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Hybrid light-emitting devices for the straightforward read-out of chiral information

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Keywords: Bipolar electrochemistry, chiral recognition, wireless light emission, conducting polymers

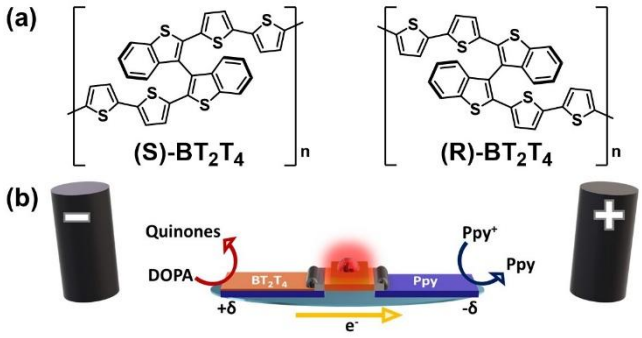
1. Introduction

Electrochemical concepts are an interesting alternative for the discrimination and quantitative analysis of chiral molecules.1-7 For example, electrodes, chemically modified with conducting polymers, have been proposed for chiral recognition and quantification in classic electrochemical setups.8 Among different electrochemical approaches, bipolar electrochemistry (BPE) has gained considerable attention in recent years with respect to analytical applications and for materials science due to interesting features related to its wireless nature.9-15 In a classic BPE experiment, anodic and cathodic reactions can be driven simultaneously on a single wireless electrode, due to the presence of an external electric field. The concept has been successfully used as a transduction mechanism for recovering analytical information, especially also in the context of chiral recognition. For example, changes in the mechanical properties of doped polypyrrole (Ppy) have been coupled with the oxidation of an enantiomer on the surface of an enantioselective material.16-18 More specifically, chiral mesoporous platinum-Ppy hybrids films have been used as enantioselective actuators.16 However, this approach relies on relative changes in current amplitude, which does not allow the analysis of enantiomeric mixtures. Recently, bipolar electromechanical read-out has also been achieved by coupling Ppy actuation with enantioselective recognition at an oligomeric compound, belonging to one of the several families of polymers endowed with inherent chirality.17,18,19 In this case, chiral discrimination is based on the difference in oxidation potentials, caused by energetically different interactions between the chiral surface and the probe in solution.20-22 During the BPE experiment the reduction of Ppy is coupled with the selective oxidation at the inherently chiral oligomers. When an external electric field is applied, the chiral bipolar object present in solution is polarized, leading to a preferential oxidation of one of the two antipodes.17,23,24 Consequently, a mechanical deformation of the conducting polymer is detected and measured only when the right enantiomer of the deposited oligomer reacts selectively with the matching molecular probe in solution. Although, this type of actuation constitutes an efficient read-out, the development of even easier and more straightforward analytical detection schemes is an interesting challenge.

A purely optical read-out of electrochemical activity, based on color changes or light emission, allows low-cost measurements of different species, chemical imaging and the design of parallel analytical arrays.25-28 An interesting option in this context is the use of light emission diodes (LED) for direct visualization of electrochemical processes.29,30 In general the analytical information is encoded by the electric current and the concomitant light emission, ensured by a direct electrical connection.31 An alternative approach is the wireless operation of such devices, either by coupling thermodynamically spontaneous reactions to the terminals of the LED,32 or by using BPE.33 In recent years, BPE has been used to power micro-LED swimmers,34,35 rocket-like LED devices,36 magnetically-stirred macro-LEDs37 or LED-based light emitting crawlers.38 The oxidation and reduction reactions, simultaneously occurring at the opposite extremities of the bipolar electrode lead to an electron flow through the integrated LED, causing a switching-on of the device.

Here we present a static bipolar on-off system, obtained by coupling three main ingredients: i) an inherently chiral oligomer, which is the site of enantioselective oxidation; ii) pristine Ppy, where the reduction reaction occurs; iii) and a micro-LED for the light emission (Scheme 1). When a sufficiently

high electric field is applied, the two redox reactions generate a selective electron flow, causing light emission from the micro-LED. The device is placed in a solution containing the enantiomers of a chiral model analyte, L- or D-3,4-dihydroxyphenylalanine (L- or D-DOPA). The selectivity of the process is based on the diastereomeric interactions between the inherently chiral oligomer and one of the stereoisomers.39 Thus, the LED will switch on only if the right enantiomer is in solution, allowing an easy and straightforward discrimination.



