RSC).

oligomer (dimer or trimer, obtained by chemical oligomerization and chromatographic separation) [91], or working in acetonitrile with films electrodeposited in the same medium on GC tips in a 3-electrode minicell. Preliminary enantiodiscrimination experiments with pharmaceutically relevant probes have also been reported [93,94]. Comparable features and enantioselection ability have also been observed by oligomeric films obtained from a spider-like, all-thiophene inherently chiral monomer with four equivalent oligomerization positions [83**] also with high 3D character (as well as providing an excellent MIP comonomer [77**,83**,95*]), confirming the general validity of the strategy. Extending the same experiments to inherently chiral electroactive films with other stereogenic elements is of huge interest. Quite recently an additional confirmation came with the outstanding enantioselection observed working on achiral electrodes in inherently chiral media [96**].

Conclusion

Many approaches have been proposed to prepare and exploit enantioselective electrode surfaces based on CECs. The main weak points encountered are (a) a kind of response unsuitable for purposes of recognition and quantification of either enantiomer in a mixture (or when it is not known *a priori* that only one enantiomer is present) by a single selector, or (b) weak and/or labile selectivity. In this context, inherently chiral electroactive oligomer films have recently resulted in a significant step further. The high torsional barriers of the atropisomeric cores regularly inserted in the electroactive conjugated systems ensure remarkable and very stable chirality properties, biunivocally linked to electroactivity; the possible presence of potentially coordinating cyclic cavities is an additional advantage. Very promising recent results have to be consolidated by (i) focusing on the deposition protocol and on the film features, to achieve clues for mechanism rationalization and to optimize performance and reproducibility, (ii) extending the study to inherently chiral oligomer/polymer films with different stereogenic elements, and (iii) testing the films with other probes as well as in other electrochemical applications and devices.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.coelec.2018.01.001](https://doi.org/10.1016/j.coelec.2018.01.001).

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

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