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Recent advances in bipolar electrochemistry with conducting polymers

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Dedication: This manuscript is dedicated to Prof. Wolfgang Schuhmann at the occasion of his 65th birthday and in recognition of his impressive contributions to the field of electrochemistry

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Abstract: Conducting polymers have been extensively studied due to their potential applications ranging from sensing to energy storage and environmental remediation. They can be easily generated by electrosynthesis and have also very interesting electrochemical features, which have been mostly examined with classic electrochemical approaches. Bipolar electrochemistry offers an attractive alternative way to synthesize and characterize the physico-chemical properties of conducting polymers. The wireless and asymmetric features of bipolar electrochemistry can be advantageously combined with the electroactivity, tunability and easy processability of conducting polymers. This synergy has been increasingly explored in recent years for the controlled electrogeneration, surface modification and characterization of different π-conjugated polymers. This review summarizes the advances in this context and discusses also some unconventional applications such as wireless light-emitting devices and actuators.

1. Introduction

Conducting polymers (CPs) have gained considerable attention due to their interesting applications ranging from sensing and energy storage/conversion to environmental remediation.[1-3] Commonly, classic electrochemical methods are used for the electropolymerization and the characterization of π-conjugated systems.[4-6] These techniques allow the evaluation of the optical, electrical and conformational changes during the charging/discharging process. Nevertheless, in order to open up different new applications for this class of materials, it is interesting to explore simple, fast and straightforward alternative methods. A promising and original option to synthesize and characterize the physico-chemical properties of CPs is the use of bipolar electrochemistry (BE).[7-11] BE is an interesting approach to generate asymmetric electroactivity on a conducting object. Briefly, in the presence of an external electric field (ε), a polarization potential difference (ΔV) is generated at the extremities of a conducting object positioned anywhere in the solution. When electroactive species are also present in the electrolyte, redox reactions can occur at both extremities of the object. Thus, as long as the ΔV exceeds the thermodynamic threshold potential required to trigger both reactions (ΔVmin), the conducting object behaves as a bipolar electrode (BPE). This concept has been extensively used in electrosynthesis,[12] photoelectrochemical cells,[13] electrochemical separation,[14] electrochemical sensing,[15] and optical detection.[16] BE has also been employed for the electrogeneration, modification and characterization of different π-conjugated polymers. The aim of the present review is to discuss the recent advances concerning the synthesis, characterization and possible applications of CPs based on the concept of BE.

2. Bipolar electro-organic synthesis

Chemically modified electrodes with CPs are obtained by electropolymerization of the correspondent monomer. Commonly this can be achieved by using classic electrochemical methods i.e. cyclic voltammetry, chronoamperometry or chronopotentiometry. In recent years anisotropic modification of conducting objects by bipolar electropolymerization,[17-19] electrochemical post-functionalization of CPs[20,21] and elaboration of CP gradients on surfaces[22-24] have been studied. In this section, we summarize the recent findings concerning the different methodologies and applications of bipolar electro-organic synthesis of CPs.

2.1. Anisotropic modification of BPEs

As stated above, when applying an electric field, the BPEs exhibit an asymmetric polarization at their extremities. In the presence of an electroactive monomer, the anodic side of the BPE triggers the electropolymerization of the monomer via its oxidation. This reaction is associated with a reduction, either of the solvent or an additional electroactive probe, on the opposite side. Such redox coupling between the opposite sides of a BPE has been widely used in the frame of electrocatalysis, electrochemical sensing and the optical read-out of the presence of electroactive species, among others also by Schuhmann's group.[25-27] The first example of bipolar electrodeposition of conducting polymers was reported by Bradley et al. In this case, the selective deposition of polypyrrole (Ppy) on the tip of carbon nanotubes was carried out.[28] In a similar approach, modification of gold plates and glassy carbon spheres in acetonitrile or ionic liquids were achieved by coupling the reduction of benzoquinone and the oxidation of pyrrole (Figure 1a).[29] Thinner and smoother films were obtained by performing bipolar electropolymerization in an ionic liquid (Figure 1b). BE was also employed for the electrodeposition of thiophene-3-carboxylic acid on an Au microfilm.[30] Such layers exhibit a higher stability and a better adhesion to the Au surface than the ones electrodeposited by classic electrochemical methods. This can eventually be attributed to the direct coupling of the reduction of quinone and the oxidation of the monomer, which decreases the potential difference required to trigger the electropolymerization, leading to less overoxidized oligomers. Dissymmetrically modified carbon nanofibers and carbon tubes, have been obtained by coupling the reduction of metal salts with the oxidation of the desired monomer.[31,32] For example, polythiophene (PTh) and Ppy have been asymmetrically deposited by coupling the oxidation of the corresponding monomer with the reduction of Au or Cu precursors. Another interesting approach is to produce asymmetric particles by controlling the oxidation state of the CPs. A two-step synthesis of asymmetric polyaniline (PANI)-alginate hydrogels particles has been reported.[33] At first Ca-alginate hydrogel beads were prepared, subsequently loaded with aniline, followed by chemical polymerization. The conducting beads were asymmetrically post-modified by overoxidizing PANI at the anodic side of the beads (Figure 1c, d).

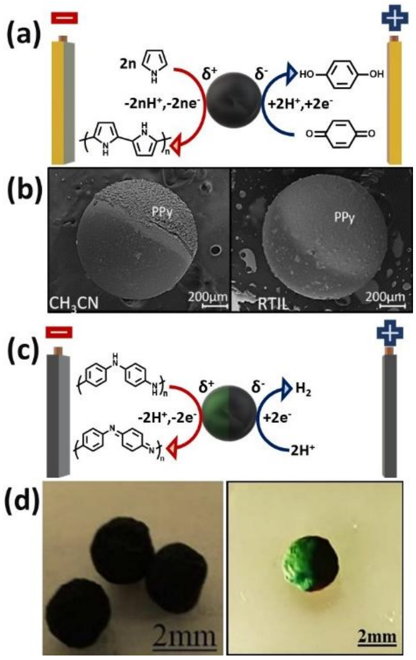


Figure 1. (a) Schematic illustration of the bipolar electrodeposition of Ppy on the surface of a glassy carbon bead BPE, exposed to an electric field between two gold feeder electrodes. The reduction of benzoquinone and the oxidation of Py occur, respectively, at the cathodic and anodic parts of the BPE. (b) Glassy carbon beads obtained by BE carried out in different solvents; (left) in acetonitrile and (right) in a room temperature ionic liquid (RTIL) (1-butyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide). Adapted from reference 29. (c) Schematic illustration of the asymmetric doping of a PANI-alginate hydrogel particle exposed to an electric field between two Pt feeder electrodes. (d) Conducting PANI-alginate hydrogel beads, before (left) and after (right) asymmetrical modification. Adapted from reference 33.

