Bipolar electrochemical rotors for the direct transduction of molecular chiral information

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Dedication: This manuscript is dedicated to Prof. Erkang Wang and Prof. Shaojun Dong at the occasion of their 90th birthdays in recognition of their important contributions to a large variety of topics in the field of electrochemistry

Abstract

Efficient monitoring of chiral information of bioactive compounds has gained considerable attention, due to their involvement in different biochemical processes. In this work, we propose a novel dynamic system for the easy and straightforward recognition of chiral redox active molecules and its possible use for the efficient measurement of enantiomeric excess in solution. The approach is based on the synergy between the localized enantioselective oxidation of only one of the two antipodes of a chiral molecule and the produced charge-compensating asymmetric proton flux along a bipolar electrode. The resulting clockwise or anticlockwise rotation is triggered only when the probe with the right chirality is present in solution. The angle of rotation shows a linear correlation with the analyte concentration, enabling the quantification of enantiomeric ratios in mixtures where the two antipodes are present in solution. This device was successfully used to simultaneously measure different ratios of the enantiomers of 3,4-dihydroxyphenylalanine and tryptophan. The versatility of the proposed approach opens up the possibility to use such a dynamic system as a straightforward (bio)analytical tool for the qualitative and quantitative discrimination of different redox active chiral probes.

Keywords: Chiral recognition, inherently chiral oligomers, bipolar electrochemistry, rotors

1. Introduction

Physico-chemical transduction of chiral information of bioactive compounds such as amino acids, sugars and proteins, has gained considerable attention in recent years, due to their involvement in different biochemical processes (Zor et al., 2019, Wu et al., 2021, Gogoi et al., 2019). For example, the efficient monitoring of D-amino acids is used as an indication of bacterial contamination in food and beverages (Rosini et al., 2020). An interesting approach for the transduction of chiral information is based on the use of electrodes modified with chiral selectors (Niu et al., 2020, Zhang et al., 2018, Yu et al., 2015, Zagotiva et al., 2021). Different conventional electrochemical systems have been designed for the study of chirality in solution, using as chiral recognition elements e.g. metal-organic frameworks (Guo et al., 2020, Wei et al., 2021, Zhou et al, 2021), β-cyclodextrin (Munoz et al., 2018,

Li et al., 2021), molecular imprinted electrodes (Iacob et al., 2015, Ratautaite et al., 2022, Wattanakit et al., 2020) or inherently chiral oligomers (Arnaboldi et al., 2015). In particular, the latter has gained considerable attention since the enantiodiscrimination of chiral analytes is related to the energetically different diastereomeric interactions between the chiral surface and the molecular target in solution, which leads to thermodynamic differences in oxidation potential values (Sannicolo et al., 2014, Arnaboldi et al., 2018). Recently, the outstanding enantioselectivity of these materials has been coupled to the wireless nature of bipolar electrochemistry (BE), in order to develop easy and straightforward read-out schemes of chiral information (Arnaboldi et al., 2020, Arnaboldi et al., 2021, Salinas et al., 2022, Salinas et al., 2021). BE is a powerful tool to produce asymmetric electroactivity on a conducting object in the presence of an external electric field (ε) (Fosdick et al., 2013, Koefoed et al., 2017, Bouffier et al., 2021, Salinas et al., 2022, Saqib et al., 2015). Under these conditions a polarization potential difference (ΔV) is generated at the extremities of a conducting object. In the presence of electroactive species, the object behaves as a bipolar electrode (BPE) when ΔV exceeds the thermodynamic threshold potential (ΔVmin), triggering redox reactions at each extremity of the device. Such wireless approach has been used in electrosynthesis (Shida et al., 2019, Bortnikov et al., 2022), electrochemical separation (Mavre et al., 2010), electroanalysis (Karimian et al., 2019, Rahn et al., 2021, Zhai et al., 2016, Zhang et al., 2014, Gao et al. 2018) and for motion generation (Han et al., 2018, Sheng Moo et al., 2018). In this context, a promising approach is to take advantage of the asymmetric electroactivity generated by BE, in order to produce wireless rotation. Such kind of dynamic behavior opens up new possibilities for analytical applications, since the speed or angle of rotation can be used as an easy and straightforward readout of chemical information. Such a dynamic response, in comparison with the previously mentioned electromechanical readouts, avoids the use of Ppy as substrate, which after several actuation cycles, might lose its mechanical stability. Wireless rotation can be simply achieved by exposing the BPE to an external magnetic field, however this is limited to the use of ferromagnetic electrodes (Dauphin et al., 2020, Dauphin et al., 2019). An alternative design of fully wireless electrochemical rotors is based on a bubble accumulation/release mechanism (Loget et al., 2011, Eßmann et al., 2017). However, in these systems the induced motion is irregular, due to the random detachment of bubbles, which limits its possible use as read-out of chemical information in solution. An interesting approach is to take advantage of the ion flux, parallel to the BPE, associated with the electron flow from the anodic to the cathodic extremity of the device. For example, the asymmetric proton flux produced during the reduction and oxidation of oxygen and L- or D-3,4-dihydroxyphenylalanine (L- or D-DOPA), respectively, has been used to develop a dynamic readout strategy of molecular chirality in solution (Arnaboldi et al., 2021).

