

## Pinpointing the Dynamic $p$ - $i$ - $n$ Junction

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The  $p$ - $i$ - $n$  junction structure that develops dynamically under an applied bias via electrochemical doping (ECD) is of key importance for the performance of light-emitting electrochemical cells (LECs). While the complex electronic and ionic processes that govern its transient formation have been extensively studied by both experiments and drift-diffusion modeling, less attention has been given to the steady-state junction as a function of voltage. Here we study the formed  $p$ - $i$ - $n$  structure of a polymer LEC at the steady state by measuring and analyzing its most distinctive feature: the current density–voltage–luminance characteristics. Unexpectedly, we find that the effective conductance of the  $p$ - $i$ - $n$  structure exhibits a positive correlation with the applied bias, a behavior not predicted by existing LEC drift-diffusion models. We attribute this discrepancy to the assumption in these models of a constant density of *mobile* ions. Hence, we present a modified model in which the ECD level—represented by the number of ions with which the organic semiconductor is doped—scales with the applied voltage, implying a voltage-dependent doping efficiency. We validate this hypothesis using electron spin resonance spectroscopy and drift-diffusion modeling, while additionally establishing that only a small fraction of the *available* ions in our system, which increases from 1% to 3% with increasing bias, contributes to the ECD and is necessary for efficient LEC operation. These findings not only provide fundamental insights into the operational mechanism of LECs but also have direct implications for the broader organic mixed ionic and electronic conductor community.

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### I. INTRODUCTION

The ability to conduct both ions and electrons is key in emerging organic electrochemical devices since it enables control of the charge concentration and, thereby, the opportunity to manipulate their charge transport. Organic materials with this ability are termed “organic mixed ionic and electronic conductors” (OMIECs). OMIECs are the core component of a wide range of electrochemical devices, including supercapacitors and batteries for energy storage, organic electrochemical transistors for biosensing and bioactuators, and light-emitting electrochemical cells (LECs) for light emission applications [1–4]. The ion transport, generally much slower than electronic transport,

gives rise to common dynamic characteristics of OMIEC devices, including time- and voltage-dependent optoelectronic, morphological, and chemical properties [3,5]. In the particular case of LECs, their OMIEC nature is the key to their characteristic and distinct operation: the *in situ* formation of a dynamic  $p$ - $i$ - $n$  junction.

LECs are electroluminescent thin-film devices, capable of large-area emission, that typically comprise three layers: an active layer sandwiched between two electrodes. The active layer is an OMIEC, and consists of a blend of a luminescent organic semiconductor (OSC) and an electrolyte [1,4]. The OSC is responsible for electronic conductivity, while the electrolyte enables ionic conductivity through its mobile ions. Some LEC architectures use, instead, ionic transition metal complexes (iTMCs) or cyanine dyes as the active layer, allowing a single material to perform both tasks [6–9]. However, they are typically blended with an additional electrolyte to increase their otherwise low ionic mobility [6–8].

The electrochemical doping (ECD) model is the well-established framework that explains the LEC operation [10,11]. When a bias voltage  $V_{\text{bias}}$  is applied, the mobile

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ions respond to the electric field and accumulate, first, at the electrode interfaces, forming electrical double layers (EDLs). The EDLs reduce the width of the injection barriers and facilitate electronic charge injection by tunneling. Their space charge is then electrostatically compensated by the redistribution of the mobile anions and cations, a process called “electrochemical doping”. As ECD progresses, two regions within the active layer start growing while increasing their electronic conductivity: a  $p$ -doped region near the anode and an  $n$ -doped region near the cathode. The region in between remains relatively free from ECD, maintaining its intrinsic (electronic) conductivity. There, holes and electrons can meet, resulting in exciton formation and subsequent light emission. The dynamic  $p$ - $i$ - $n$  junction has emerged. Eventually, the device reaches a steady state when there is no net ionic current; the ECD process is completed, and the  $p$ - $i$ - $n$  structure is constant in time—with developed doping profiles that resemble those of linearly graded  $p$ - $n$  junctions [11]. Because of its self-organizing nature, the boundaries between the  $p$ -doped,  $n$ -doped, and intrinsic regions are not distinctly defined. This is why the  $p$ - $i$ - $n$  junction is also often referred to as a “ $p$ - $n$  junction” [10,12–14]. Here we opt for the “ $p$ - $i$ - $n$  junction” terminology for convenience.

Regardless of the terminology, the developed junction structure plays a key role in determining the device efficiency. On the one hand, the thickness and ECD level of the different regions determine the electrical properties of the device, enabling its characteristic low-voltage operation [10,11]. On the other hand, detrimental effects arise when, for example, the emissive intrinsic region is located either too close to the electrodes—where the emission can be heavily quenched—or at a destructive interference site [14–17]. In static  $p$ - $i$ - $n$  junctions, such as  $p$ - $i$ - $n$  organic light-emitting diodes (OLEDs), excitons are often confined within a distinct emission layer through purposely designed blocking layers, which additionally prevent light losses via exciton-polaron quenching (EPQ), while maintaining low Ohmic losses [18]. However, the self-organizing nature of the LEC’s dynamic  $p$ - $i$ - $n$  junction comes at a cost: exciton formation occurs in direct contact (and even overlap) with the doped regions, leading to severe EPQ and subsequent luminance reduction [19–21]. This trade-off emphasizes the importance of controlling and understanding the LEC’s  $p$ - $i$ - $n$  junction structure [19].

In this regard, significant efforts have been made to understand the transient dynamics and junction formation both experimentally [10,13,14,22–27] and through drift-diffusion (DD) numerical modeling [11,14,28–31]. Despite the extensive research in the field, the dependence on  $V_{\text{bias}}$  of the developed  $p$ - $i$ - $n$  junction at steady-state operation has been somewhat overlooked. Numerical drift-diffusion models have focused primarily on transient dynamics at a single, constant  $V_{\text{bias}}$ , ignoring the effect that  $V_{\text{bias}}$  itself has on the resulting  $p$ - $i$ - $n$  structure. Furthermore, these models

typically assume that all the ions present in the active layer are (equally) *mobile* and therefore participate either in the EDL or in the ECD process at the steady state, inherently assuming a liquid-like ion-transport mechanism. However, previous experimental studies have hinted that the number of *mobile* ions is considerably less than the number of ions available in the active layer in the form of salt complexes [17,29,32]. With this in mind, our study focuses on understanding the steady-state characteristics of the dynamic  $p$ - $i$ - $n$  junction.