Recently, Inagi's group used alternating current (AC) bipolar electrosynthesis for the growth of CP fibers without the need of porous membranes as a template. For example, 1-D electropolymerization of 3,4-ethylendioxythiophene (EDOT) results in polymer fibers at both extremities of Au wires.[34] A strong variation of the morphology, propagation rates and degree of branching of the wires, as a function of the frequency, solvent and supporting electrolyte was observed. With a similar philosophy, the AC bipolar electropolymerization of EDOT in micro-spaces has been reported. The confined space, where the electropolymerization is carried out, generates linear PEDOT fibers, due to the limited access of the monomer to the end of the fiber.[35] Such an approach has been used for the fast and selective wiring of metal conductors. In addition, this method has been used to produce PEDOT-Pt hybrid fibers[36] and in-plane CP films (Figure 2a, b).[37] Such polymeric patterns present an anisotropic electrical character, due to a difference in doping rate triggered during the AC bipolar electropolymerization[38].

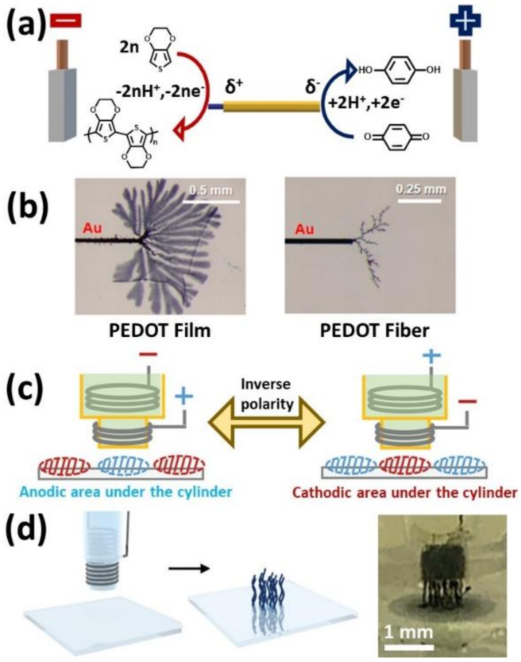


Figure 2. Schematic illustration of the bipolar electrodeposition of PEDOT on the surface of an Au wire BPE exposed to an electric field between two Pt feeder electrodes. The reduction of benzoquinone and the oxidation of EDOT occur, respectively, at the cathodic and anodic sides of the BPE. (b) Optical pictures of a PEDOT film and fiber obtained by applying different frequencies; 5 Hz (left) and 50 Hz (right). Adapted from reference 37. (c) Schematic illustration of the tubular bipolar set-up by inverting the polarity of a BPE surface under AC-conditions. (d) Graphical representation and photograph of a perpendicular PEDOT fiber array on the BPE. Adapted from reference 40.

An interesting alternative is the use of unconventional bipolar set-ups to produce localized surface modifications. For example, local deposition of poly-3-methylthiophene (P3MT) was carried out by using a tubular bipolar electrochemical set-up (Figure 2c).[39] As it can be seen, the shape and arrangement of the feeder electrodes causes the formation of two well-defined polarized areas on the surface of the BPE. This enables localized electropolymerization underneath the negative feeder electrode. Such a set-up allows obtaining well-defined spots of CP with a controlled size.

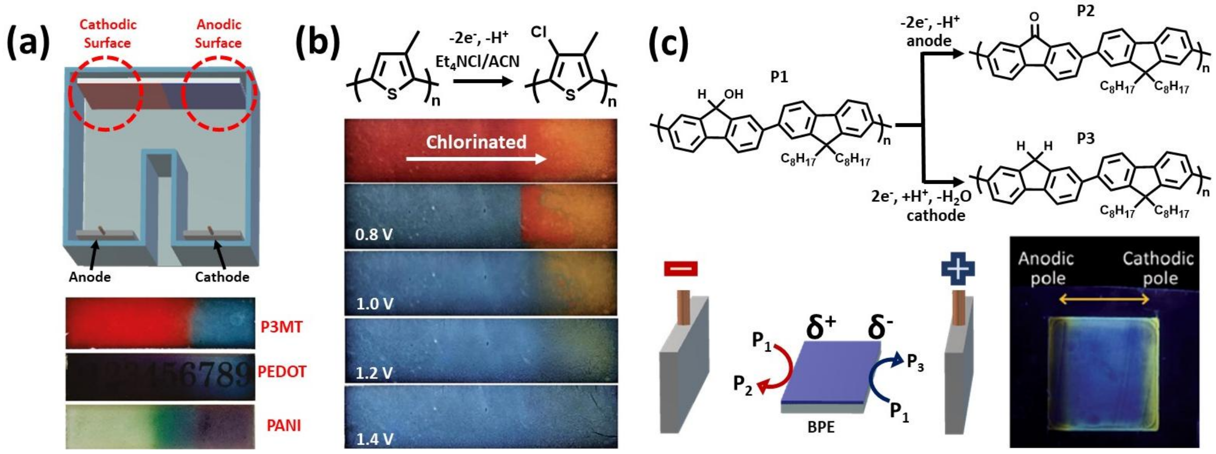


Figure 3. (a) (Top) Schematic illustrations of a U-type electrolytic cell containing the feeder electrodes and the BPE. (Bottom) Optical pictures of doped P3MT, PANI and PEDOT films. Adapted from reference 43. (b) (Top) Electrochemical chlorination reaction of P3MT. (Bottom) Optical pictures of the chlorinated P3MT film before and after anodic doping at different doping potentials (indicated in the figure). Adapted from reference 42. (c) (Top) Anodic and cathodic reactions of co-Poly-(9-fluorenol)-(9,9-dioctyfluorene) (P1). (Bottom) Schematic illustration of the bipolar setup (left) and optical pictures of the CP under UV irradiation with a composition gradient. Adapted from reference 46.