Herein, we report a wireless electrochemical rotor where the angle of rotation is intimately related to the chirality of the molecules present in solution. The proposed system takes advantage of a localized electrophoretic mechanism, induced by the redox reactions at each extremity of the BPE and the high enantioselectivity of inherently chiral oligothiophenes, deposited on the rotor, with respect to the enantiomers of a chiral analyte present in solution. The synergy of these ingredients allows the design of a novel dynamic device, coupling the reduction of protons with the localized enantioselective oxidation of a chiral probe on the inherently chiral oligomers. The generated charge-compensating asymmetric proton flux along the BPE induces an enantiospecific clockwise or anticlockwise rotation. It is important to highlight that the present work takes advantage of the synergy between different approaches developed in our group (Arnaboldi et al., 2020, Arnaboldi et al., 2021a, Arnaboldi et al., 2021b), in which chiral recognition is combined with an electrophoretic mechanism, that is then exploited to induce different types of motion. In the present contribution, the localized electrophoretic mechanism together with the enantioselectivity of the oligomers allows

for the first time designing a novel type of readout device, for which the angle of a rotor is directly correlated with the chirality of the probe in the solution.

2. Experimental

2.1. Reagents

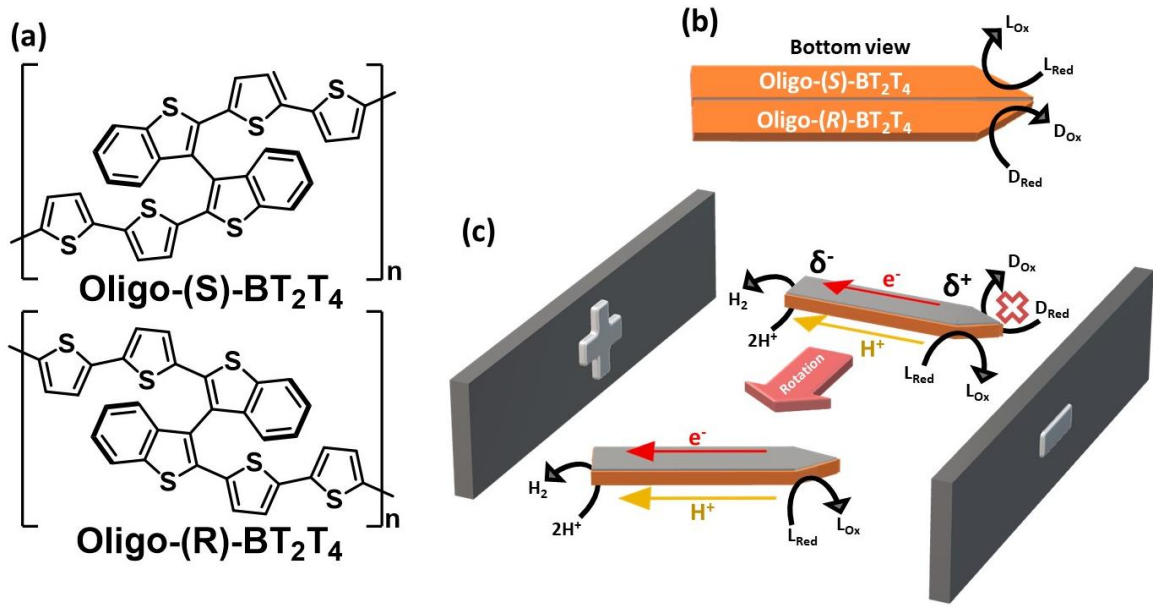
Acetonitrile (ACN, Sigma-Aldrich), LiClO4 (Aldrich, 99%), D- and L-3,4-dihydroxyphenylalanine (Aldrich, ≥99%), D- and L-tryptophan (Aldrich, ≥99%), Pt foil (Goodfellow, 99.95%, 0.1 mm of thickness) and glassy carbon beads (Alfa Aesar, d = 200-400 µm) were used as received. Enantiopure (R)- or (S)-2,2′-bis(2-(5,2′-bithienyl))-3,3′-bithianaphthene ((R)-BT2T4 and (S)-BT2T4, Scheme 1a) were synthesized following a published method (Sannicolo et al., 2014). All solutions were prepared with deionized water (MilliQ Direct®)

