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# Spatial Control of p−n Junction in an Organic Light-Emitting Electrochemical Transistor

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*Supporting Information*

**ABSTRACT:** Low-voltage-operating organic electrochemical light-emitting cells (LECs) and transistors (OECTs) can be realized in robust device architectures, thus enabling easy manufacturing of light sources using printing tools. In an LEC, the p−n junction, located within the organic semiconductor channel, constitutes the active light-emitting element. It is established and fixated through electrochemical p- and n-doping, which are governed by charge injection from the anode and cathode, respectively. In an OECT, the electrochemical doping level along the organic semiconducting channel is controlled via the gate electrode. Here we report the merger of these two devices: the light-emitting electrochemical transistor, in which the location of the emitting p−n junction and the current level between the anode and cathode are modulated via a gate electrode. Light emission occurs at 4 V, and the emission zone can be repeatedly moved back and forth within an interelectrode gap of 500 μm by application of a 4 V gate bias. In transistor operation, the estimated on/off ratio ranges from 10 to 100 with a gate threshold voltage of −2.3 V and transconductance value between 1.4 and 3 μS. This device structure opens for new experiments tunable light sources and LECs with added electronic functionality.

The past decade has seen a rapid advancement of luminescent organic conjugated polymers, showcasing notable commercial applications, such as large-area lightings and mobile phone displays utilizing organic light-emitting diode (OLED)[1,2] technology. The basic principle of the OLED has been combined with the current modulation properties of the organic field-effect transistor, yielding the organic light-emitting transistor.[3−5] Of particular interest, ambipolar transistor geometries, in which the light-emitting zone is spatially controlled, have been presented.[5] Another light-emitting component, the electrochemical light-emitting cell (LEC),[6−22] has been established as an interesting alternative to OLEDs that has several attractive properties, such as a low turn-on voltage and relative insensitivity to the choice of electrode work function as well as to the thickness of the active organic polymer.[6,7] The basic principle of the LEC has been utilized in organic transistors,[23] yielding devices that emit light but where spatial control of the emitting zone has not been achieved.

A conventional LEC usually comprises an intimate blend of a conjugated luminescent polymer and an electrolyte, but it can also be constructed in a bilayer configuration where the two compounds are stacked in separated layers.[18] The working mechanisms of these two classes of LEC are essentially the same: as long as a sufficiently large voltage is applied to the device, ions migrate toward the electrodes to compensate for the injected charge, leading to p- and n-doped regions of the polymer as a result of electrochemical redox reactions. The doped regions grow in size until they meet and form a p−n junction, where holes and electrons recombine radiatively after flowing through the highly conductive and doped polymer films. This p−n junction dynamically dissipates/reforms when the voltage is released/applied.[15]

In a typical LEC, the p−n junction is formed at a fixed position after complete electrochemical doping of the conjugated polymer film. Efforts have been made to tune the junction position by varying the materials such as the light-emitting polymer,[12] the electrolyte,[8,11] or the electrodes.[19] Processing methods such as thermal annealing[13] as well as the operation protocols[14] likewise change the junction location. However, no reports of in situ spatial control of the p−n junction in a single LEC device have been published. Although the light-emitting zone can be spatially modified in a lateral OLED by employing a field-effect gating configuration,[5] incorporating the conventional gate dielectric and metallic gate onto an LEC does not lead to any analogous effect.[23,24] We believe this is mainly because the electrostatic effect is not sufficient to modulate the essential electrochemical reaction in an LEC.[15]

By employing an electrochemically active conducting polymer material as a gate electrode, we have fabricated a three-electrode device, the light-emitting electrochemical transistor (LECT), in which the p−n junction is established between bottom electrodes, here designated as the cathode (negative electrode) and the anode (positive electrode), and spatially controlled by the top gate. The device (structure shown in Figure 1a) is based on a bilayer LEC, which consists of the light-emitting polymer poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and an ion-conductive electrolyte composed of poly(ethylene oxide) (PEO) and the salt $CF_3SO_3K$. These two active materials are separately stacked on top of Au bottom cathode and anode electrodes. The electroactive polymer poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) is deposited onto the bilayer LEC as a gate terminal to modulate the ion distribution in the electrolyte layer. Besides providing sufficient ions for the electrochemical doping, the electrolyte layer electronically insulates the gate electrode from the light-emitting polymer.