Recently Zhou et al. performed AC bipolar electropolymerization of EDOT in the same bipolar set-up. In this case, a template-free perpendicular growth of PEDOT fiber arrays was achieved (Figure 2d).[40] Also a split templated BPE was used for the synthesis of one-dimensional poly-3-thiophenetrifluoroborate nanowires.[41] In this work, the BPE was composed of two ITO electrodes connected with each other and placed parallel to the feeder electrodes. The electrosynthesis of the nanowires was carried out on an ITO electrode, templated with anodic aluminum oxide.

2.2. Doping gradients

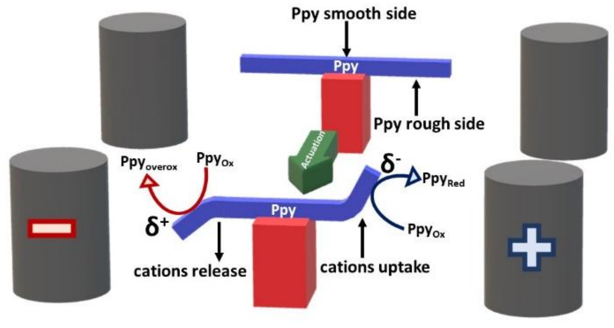
Commonly, in the presence of an applied electric field, a gradient of polarization potential is established along the BPE. Such a potential distribution is of particular interest when π-conjugated polymers are deposited on the surface of the BPE, due to the possible formation of doping gradients. In the presence of an electric field, a neutral CP experiences an asymmetric polarization that follows the shape of the corresponding potential distribution. For example, in a classic BP setup, an approximately linear polarization gradient is obtained, causing also the formation of a linear gradient of charges in or on the polymer matrix. Such a concept of doping gradient was first reported by Inagi et al. for the elaboration of bipolar patterns in CPs. In this work, P3MT deposited on the surface of an ITO electrode, was used as BPE in a U-type bipolar cell. In the presence of an electric field the potential distribution follows a sigmoidal shape, causing the oxidation of the P3MT film on the anodic side of the BPE,[42] evidenced by the characteristic color change from the red (neutral) to the blue (p-doped) state of P3MT. The same concept has been exploited for the formation of doping gradients in PANI and PEDOT (Figure 3a).[43] Furthermore, localized patterns have been obtained with a tubular bipolar electrochemical set-up (Figure 2c), which allows generating extremely steep potential gradients.[44] In addition, such doping regions can be used for the post-functionalization of the polymers. For example, P3MT has been post-functionalized by a localized anodic chlorination of the thiophene ring (Figure 3b) during the p-doping process.[39,42] Following a similar concept, the electro-click reaction between an azide-functionalized PEDOT and substituted alkyne groups with electrogenerated Cu (I) as catalyst was reported.[45] With this method hydrophobicity-hydrophilicity gradients or modification with visible markers were induced. The asymmetric polarization of the BPE, under the appropriate synthetic conditions, can also produce simultaneously two different materials of interest (paired electrochemical synthesis) from a single precursor. In this context, bipolar electrochemical oxidation and reduction of co-Poly-(9-fluorenol)-(9,9-dioctyfluorene) (P1), deposited on a boron-doped diamond plate, was performed (Figure 3c).[46] Under UV-irradiation the emission of the obtained film is gradually changing from yellow to blue and dark orange from the cathodic to the anodic pole of the BPE, confirming the electrosynthesis of P3 and P2.

3. Wireless actuation

Actuation of conducting polymers is an interesting feature induced by the swelling or shrinking of their structure during the charging/discharging process. When a conducting polymer is charged, insertion or release of ions and solvent has to occur in order to retain electroneutrality. This causes swelling or shrinking of the polymer structure. According to the electrochemically stimulated conformational relaxation model (ESCR), four conformational changes occur: swelling, shrinking, compaction and relaxation.[47,48] This model has been studied by Otero’s group, evaluating the coulo-dynamic response during the actuation of Ppy strips in a classic three electrode system.[49-51] Actuation of CPs in a bipolar electrochemical set-up is an interesting alternative, due to the wireless nature of the experiment. This can have tremendous advantages and we summarize recent findings in the following.

3.1. Mechanism of wireless actuation

The simplest mechanism of bipolar electrochemical actuation of CPs involves a double breaking of symmetry. Most importantly, the presence of the electric field causes an asymmetric polarization of the polymer film, which triggers opposite electrochemical reactions at both extremities of the BPE (Scheme 1). As in classic electrochemical experiments, any redox half-reaction in the polymer matrix is accompanied with a change in volume, caused by the uptake or release of ions. Thus in a BE experiment, the polymer film experiences an asymmetric change of volume at both extremities. The side where the swelling or shrinking process occurs depends directly on the initial composition of the polymer film. For example, when an oxidized CP strip is used as BPE, the reduction of the polymer induces a release of anions and therefore shrinking is observed at the cathodic side. Consequently, the overoxidation, which occurs at the anodic extremity, is accompanied by an uptake of anions and leads to swelling. However, when the same CP strip is doped with quite bulky anions, which are trapped inside the polymer matrix, swelling and shrinking take place in the opposite positions, because cation flux is now used to maintain electroneutrality. The second type of symmetry break is related to the intrinsic anisotropy in surface roughness of the polymer film. In a classic electropolymerization experiment, carried out on a flat electrode surface, the obtained film has one smooth face in contact with the electrode and a rough one in contact with the solution. This difference in surface roughness causes an asymmetric uptake or release of ions, which is responsible for an overall bending of the polymer in one direction.



Scheme 1. Schematic Illustration of the mechanism of wireless actuation of a Ppy strip (blue) placed between two feeder electrodes before and after applying an electric field.

For example, when an oxidized Ppy strip, doped with dodecylbenzenesulfonate, is exposed to an electric field, cations enter at the cathodically polarized extremity preferentially from the rough bottom face, thus causing an upward motion (Scheme 1).[52] On the other hand, the cation release at the anodic side, occurring preferentially also through the bottom face, triggers a downward motion (Scheme 1). Thus, the type of actuation can be controlled by the size and concentration of the anions and cations, and the kinetics of the process can be changed by tuning the applied electric field. Finally, a third category of symmetry break relies on the irreversible overoxidation of one side of the polarized polymer film, leading to a local increase in stiffness. This asymmetric mechanical behavior has been observed for oxidized Ppy strips when exposed to an electric field with alternating polarity.[53] During the first polarization pulse, the anodic side of the strip undergoes an irreversible overoxidation. During the subsequent polarization cycles the overoxidized side is electrochemically inactive, leading to a crawling type motion, supported by the reversible bending/stretching process occurring at the still electroactive opposite extremity.