2.2. Electropolymerization of enantiopure (R)-BT2T4 and (S)-BT2T4.

A bifunctionalized oligo-(R) and oligo-(S)-BT2T4 was designed, in order to break the symmetry of the device. In such a system the oxidation of a given enantiomer takes place selectively only on one half of the anodic extremity of the bipolar electrode where the oligomer with the matching appropriate chirality is immobilized. This produces an asymmetric proton flux. The electrogeneration of the enantiopure oligo-(S)-BT2T4 and oligo-(R)-BT2T4 was carried out on the surface of a Pt foil acting as a working electrode in a conventional three-electrode electrochemical cell containing a 0.1 M LiClO4/ACN solution and 1 mM of the (R)- or (S)-enantiopure monomers. The counter electrode was a platinum mesh together with a Ag/AgCl reference electrode. Oligo-(S)-BT2T4 and oligo-(R)-BT2T4 were synthesized by cyclic voltammetry, v = 0.1 V s-1, Ei = 0.0 V and Ef = 0.9 V vs Ag/AgCl during 20 cycles. After the deposition of the (S)-enantiopure oligothiophene, the modified Pt foil was rotated 180° to allow the deposition of the oligothiophene with the opposite configuration (Scheme S1). Then, the bifunctional electrode was cut to obtain a device with a rectangular shape with approximate final dimensions of 1.1 cm length by 0.2 cm width (Scheme 1b). In order to distinguish more clearly both extremities, the anodically polarized end was tailored with an arrow shape for the rotation experiments. Finally, the upper face of the rotors (mono and bifunctional) was cleaned carefully with acetone to remove completely the oligomers. For the concentration dependence study and the enantiomeric excess measurements, monofunctional oligo-(S)- and oligo-(R) rotors were used.

2.3. Bipolar electrochemistry measurements

For the wireless recognition, the bifunctional rotor was placed at the center a conventional bipolar cell, with the oligomer-modified face in contact with the aqueous solution. Two Pt covered glass plates were positioned as feeder electrodes at the extremities of the cell at a distance of 7 cm. Dynamic bipolar recognition was carried out in an aqueous solution containing 5 mM LiClO4 in the presence of 5 mM L- or D-DOPA. For concentration dependence experiments, 1.7, 2.5, 5, 7, and 10 mM L-DOPA solutions were analyzed. For the double recognition system, the enantiopure monofunctional oligo-(R)- and oligo-(S) rotors were placed in parallel at the center of a bipolar cell. Double dynamic bipolar enantiomeric recognition was carried out in an aqueous 5 mM LiClO4 solution in the presence of a 50:50 and 10:90 mixture of L-:D-DOPA, or 50:50 and 30:70 mixture of L-:D-Tryptophan, at a constant applied electric field (0.56 V cm-1). Experiments were monitored by using a charge-coupled device (CCD) camera (CANON EOS 70D, Objective Canon Macro Lens 100 mm 1:2.8). Images were processed with ImageJ software. The readout time for all the experiments was 3 sec.



