

Bipolar Electrochemistry of Electrochemically Doped Luminescent Conjugated Polymers

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Introduction

Polymer light-emitting electrochemical cell (PLEC) contains a mixture of luminescent conjugated polymer and polymer electrolyte. A sufficiently large external voltage bias causes *in situ* electrochemical p- and n-doping of the polymer next to the driving electrodes. The doping fronts propagate inward until they meet to form an electroluminescent p-n junction. [1]

Bipolar electrochemistry is an electrochemical phenomenon where an electrically floating conductor (a bipolar electrode or BPE) induces redox reactions at its extremities if a sufficient potential difference is applied to the driving electrodes of an electrochemical cell. [2]

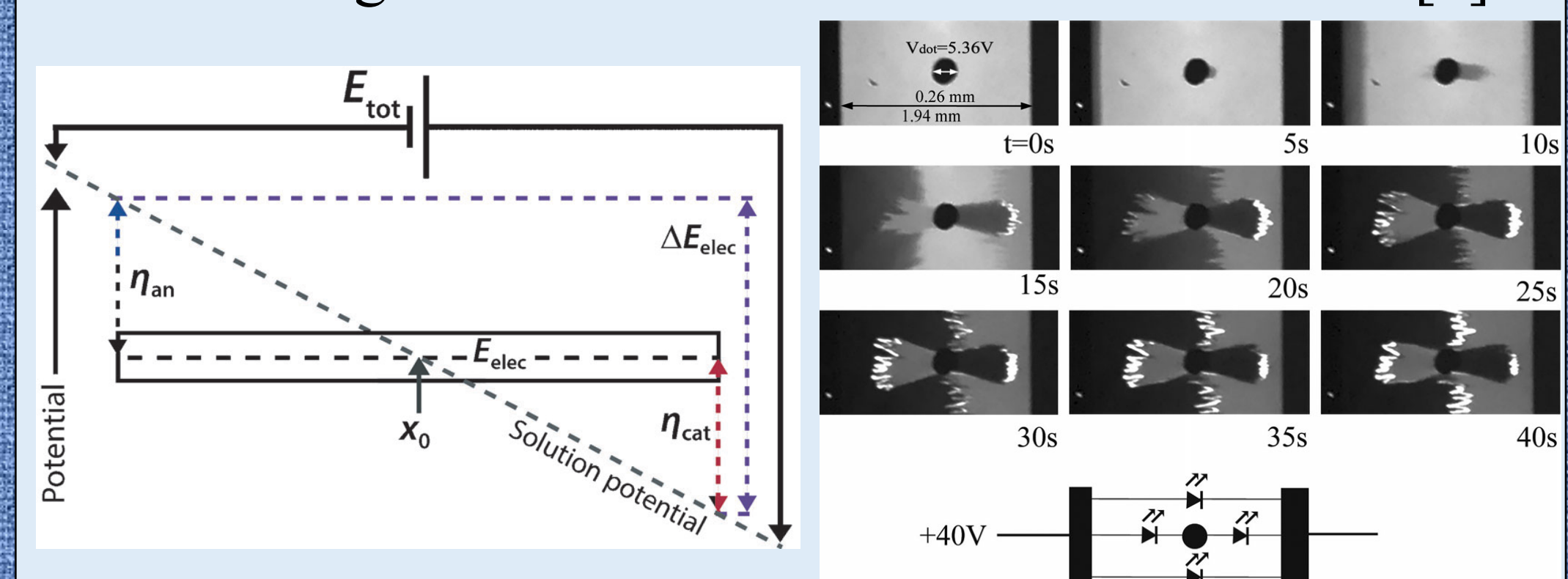


Figure 1: Left: Scheme of a bipolar electrode in an electric field. [2] Right: Planar PLEC with aluminum disc BPE embedded. Top part shows time-lapse fluorescence images of the cell. Lower part shows the equivalent circuit of the cell when fully emitting. [3]

Motivation

Electrochemistry involving a bipolar electrode has become an increasingly versatile and powerful method in novel material manufacture. These bipolar electrochemical systems typically involve metal/carbon conductors and a liquid electrolyte. Recently, our group demonstrated that bipolar electrochemistry could also be combined with solid-state electrochemistry in a PLEC. [3] In this study, we use a micromanipulated vacuum probe station and fluorescence imaging to induce and visualize bipolar electrochemical redox reactions in an extremely large planar PLEC.