In this work, we compare the experimental steady-state current density–voltage–luminance ( $j$ - $V$ - $L$ ) characteristics of a polymer-based LEC with the state-of-the-art LEC drift-diffusion model for voltages above the energy gap ( $V_{\text{bias}} > E_g/q$ ); that is, once the  $p$ - $i$ - $n$  junction has formed. The measured and modeled  $j$ - $V$  characteristics reveal opposing trends in the reorganization of the  $p$ - $i$ - $n$  structure as a function of  $V_{\text{bias}}$ . To further investigate the origin of this discrepancy, we perform fast  $I$ - $V$  scans, capturing a snapshot of the experimental  $p$ - $i$ - $n$  junction at each steady state and allowing us to pinpoint its origin to the dependence of the intrinsic region width on  $V_{\text{bias}}$ . To explain the experimental results, we propose a scenario in which the number of accessible and mobile ions ( $\rho$ )—and, thus, that are available for ECD—scales with  $V_{\text{bias}}$ . We validate this hypothesis through *in operando* electron spin resonance (ESR) spectroscopy, additionally finding that only about 1%–3% of the existing ions in the active layer contribute to the ECD. Furthermore, we show that drift-diffusion simulations incorporating a positive and reversible dependence of mobile ion concentration on  $V_{\text{bias}}$  qualitatively reproduce the experimental results. Finally, we discuss the possible microscopic physical origin of this effect and its implications for device performance.

## II. RESULTS

### A. Model system and assumptions

We choose a well-known and well-studied polymer-based LEC as the model system to investigate its  $p$ - $i$ - $n$  junction at the steady state. The device consists of a simple three-layer structure: indium tin oxide (ITO) (anode)/active layer/Al (cathode), with the active layer consisting of a blend of the electroluminescent conjugated polymer Super Yellow (SY), and the electrolyte hydroxyl-capped trimethylolpropane ethoxylate (TMPE-OH; ion transporter) and  $\text{KCF}_3\text{SO}_3$  (salt), which provides the mobile ions [33]. SY has a nominal fundamental energy gap  $E_g$  of 2.6 eV, as determined from the redox onset potentials in thin-film cyclic voltammetry [33,34]. All the optoelectronic characterization is performed under constant and controlled room temperature conditions. See Appendix A and Fig. 7 therein for further details on device fabrication, structure, and energy levels.

The same device structure is used to simulate the optoelectronic characteristics with use of the one-dimensional drift-diffusion model provided by and implemented in SETFOS version 5.4 from Fluxim. This implementation represents the state-of-the-art LEC drift-diffusion model and assumptions widely adopted by the research community. Here we highlight some of these relevant assumptions that should be considered before proceeding (see Appendix A for complete details). A symmetric Ohmic injection barrier of 0.1 eV at each electrode interface is used, deliberately omitting injection from realistic EDLs, while still capturing its practical effect. This is because our model does not account for injection through the EDLs, which requires a tunneling injection model. However, this assumption does not affect the results presented, as further justified in Appendix A and later validated by the experimental data. Figure S1(a) in Supplemental Material [63] displays the zero-bias band diagram (continuous line) for the modeled LEC. To keep the model as straightforward as possible, a constant and equal hole and electron mobility  $\mu$  is chosen, which leads to a centered intrinsic region and emission. To maintain the charge neutrality, the same density of anions and cations is used, which is referred to indistinctly as the “total ion density”  $\rho$ , unless otherwise stated. All the ions are assumed to be equally mobile and to electrically respond to the applied voltage. Moreover, in this model, the total ion density is further assumed to be constant and independent of  $V_{\text{bias}}$ , an assumption commonly adopted in LEC modeling and that will be referred to as  $\rho_{\text{const}}$ . The Einstein-Smoluchowski equation, which relates the diffusion coefficient  $D$  to the mobility  $\mu$ , is assumed to hold for the ionic and electronic charges:

$$qD = \mu k_B T, \quad (1)$$

where  $q$  is the charge of the particle,  $k_B$  is the Boltzmann constant, and  $T$  is the temperature.

### B. The steady-state $j$ - $V$ characteristics of an LEC

One of the most distinguishing signatures of a  $p$ - $i$ - $n$  junction is its  $j$ - $V$  characteristics. In this section, we start by using the prevailing and established drift-diffusion model (hereafter referred to as  $\rho_{\text{const}}$ ) in the literature to simulate the  $j$ - $V$  characteristics of an LEC and later compare them with the experimental data [11,14,30]. In a dynamic  $p$ - $i$ - $n$  junction, these characteristics depend on the voltage scanning rate unless sufficient time is given for the system to reach a steady state at each voltage step. The steady state is achieved once the voltage and current stay constant over time, signaling the end of net ion movement (the electrodes are blocking contacts for the ions). In a DD model, this is mathematically translated into solving the differential Poisson and continuity equations with all time-derivative terms set to zero. Thus, mathematically,

the steady state is both accessible and relatively easy to obtain.

Figure 1(a) shows the simulated ( $\rho_{\text{const}}$  model, dashed black line) and experimental (stars) steady-state  $j$ - $V$  curve of an LEC. We first focus on the modeled curve and the  $V_{\text{bias}} > 2.4$  V region—that is, when the potential barrier ( $E_g/q$  of the OSC) for the ECD has been surpassed. A total ion density  $\rho_{\text{const}}$  of  $5 \times 10^{18} \text{ cm}^{-3}$  was used in the simulation. We observe a linear current-voltage trend, resembling Ohmic behavior, i.e.,  $j \propto V_{\text{bias}}$ . Figure 1(b) shows an effective conductance representation of the data from Fig. 1(a), calculated as

$$G_{\text{eff}} = \frac{I}{(V_{\text{bias}} - V_g)}, \quad (2)$$

where  $I$  is the current and  $V_g = 2.4$  V ( $E_g/q$  minus 0.2 V from the injection barriers). The goal is to compare the conductance of the developed  $p$ - $i$ - $n$  structure at different voltages when the potential barrier  $V_g$  has been overcome. We observe that the device’s  $G_{\text{eff}}$  decreases with applied bias.

*A priori*, the linear behavior observed for  $V_{\text{bias}} > 2.4$  V in Fig. 1(a) (dashed line) might seem inconsistent with the behavior expected from an OSC device under space-charge-limited (SCL) current (SCLC) conditions:

$$j_{\text{SCLC}} \propto \frac{(V_{\text{bias}} - V_{\text{BI}})^2}{d^3}, \quad (3)$$

where  $d$  is the thickness of the space-charge region and  $V_{\text{BI}}$  is the built-in voltage. Strictly speaking, this equation is valid only for a unipolar device with neither doping nor traps. However, since a superlinear behavior with voltage is still expected for bipolar devices [35] or in the presence of traps [36], the following reasoning still holds.

A closer look, with the help of Figs. 1(c) and 1(b), clarifies this apparent inconsistency. Figure 1(c) shows the modeled ion density profiles across the active layer at three different values of  $V_{\text{bias}}$ , indicated by the corresponding symbols in Fig. 1(a). The position  $x$  in the active layer is normalized to  $d_{\text{AL}}$ , with 0 and 1 corresponding to the anodic and cathodic interface, respectively. At the steady state, all the anions and cations (filled and open symbols, respectively) not locked in the EDLs are compensated by holes and electrons, respectively, effectively eliminating the space charge in the  $p$ - and  $n$ -doped regions. From now on, the ion profiles will serve as a proxy for the ECD, and both terms will be used interchangeably unless otherwise stated.