Scheme 1. (a) Chemical structures of the two enantiomers of BT2T4 oligomers. (b) Bottom view of the bifunctionalized bipolar rotor. (c) Schematic illustration of the bifunctionalized rotor in an upside-down configuration, with a representation of the associated chemical reactions and the charge-compensating asymmetric proton flux. In such bifunctionalized devices, the oxidation of an antipode takes place selectively only on one half of the anodic extremity of the BPE. The orange and grey parts stand for oligo-BT2T4 and Pt foil, respectively. The distance between the feeder electrodes is 7 cm and the length of the bipolar object is approximately 1.1 cm.

3. Results and discussion

The dynamic behavior of the bioanalytical rotors was evaluated by placing the bifunctional device at the center of a bipolar cell at the air/water interface of a 5 mM LiClO4 solution, in the presence of the enantiomers of a chiral model analyte, D- or L-DOPA. In order to avoid lateral or linear motion of the BPE, the device was supported by a thin glass tube axis, fixed at the bottom of the cell. Theoretically, when a high enough electric field is applied, an asymmetric polarization of the BPE occurs, inducing the corresponding redox reactions. Under these conditions the oxidation of the chiral probe and the reduction of protons take place producing a charge-compensating proton flux along the BPE (Scheme 1b). However, in order to induce rotation, a double break of symmetry of the system is needed. The first break of symmetry is related to the design of the BPE. Due to the diastereomeric interactions between the inherently chiral oligomer having a certain configuration, (R) or (S), and the matching chiral probe in solution, the oxidation of the latter takes place selectively only on one half of the anodic extremity of the BPE, producing an asymmetric proton flux (Schemes 1c and S1b) at one edge of the object. Thus, according to the spatial position of the inherently chiral oligomer involved in the enantioselective oxidation, a clockwise or a counterclockwise rotation can be generated. In order to illustrate the formation of the asymmetric proton flux initiated at the anodically polarized part of the BPE, the double modified bipolar rotor was immobilized at the air/water interface of a 5 mM LiClO4, 5 mM L-DOPA solution (Figure S1). Glassy carbon beads (d = 200-400 µm) were positioned at the anodic extremity of the bifunctionalized BPE as tracking particles. Under a constant electric field (0.7 V cm-1) a circular hydrodynamic pattern can be observed; only on the oligo-(R) side of the BPE, where the oxidation of D-DOPA enantiomer is favored (Figure S1). The second break of symmetry involves the position of the support axis along the BPE. Since the proton flux is generated at the object's anodic end, the torque force that produces rotation decreases when the support axis is positioned closer to this extremity. In order to illustrate

this phenomenon, the dynamic behavior of two bipolar rotors, with the support axis located at different positions, was monitored in a 5 mM LiClO4, 5 mM L-DOPA solution at a constant electric field of 0.7 V cm-1 (Figure S2). The BPE with the support axis close to the cathodic extremity shows a pronounced anticlockwise rotation, whereas the device with the support axis close to the anodic end leads to no significant rotation. Therefore, for all the bipolar enantiomeric recognition measurements, the support axis was positioned at the cathodic extremity of the BPE.