SCHEME 1. (a) Chemical stuctures of the inherently chiral oligomers (b) Schematic illustration of the bipolar set-up used for the wireless discrimination of D- and L-DOPA based on light emission by the LED. The orange part stands for the BT2T4 oligomer, whereas dark blue symbolizes the Ppy film. Light blue illustrates the air/water interface. The distance between the feeder electrodes is 5 cm and the length of the bipolar object is 1.8 cm.

2. Materials and Methods

2.1. SYNTHESIS OF THE POLYPYRROLE FILM

The polypyrrole film (Ppy) was synthesized according to previous reports (Scheme S1).16-18 In brief, electropolymerization of pyrrole (Sigma Aldrich) was carried out in an aqueous solution of 0.25 M dodecylbenzene sulfonate (DBS, Sigma Aldrich) and 0.2 M monomer by chronopotentiometry applying 4 mA for 1.5 hrs. Two gold coated glass slides were used as working and counter electrode, respectively and Ag/AgCl as a reference electrode. After polymerization, the polymer coated substrate was washed with water, dried and used for further oligomerization of chiral monomer i.e. 2,2’-bis[2-(5,2’-bithienyl)]-3,3’-bithianaphthene (BT2T4). All solutions were prepared with deionized water (MilliQ Direct-Q®).

2.2. ELECTROSYNTHESIS OF ENANTIOPURE OLIGO-(R) OR OLIGO-(S)-2,2’-BIS[2-(5,2’-BITHIENYL)]-3,3’-BITHIANAPHTHENE (OLIGO-(R) OR OLIGO-(S)-BT2T4)

Enantiopure oligo-(R) and oligo-(S)-BT2T4 films were obtained following previously optimized procedures,17,18,23,24 in order to avoid changes of the onset potential of the devices, which might occur when changing the film thickness. Electrodeposition was carried out in a 0.1 M LiClO4/ACN solution containing 1 mM of monomer by chronopotentiometry applying 1.5 mA for 40 minutes. The Ppy substrate was used as working electrode together with a Pt mesh and Ag/AgCl as counter and reference electrodes, respectively. After deposition, the oligo-(3,3’-dibenzothiophene)-polypyrrole hybrid films were peeled off from the gold substrate and cut into strips of 7 mm x 3 mm (Scheme S1).

2.3. BIPOLAR CHIRAL RECOGNITION

The bipolar devices were assembled by connecting a strip of the corresponding oligo-(3,3'-dibenzothiophene)-polypyrrole hybrid film and a non-modified Ppy strip to the anode and the cathode of a miniaturized red light-emitting diode (LED, 0603 SMD diode, Wurth Elektronik, 1.60 mm × 0.8 mm) (Scheme 1). In brief, the polymer strips with the desired dimensions and the LED were attached to a glass support using double-sided adhesive tape. Afterwards a small volume of agar silver paint (Agar scientific Ltd.) was employed to establish electric connection between the polymer strips and the LED. The total length of the final bipolar device is 1.5 cm. For the bipolar recognition, the enantiopure oligo-(R)- or oligo-(S)-BT2T4-LED-Ppy device was fixed in the center of a bipolar cell. Two graphite feeder electrodes were positioned at the extremities of the cell at a distance of 5 cm. Light emitting bipolar recognition was carried out in 5 mL of an aqueous solution containing 0.2 M $LiClO_4$ in the presence of 5 mM L- or D-DOPA. For concentration dependence experiments, 1, 3, 5 and 10 mM L-DOPA solutions were analyzed with an oligo-(S)-(3,3'-dibenzothiophene)-LED-Ppy system. For the double recognition system, the enantiopure oligo-(R)- and oligo-(S)-BT2T4-LED-Ppy bipolar devices were fixed in parallel at the center of a bipolar cell. Double light emitting bipolar recognition was carried out in an aqueous 0.2 M $LiClO_4$ solution in the presence of a 2:1 mixture of D:L-DOPA (3.4 mM:1.7 mM, respectively) at a constant applied electric field (3.4 V cm-1). Experiments were monitored by using a CCD camera (CANON EOS 70D, Objective Canon Macro Lens 100 mm 1:2.8). Images were processed with Image J software.