Thus, a distinct graded  $p$ - $i$ - $n$  structure is observed: two triangular doped regions—the  $p$ -doped region (next to the anode) and the  $n$ -doped region (next to the cathode)—that surround an ion-depleted intrinsic region (highlighted with the color-coded rectangles). The intrinsic region width  $d_i$

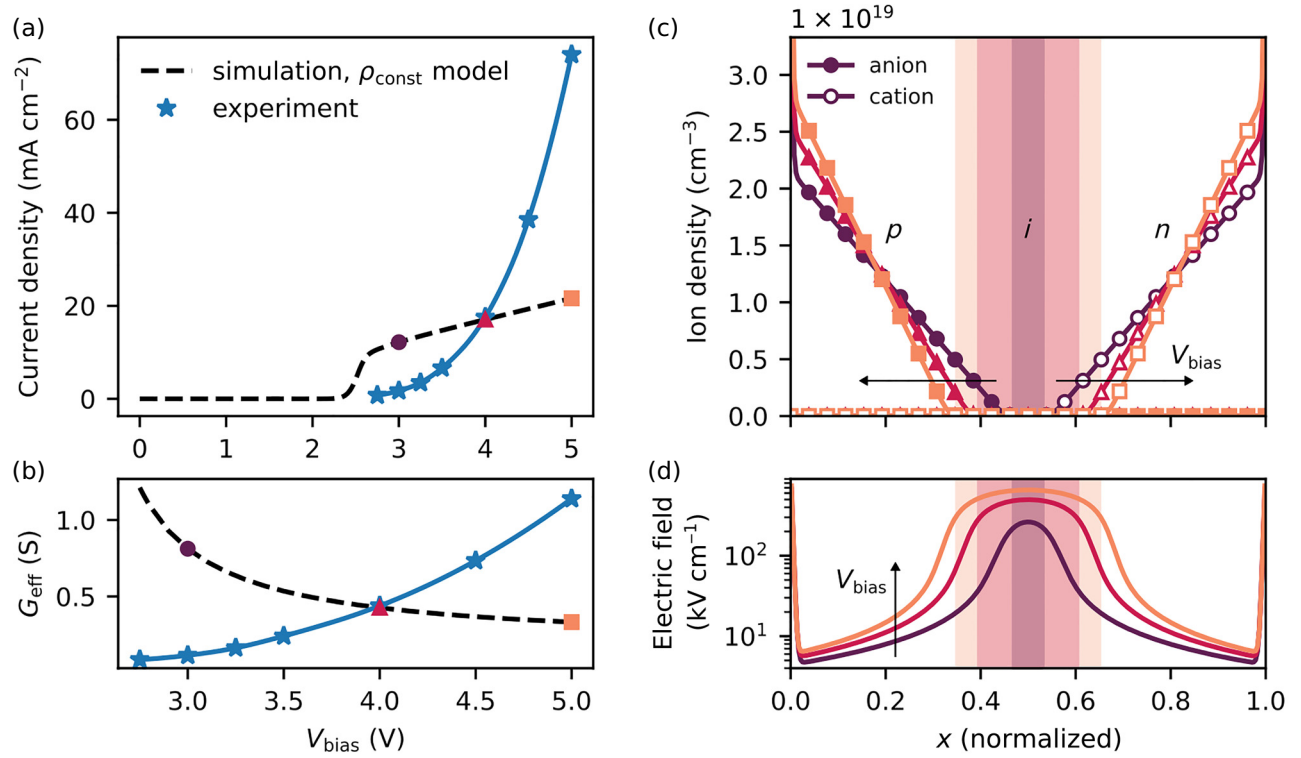


FIG. 1. Experimental vs drift-diffusion simulation data of an LEC's  $j$ - $V$  characteristics. (a) Experimental  $j$ - $V$  characteristics of the LEC at the quasi-steady-state (stars; the continuous blue line is a guide for the eye) and the modeled steady-state characteristics with  $\rho_{\text{const}}$  obtained with drift-diffusion simulation (dashed black line, with total ion density  $\rho_{\text{const}} = 5 \times 10^{18} \text{ cm}^{-3}$ ). Figure S5 in Supplemental Material [63] shows the corresponding experimental luminance-voltage plot. (b) Effective conductance  $G_{\text{eff}}$  representation of the experimental and simulated data in (a); see the main text for further details. (c) Simulated ion density and (d) electric field as a function of the position in the active layer (normalized to  $d_{\text{AL}}$ ) at the three steady-state voltages indicated by the corresponding symbols and colors in (a),(b). The color-coded shaded areas highlight the intrinsic region, and the arrows indicate the trend with increasing  $V_{\text{bias}}$ .

is defined as the region where the (local) ion density  $\varrho(x)$  is 1% or less of  $\rho_{\text{const}}$ . This choice for defining  $d_i$  is somewhat arbitrary; in the dynamic  $p$ - $i$ - $n$  junction the borders between the  $p$ -doped, intrinsic, and  $n$ -doped regions are smoother compared with those in a classical  $p$ - $i$ - $n$  junction (e.g., a  $p$ - $i$ - $n$  OLED). This definition is not fundamental and does not alter the underlying physics. For further discussion, see Figs. 8 and 9, as well as the corresponding text in Appendix B.

More interestingly, Fig. 1(c) also highlights that the simulated dynamic  $p$ - $i$ - $n$  doping structure is dependent on  $V_{\text{bias}}$ . As  $V_{\text{bias}}$  increases, the linearly graded ion profiles become steeper, thinning the doped regions and, consequently, widening the intrinsic region. Because of this thinning, the doped regions become more conductive as the effective doping density increases (the same number of ions now occupies a smaller volume). In contrast, the widening of the intrinsic region is concomitant with a larger space-charge region, effectively decreasing the capacity of the  $p$ - $i$ - $n$  structure to conduct current—see Eq. (3). The decrease in  $G_{\text{eff}}$  shown in Fig. 1(b) is now evident: the  $p$ - $i$ - $n$  structure reorganizes into a less

conductive state with  $V_{\text{bias}}$ , with the widening of the intrinsic region being the most penalizing factor for  $G_{\text{eff}}$ . In the  $j$ - $V$  representation [Fig. 1(a)], the expected superlinear  $j$  dependence on voltage is compensated by the increase of  $d_i$ . Interestingly, this trade-off results in the observed linear dependence of the current on voltage.