In order to further characterize the important parameters governing the rotation mechanism, we have studied the influence of the applied electric field on the amplitude of the rotation angle. A bifunctionalized bipolar rotor was placed at the center of a bipolar cell containing a 5 mM LiClO4, 5 mM of D- or L-DOPA solution. Once again, under these conditions the triggered redox reactions that occur at the two extremities of the bipolar electrode are the oxidation of DOPA enantiomers and the reduction of protons. The reduction of protons takes place under our experimental conditions at the surface of the platinum extremity of the bipolar rotor with almost no overpotential with respect to the thermodynamic standard potential (0 V vs NHE) and it is thus the kinetically most favorable process. In the presence of D-DOPA, the chiral recognition device shows a clockwise rotation, since the asymmetric proton flux is produced only at the side modified with the oligo-(R)-BT2T4 (Figure 1a and Video S1). In addition, a continuous increase of the rotation angle as a function of the applied electric field is observed. On the contrary, in the presence of L-DOPA, an anticlockwise rotation is obtained, since the oxidation of the chiral probe occurs only at the side modified with the oligo-(S)-BT2T4 (Figure 1b and Video S2). Such an opposite dynamic behavior is attributed to the different thermodynamic interactions between the inherently chiral oligomers and the two enantiomeric probes. It has already been demonstrated by differential pulse voltammetry experiments (DPV) that the oxidation of DOPA antipodes on an enantiopure oligomer surface occurs at two significantly different potential values (i.e., 0.3 V and 0.9 V vs Ag/AgCl, for L- and D-DOPA, respectively) (Arnaboldi et al., 2020, Arnaboldi et al., 2021). Such a thermodynamic difference can be exploited in bipolar experiments to transform exclusively one of the two enantiomers of DOPA at the BPE if the polarization potential difference is tuned properly.

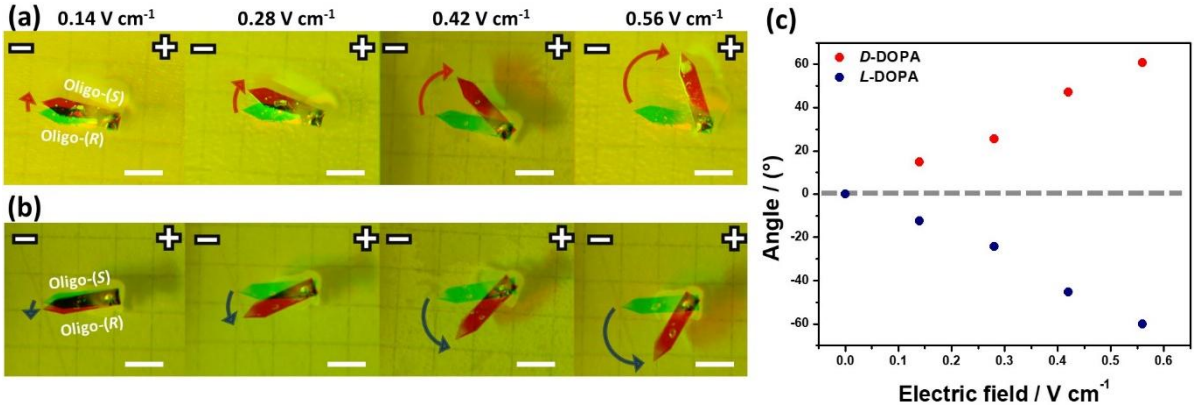


Figure 1. Optical pictures of the dynamic response of a bifunctional rotor, recorded during the electrooxidation of (a) D- or (b) L-DOPA, at different applied electric fields (indicated in the figure). Initial and final positions of the BPE during wireless rotation are indicated in green and red, respectively. Scale bar 5 mm. (c) Angle of rotation as a function of the applied electric field for a double modified bipolar rotor in a 5 mM LiClO4 solution containing 5 mM D- or L-DOPA (red and blue dots, respectively). The readout time for all the experiments is 3 sec.

By plotting the angle of rotation, recorded for the clockwise and anticlockwise motion, as a function of the applied electric field, it is possible to obtain a specular linear tendency for the oxidation of