Figure 2: A Janis ST-500 micromanipulated probe station.

Results

A 60V voltage bias was applied between a pair of metallic probes, which were brought into contact with the polymer film. Figure 3(iii) provides a visual account of the dynamic doping process which cause the increase of probe current and strong PL quenching. EL in Figure 3(iii)(b)-(d) is the result of radiative recombination of injected electrons and holes in the PLEC junction under forward bias. EL disappeared when the applied voltage bias was removed, revealing a sharp boundary between the p- and n-doped regions, which were called p- and n-doped BPE regions.

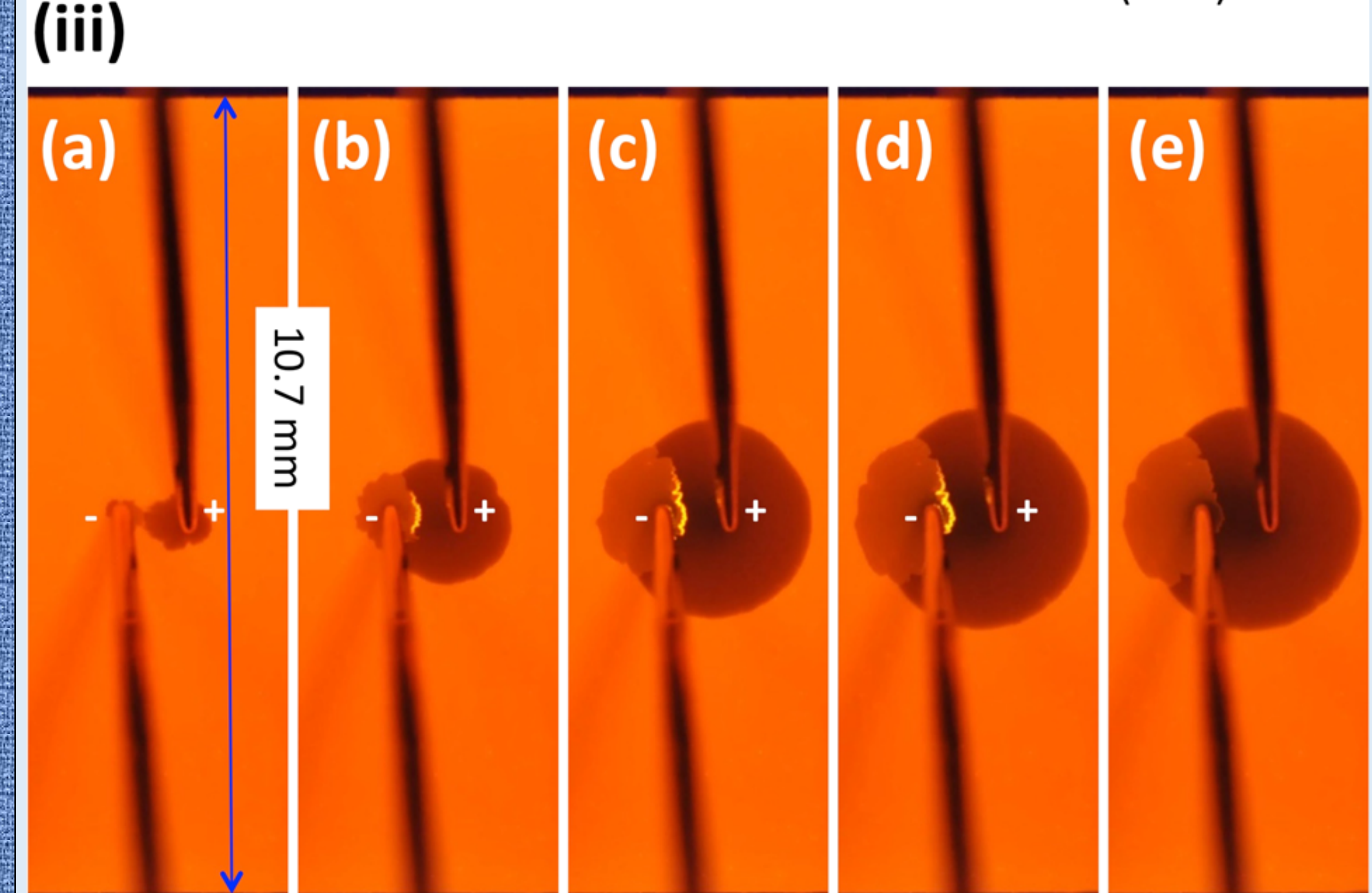
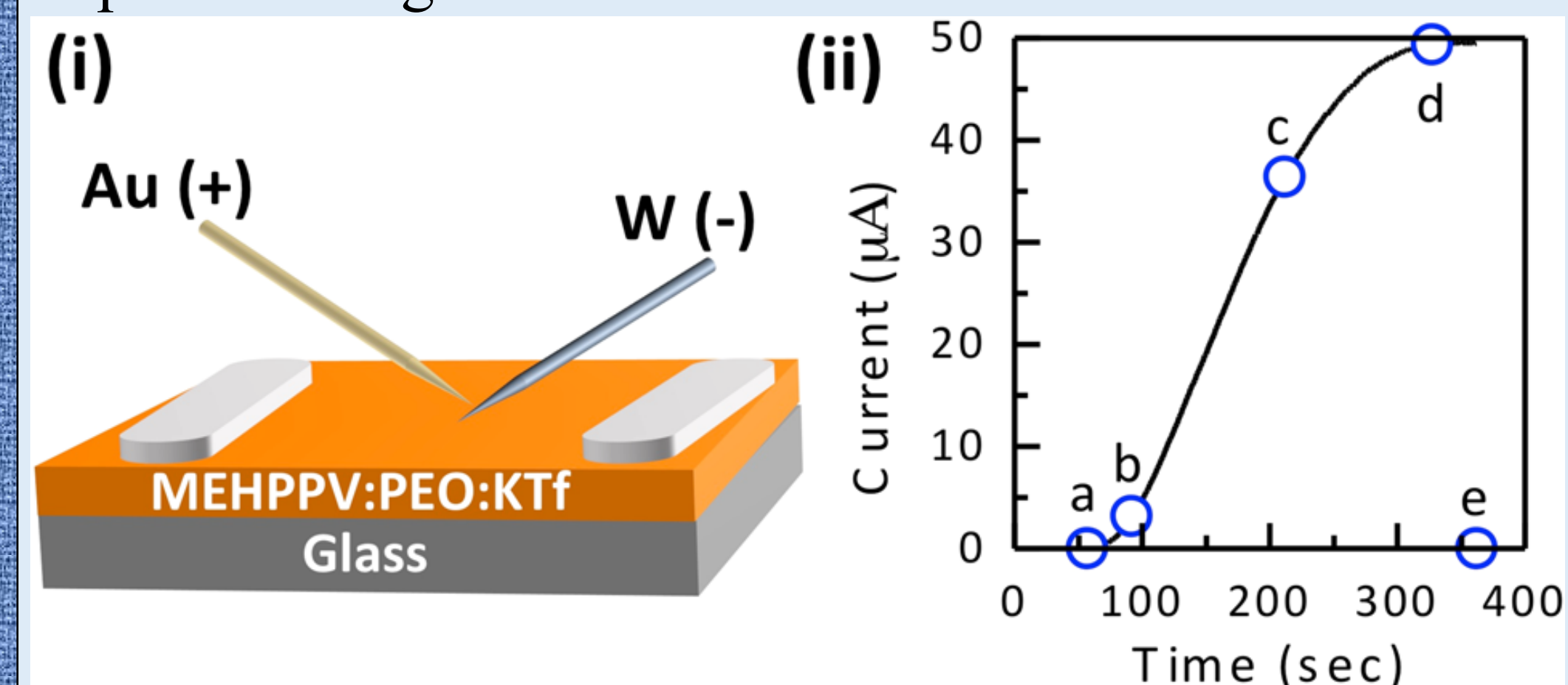