3. Results and Discussion

In order to evaluate the electric field required to switch on the LED integrated in the bipolar electrode, a non-enantioselective Ppy-LED-Ppy system was tested first. The device was placed, at the center of a bipolar cell containing an aqueous 0.2 M $LiClO_4$ solution. When a high enough electric field is applied in such a set-up, the bipolar electrode gets sufficiently polarized at its extremities to induce redox reactions. They primarily lead to the oxidation and reduction of doped Ppy at the anode and cathode of the LED, respectively, powering the light emission of the diode. At low electric field values (below 3 V cm-1) there is not enough driving force to induce these redox reactions, thus the LED remains in the off-state (Figure S1a). Once the electric field reaches a threshold value of around 3 V cm-1, the polarization potential difference with respect to the surrounding solution gets high enough to trigger the oxidation and reduction of doped Ppy at the extremities of the bipolar electrode. This creates an electron flow from the anodic to the cathodic side of the LED and thus concomitant light emission. As can be seen from Figure S1a and b, the emitted light intensity is a function of the applied electric field value.

After the evaluation of the threshold potential, we studied enantiomeric discrimination by using the light emitting chiral recognition device. Two independent oligo-(R)-BT2T4-LED-Ppy devices were placed, separately, at the center of a bipolar cell containing an aqueous 0.2 M $LiClO_4$ solution containing 5 mM of D- or L-DOPA. In this case the triggered redox reactions that occur at the extremities of the bipolar electrode are: i) the oxidation of DOPA and ii) the reduction of doped-Ppy (Scheme 1). In the presence of D-DOPA, the threshold potential of the (R) chiral recognition device is slightly lower (2.8 V cm-1 ± 0.1 V cm-1), than the one observed for the non-modified device, whereas in the presence of L-DOPA the potential shifts to significantly higher anodic values (above 4 V cm-1 ± 0.1 V cm-1) (Figure 1a and b). Thus, the oligo-(R)-BT2T4-LED-Ppy selectively recognizes D-DOPA, which results in a strong light emission, whereas no light is observed when L-DOPA is in solution. The specular behavior was observed when the oligo-(S)-BT2T4-LED-Ppy was used in the presence of 5 mM D- or L-DOPA. (Figure S2a and b). The difference in threshold potential observed in both cases is attributed to a change in diastereomeric interactions between the inherently chiral oligomer and the two enantiomeric probes. Previous work has already demonstrated the possibility to discriminate

chiral analytes in terms of a difference in peak potentials recorded by differential pulse voltammetry.17,18 In fact, the peak difference obtained for the oxidation of the two DOPA enantiomers on an oligomer modified surface with a given chirality was found to be between 200 and 300 mV. Such a high thermodynamic difference in a traditional electrochemical set-up translates directly into a shift of the applied electric field observed in BPE. Thus, in the presence of one specific oligomer the right chiral probe is oxidized exclusively. In addition to the recognition achieved by the difference in threshold potential, a considerable change in light intensity is also observed at higher electric field values. For example, when D-DOPA is electrooxidized on the surface of the oligo-(R)-BT2T4, a much stronger light emission was obtained, in comparison with the electrooxidation of L-DOPA with the same device. A similar but opposite behavior is obtained when oligo-(S)-BT2T4 is used to oxidize L- or D-DOPA. Although at very high electric field values both enantiopure oligomers can induce oxidation of a given probe molecule, the presence of the right chiral probe promotes the oxidation kinetics on the oligomer with the right configuration, thus providing a higher current across the LED and causing an increase in light intensity. This is also consistent with the difference in bending rates at high electric field, observed in previous works.17

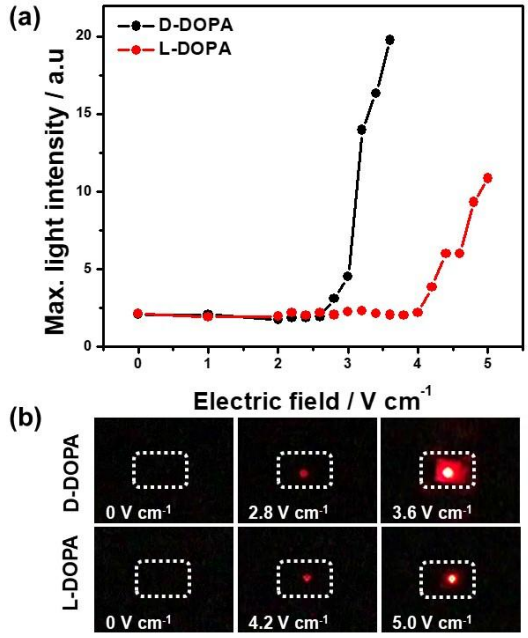


FIGURE 1. (a) Maximum light intensity as a function of the applied electric field for two independent oligo-(R)-BT2T4-LED-Ppy bipolar electrodes in an aqueous solution of 0.2 M LiClO4 containing 5 mM D-DOPA or L-DOPA (black and red dots respectively). (b) Optical pictures of the oligo-(R)-BT2T4-LED-Ppy bipolar electrodes at different applied electric fields, (indicated in the figure) in the presence of D- or L-DOPA, respectively. The readout time for all the experiments is 20 sec.