both DOPA enantiomers (Figure 1c). This angle is intimately related to the polarization potential difference ΔV between the two extremities of the BPE when the electric field is applied. The generated ΔV can be expressed as $\Delta V = \varepsilon l \cos \alpha$, where l is the length of the bipolar rotor and α is the angle with respect to the electric field lines. Since the overall polarization of the object is the driving force for the rotation, in theory the bipolar rotor should stop its rotation when ΔV drops below the thermodynamically defined ΔVmin. In order to confirm this hypothesis, the theoretically generated polarization potential difference as a function of the angle of rotation (ΔVtheo) was calculated for different applied electric field values (Figure S3, see supporting information for more details). As expected, the maximum ΔVtheo, for all applied electric field values, is obtained when the BPE is oriented orthogonal with respect to the feeder electrodes. This value decreases as the angle of rotation increases. By calculating the corresponding experimentally observed polarization potential difference (ΔVexp), it is possible to identify the ΔVmin required to power the rotation, being approximately 300 mV (Figure S3, red dots). This value is in good agreement with the theoretical ΔVmin, calculated from the reported peak potential for the oxidation of DOPA (300 mV) and the standard reduction potential of protons on Pt (0 V) (Arnaboldi et al., 2021).

After demonstrating the possibility of chiral discrimination by a dynamic on-off response, the next step was to evaluate whether this approach allows a quantitative analysis of chiral molecules. Therefore, the amplitude of the rotation angle was measured as a function of the enantiomer concentration. In order to simplify the experimental methodology for bioanalytical applications, these experiments were carried out with a monofunctional rotor (Schemes S1a). Five L-DOPA concentrations were analyzed (1.7, 2.5, 5, 7 and 10 mM) with the monofunctionalized oligo-(S) rotor, by applying a constant electric field (0.56 V cm-1) (Video S3). As it can be seen, a plot of the angle of rotation as a function of L-DOPA concentration reveals a linear correlation (R2 = 0.98) (Figure 2) in the selected range of concentrations. This result illustrates the possible use of such bipolar rotors as bioelectroanalytical tool for the quantitative measurement of chiral probes in solution.

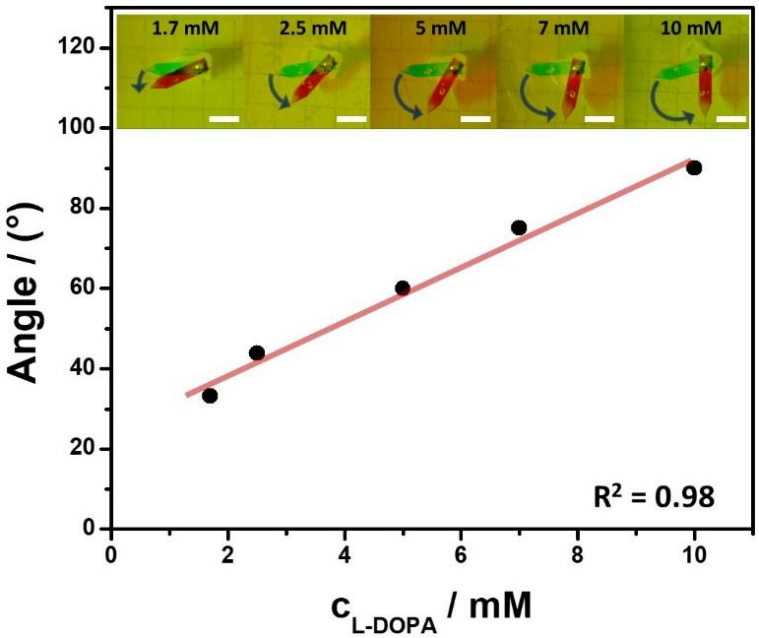
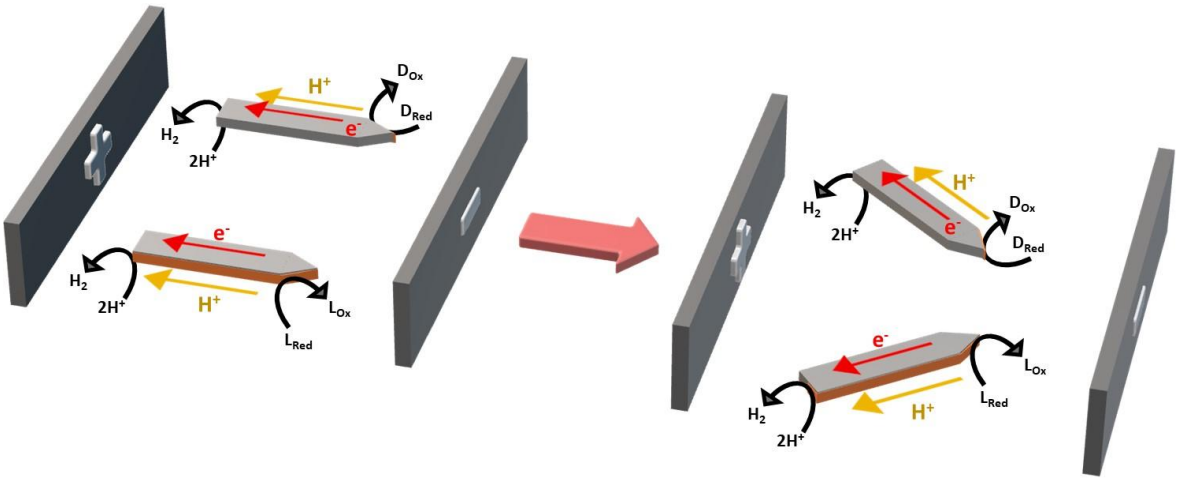


