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Double-Gate Light-Emitting Electrochemical Transistor: Confining the Organic p–n Junction

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Supporting Information

ABSTRACT: In conventional light-emitting electrochemical cells (LECs), an off-centered p–n junction is one of the major drawbacks, as it leads to exciton quenching at one of the charge-injecting electrodes and results in performance instability. To combat this problem, we have developed a new device configuration, the double-gate light-emitting electrochemical transistor (DG-LECT), in which the location of the light-emitting p–n junction can be precisely defined via the position of the two gate terminals. Based on a planar LEC structure, two gate electrodes made from an electrochemically active conducting polymer are employed to predefine the p- and n-doped area of the light-emitting polymer. Thus, a p–n junction is formed in between the p-doped and n-doped regions. We demonstrate a homogeneous and centered p–n junction as well as other predefined junction patterns in these DG-LECT devices. Additionally, we report an electrical model that explains the operation of the DG-LECTs. The DG-LECT device provides a new tool to study the fundamental physics of LECs, as it dissects the key working process of LEC into decoupled p-doping, n-doping, and electroluminescence.

Solid-state light-emitting electrochemical cells (LECs) have emerged as a promising candidate for next-generation lighting and display applications in recent years. LECs possess the advantages of low operating voltage, high power efficiency,[1,2] insensitivity to the film thickness, and choice of electrode materials,[3,4] consequently giving rise to a facile fabrication scheme.[4−6] The operation mechanism of LECs is governed by the fact that the active material is electron- and ion-conductive, electrochemically active, and luminescent, which makes it a unique component that has no inorganic counterpart.

A conventional LEC consists of two electrodes, a light-emitting polymer (LEP) and an electrolyte, with the two latter components either blended or phase-separated.[7] Once a voltage larger than the band gap of the LEP is applied to the device, ions migrate toward the electrodes to compensate the injected charge, leading to electrochemical n- and p-doping of the LEP. The doped regions grow in size until they meet and form an organic p–n junction, where holes and electrons recombine radiatively after flowing through the highly conductive doped polymer film. In an unoptimized LEC based upon the commonly used polymer MEH-PPV (poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene]), the emission zone is usually located in the vicinity of the cathode (negative electrode),[8−11] because p-doping is dominant over n-doping. Two causes are suggested for this unbalanced electrochemical doping: (1) an undesired side reaction between the electrolyte and the injected charges takes place at the cathodic interface and blocks continuous n-doping;[10] (2) the hole mobility increases nonlinearly with an increased p-doping level in MEH-PPV so that an equilibrium system with a relatively higher p-doping fraction is more energetically favorable.[12] This off-center emission zone is a major drawback in LEC devices. It leads to exciton quenching at the electrode[13] and/or doping-induced short circuit formation,[14] which plays a detrimental role in the lifetime and efficiency of LECs. Efforts have been devoted to moving or confining the emission zone toward the center in between the two electrodes, by changing the materials of LEPs,[15] the electrolyte,[16,17] and the charge-injecting contacts.[11] Other than varying the materials, it is also possible to affect the junction position by changing the device configuration and architecture. Tang has recently demonstrated a vertical trilayer LEC where an intermediate layer is utilized to separate p- and n-doping to dictate the junction position.[18] However, in the report from Tang no direct visual evidence was revealed that the emissive junction was actually confined to the center of the vertical structure. We have previously demonstrated that in a three terminal light-emitting electrochemical transistor (LECT) the position of the junction can be in situ controlled by a gate terminal that dictates the doping level of the LEP.[19] In this device we were able to move the emissive junction back and forth within a 500 μm wide gap, but the curvy shape and nonuniform lighting profile make it not very useful in a practical application. Zhou[20] and Yumusak[21,22] also observed in their LECT devices that the light intensity can be modulated by the gate terminal. Here, we present a new device configuration, the double-gate light-emitting electrochemical transistor (DG-LECT), and we show that in this DG-LECT a localized junction with a more homogeneous profile can be achieved.

Similar to its predecessor, the DG-LECT was fabricated based upon the bilayer LEC structure[7] where a stack of electrolyte and LEP was placed on top of two bottom electrodes with an interelectrode distance of 500 μm (Figure 1a). Here, we used MEH-PPV as the LEP and a mix of poly(ethylene oxide) (PEO) and the salt KCF_3SO_3 as the electrolyte. A pair of gate electrodes with a spacing of ~75 μm was laminated onto the top of the stack. We chose a ready-