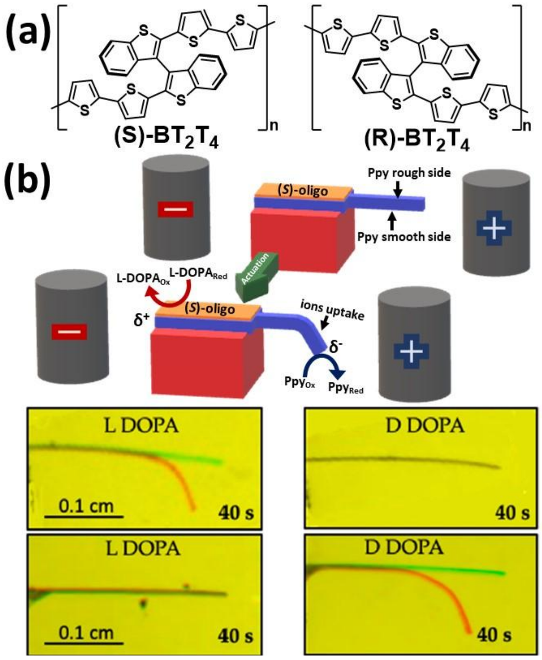


Figure 4. (a) Chemical structures of the two enantiomers of BT2T4 oligomers. (b) (Top) Schematic illustration of the bipolar cell used for wireless discrimination of D- and L-DOPA before and after applying the electric field. The orange part symbolizes the (S)-BT2T4 oligomer, whereas the blue color indicates the Ppy film. (bottom) Bipolar enantioselective electrooxidation of L- and D-DOPA (5 mM) on the surface of oligo-(S)-BT2T4 (left), and oligo-(R)-BT2T4 (right) deposited on Ppy. The initial state (green) and final state (red) of the Ppy cantilever during electromechanical deformation is presented. Adapted from reference 57.

3.2. Applications of wireless actuation

In most examples of wireless actuation of CPs, one extremity of the asymmetrically polarized film serves as a reaction site for a given molecule of interest, whereas the opposite end acts as a transducer by generating motion. For example, a linear response in terms of mechanical deformation, as a function of H2O2 concentration, has been reported when using an oxidized free-standing Ppy strip as BPE. The actuation is caused by the reduction of the charged Ppy, whereas at the anodic side H2O2 oxidation occurs.[54] The same approach was used for the biosensing of glucose. In this case, the enzyme glucose oxidase was immobilized on one side of an oxidized Ppy strip, affording a Michaelis-Menten type correlation between glucose concentration and degree of bending. More recently, the BE approach has also been explored for the transduction of chirality across different length scales, from the molecular up to the macroscopic level. Assavapanumat et al. reported the first wireless enantioselective actuator, coupling chirality with the electromechanical properties of a Ppy film, by using an imprinted hybrid platinum-Ppy surface.[55] The mechanical deformation of the Ppy strip is directly related to the difference in oxidation kinetics of the two enantiomers of mandelic acid. However, the enantioselectivty is based on the relative difference in conversion efficiency, making it intrinsically impossible to detect both enantiomers if they are simultaneously present in the same mixture.

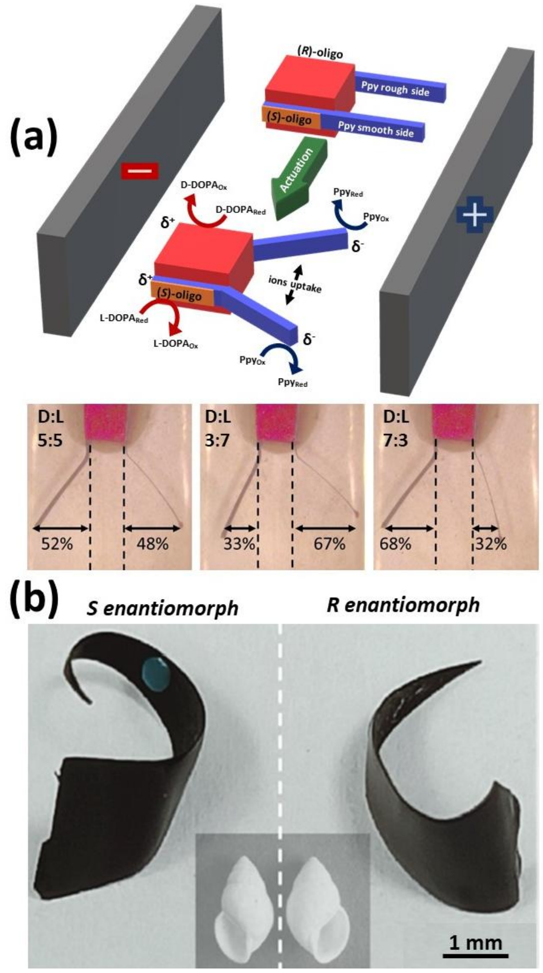


Figure 5. (a) (Top) Schematic illustration of the bipolar electrochemical setup used for wireless enantiomeric excess detection of mixtures of L- and D-DOPA before and after applying the electric field. The orange part stands for the (S)-BT2T4 oligomer, whereas blue symbolizes the Ppy film. (Bottom) Bipolar electrochemical experiments for the enantiomeric excess determination of solutions with different molar ratios between D- and L-DOPA probes (indicated in the figure). Adapted from reference 58. (b). Optical pictures of the two (R)- and (S)-enantiomorphs recovered at the end of the bipolar experiments, illustrating the transmission of a chiral information from the molecular up to the macroscopic scale. Adapted from reference 59.

An alternative is the use of inherently chiral oligomers, where the discrimination of the enantiomers of chiral analytes is based on thermodynamic differences in oxidation potential, caused by energetically different diastereomeric interactions between the chiral surface and the molecular target in solution.[56] For example, a hybrid Ppy film modified with inherently chiral oligomers, i.e. oligo-(3,3'-dibenzothiophene) (oligo-BT2T4) (Figure 4a), was used as BPE for the absolute enantiomeric discrimination of L- or D-3,4-dihydroxyphenylalanine (L- or D-DOPA) (Figure 4b).[57] In this work, the induced redox reactions lead to well-pronounced wireless actuation when DOPA with the appropriate chirality is present in solution, whereas absolutely no electromechanical response is measured for the wrong enantiomer (Figure 4b). In addition, a linear response for the degree of bending as function of the analyte concentration was obtained. Following this concept, the enantiomeric excess of unbalanced mixtures of L- and D-DOPA can be determined by using simultaneously both hybrid Ppy films, modified respectively with the S- and R-oligo-BT2T4 oligomer, as BPEs (Figure 5a).[58] A correlation between the degree of actuation and the concentration of the corresponding analyte in solution was obtained. In a very recent work, the propagation of chiral information along different scales could be achieved. In this case a hybrid sandwich BPE, composed of Ppy and both S- and R-oligo-BT2T4, was exposed to either L- or D-DOPA in solution.[59] In the presence of an electric field, macroscopic enantiomorphs are formed through chirospecific curling, thus transducing the presence of chirality at the molecular scale (Figure 5b).