Figure 2. Angle of rotation as a function of L-DOPA concentration obtained for the electrooxidation of L-DOPA in a 5 mM LiClO4 solution at a constant applied electric field (0.56 V cm-1). Inset: optical pictures of the dynamic response of the monofunctional oligo-(S) rotor, at different L-DOPA concentrations. Initial (green) and final position (red) of the BPE during wireless rotation. Scale bar 0.5 cm. The readout time for all the experiments is 3 sec.

Based on these results, the possible simultaneous quantification of both DOPA enantiomers with a double bipolar rotor system was studied. In this case, two monofunctionalized rotors, oligo-(R)- and oligo-(S), were placed parallel to each other at the center of a bipolar cell containing a 5 mM LiClO4 aqueous solution (Schemes 2 and S1a). Theoretically, since the oligothiophenes are deposited on the opposite sides of the bipolar rotors, in the presence of both chiral probes, at a constant electric field (0.56 V cm-1), both devices should rotate in a clockwise and anticlockwise direction, and their angle of rotation should be correlated with the concentration of the corresponding enantiomer. For this proof-of-concept, ratios of 50:50 and 10:90 L-:D-DOPA have been chosen. As can be seen, for the racemic mixture, the dynamic response of both bipolar rotors is perfectly specular, showing a clockwise and anticlockwise rotation for the (S) and (R) bipolar rotor, respectively, with an angle of rotation that correlates with the enantiomeric ratio in solution (Figure 3a). However, when the measurement is carried out in a 10:90 solution, the (R) bipolar rotor presents a more pronounced rotation angle than the (S) device (Figure 3b and Video S4). The rotation angles for the oxidation of D- (80.9°) and L-DOPA (9.9°) correlate with the 10:90 L-:D-DOPA ratio present in solution.



Scheme 2. Schematic representation of the double monofunctional rotor set-up used for the simultaneous quantification of enantiomers with a representation of the associated chemical reactions and the charge-compensating asymmetric proton flux. The orange and grey parts stand for the BT2T4 oligomers and Pt foil, respectively. The distance between the feeder electrodes is 7 cm and the length of the bipolar object is approximately 1.1 cm.