Figure 3: *In situ* electrochemical doping induced with a pair of biased probes. The cell was heated at 340 K under vacuum in a probe station. (i) A schematic of the planar LEC and biased metallic probes. (ii) Probe current as a function of time at a bias voltage of 60 V. (iii) Time-lapse fluorescence images of the polymer film.

The probes were repositioned to contact the aluminum driving electrodes, and a voltage of 800V was applied. This created a unique situation where the PLEC film between the driving electrodes contained regions of doped polymer that were not in direct contact with the driving electrodes. The lighter color of doped BPE in Figure 4(iii)(a) reveals that some dedoping had occurred during 385s it took to reposition the probes. Figure 4(iii)(b) shows new, corn-shaped doping originating from both core BPE regions after the application of 800V bias on both driving electrodes.

Discussion

We learned that a metallic disc deposited between the driving electrodes in a planar PLEC could function as a bipolar electrode. Since the luminescent polymer MEH-PPV can be doped to exhibit metallic conductivity, the doped BPE regions functioned as bipolar electrodes due to their elevated conductivity.

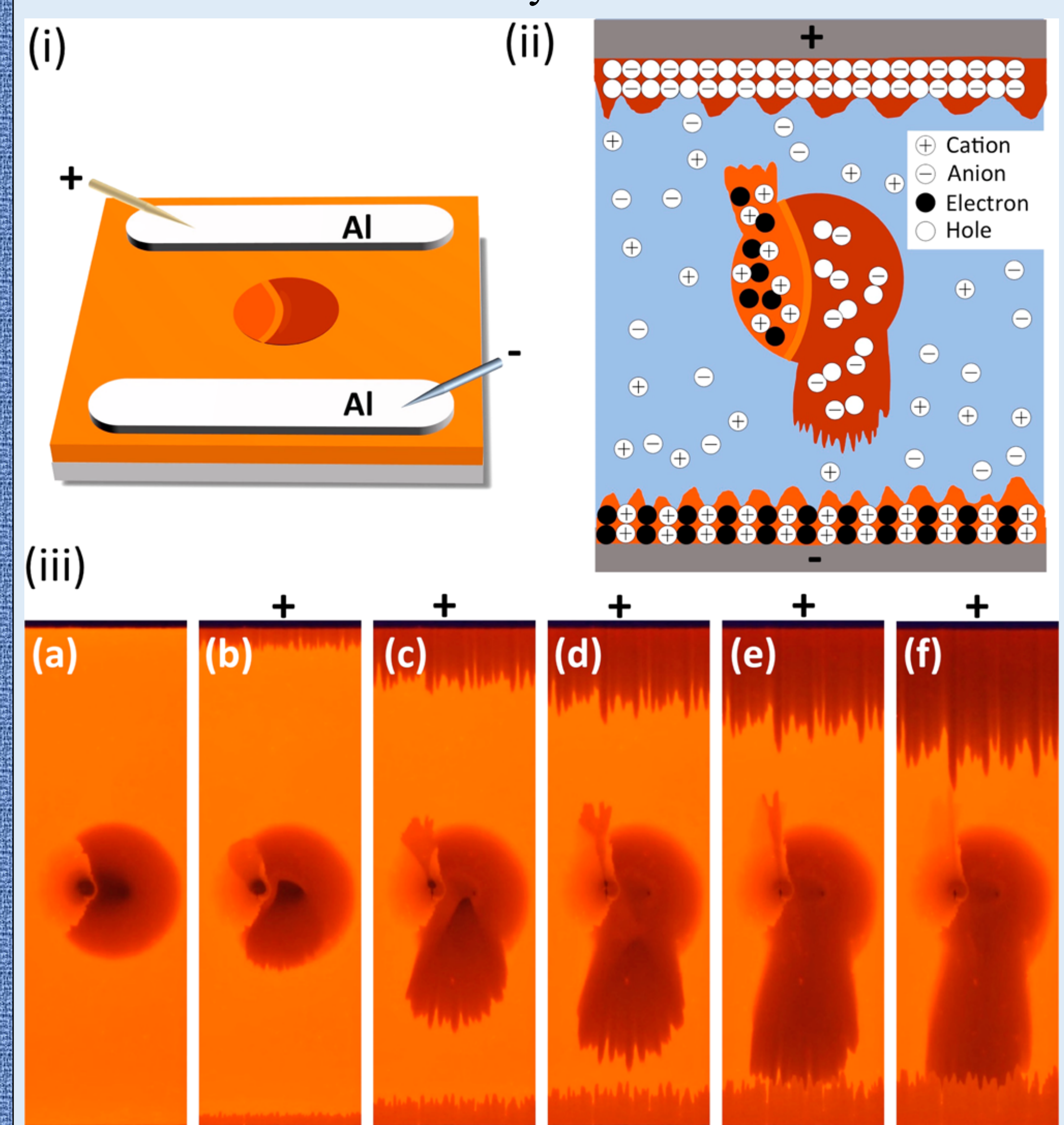


Figure 4: *In situ* electrochemical doping driven by a pair of aluminum electrodes. (i) Schematic of the planar LEC showing the positions of the biased probes. (ii) A schematic showing the electronic and ionic charge carriers in the LEC film. (iii) Time-lapse PL images of the cell after the application of an 800 V bias across the driving electrodes.

Two important facts should be noted.

- First, the induced doping from both p- and n-doped BPE regions did not originate from the extremities of the large doped shell but rather from the much smaller core regions. This observation confirms that only the more conductive core regions had sufficiently elevated conductivity to function as BPEs.
- Second, the doped BPEs are separated by a less quenched, quasi-intrinsic region, and both doped BPEs promoted only one type of doping. Figure 5 uses the p-doped BPE as an example to illustrate the doping processes involving the p-doped BPE core and the surrounding polymer.

Figure 5 shows the BPE shell on the RHS loses an electron to the core and is oxidized. The BPE core on the LHS retain the injected electron and eject a negative

counterion across the boundary because of large potential energy barrier. Similar arguments can also be made to explain the fact that only n-doping is observed from the n-doped BPE. The doped polymer BPE induces a doping reaction on one extremity that is balanced by a dedoping reaction on the opposite extremity.