In a recent approach, actuators that respond to a double stimulus such as an electric field and light were proposed. A hybrid Ppy-TiO2 film, modified with methylene blue as a sensitizer, was used as BPE for the design of a wireless on/off switch.[60] Under illumination electron-hole pairs are produced in the TiO2 layer, which, in the presence of a potential gradient, move towards the Ppy extremities. This triggers the oxidation and reduction at both sides of the BPE, leading to the deformation of the polymer. Another interesting aspect is the use of freestanding-Ppy tubes with different inner and outer diameters as BPE for wireless electropumping. The electric field induces asymmetric polarization of the Ppy tube, triggering the simultaneous swelling and shrinking at the opposite ends of the tube.[61] By applying an AC electric field, a pumping effect can be induced, causing the uptake of liquid at one side of the tube and its expulsion at the opposite end.

4. Conducting polymers for wireless light emission

Currently, the majority of the reported examples of the use of CP for the design of wireless light emitting systems are based on the concept of solid-state electroluminescence.[62,63] Briefly, a polymer light-emitting electrochemical cell (PLEC) composed of a polymer electrolyte, i.e. a polyethylene oxide/lithium salt complex, and a luminescent conjugated polymer, is used. When the PLEC is connected to two metal electrodes and a sufficient potential bias is applied, the in-situ electrochemical p- and n-doping of the luminescent CP occurs. At a constant potential, the doping regions expand until they meet to form a p-n junction. The electroluminescence is caused by the transfer of charge carriers across the p-n junction. These systems are different from the classic organic or polymer light-emitting diodes, due to the doping and junction formation. When introducing a conductor or semiconductor material, positioned on the surface of the PLEC, a polarization of the device occurs, creating a BPE. This changes the doping pattern and the emission profiles of the PLECs (Figure 6a). The combination between BE and PLEC gives rise to a new concept known as solid-state bipolar electroluminescence. In this section, we summarize the recent findings in this context and discuss some examples of CP used for the design of wireless light emitting systems.

4.1. Solid-state bipolar electroluminescence

First, it is important to highlight that in order to build PLECs devices the luminescent conjugated polymer should be able to exhibit p- and n-doping processes and the polyelectrolyte should be able to compensate the produced charges. Poly-[5-(2-ethylhexyloxy)-2-methoxy-1,4-phenylenevinylene], (MEH-PPV), and poly-(ethylene oxide) (PEO), as well as potassium triflate (KTf) are used in the majority of the examples as luminescent CP and polyelectrolyte, respectively (Figure 6a).

BPEs are placed on the surface of PLEC devices in order to create multiple junctions or “bulk homojunction cells”, that enhance the overall light emission.[64,65] The basic principle of solid-state bipolar electroluminescence was presented for the first time by Gao’s group.[66] In their work, a planar PLEC connected to Au and Al feeder electrodes was used. An aluminum disk was placed in the center of the PLEC as BPE. The electroluminescent device exhibits the dynamic in-situ electrochemical p- and n-doping process on the feeder electrodes and around the asymmetrically polarized BPE. Localized light emission is caused by the formation of four distinct p-n junctions, for which the intensity is proportional to the local current density; two originate from the splitting of the main p-n junction generated by the feeder electrodes by the positioning of the aluminum disk, and two additional junctions are induced by the p- and n-doping fronts released from the BPE (Figure 6b). Horizontal and vertical 1D and 2D arrays of metallic BPEs made of Au, Al and Ag have been reported.[67-70] In all cases, the individual disks of the BPE array induce a visible electrochemical p- and n-doping within the luminescent CP. The growth and overlapping of the doping regions as a function of time has been observed. This creates localized p-n junctions between the metal disks, which causes strong light emission. In a recent work, Hu et al. developed a planar PLEC array of 27×21 or 46×36 silver nanoparticle disks (Figure 7a).[71] The wireless redox doping reactions induced on the BPEs lead to the simultaneous formation of over a thousand of light emitting p-n junctions uniformly distributed throughout the PLEC. An interesting alternative is employing doped CP as BPE in order to generate the light emitting p-n junctions. Hu et al. used the p- and n-doped regions, formed at the center of a PLEC, as BPEs, in order to induce in a wireless manner redox doping.[72] Finally, laser illumination was exploited to trigger localized photoconductivity in the PLEC.[73] Under the influence of an applied electric field, the light induced BPE generates the characteristic p-doping region and the reduction of the photosensitizer present in the polyelectrolyte mixture.

4.2. Alternative wireless light emitting systems

An interesting approach is the asymmetric generation of electrochemiluminescence (ECL) on one side of a π-conjugated polymer. Villani et al. generated bipolar ECL from luminol and H2O2 on freestanding PEDOT and Ppy films (Figure 7b).[74] Under these conditions, the anodic part of the films presents a broad and edge-confined light emitting region for Ppy and PEDOT, respectively. In addition, the asymmetric generation of O2, induces bubble propulsion of the polymers. A promising alternative is the design of hybrid polymer-microelectronic devices, in which miniaturized light emitting diodes (μ-LED) are functionalized with CP. In a recent work, a Ppy-μ-LED hybrid BPE, that emits light combined with electromechanical motion in the presence of an applied electric field, was reported.[75] As stated above, actuation of the Ppy strips is triggered by the presence of two asymmetry inducing components, a difference in surface roughness and different oxidation states of the two extremities. In addition, light emission is caused by the simultaneous oxidation/reduction reactions, occurring at the opposite ends of the Ppy, leading to an electron flow through the integrated LED. Finally, the possible readout of chiral information by the combination of the enantioselective oxidation of a chiral probe with the emission of light produced from a LED has been reported very recently.[76] A static hybrid oligo-BT2T4-LED-Ppy bipolar device was designed based on the coupling of the selective oxidation of a chiral probe on the surface of an inherently chiral oligomer and the reduction of an oxidized Ppy strip (Figure 7c). The wirelessly induced electrochemical reactions trigger the switching-on of the devices only when the correct chiral probe is present in solution.