The  $d_i$  increase can be qualitatively explained by the drift-diffusion equations for the ions (see Sec. A of Supplemental Material [63]). At the steady state there are no net ionic currents, so the ionic drift and diffusion currents are equal. For example, for the anionic current in a one-dimensional model,  $j_{\text{a,drift}} = j_{\text{a,diffusion}}$ , and thus

$$q\mu_a\varrho_a\frac{dV}{dx} = qD\frac{d\varrho_a}{dx}, \quad (4)$$

where  $q$  is the elementary charge,  $\mu_a$  the mobility,  $\varrho_a$  the anion density, and  $D$  the diffusion coefficient. The Einstein-Smoluchowski relation further simplifies Eq. (4) to the following identity:

$$q\varrho_a\frac{dV}{dx} = k_B T \frac{d\varrho_a}{dx}. \quad (5)$$

If  $V_{\text{bias}}$  is now, for instance, increased, this equality is broken, and the system needs to relax to a new steady state. A stronger electric field develops across the device [see Fig. 1(d) and the band diagrams in Fig. S1(a) in Supplemental Material [63]], leading to an increase in the drift current—left side of Eq. (5). To relax to the new steady state, the ions will reorganize so that the diffusion current compensates for the increased drift current. Therefore, a higher anion density gradient can be sustained, which translates into a steeper ion profile and the increase of  $d_i$ ; see Figs. 1(c) and 1(d) and the direction of the arrows.

How do these predictions compare with the steady-state  $j$ - $V$  characteristics of a real LEC? Let us now shift our focus to the experimental data. The measured  $j$ - $V$  characteristics of a polymer LEC are presented in Fig. 1(a) (blue stars). We note that experimentally only a quasi-steady-state (QSS) can be attained, a fact that we thoroughly address in the next section. For completeness, Fig. S5 in Supplemental Material [63] shows the QSS luminance for the device in Fig. 1(a) (filled symbols), which shows that the device is functional and performing in line with previous reports for this system [14,37].

At this point, we highlight the fundamental discrepancy between the modeled data and the measured data. The measured current density shows a superlinear dependency on  $V_{\text{bias}}$ , in contrast to the linear dependency predicted by the  $\rho_{\text{const}}$  assumption. The equivalent effective conductance plot [Fig. 1(b)] reveals a more pronounced discrepancy, with  $G_{\text{eff}}$  increasing superlinearly with  $V_{\text{bias}}$  for the experimental data, compared with the decrease exhibited by the  $\rho_{\text{const}}$  model. We note that a more realistic model for the electronic mobility, such as a Poole-Frenkel type or the extended Gaussian disordered model (EGDM) [38], also

fails to replicate the experimental data (see Fig. S2 in Supplemental Material [63]).

This discrepancy indicates that when  $V_{\text{bias}}$  is changed, the ECD rearrangement occurs in different ways in the simulation and the experiment. The fingerprint of this rearrangement can be traced by following the transients toward the steady state. In the next section, we analyze this fingerprint.

### C. Capturing the steady-state $j$ - $V$ characteristics: The fingerprint of ion rearrangement

Another way to simulate the steady state is to numerically solve the DD equations in the transient domain until a steady-state condition is reached. In a constant-voltage driving scheme, the device response is simulated until the current reaches a constant value, signaling the attainment of the steady state. Figure 2(a) illustrates this process; it shows the current transient (solid line, right axis) after a stepwise change in  $V_{\text{bias}}$  (dashed line, left axis). In this transient, the device starts at its steady state for  $V_{\text{bias}} = 3$  V, as seen from the initially constant  $j$ . After a certain time, the voltage is instantly changed to 4 V, the current peaks, and then asymptotically decreases to its corresponding steady-state value. Similarly, when  $V_{\text{bias}}$  is lowered stepwise from 5 to 4 V, the current first dips and then asymptotically increases toward its new steady-state value. The asymptotic values at each step can be used to construct the steady-state curve, as indicated by the triangles in Fig. 2(a) plotted in Fig. 2(b). The same process for infinitesimal  $V_{\text{bias}}$  steps would give rise to the curve presented in Fig. 1(a) (dashed line) and replotted in Fig. 2(b) as the continuous line.

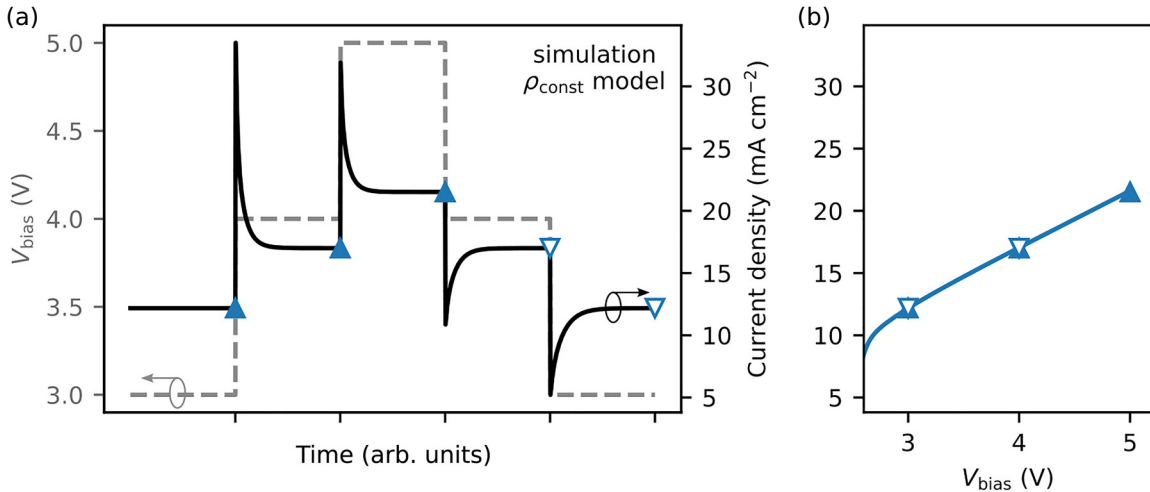


FIG. 2. Simulated staircase transient for the  $\rho_{\text{const}}$  model and obtaining of the  $j$ - $V$  characteristics. (a) Simulated constant-voltage driving staircase scheme (dashed gray line, left axis) and the corresponding current density transient (black line, right axis). The triangles indicate the steady state  $j$  during the forward staircase scan (upward filled triangles) and the reverse staircase scan (downward open triangles). (b) Close-up of the simulated steady-state data presented in Fig. 1(a). The triangles correspond to the steady-state values obtained in (a). Note that the upward and downward triangles overlap, highlighting the lack of hysteresis in the modeled data.