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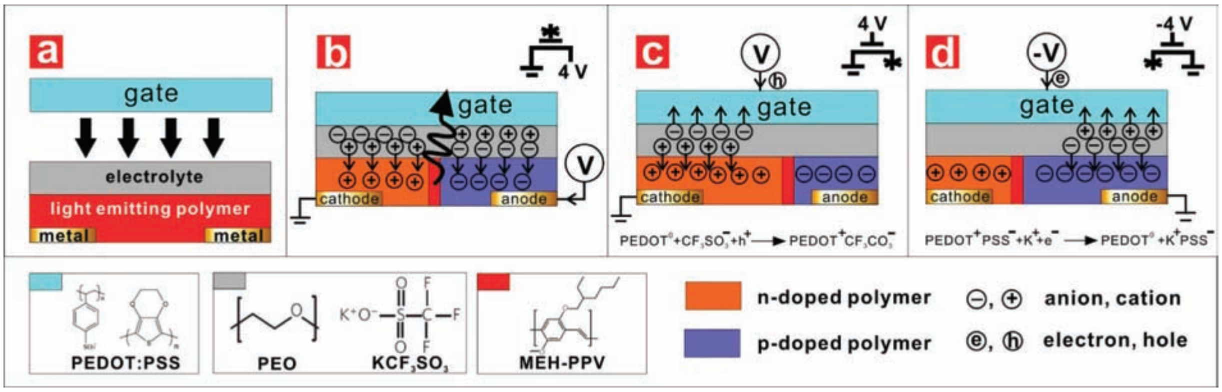

**Figure 1.** Structure, materials, and three working modes of the LECT. (a) An LECT is made by laminating a PEDOT:PSS gate onto a bilayer LEC. (b) In *emission mode*, a voltage is applied between the cathode and anode to facilitate the electroluminescence. (c) In *n-doping mode*, a positive voltage is applied between the gate and cathode, broadening the n-doping from the cathode. (d) In *p-doping mode*, a negative voltage between the gate and anode gives rise to the growth of the p-doping region from the anode.

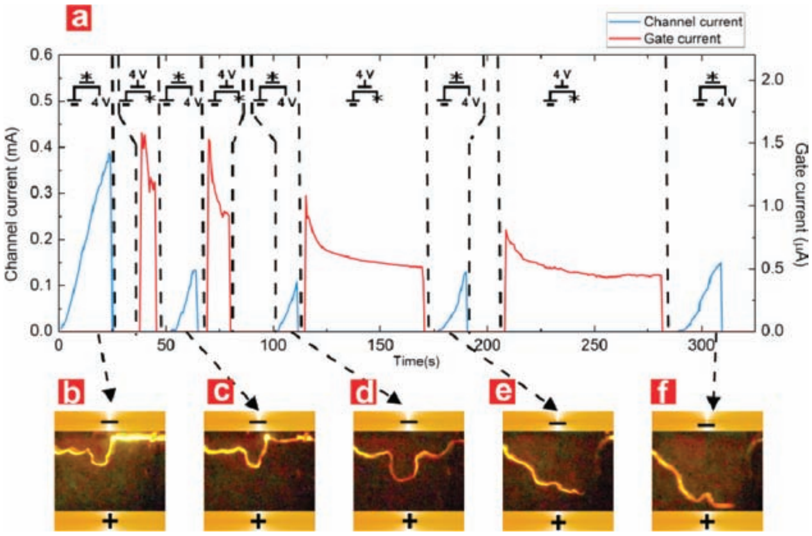

**Figure 2.** Evolution of the light emission zone of an LECT as it was switched between n-doping and emission modes. (a) Electrical characteristics of the LECT during this process. Sections with zero current (e.g., between 80 and 100 s) exist because of handling time for probes and connections. (b) Initialization of the p−n junction. (c−f) Development of the position of the junction after application of each n-doping mode.

We further introduce three operation modes of the device: (I) In *emission mode*, a voltage larger than the energy gap of the light-emitting polymer is applied between the anode and the cathode, ensuring electronic charge carrier injection into the polymer from the bottom electrodes. Reduction occurs at the cathode and oxidation at the anode. This enables a pristine LECT to initialize the formation of p- and n-doped regions and thus light emission along the p−n junction (Figure 1b). (II) In *n-doping mode*, a positive voltage is applied between the gate and the cathode, leaving the anode floating. We anticipate this operation to induce oxidation in the PEDOT:PSS gate accompanied by migration of anions from the electrolyte. The cations in excess are then free to diffuse into the MEH-PPV to further n-dope the polymer (Figure 1c). (III) In *p-doping mode*, a negative voltage is applied between the gate and the anode, leaving the cathode floating. Conversely to (II), we expect this to result in p-doping of the emitting polymer (Figure 1d). The half-reactions involving PEDOT:PSS and ions are shown in Figure 1c,d, respectively. Therefore, depending on the sign and magnitude of the gate voltage, the balance of the p- and n-doped regions within the MEH-PPV film can be controlled in situ. As illustrated in Figure 1, we therefore expect the position of the light-emitting p−n junction to shift toward the anode (cathode) in n-doping (p-doping) mode.