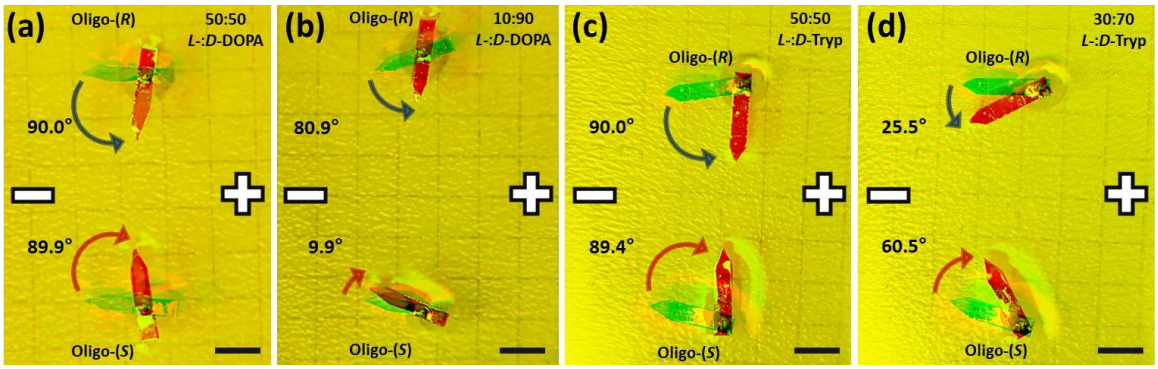


Figure 3. Optical pictures of the dynamic response of two monofunctional rotors, oligo-(R) and oligo-(S), obtained during the respective bipolar electrooxidation of enantiomeric mixtures; L-:D-DOPA ratios (a) 50:50 and (b) 10:90, and L-:D-Tryp ratios (c) 50:50 and (d) 30:70, in a 5 mM LiClO4 solution.

Initial (green) and final position (red) of the BPE during wireless rotation. Scale bar 0.5 cm. The readout time for all the experiments is 3 sec.

After these first proof-of-principle experiments, the possibility of replacing DOPA with an alternative chiral bioanalyte has been explored in order to verify the general validity of the proposed mechanism. The dynamic response of the double bipolar rotor system was evaluated in the presence of both enantiomers of Tryptophan, with ratios of 50:50 and 30:70 L-:D-Tryp at a constant electric field (0.56 V cm-1). In this case, the previously reported DPVs have shown that the diastereomeric interaction between the (S)-oligomer and the D-Tryp is thermodynamically more favorable (-0.3 V and 0.4 V vs Ag/AgCl, for D- and L-Tryp, respectively), presenting a peak to peak separation between D- and L-antipodes of approximately 700 mV (Salinas et al., 2021). Both monofunctionalized rotors were placed parallel to each other at the center of a bipolar cell containing an aqueous 5 mM $LiClO_4$ solution. As expected, in the racemic mixture, the dynamic response of both bipolar rotors is perfectly specular, showing the characteristic clockwise and anticlockwise rotation for the (S) and (R) bipolar device, respectively. Furthermore, the angle of rotation correlates with the ratio of both enantiomers in solution (Figure 3c). When the measurement is carried out in an unbalanced solution, the (S)-bipolar rotor presents a larger amplitude of rotation than the (R) device (Figure 3d), with values of the rotation angle, for the oxidation of L-Tryp (25.5°) and D-Tryp (60.5°), that are in agreement with the 30:70 L-:D-Tryp ratio in solution.

4. Conclusions

In conclusion, an original bioanalytical system has been designed by coupling in a bipolar electrochemical set-up the reduction of protons with the spatially localized enantioselective oxidation of a chiral probe. These reactions occur on the surface of a mobile bipolar electrode, modified in an asymmetric way with inherently chiral oligomers. Rotational motion of the bipolar electrode is triggered by a charge-compensating asymmetric proton flux along only one edge of the object, resulting in an enantiospecific clockwise or anticlockwise rotation as a function of the stereoisomer present in solution. The amplitude of the rotation can be controlled by the applied electric field, allowing to selectively oxidize only one of the two enantiomers of the biological model analyte DOPA. In addition, the angle of rotation is found to be directly proportional to the analyte concentration. In addition, this concept of wireless enantioselective rotation has been successfully used for the quantification of the ratio between the two DOPA antipodes present in solution. The approach is generic, since analog dynamic bioanalytical information can be also obtained with other chiral analytes, as has been exemplified for the amino acid tryptophan. In addition, the interplay between the functionalized rotors, the chiral analytes and the applied electric field, allows a fine-tuning of the specificity of the analytical system. The versatility of the proposed system opens up the possibility to use it as a straightforward analytical tool for the qualitative and quantitative discrimination of different redox active chiral probes.

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Graphical abstract


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