The simulated transient behavior of the current while  $V_{\text{bias}}$  is stepped up or down offers an additional view of the picture shown in Fig. 1. Let us follow that. Immediately after the instant rising  $V_{\text{bias}}$  step (e.g., 3 to 4 V), the device has momentarily the same  $p$ - $i$ - $n$  structure; the ions have not had time to rearrange themselves and, therefore, the current scales approximately as Eq. (3), since  $d_i$  has not changed. With time, the ions reorganize to form a less conductive  $p$ - $i$ - $n$  structure [as shown in Figs. 1(c) and 2(a) and Fig. S3 in Supplemental Material [63] for the transient evolution], and therefore the current decreases until the new steady state is attained. A similar argument holds for the downward  $V_{\text{bias}}$  scan (e.g., from 5 to 4 V); the  $p$ - $i$ - $n$  structure rearranges now from a low conductive state to a higher conductive state—see the current dips in Fig. 2(a). Naturally, this state is the same as the one obtained by the upward step from 3 to 4 V [see the overlap of the triangles in Fig. 2(b)] and shows that no hysteresis is present in the model, as expected. This overall behavior can thus be interpreted as a fingerprint of ion reorganization.

We now shift to the experimental data and to the explanation of how the measured steady-state  $j$ - $V$  characteristics from Fig. 1(a) were obtained. Unfortunately, the experimental steady state is more complicated to attain than the modeled one. Device degradation and long timescales (e.g., very slow-moving ions) are always at play, so the monitored current never stabilizes, and the device never reaches a “true” steady state. However, a good approximation of the steady state can be taken when the change in current with time is sufficiently small. In this study, this was achieved by continuously applying a bias voltage until the relative rate of change with time of the current density  $j$  was less than  $9 \times 10^{-5} \text{ s}^{-1}$  (see Appendix A for details). This defined our designated experimental steady state, hereafter referred to as the “quasi-steady-state”. Figure 3 summarizes how the  $j$ - $V$  curve presented in Fig. 1(a) was obtained (note that these data were recorded on a different device). Technical details regarding the measuring protocol can be found in Appendix A, but the key points are summarized below.

The device was prebiased with a constant current density  $j$  of  $12.5 \text{ mA cm}^{-2}$  for approximately 20 min. The current and time settings ensured that the measurement started with an already existing  $p$ - $i$ - $n$  junction close to its QSS (see Fig. S6 in Supplemental Material [63] for the transients). Immediately afterwards, the voltage staircase protocol shown in Fig. 3(a) (dashed gray line, right axis) was applied, and the current transient was recorded (black line, left axis). The time steps ensured the attainment of the QSS condition, corresponding to the last recorded  $j$  value of each  $V_{\text{bias}}$  step—star symbols in Fig. 3(a), later projected to Fig. 3(b). After the highest  $V_{\text{bias}}$  had been reached, a reverse staircase scheme was applied down to the initial voltage, with the use of symmetric time steps,

and the steady-state values are plotted in Fig. 3(b) as open triangles.

Figures 3(c) and 3(d) show a close-up of the transient upon a step up [Fig. 3(c)] or step down [Fig. 3(d)] of  $V_{\text{bias}}$ , respectively. Figure 3(c) shows that immediately after the increase of  $V_{\text{bias}}$  from 3.00 to 3.25 V,  $j$  abruptly increases from 3.1 to 4.6  $\text{mA cm}^{-2}$  (filled triangle and open square) and, later, asymptotically increase to 6.2  $\text{mA cm}^{-2}$  at the QSS (filled square, representing a 30% increase). Conversely, Fig. 3(d) shows that immediately after the decreasing  $V_{\text{bias}}$  step (from 3.5 to 3.25 V),  $j$  abruptly decreases from 12.9 to 9.3  $\text{mA cm}^{-2}$  (filled triangle and open square) and, later, asymptotically decreases to 7.8  $\text{mA cm}^{-2}$  at the QSS (filled square, representing a 16% decrease). Comparison of Figs. 3(c) and 3(d) highlights the small hysteresis present in the experimental  $j$ - $V$  curve; the downward staircase scan shows a slightly higher QSS current for the same  $V_{\text{bias}}$  [see also Figs. 3(a) and 3(b), open vs filled stars].

Overall, Fig. 3 reveals three main features regarding the current behavior: (1) an abrupt change after each  $V_{\text{bias}}$  step, (2) a gradual transient, and (3) a hysteresis effect. Feature (1) is the most intuitive; the current increases (decreases) abruptly with increasing (decreasing) driving voltage as one would expect in a static  $p$ - $i$ - $n$  junction (e.g., a  $p$ - $i$ - $n$  OLED or a classical diode), since the ions have not had time to respond to the change in the electric field. Feature (2) is more interesting, since it corresponds to the ions reorganizing to a new ECD structure in response to the new electric field. Specifically, the transient rise (decline) in current after increase (decrease) of  $V_{\text{bias}}$  indicates that the  $p$ - $i$ - $n$  junction reorganizes into a more (less) conductive state. These measured trends show behavior exactly opposite that predicted by the  $\rho_{\text{const}}$  model in Fig. 2(a). Feature (3)—the relatively small hysteresis—is consistent with a slow underlying ECD process, as seen by the higher QSS currents observed in the downward staircase scans [Fig. 3(b)]. The latter also indicates that degradation does not dominate during the timescale of the measurement. The “true” steady state was most likely attained during neither the upward nor the downward staircase scan; hence, the name “quasi-steady-state.”

Regardless, the key message taken from the experimental data remains the same: the *fingerprint* of ion reorganization exhibits a trend opposite that expected from the  $\rho_{\text{const}}$  model. It is important to emphasize that this conclusion is further confirmed by the downward  $V_{\text{bias}}$  scan, which shows the same superlinear  $j$ - $V$  characteristics [see Fig. 3(b)]. This consistency indicates that the reorganization process associated with feature (2) is reversible and not merely a consequence of an incomplete transient toward the *true* steady state, which would instead correspond to feature (3). At this point, it is not clear from where the experimental  $V_{\text{bias}}$  dependence of the  $p$ - $i$ - $n$  structure’s charge-transport capability originates. In the next section, we attempt to pinpoint its origin.