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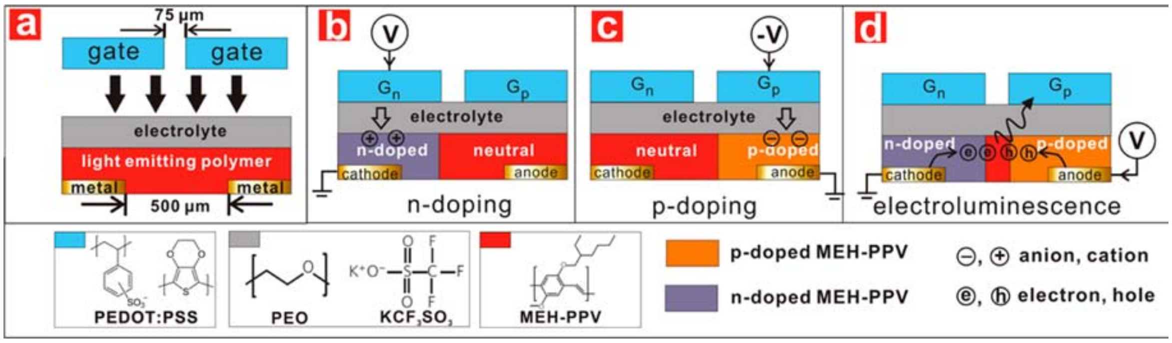

Figure 1. Materials, structure, and operation modes for DG-LECT. (a) Device structure. (b) n-Doping mode. (c) p-Doping mode. (d) EL mode.

made foil coated with poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) as the gate materials due to its high electrochemical capacity and excellent optical transparency.

We then define the following three operation modes of the device, as shown in Figure 1b−1d: (1) In *n-doping mode*, a positive voltage (+5 V) is applied at the gate (termed as G$_n$) vs the cathode; (2) In *p-doping mode*, a negative voltage (−5 V) is applied to the gate (termed as G$_p$) vs the anode; (3) In the *electroluminescence (EL) mode*, a potential larger than the LEP's band gap is applied between the anode and cathode. We anticipate that the n-doping mode leads to further oxidation in the PEDOT phase of the left-hand gate accompanied by the migration of anions from the electrolyte to the gate electrode, so that the excess cations are free to diffuse into the LEP to cause n-doping of the polymer bulk. Conversely to this n-doping process, p-doping includes that the right-hand gate is reduced and that anions migrate into the LEP to cause p-doping of the LEP. We expect that after sufficient n- and p-doping driven by the two gate terminals, the operation in EL mode will lead to a light emission zone established in between the predefined p-doped and n-doped regions, as illustrated in Figure 1d.

As the doping level of a conjugated polymer, such as polythiophene[23] or MEH-PPV,[24,25] is increased, the electrical resistance of the polymer bulk typically decreases by orders of magnitude. The electrical doping-induced change in resistance was characterized for the MEH-PPV material. To achieve this in an electronically conducting material that also is electrochemically active, a fast DC voltage sweep is required. This ensures that only an insignificant rearrangement of the included ions occurs during the electrical measurement event.[26] We performed the electrical characterization in 10^{-5} Pa vacuum at a temperature of 70 °C. The DG-LECT was initially operated in the p-doping mode for 11 individual doping periods (each period lasts for about 6 s), which results in p-doping of the MEH-PPV beneath the G$_p$ electrode. The resistance between the cathode and the anode was measured after each p-doping cycle and is given in Figure 2. The first data point (cycle 0) indicates the resistance of MEH-PPV in its pristine undoped state. The resistance decreases continuously during the first periods and saturates during the last few periods. Subsequently, 11 periods of n-doping were carried out to n-dope the MEH-PPV phase beneath the G$_n$, and a similar trend in the decrease of the resistance is found; see Figure 2. To explain this change in resistance vs doping periods, a simple electrical model is proposed; see the inset of Figure 2. We divide the resistance of MEH-PPV into three components: R_p and R_n corresponds to the resistance of the MEH-PPV beneath the G$_p$ and G$_n$, respectively; R$_i$ is associated with the component located in between R_p and R_n, which remains undoped during the two doping processes. At cycle 0, the resistance of pristine MEH-PPV (1170 MΩ) is equal to the sum of R_p, R_n, and R_i. After 11 p-doping cycles R_p decreases by orders of magnitude and becomes negligible. The total measured resistance 560 MΩ (cycle 11) then equals $R_n + R_i$, which causes the resistance saturation during p-doping cycles. Similarly, after the 11 periods of n-doping, the measured resistance of 155 MΩ (cycle 22) corresponds to R_i. This remaining undoped part of MEH-PPV leads to the resistance saturation during n-doping cycles. The resulting resistance of 155 MΩ vs the initial resistance of 1170 MΩ agrees with the total length of the undoped region (75 μm) vs the total channel length (500 μm), i.e. ~15%.