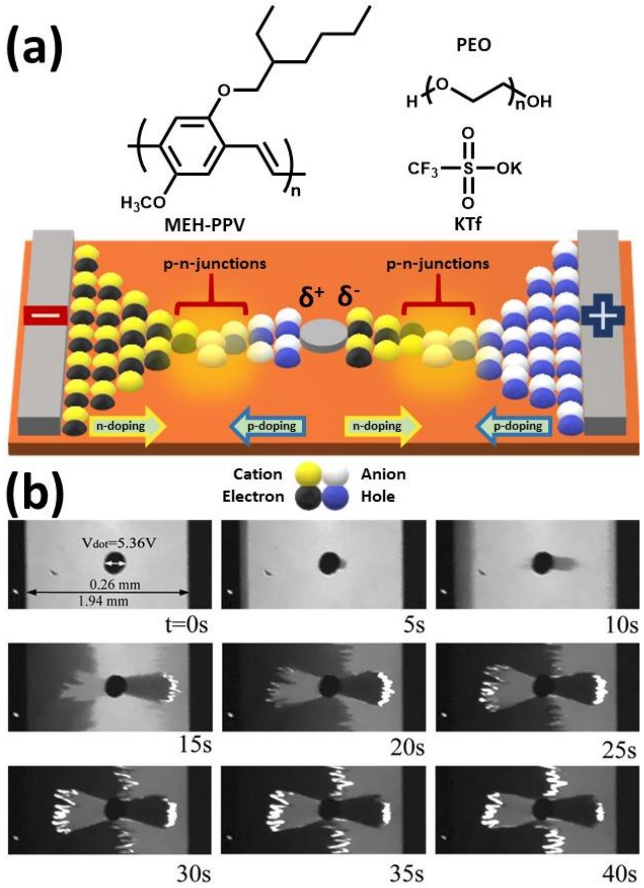


Figure 6. (a) Chemical structures of a luminescent CP and polyelectrolytes, respectively, and a scheme of a PLEC with a BPE disk positioned between the feeder electrodes illustrating the doping propagation and formation of light emitting p–n junctions. b) Time-lapse fluorescence images of a planar cell consisting of Au and Al feeder electrodes, and a single aluminum disc as BPE. Adapted from reference 66.

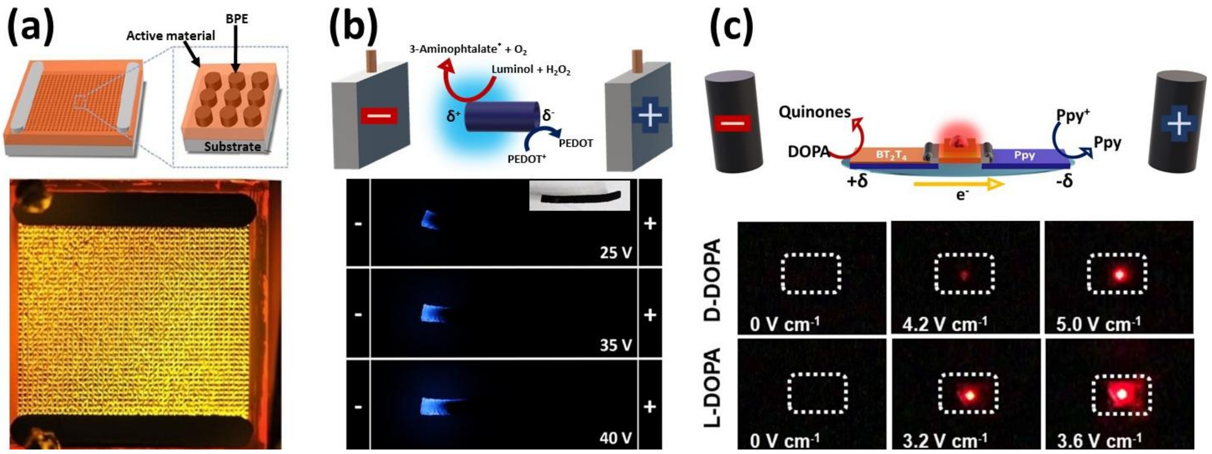


Figure 7. (a) (Top) Schematic illustration of a planar PLEC with a BPE array composed of 27×21 printed Ag-NP disks, embedded in the polymer layer. (Bottom) A planar PLEC with 46×36 BPEs operated at 400 V and 360 K. Adapted from reference 71. (b) (Top) Scheme of the bipolar setup used for the ECL emission, using a PEDOT film as BPE. (Bottom) Optical pictures of the ECL emission on a

PEDOT film used as BPE at different applied potentials (indicated in the figure). The inset shows the initial state of the PEDOT BPE. Adapted from reference 74. (c) (Top) Schematic illustration of the bipolar set-up used for the wireless discrimination of D- and L-DOPA based on light emission by an integrated LED. The orange part stands for the BT2T4 oligomer, whereas dark blue symbolizes the Ppy film. The light blue color illustrates the bottom of the cell. (Bottom) Optical pictures of the oligo-(S)-BT2T4-LED-Ppy bipolar electrodes at different applied electric fields, (indicated in the figure) in the presence of D- or L-DOPA, respectively. Adapted from reference 76.

5. Summary and Outlook

In this review different advances in BE, based on the use of CPs as BPEs were discussed. The versatility of BE is demonstrated by different applications ranging from electro-organic synthesis, (chiral) actuation and light emission. All these systems reflect the inherent advantages of BE, such as its wireless nature and the occurrence and tunability of simultaneous reduction/oxidation processes at opposite ends of the bipolar object. Site-selective surface modification of different macro- micro- and nano-objects involving CPs have been successfully achieved in order to produce films, fibers or gradient surfaces. The intrinsic asymmetry provided by this technique has been used to trigger motion and light emission via contraction/expansion or electroluminescent processes, respectively. Wireless actuation and/or light emission have been proposed as straightforward read-outs of chemical information, allowing the transduction of an analytical signal for qualitative and quantitative measurements.

Finally, it is worth mentioning that the objectives of the research efforts in recent years were to improve the sensitivity and selectivity of BPEs; to make the set-ups affordable, portable, robust and user-friendly; to scale down the size of the BPEs; to elucidate reaction mechanisms; and to simplify materials preparation and patterning schemes. However, in addition to these ongoing efforts, there are still important challenges that need to be addressed, like for instance the implementation of arrays of polymeric BPEs in imaging applications that require large areas. The number of opportunities in this field is still growing, considering that bipolar electrochemistry is a straightforward concept providing innovative solutions to long-standing issues in electrochemistry.