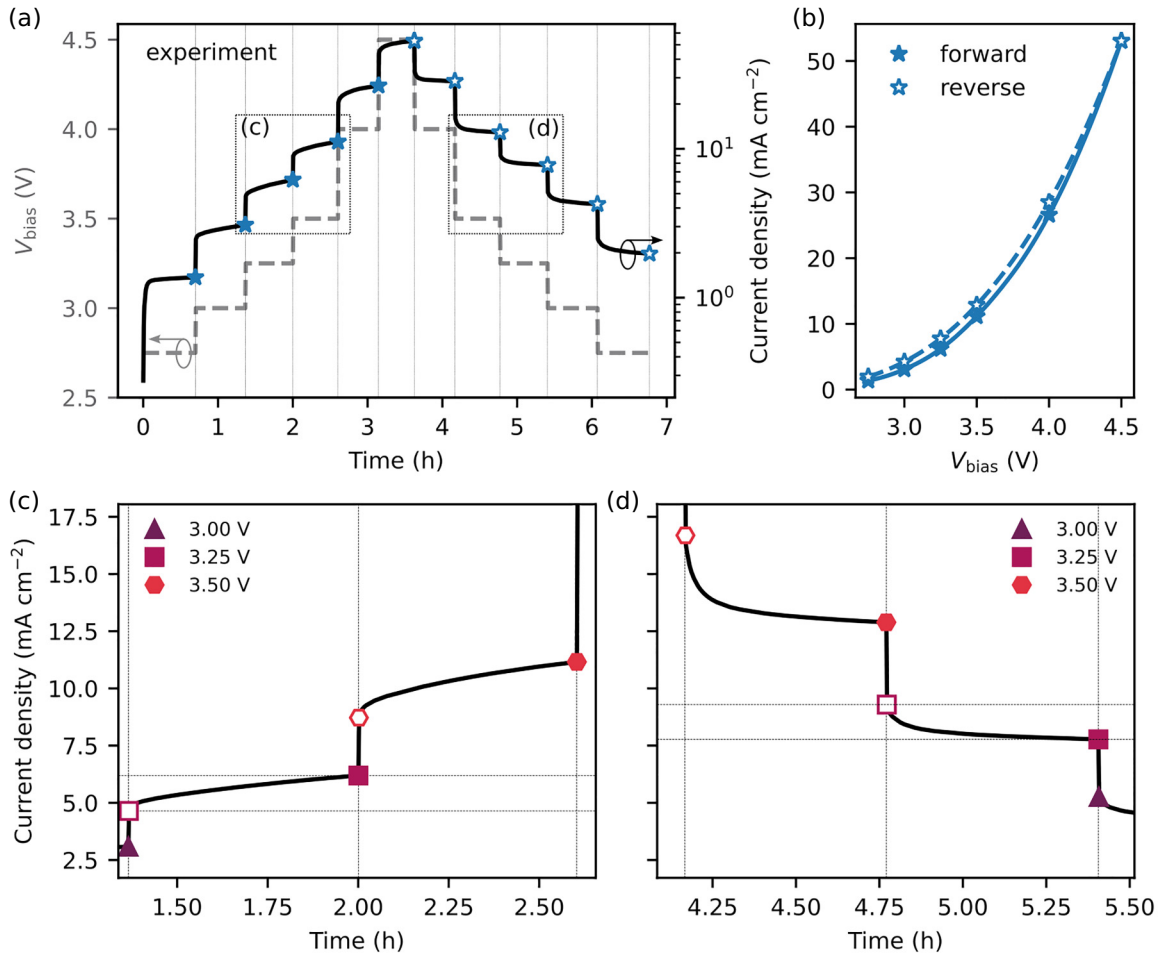


FIG. 3. Experimental staircase transient and obtaining of the quasi-steady-state  $j$ - $V$  characteristics. (a) Bias-voltage staircase scheme (dashed gray line, left axis) and the corresponding transient evolution of the current density (solid line, right axis). The QSS values for the current density were derived when the current change had leveled off (filled and open stars for the upward and downward  $V_{\text{bias}}$  scan, respectively). (b) QSS  $j$ - $V$  of the LEC during forward and reverse bias scans, as obtained from (a); the lines are a guide for the eye. (c),(d) Close-up of the current transients indicated by the boxes in (a). The vertical dotted lines indicate a  $V_{\text{bias}}$  change. The open symbols indicate the initial current density and the filled symbols indicate the QSS current density for  $V_{\text{bias}}$  indicated in the legend. The two horizontal dotted guidelines indicate the initial and final current densities for  $V_{\text{bias}} = 3.25$  V.

#### D. Snapshots of the dynamic $p$ - $i$ - $n$ junction

To further investigate the measured dynamically developed  $p$ - $i$ - $n$  structure, we present a  $j$ - $V$ -snapshot technique. Briefly, we perform fast  $I$ - $V$  scans immediately after the device has reached the QSS to obtain the  $j$ - $V$ - $L$  characteristics. With this strategy, it is possible to capture the signature of the developed  $p$ - $i$ - $n$  junction at each  $V_{\text{bias}}$  value.

“Fast” is a relative term. What does it imply in this context? Here it means performing  $I$ - $V$  scans fast enough so that the ions, and therefore the ECD profiles, do not have time to respond to the changes in the electric field due to their comparatively lower mobility relative to the electronic charges. With this approach the  $p$ - $i$ - $n$  structure behaves, effectively, as if the ion motion were frozen during the scan. A similar approach was applied in an

iTMC-based LEC by Lenés *et al.* [23] to study the ECD transients and by Tordera *et al.* [39] to examine the stabilization of the ECD dynamic configuration using pulsed-current driving. In the present study, the same driving protocol as presented in Fig. 3(a) was used, but an additional (fast)  $I$ - $V$  scan at the quasi-steady-state was performed. To avoid confusion with the terminology, we define  $V_{\text{bias}}$  as the voltage at which the device has been preconditioned before the fast  $I$ - $V$  scan to reach the QSS [that is, the voltages shown in Figs. 1(a) and 3]. In contrast, the rapidly changing voltage applied during the fast  $I$ - $V$  scan itself is referred to as “voltage.”

By ensuring that the forward and backward fast  $j$ - $V$  curves overlap, we can verify that the  $p$ - $i$ - $n$  junction (and the ions) indeed remain unaffected during the measurement. We initially tested different voltage scan rates to find

a balance between speed and signal quality. Scans completed in less than 2 s yielded a good overlap; although minimal ion movement had occurred, the same trends and features observed at faster scan rates were still present. Further details can be found in Appendix A. Figure S8 in Supplemental Material [63] illustrates the overlap between forward (filled symbols) and reverse (open symbols) fast  $I$ - $V$  scans for both the current and the luminance as a function of voltage. The overlap is nearly perfect for most curves, making the two scan directions indistinguishable and validating the  $j$ - $V$ -snapshot approach.

Figure 4 and Fig. S9 in Supplemental Material [63] present the results of the  $j$ - $V$ -snapshot approach for the upward (downward)  $V_{\text{bias}}$  staircase, along with results for the luminance and the current efficacy (CE). The QSS values are shown as blue stars. Figure S7 in Supplemental Material [63] presents the staircase data [equivalent to Fig. 3(a) but for a different device], where the effect of the fast  $I$ - $V$  scans appears as a current dip at the very end of each  $V_{\text{bias}}$  step. While this dip indicates that some ion movement has occurred during the fast scans, the system fully recovers in less than 5 min. We note that while faster scans resulted in significantly smaller dips (i.e., less perturbation) at the cost of increased noise in the current signal, the observed trends were the same.