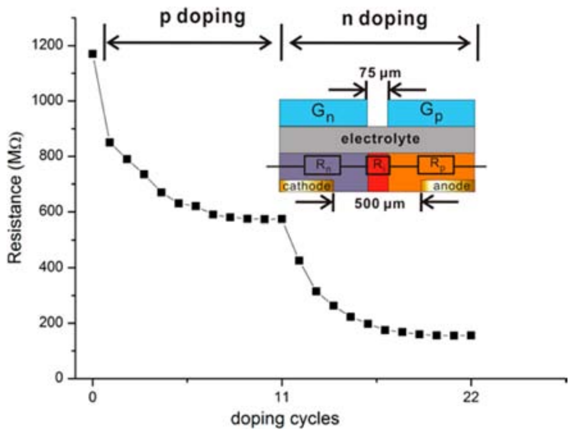

Figure 2. Doping induced electrical resistance change. The inset shows the electrical model of the MEH-PPV layer.

From the aforementioned experiment we confirm that both p- and n-doping occur to a large extent as we find a significant change in resistance during both doping processes. It is known that in LECs the electrochemically doped region of a thin organic semiconductor film can propagate away from the proximity of the charge-supplying electrode.[15,27−29] This occurs because the doping process makes the thin film highly conducting; thus the doped organic thin film can serve as its own electrode. Photoluminescence (PL) is a commonly used technique to study the steady state doping profile or the doping front propagation in LECs. In the PL process, an electron in the ground state of the polymer is excited across the band gap, by the absorption of an incident photon, which then reradiates as a photon. PL quenching is expected to occur for doped MEH-PPV because (electrochemical) doping creates states within the band gap to which an exciton can decay nonradiatively.[24] A

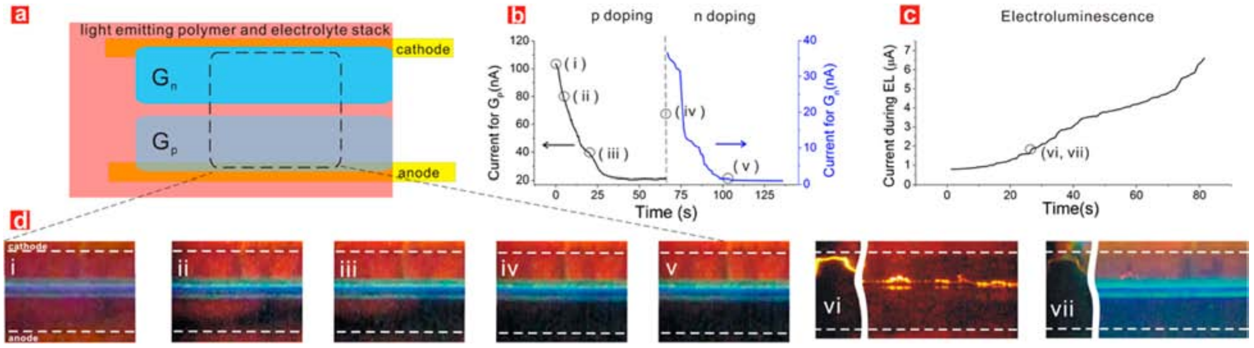

Figure 3. PL and EL characterization for the DG-LECT. (a) A structural sketch of DG-LECT. (b) The gate current response in p- and n-doping mode. (c) The current through cathode and anode during EL mode. (d) The corresponding photos as marked in (b) and (c): (i)−(v) PL response during p- and n-doping mode. (vi) EL photo without external light source. (vii) EL photo under UV exposure. We note that in the left part of (vi) and (vii), the light emission corresponds to a part of the device without gate terminal coverage. The average duration was about 40 s for both p- and n-doping.

pristine DG-LECT device (structural sketch shown in Figure 3a) was operated in the p-doping mode for 65 s, followed by n-doping mode for another 65 s; see Figure 3b. During the doping processes, several PL images were recorded, as shown in Figure 3d. The photos were recorded from the top of the DG-LECT with the transparent gate facing the camera. The blue line across the device, in the middle of the photos in Figure 3d(i)−3d(v), indicates the spilt of the gate electrode. The upper (lower) part of the photos shows the n-doping (p-doping) region. Figure 3d(i) displays the PL response of a pristine undoped device, and Figure 3d(ii)−3d(iv) show PL quenching associated with p-doping. The p-doping front is propagating from the anode toward the middle of the junction. We note that the p-doping front does not cross the line that separates the two gates. This is due to the lack of an electric field to promote p-doping outside the region of the G_p.

However, we did not observe any major PL quenching effect underneath G_n during the n-doping process, as indicated in Figure 3d(iv) and 3d(v). We speculate that it is due to the following two reasons: (1) the n-doping induced PL quenching is known to be less apparent than that of p-doping especially at a low doping level;[25,27,29] (2) the coverage of the translucent electrolyte and the PEDOT:PSS electrode additionally weaken the visual effect.