After demonstrating the possibility of chiral discrimination by an on-off light emission, the next step was to evaluate whether quantitative analysis of chiral molecules can be achieved. The light intensity was measured as a function of the enantiomer concentration. Four L-DOPA concentrations were analyzed (1, 3, 5, 10 mM) with an oligo-(S)-BT2T4-LED-Ppy bipolar device by applying a constant electric field (3.4 V cm-1). For each concentration, the average of the light intensity over 15 seconds has been calculated. This is necessary to take into account fluctuations of the light intensity during the experiment, in particular at low concentrations, probably caused by a fast consumption of the analyte in the bipolar cell. Nevertheless, the plot of the average light intensity as a function of L-

DOPA concentration reveals a linear correlation (R2= 0.993) (Figure 2). This illustrates the possible use of such hybrid polymer-microelectronic devices as an analytical tool for the qualitative and quantitative measurement of chiral probes.

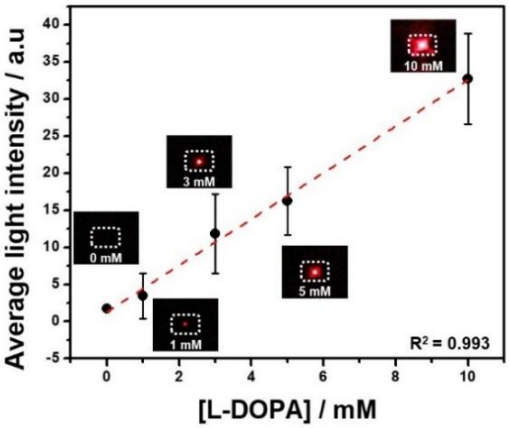
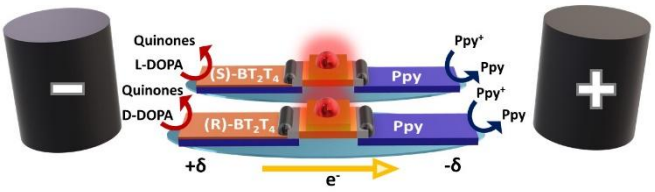


FIGURE 2. Average light emission as a function of L-DOPA concentration measured by the enantioselective oxidation of L-DOPA on a (S)-BT2T4-LED-Ppy bipolar device, in a 0.2 M LiClO4 solution at a constant applied electric field (3.4 V cm-1). Inset; Optical pictures of the (S)-BT2T4-LED-Ppy bipolar device at different L-DOPA concentrations (indicated in the figure). The error bars represent the variation of the light intensity over 15 seconds of experiment.



SCHEME 2. Illustration of the double light-emitting bipolar recognition of DOPA enantiomers. The orange part stands for the BT2T4 oligomers, whereas blue symbolizes the Ppy film. The distance between the feeder electrodes is 5 cm and the length of the bipolar electrode is 1.8 cm.

Finally, the possibility to simultaneously detect both DOPA enantiomers with a double light-emitting device was studied. In this case, oligo-(R)- and oligo-(S)-BT2T4-LED-Ppy devices were placed parallel to each other in the center of a bipolar cell containing an aqueous 0.2 M LiClO4 solution (Scheme 2). In theory, in the presence of both chiral probes, at a constant electric field (3.4 V cm-1), both devices should switch-on and their light intensity should be correlated with the concentration of the corresponding enantiomer. For this measurement, a ratio of 2:1 D:L-DOPA (3.4 mM:1.7 mM, respectively) has been chosen for a proof-of-principle experiment. The light intensity was measured once the steady state light intensity was reached (50 seconds). As it can be seen from the optical picture (Figure 3), under these conditions, the oligo-(R)-BT2T4-LED-Ppy device emits a brighter light than the (S)-BT2T4-LED-Ppy. When comparing the steady state light intensity for the oxidation of D- (27.7 a.u) and L-DOPA (15.4 a.u), the values seem to be coherent with the 2:1 D-DOPA/L-DOPA ratio present in solution. At this time scale the high light intensity can be caused by the presence of an additional redox process powering the devices. A first possibility is the oxidation of non-chiral redox compounds produced during the decomposition of DOPA, i.e. dopamine. Thus the response of the oligo-(S)-BT2T4-LED-Ppy device was tested in a 5 mM L-DOPA solution in the absence and presence (2.5 mM) of dopamine (Figure S3). In the presence of dopamine, a slightly lower light intensity, but