We first focus on Figs. 4(a) and 4(b), where each curve can now be interpreted as the  $j$ - $V$ - $L$  characteristics of a static  $p$ - $i$ - $n$  structure. The reader will notice that each curve resembles that of a typical organic  $p$ - $i$ - $n$  OLED structure exhibiting three distinct regimes and with a built-in voltage  $V_{\text{BI}}$  of approximately 1.8 V (lower than the OSC's  $E_g$ ): (1) the shunt current regime ( $V < V_{\text{BI}}$ ), where  $j \propto V$  and no light emission is observed; (2) the exponential regime ( $V \approx V_{\text{BI}}$ ), with the current following the Shockley equation and where the onset of light emission is observed, and (3) the SCL regime ( $V \gg V_{\text{BI}}$ ) [40]. For qualitative comparison, the dotted lines show the different functional dependencies of  $j(V)$ : a linear dependence in regions 1 and 3 and an exponential dependency in region 2. The curves show significant overlap at different  $V_{\text{bias}}$  values until the end of region 2, where they begin to diverge. In region 3, the curves exhibit a superlinear dependence, as highlighted by the comparison with the linear dependency of the dotted line. In the SCL regime, the current and luminance increase with  $V_{\text{bias}}$ . Figures S9(a) and S9(b) in Supplemental Material [63] show the equivalent plots for the downward  $V_{\text{bias}}$  scan.

Figures 4(c) and S9(c) in Supplemental Material [63] show that the CE decreases monotonically with  $j$  at a given  $V_{\text{bias}}$  (e.g., see the dark circles). Additionally, a reduction of CE with  $V_{\text{bias}}$  is observed, as indicated by the vertical downward shift of the CE curves. For example, the device biased at 5.00 V exhibits a less efficient  $p$ - $i$ - $n$  structure than the device biased at 2.75 V at the same current density. The trends for the upward and downward  $V_{\text{bias}}$  staircase

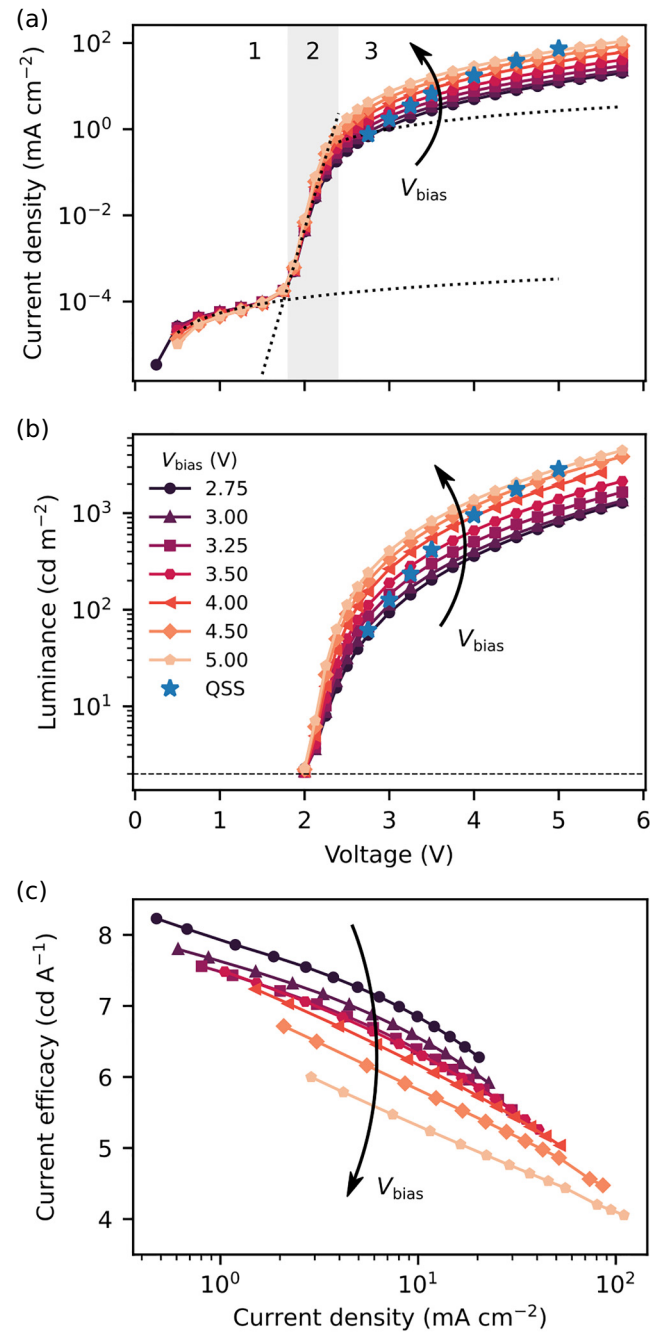


FIG. 4. Experimental  $j$ - $V$  snapshots of the LEC at different values of  $V_{\text{bias}}$ . (a) Current density vs voltage at different values of  $V_{\text{bias}}$  [as indicated in the legend in (b)] corresponding to the protocol performed in Fig. 3. The shaded area and numbers mark the three characteristic regimes of an organic  $p$ - $i$ - $n$  device: shunt (1), exponential (2), and space charge-limited (3) regimes. The dotted lines represent different functional dependencies of  $j(V)$ : linear in regions 1 and 3, and exponential in region 2. (b) Luminance vs voltage at different values of  $V_{\text{bias}}$ . The dashed horizontal line indicates the minimum detectable photocurrent. (c) Current efficacy as a function of the current density. The blue stars in (a),(b) correspond to the steady-state values obtained as in Fig. 3. The arrows in the figures indicate the direction of increasing  $V_{\text{bias}}$ .

scans are the same for current, luminance, and CE (see Fig. 4 and Fig. S9 in Supplemental Material [63]). The only difference is that the variation in the SCL currents with  $V_{\text{bias}}$  is smaller for the downward case, as seen in the closer spacing of the curves in Fig. S9(a) in Supplemental Material [63].

The overlap of the curves until the exponential regime (region 2) indicates that the resistance of the injection layers (EDLs) and the transport layers (i.e., the  $p$ - and  $n$ -doped regions) remains relatively unaffected by  $V_{\text{bias}}$ . If there were significantly different potential drops outside the SCL region, the  $j$ - $V$  curves would shift horizontally. The remarkably high quality of the EDLs is evident from the fact that  $V_{\text{BI}}$  (and the light emission onset) is well below  $E_g/q$  of SY (approximately 1.8 V vs approximately 2.6 V, respectively). This suggests the formation of quasi-Ohmic-contacts at the electrodes, further supporting the assumption of Ohmic injection in the simulations. We remind the reader that in its unbiased state, this LEC device has hole and electron injection barriers of 0.4 and 1.6 eV, respectively (Fig. 7). The detection of light emission as early as 2.0 V is consistent with the well-established wide distribution of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) density of states (DOS) of disordered OSC films, also observed in thin-film SY devices (a Gaussian DOS with  $\sigma = 0.14$  eV) [38,41]. We also note that a universal subgap electroluminescence has been observed in SY OLEDs, and the early onset of light emission in our device is in line with this behavior, further supporting the formation of low injection barriers [42].