Operation of the LECT in alternating emission mode and n-doping mode is shown in Figure 2. The device was first operated in emission mode at 4 V to initiate the p−n junction and establish light emission. Similar to previously published LECs using the same materials system,[8,11,14,15] our LECT emitted light closest to the cathode (Figure 2b). The p-doped region was then relatively larger than the n-doped zone, which is tentatively attributed to parasitic side reactions occurring at the cathodic interface.[14] The junction exhibited an inhomogeneous curvy shape, possibly as a result of inhomogeneity of the drop-cast electrolyte layer,[9] within the MEH-PPV emitting layer, or along their common interface. The LECT was then operated in n-doping mode, driven by applying a gate bias voltage of 4 V during a period of 6 s, to generate moderate electrochemical n-doping. During the following period of emission mode operation, we observed a slight shift of the recombination zone toward the anode (Figure 2c). This indicates the growth of the n-doping area outward from the cathode as well as some dedoping of the p-doped area. As we repeated the n-doping and emission modes alternatively for

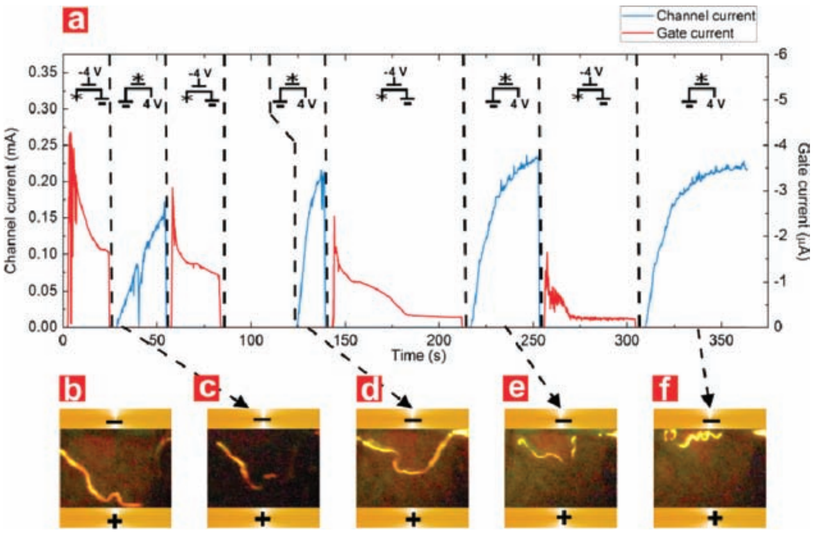

**Figure 3.** Evolution of the light emission zone of an LECT as it was switched between p-doping and emission modes. (a) Electrical characteristics of the LECT during this process. Sections with zero current (e.g., between 85 and 120 s) exist because of handling time for probes and connections. (b) Junction image from the previous n-doping mode (identical to Figure 1f), as a reference for comparison. (c−f) Evolution of the position of the junction after application of each p-doping mode.

three more cycles, we observed that the light emission zone gradually moved toward the anode, and finally, a large fraction of the p−n junction actually reached the border of the anode (see Figure 2d−f). This process demonstrates further expansion of the n-doped region and reduction of the p-doped area due to the migration of cations into and anions out of the MEH-PPV film. It can be concluded from this experiment that applying a positive gate voltage during n-doping mode results in growth (reduction) of the n-doped (p-doped) zone that pushes the p−n junction toward the anode.

Immediately following the experiment shown in Figure 2, the same device was operated in alternating emission mode and p-doping mode for four cycles. As can be seen from Figure 3, here the light-emitting zone moved back toward the cathode after each set of p-doping and emission mode experiments, indicating regrowth of the p-doped area and successive diminution of the n-doped region. We conclude from this operation that a negative gate voltage drives the electrolyte anions to migrate into the MEH-PPV polymer, which promotes p-doping and forces the p−n junction to move toward the cathode. The whole process cycle described in Figures 2 and 3 could be repeated several times with similar results, apart from a gradual decrease in light intensity.