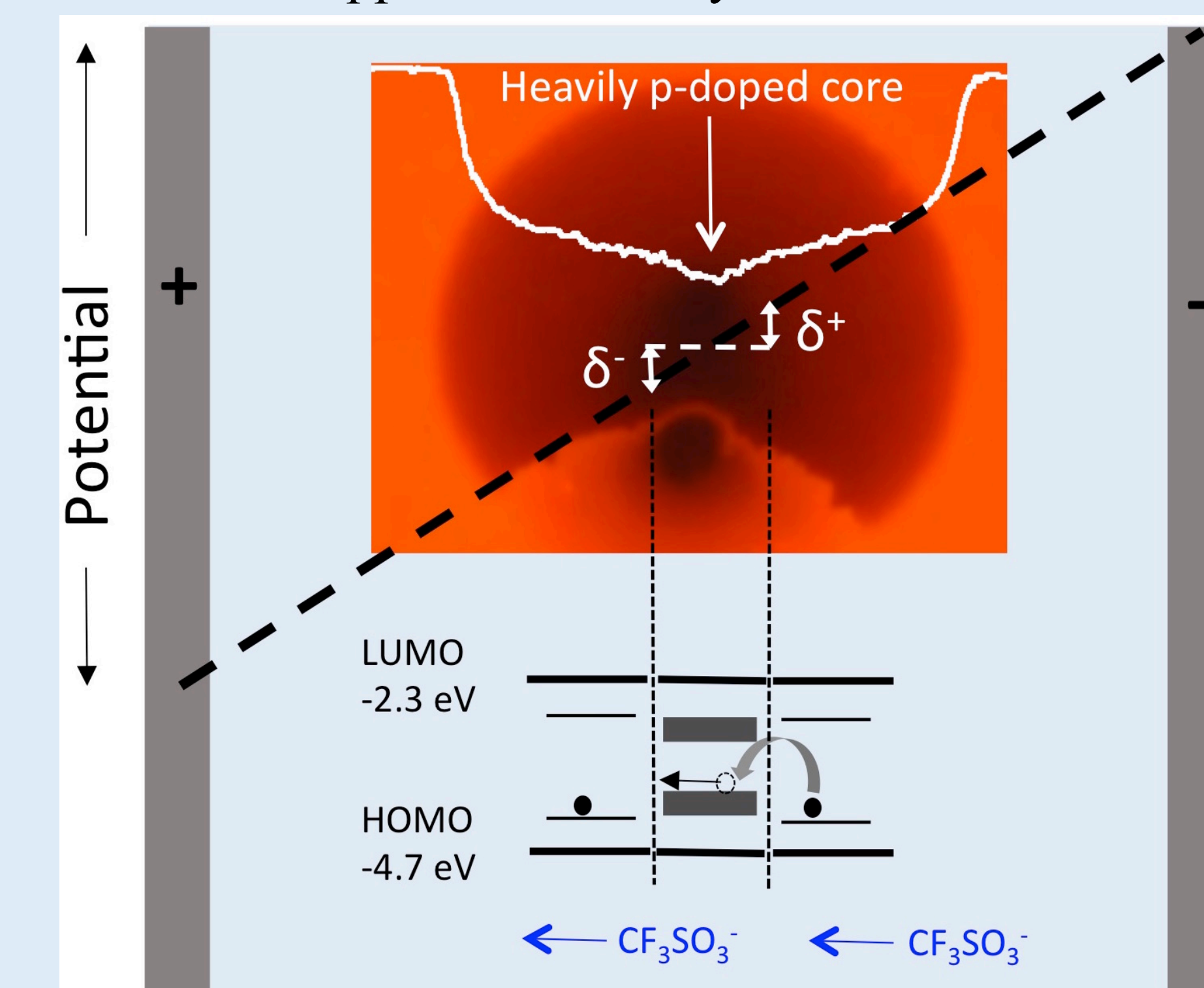


Figure 5: Schematic representation of the doping processes around a p-doped BPE under bias. The white trace is the PL intensity across the entire p-doped BPE through its core. The thick, black dashed line represents the potential. The horizontal white dashed line represents the potential of the p-doped BPE core. The lower portion shows the energy level diagrams of the BPE core and its outer regions.

Conclusions

In summary, we studied the electrochemical and bipolar electrochemical doping of a mixed polymer conductor in a solid-state electrochemical cell. We demonstrated, for the first time, that a doped polymer could function as a bipolar electrode to induce redox doping reactions wirelessly. In the p-doped BPE, electrochemical p-doping is induced on one end which is balanced by a reductive dedoping reaction on the opposite end. In the n-doped BPE, only electrochemical n-doping is observed which is balanced by an oxidative dedoping reaction.

References

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