After operating the DG-LECT in the p- and n-doping processes (during 65 s + 65 s), the device was biased at 5 V in the EL mode; see Figure 3c. This gives us information about where exactly the light-emitting junction is positioned in between the electrodes. During the EL mode the electric current increases with time which indicates that the doping level in MEH-PPV keeps increasing. An image of the entire emitting junction is given in Figure 3d(vi) and 3d(vii). The latter image shows the emitting junction under exposure to UV light. It is clear from the right part of Figure 3d(vi) that the light emission zone is confined to the middle of the channel, coinciding with the cut that separates the two gate electrodes. For comparison, we leave a small portion of the channel uncovered by any gate electrode; see the left part of Figure 3d(vi). Clearly, the part of the channel located outside the double-gate configuration displays a light-emitting junction positioned adjacent to the negative electrode. From this we draw the conclusion that the n-doping process caused by the G_n is effective and manages to n-dope the entire LEP from the cathode to the center of the channel. It is also worth mentioning that if one alters the n-doping and p-doping sequence (i.e., the n-doping process is performed followed by the p-doping mode), the resulting emission junction again is positioned in the center of the channel, right under the gap between the two gate electrodes.

Moreover, we made a DG-LECT including a G_n−G_p double gate configuration defined as a zigzag-shaped pattern; see Figure 4a and 4b. The p- and n-doping processes were successively carried out followed by biasing the device in the EL mode. The emission junction displays a pattern that fully mimics the predefined zigzag pattern; see Figure 4c. This result further proves that the light emission junction can be fully defined using the double-gate configuration providing control over the p- and n-doping regions. We find that the light intensity is slightly stronger when the emitting junction is located relatively closer to the cathode as compared to the anode. This is due to the fact that the p-doped MEH-PPV is relatively more conductive than the n-doped MEH-PPV[25] so that the electric current running along the channel encounters a

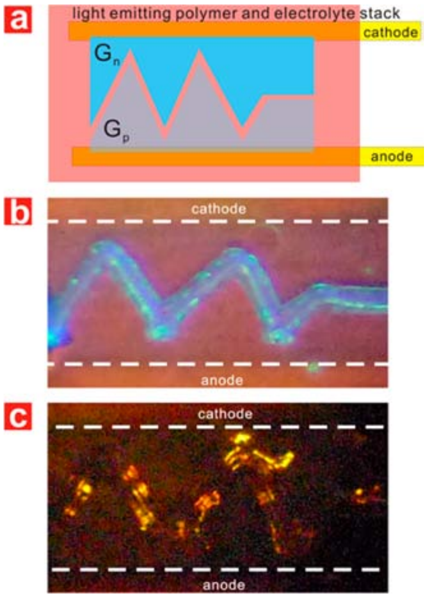

Figure 4. DG-LECT with zigzag-patterned double gate. (a) The structural sketch. (b) A pristine device. (c) A device at EL mode, after being operated under p- and n-doping mode.

relatively smaller electric resistance, thus producing a larger number of luminescent excitons.

Similar to other unoptimized devices,[30,31] while operating in the EL mode, the emitting p−n junction of our DG-LECT slowly moves (5−7 min) along the channel toward the negative electrode due to the dominant p-doping over n-doping. To establish a stable p−n junction, continuous enhancement of the n-doped region is required in order to balance the prevailing p-doping process. This is successfully achieved as follows: After establishing the light-emitting junction within the channel, we apply the n-doping process and EL mode simultaneously; i.e., the voltages applied at G_n and cathode are both 5 V, while the anode electrode is grounded. This device operation protocol manages to keep the junction fixed in the same position for about 2 h; however, the light intensity gradually decreases. Due to this lifetime limit of our device, we could not continue to operate and monitor the device for more than 2 h. We speculate that the short lifetime issue is attributed to the fact that all the manufacturing was carried on in ambient atmosphere and that water-based solutions were used to achieve the electrolyte layer. Water and oxygen residues stored in our DG-LECT devices after manufacturing can potentially deteriorate the operational lifetime.[32]

In summary, we report the double-gate light-emitting electrochemical transistor in which the p- and n-doping of an LEP can be controlled and defined by two electrochemical gate electrodes. Thus, the organic p−n junction can be in situ formed and its exact lateral position can be precisely defined. With the DG-LECT configuration the light-emitting p−n junction can be assured to be located away from the charge injecting electrodes, thus avoiding exciton quenching at the electrodes and establishing an emitting zone that is stable at a specific location within the channel. Our findings show promise for the improvement of the device lifetime and/or the emission efficiency, and we intend to investigate and further explore this in future experiments. Also, in the DG-LECT the electrochemical p-doping and n-doping processes are decoupled from each other and from the electroluminescent operational mode. This offers a tool to further study the operation mechanism of the LEC devices.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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