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Keywords: Conducting polymers • bipolar electrochemistry • Electro-organic synthesis • Light emitting systems • Actuation

References

[1] J. Heinze, B. A. Frontana-Uribe, S. Ludwigs, Chem. Rev. 2010, 110, 4724-4771.

[2] J. G. Ibanez, M. E. Rincon, S. Gutierrez-Granados, M. Chahma, O. A. Jaramillo-Quintero, B. A. Frontana-Uribe, Chem. Rev. 2018, 118, 4731-4816.

[3] G. De Alvarenga, B. M. Hryniewicz, I. Jasper, R. J. Silva, V. Klobukoski, F. S. Costa, T. N. M. Cervantes, C. D. B. Amarala, J. T. Schneider, L. Bach-Toledo, P. Peralta-Zamora, T. L. Valerio, F. Soares, B. J. G. Silva, M. Vidotti, J. Electroanal. Chem. 2020, 879, 114754.

[4] A. Yassin, M. Oçafrain, P. Blanchard, R. Mallet, J. Roncali, ChemElectroChem 2014, 1, 1312-1318.

[5] J. G. Martinez, M. Ayán-Varela, J. I. Paredes, S. Villar-Rodil, S. D. Aznar-Cervantes, T. F. Otero, ChemElectroChem 2017, 4, 1487-1497.

[6] G. Salinas, B. A. Frontana-Uribe, ChemElectroChem 2019, 6, 4105-4117.

[7] L. Bouffier, D. Zigah, N. Sojic, A. Kuhn, Annu. Rev. Anal. Chem. 2021, 14, 65-86.

[8] S. E. Fosdick, K. N. Knust, K. Scida, R. M. Crooks, Angew. Chem. Int. Ed. 2013, 52, 10438-10456.

[9] L. Koefoed, S. U. Pedersen, K. Daasbjerg, Curr. Opin. Electrochem. 2017, 2, 13-17.

[10] N. Karimian, P. Hashemi, A. Afkhami, H. Bagheri, Curr. Opin. Electrochem. 2019, 17, 30-37.

[11] C. A. C. Sequeira, D. S. P. Cardoso and M. L. F. Gameiro, Chem. Eng. Commun. 2016, 203, 1001.

[12] N. Shida, Y. Zhou, S. Inagi, Acc. Chem. Res. 2019, 52, 2598−2608.

[13] G. Loget, G. Li, B. Fabre, Chem. Commun. 2015, 51, 11115-11118.

[14] R. K. Anand, E. S. Johnson, D. T. Chiu, J. Am. Chem. Soc. 2015, 137, 776-783.

[15] O. Klett, L. Nyholm, Anal. Chem. 2003, 75, 1245-1250.

[16] S. Wu, Z. Zhou, L. Xu, B. Su, Q. Fang, Biosens. Bioelectron. 2014, 53, 148-153.

[17] N. Shida, S. Inagi, Chem. Commun. 2020, 56, 14327.

[18] Z. Chen, E. Villani, S. Inagi, Curr. Opin. Electrochem. 2021, 28, 100702.

[19] S. Inagi, Polymer Journal 2019, 51, 975-981.

[20] S. Inagi, T. Fuchigami, Macromol. Rapid Commun. 2014, 35, 854-867.

[21] T. Kurioka, S. Inagi, Chem. Rec. 2021, 21, 1-14.

[22] S. Inagi, Polymer Journal 2016, 48, 39-44.

[23] C. Qin, Z. Yue, Y. Chao, R. J. Forster, F. O. Maolmhuaidh, X. F. Huang, S. Beirne, G. G. Wallace, J. Chen, Appl. Mater. Today 2020, 21, 100804.

[24] Y. Zhou, N. Shida, I. Tomita, S. Inagi, Angew. Chem. Int. Ed. 2021, 133, 14741-14750.

[25] V. Eßmann, S. Barwe, J. Masa, W. Schuhmann, Anal. Chem. 2016, 88, 8835-8840.

[26] C. Santana-Santos, F. Conzuelo, V. Eßmann, M. Bertotti, W. Schuhmann, Anal. Chim. Acta 2019, 1087, 36-43.

[27] V. Eßmann, J. Clausmeyer, W. Schuhmann, Electrochem. Commun. 2017, 75, 82-85.

[28] S. Babu, P. Ndungu, J. C. Bradley, M. P. Rossi, Y. Gogotsi, Microfluid. Nanofluid. 2005, 1, 284-288.

[29] S. Kong, O. Fontaine, J. Roche, L. Bouffier, A. Kuhn, D. Zigah, Langmuir 2014, 30, 2973-2976.

[30] F. Gholami, A. Navaee, A. Salimi, R. Ahmadi, A. Korani, R. Hallaj, Sci. Rep. 2018, 8, 15103.

[31] M. Ongaro, A. Gambirasi, M. Favaro, A. Kuhn, P. Ugo, Electrochim. Acta 2014, 116, 421-428.

[32] G. Loget, V. Lapeyre, P. Garrigue, C. Warakulwit, J. Limtrakul, M. H. Delville, A. Kuhn, Chem. Mater. 2011, 23, 2595-2599.

[33] A. Srinivasan, J. Roche, V. Ravaine, A. Kuhn, Soft Matter 2015, 11, 3958-3962.

[34] Y. Koizumi, N. Shida, M. Ohira, H. Nishiyama, I. Tomita, S. Inagi, Nat. Commun. 2016, 7, 10404.

[35] M. Ohira, Y. Koizumi, H. Nishiyama, I. Tomita, S. Inagi, Polymer Journal 2017, 49, 163-167.

[36] Y. Koizumi, M. Ohira, T. Watanabe, H. Nishiyama, I. Tomita, S. Inagi, Langmuir 2018, 34, 7598-7603.

[37] T. Watanabe, M. Ohira, Y. Koizumi, H. Nishiyama, I. Tomita, S. Inagi, ACS Macro Lett. 2018, 7, 551-555.

[38] N. Shida, T. Watanabe, I. Tomita, S. Inagi, Synth. Met. 2020, 266, 116439.

[39] T. Kuwahara, K. Sato, M. Kondo, M. Shimomura, Synth. Met. 2014, 198, 274-276.