We note that the channel current flowing from cathode to anode in each separate light emission mode measurement (Figures 2 and 3) increased with time. This indicates a rise of conductivity along the channel due to electrochemical doping. However, we observed no corresponding displacement of the p−n junction in this mode of operation. Therefore, we conclude that during emission modes, p- and n-doping take place simultaneously and counterbalance each other and that the electrochemical reaction causing the shift of the p−n junction is solely contributed by the gate current during the n- and p-doping modes. Thus, it is reasonable to assume that the change in area, or actually in volume, of the p-doped region is proportional to the accumulated charge that is transported by the p-doping gate current, with an analogous relation for the n-doped region. We investigated this by plotting the doped area, relative to the initial position of the light-emitting zone, versus the accumulated doping charge as calculated by integration of the gate current (Figure 4). Indeed, this relation is close to linear for both the p-doping and n-doping modes, supporting the conclusion that the shift in emission zone position is entirely controlled via the gate signal.

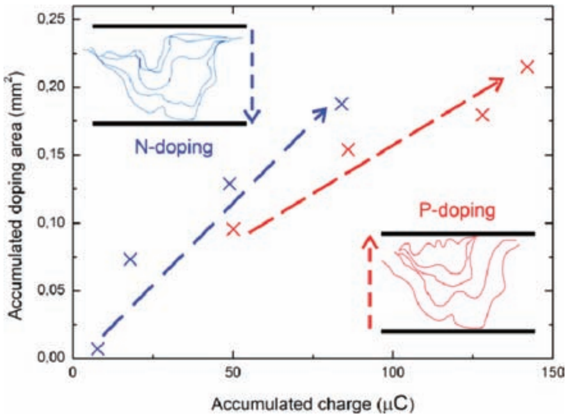

**Figure 4.** Accumulated doping areas in n-doping and p-doping modes vs corresponding electric charge. The insets show the superposition of each p−n junction position in the n-doping and p-doping modes.

The LECT device exhibits several similarities to organic electrochemical transistors with respect to the current−voltage characteristics.[25] As the electrochemical state of the LECT channel is changed by the gate electrode potential, the current between the cathode and anode is controlled. The channel current passes through both the p-doped and n-doped regions and also through the emitting junction; each region exhibits its own specific resistance value. Thus, the gate-controlled current modulation is simply governed by the fact that a change in gate voltage controls the balance between the p-doped and n-doped regions. In addition, at an elevated gate voltage, either the p-doped or the n-doped region starts to extend across the entire channel (almost the case in Figure 2f). This should be reflected in a steep increase in the channel current versus the gate voltage. In Figure 5, the channel transfer characteristics for the

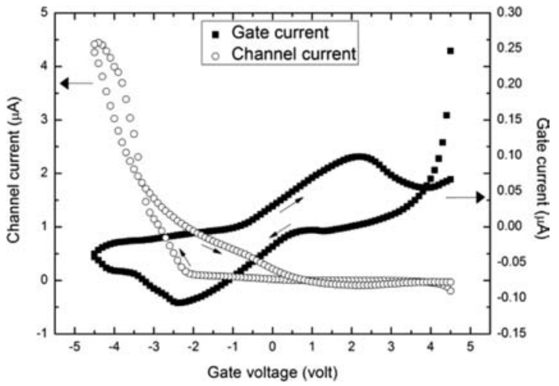

**Figure 5.** Transfer curve and gate current recorded at a sweep rate of 13 mV/s. The voltage between the cathode and anode was 1 V, and the gate was swept from +4.5 to −4.5 V.

LEC are given for a sweep rate of 13 mV/s. Here the channel current on/off ratio, estimated for the gate voltages of 0 and 4 V, ranged from 10 to 100, and the transconductance value beyond the gate threshold voltage (−2.3 V) was found to be in the range from 1.5 to 3 μS. Transistor transfer characteristics were measured for several different devices and under different electrical biasing conditions. We found large variations in the transfer characteristics from device to device and typically also large hysteresis effects at relatively higher sweep rates.

To summarize, we have introduced the LECT structure where a p−n junction can be spatially controlled by tuning the n- and p- doping regions within the polymer using a PEDOT:PSS gate. The light-emitting p−n junction can be moved back and forth within an interelectrode gap of 500 μm under a voltage bias of around 4 V. This configuration offers a method to study the fundamental physics and characteristics of the crucial p−n junction of LECs. The LECT device provides an in situ method for controlling the emitting zone of an electroluminescent device, which potentially offers the possibility of modulating the light output characteristics. Further, transistors combined with light emitters define a smart pixel circuit, which combines circuit addressability with active control of the light emission characteristics; our LECT device combines both of these features in one and the same device configuration. Thus, our findings open the door to including LECs in matrix-addressed and/or tunable lighting or display 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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