with the same onset potential was observed. This is attributed to a possible passivation of the electrode surface caused by the products obtained during the oxidation of dopamine. Thus, the oxidative transformation of such compounds cannot be at the origin of the sustained light emission and only DOPA seems to be involved at the □+ extremity. However, at the □- side of the LED, proton reduction can also occur. Initially it will be combined with the simultaneous reduction of Ppy+, but once all the Ppy+ has been reduced during a first induction period, proton reduction ensure alone the cathodic electron transfer. This is in agreement with the fact that a steady state light emission is only reached once all the Ppy is in the reduced state, and before that rather important fluctuations in light intensity can be observed (see the error bars in Figure 2 for short term experiments). The undoped-Ppy film of the steady state should in principle behave like an insulator, however, we can consider that at the beginning of the bipolar experiment only oligomers with a short chain length are reduced40 due to the large electroactive window of Ppy (from -0.8 V to 0.6 V vs Ag/AgCl).41,42 The remaining long chain Ppy oligomers can then behave like a classic electrode, allowing the proton reduction.41,43 As the oxidation of DOPA is accompanied by a release of protons, which move towards the cathodic side of the LED in order to maintain electroneutrality, this also favors proton reduction at the □- extremity. Therefore, the long-term steady state light emission is powered by the oxidation of DOPA and the reduction of protons. It is worth mentioning that the proton consumption and their transport from the anodic to the cathodic side is beneficial for the light emission, since at too low pH values the protonated form of DOPA might be produced (H4A+) (Figure S4).44 The formation of this species would slow down the redox processes at the bipolar electrode, due to its higher oxidation potential, and thus lead to a decrease in light intensity.

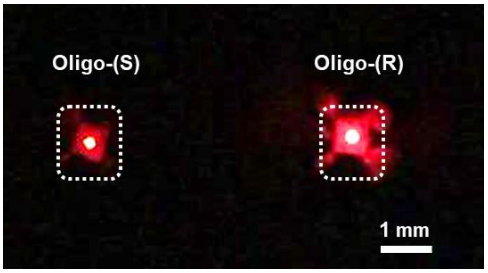


FIGURE 3. Optical picture of the steady state light emission of the double oligo-(S)- and oligo-(R)-BT2T4-LED-Ppy device, recorded in a 0.2 M LiClO4 solution containing a 2:1 ratio of D:L-DOPA (3.4 mM:1.7 mM) at a constant applied electric field (3.4 V cm-1).

3. Conclusion

Light emitting diodes have been used for a straightforward optical readout of chiral information based on bipolar electrochemistry. A hybrid polymer-microelectronic device modified with intrinsically chiral oligomers has been designed. The wireless light emission can be modulated by the applied electric field in order to selectively oxidize only one of the DOPA enantiomers. The average light intensity is found to be directly proportional to the analyte concentration. Consequently, using a double light-emitting device allows determining the ratio between the individual concentrations of each enantiomer and thus opens the possibility to employ this method for the quantification of enantiomeric excess in mixtures of two enantiomers. Finally, the presented simple approach opens up an alternative and complementary strategy for chiral discrimination with respect to more conventional spectroscopic methods such as chiroptical measurements. A standard power supply is the main ingredient necessary to perform these experiments and extract qualitative on/off information. The set-up can be eventually completed with a camera if the light intensity needs to be

quantified in order to calculate enantiomeric excess values. We therefore expect that the concept can be generalized in the future in order to detect in a similar straightforward way other redox active chiral species.

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Supporting information

Additional supporting information may be found in the online version of this article at the publisher's website.

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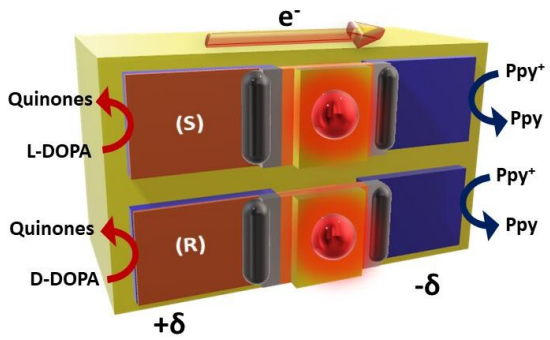
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Graphical Abstract



Electrochemical chiral recognition is transduced in a wireless way into enantioselective light emission from a LED