[40] Y. Zhou, N. Shida, Y. Koizumi, T. Watanabe, H. Nishiyama, I. Tomita, S. Inagi, J. Mater. Chem. C 2019, 7, 14745.

[41] Y. Zhou, N. Shida, Y. Koizumi, K. Endo, I. Tomita, S. Inagi, Macromolecules 2020, 53, 8123-8130.

[42] S. Inagi, Y. Ishiguro, M. Atobe, T. Fuchigami, Angew. Chem. Int. Ed. 2010, 49, 10136-10139.

[43] Y. Ishiguro, S. Inagi, T. Fuchigami, Langmuir 2011, 27, 7158-7162.

[44] Y. Ishiguro, S. Inagi, T. Fuchigami, J. Am. Chem. Soc. 2012, 134, 4034-4036.

[45] N. Shida, Y. Ishiguro, M. Atobe, T. Fuchigami, S. Inagi, ACS Macro Lett. 2012, 1, 656-659.

[46] S. Inagi, H. Nagai, I. Tomita, T. Fuchigami, Angew. Chem. Int. Ed. 2013, 52, 6616-6619.

[47] T. F. Otero, L. Valero, J. G. Martinez, Electrochim. Acta 2017, 246, 89-96.

[48] T. F. Otero, M. Alfaro, V. Martinez, M. A. Perez, J. G. Martinez, Adv. Funct. Mater. 2013, 23, 3929-3940.

[49] T. F. Otero, Electrochim. Acta 2016, 212, 440-457.

[50] M. Fuchiwaki, J. G. Martinez, T. F. Otero, Adv. Funct. Mater. 2015, 25, 1535-1541.

[51] M. Fuchiwaki, J. G. Martinez, T. F. Otero, Electrochim. Acta 2016, 195, 9-18.

[52] B. Gupta, B. Goudeau, A. Kuhn, Angew. Chem. Int. Ed. 2017, 56, 14183-14186.

[53] B. Gupta, B. Goudeau, P. Garrigue, A. Kuhn, Adv. Funct. Mater. 2018, 28, 1705825.

[54] L. Zhang, B. Gupta, B. Goudeau, N. Mano, A. Kuhn, J. Am. Chem. Soc. 2018, 140, 15501-15506.

[55] S. Assavapanumat, B. Gupta, G. Salinas, B. Goudeau, C. Wattanakit, A. Kuhn, Chem. Commun. 2019, 55, 10956-10959.

[56] S. Arnaboldi, T. Benincori, R. Cirilli, W. Kutner, M. Magni, P. R. Mussini, K Noworyta, F. Sannicolò Chem. Sci. 2015, 6, 1706-1711.

[57] S. Arnaboldi, B. Gupta, T. Benincori, G. Bonetti, R. Cirilli, A. Kuhn, Anal. Chem. 2020, 92, 10042-10047.

[58] S. Arnaboldi, G. Salinas, G. Bonetti, R. Cirilli, T. Benincori, A. Kuhn, ACS Meas. Au 2021, in press, DOI: 10.1021/acsmeasuresciau.1c00011

[59] S. Arnaboldi, B. Gupta, T. Benincori, G. Bonetti, R. Cirilli, A. Kuhn, Chem. Mater. 2020, 32, 10663-10669.

[60] A. A. Melvin, B. Gupta, K. Tieriekhov, W. Nogala, P. Garrigue, S. Reculusa, A. Kuhn, Adv. Funct. Mater. 2021, 31, 2101171.

[61] B. Gupta, L. Zhang, A. A. Melvin, B. Goudeau, L. Bouffier, A. Kuhn, Chem. Sci. 2021, 12, 2071-2077.

[62] J. Gao, Curr. Opin. Electrochem 2018, 7, 87-94.

[63] S. Hu, J. Gao, Adv. Funct. Mater. 2019, 30, 1907003

[64] C. Tracy, J. Gao, J. Appl. Phys. 2006, 100, 104503.

[65] C. Tracy, J. Gao, Appl. Phys. Lett. 2005, 87, 143502.

[66] S. Chen, G. Wantz, L. Bouffier, J. Gao, ChemElectroChem 2016, 3, 392-398.

[67] S. Hu, J. Gao, ACS Appl. Mater. Interfaces 2019, 11, 1117-1124.

[68] S. Hu, J. Gao, Electrochim. Acta 2019, 304, 184-191.

[69] J. Gao, S. Chen, F. AlTal, S. Hu, L. Bouffier, G. Wantz, ACS Appl. Mater. Interfaces 2017, 9, 32405-32410.

[70] S. Hu, J. Gao, J. Phys. Chem. C 2018, 122, 9054-9061.

[71] S. Hu, J. Gao, ChemElectroChem 2020, 7, 1748-1751.

[72] S. Hu, X. Chi, S. Chen, F. AlTal, J. Gao, J. Phys. Chem. C 2017, 121, 8409-8415.

[73] F. AlTal, J. Gao, J. Am. Chem. Soc. 2018, 140, 9737-9742.

[74] E. Villani, N. Shida, S. Inagi, Electrochim. Acta 2021, 389, 138718.

[75] B. Gupta, M. C. Alfonso, L. Zhang, C. Ayela, P. Garrigue, B. Goudeau, A. Kuhn, ChemPhysChem 2019, 20, 941-945.

[76] G. Salinas, S. Arnaboldi, G. Bonetti, R. Cirilli, T. Benincori, A. Kuhn, Chirality, 2021, in press. DOI:10.1002/chir.23370.

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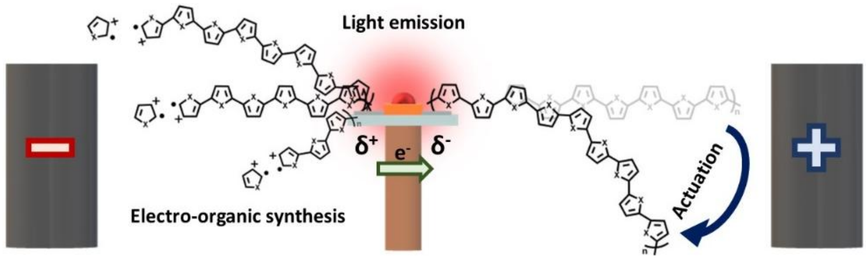

Bipolar electrochemistry is discussed in this review as an interesting alternative for the controlled electrogeneration, surface modification, characterization and actuation of different π-conjugated polymers.