We now focus on the fact that the curves in Fig. 4(a) and Fig. S9(a) in Supplemental Material [63] begin to diverge as the current becomes SCL. In this region, the curves are superlinear and parallel to each other, indicating a similar SCL mechanism, which is more clearly seen in the reduced voltage plot presented in Fig. S10 in Supplemental Material [63]. The most susceptible region to space-charge limitations is, naturally, the intrinsic region (and its vicinity). Therefore, the increased SCL current with increasing  $V_{\text{bias}}$  suggests that the increased conductance of the  $p$ - $i$ - $n$  junction originates from the formation of a more conductive intrinsic region. In Fig. 4(b) and Fig. S9(b) in Supplemental Material [63] the increasing luminance trend with increasing  $V_{\text{bias}}$  directly correlates with this increase of conductance: a higher current results in a higher exciton formation rate and a higher luminance. The fact that the same  $V_{\text{bias}}$ -dependent trend is recovered in the downward staircase further confirms the reversibility of the process and aligns with the ion rearrangement fingerprint observed from the transients (Fig. 3). The minor difference between the upward and downward  $V_{\text{bias}}$  scans is attributed to the previously discussed hysteresis effect [see Fig. 3(b)].

More interesting is perhaps the CE as a function of the current density [Fig. 4(c) and Fig. S9(c) in Supplemental Material [63]], as it combines electrical and optical data, providing further evidence of the described  $p$ - $i$ - $n$  rearrangement with a change in  $V_{\text{bias}}$ . On the one hand, the observed monotonic decrease of the CE with increasing current is attributed to the efficacy roll-off caused by increased exciton-polaron quenching, which likely outweighs the roll-on observed in SY-based OLEDs due to triplet-triplet annihilation contributing to singlet-exciton generation [43,44]. On the other hand, the shift to lower CE with increasing  $V_{\text{bias}}$  shows that as the  $p$ - $i$ - $n$  junction rearranges into a more conductive state, it also becomes less efficient.

So far, we have identified the intrinsic region as the origin of the conductance dependence of the  $p$ - $i$ - $n$  junction on  $V_{\text{bias}}$ . However, in a striking contradiction to expectations, the  $\rho_{\text{const}}$  model (Fig. 1) predicts that the intrinsic region actually becomes less conductive—through its widening—when  $V_{\text{bias}}$  increases. What, then, could explain the more conductive intrinsic region in our measured device? One possible explanation is a temperature rise—hopping transport in OSCs is temperature activated—but this is ruled out since the measurements were conducted under controlled and constant temperature conditions (see Appendixes A and D) [45,46].

With the temperature explanation ruled out, the origin must instead come from a change in the device's doping structure. Let us consider a thought experiment: Imagine we have a  $p$ - $i$ - $n$  device of a constant thickness, where we focus solely on its electrical properties. If we now want to increase its conductivity, there are two approaches: (1) reduce the width  $d_i$  of the intrinsic region—and the most resistive region—while increasing the width of the doped regions, and (2) increase the doping level of the  $p$ - and  $n$ -doped regions. In a static  $p$ - $i$ - $n$  device (e.g., a  $p$ - $i$ - $n$  OLED), where the structure is fabricated layer by layer, these two approaches—decreasing  $d_i$  and increasing the doping level—can be controlled independently during layer deposition. However, in a dynamic  $p$ - $i$ - $n$  junction (an LEC), the widths of the  $p$ -doped, intrinsic, and  $n$ -doped regions and the ECD level (i.e., ion-compensated polarons) are interdependent. For example, increasing the total number of ions naturally leads to a thinner intrinsic region, and vice versa [see Appendix B and Fig. 8(b) therein].

Hence, we propose that the increase in conductivity of the  $p$ - $i$ - $n$  structure is due to an increase in the ECD density as  $V_{\text{bias}}$  increases. In this scenario, the predicted increase of  $d_i$  with increasing  $V_{\text{bias}}$  [Fig. 1(c)] can be compensated by the decrease of  $d_i$  caused by the increased ECD density. Since we have shown that the measured effects are reversible, the same reasoning applies to the decrease in  $G_{\text{eff}}$  with decreasing  $V_{\text{bias}}$ . To validate this hypothesis, we measure the ECD density as a function of applied bias by ESR spectroscopy.

### E. Measurement of the electrochemical doping density

ESR spectroscopy can be used to quantify the ECD and the molecular-doping levels in LECs and OLEDs, respectively, during operation [22,47,48]. The ESR signal is generated by the spin resonance condition of the unpaired electrons and holes in the device, and its intensity is proportional to their number. In LECs, the ESR signal is attributed to the ion-compensated polarons, meaning that the number of measured spins provides a measure of the number of electrochemical dopants. The spins in the EDLs are not observed due to their degenerate Pauli-paramagnetic state. For more detailed information on the technique, see Ref. [22].

In this work, we use ESR spectroscopy to measure the ECD density as a function of the applied bias in the LEC under operation. We used a constant-current staircase protocol, using an  $I_{\text{bias}}$  staircase scheme instead of a  $V_{\text{bias}}$  staircase scheme, to minimize the temperature runaway caused by a positive feedback loop between voltage, current, and temperature (see Appendix A for details and Fig. S11 in Supplemental Material for the transients [63]). Data for  $j > 40 \text{ mA cm}^{-2}$  were disregarded due to significant self-heating, for which we estimated a temperature rise of more than  $40^\circ\text{C}$  at the applied electrical power [46]. The total ECD of the device was measured without distinguishing between  $p$ -type doping and  $n$ -type doping. Specific details on the measurement protocol and data analysis can be found in Appendix A.

Figure 5 shows the spin density and the number of spins, derived from the ESR measurements, as a function of the current density, revealing a monotonically increasing spin density—i.e., ECD—with increasing  $j_{\text{bias}}$ . These results align with the hypothesis presented in the previous section. Additionally, we can quantify the amount of ECD occurring in the LEC. The measured ECD density at the QSS is on the order of approximately  $2 \times 10^{18} \text{ cm}^{-3}$ , for current densities in the range of a few tens of milliamperes per square centimeter. This ECD density is significantly lower than the density of potentially available ions in the active layer (i.e., those added in the form of neutral salt complexes during fabrication), which is on the order of approximately  $8.5 \times 10^{19} \text{ cm}^{-3}$ . This implies that only up to approximately 3% of the ions present in the device contribute to the ECD. If the ESR-silent charges from the EDLs are accounted for, the total proportion of ions participating in the LEC operation is estimated to be up to approximately 4%.

Our results partially contrast with those reported by Katsumata *et al.* [22] and Sakanoue *et al.* [48], where approximately 100% of the anions formed  $p$ -type doping but only less than 5% of the cations formed  $n$ -type doping. However, both studies used an ionic liquid-based LEC with unbalanced doping that led to emission forming close to the cathode, potentially caused by electrochemical side reactions of the cations at the cathode. Sakanoue *et al.*

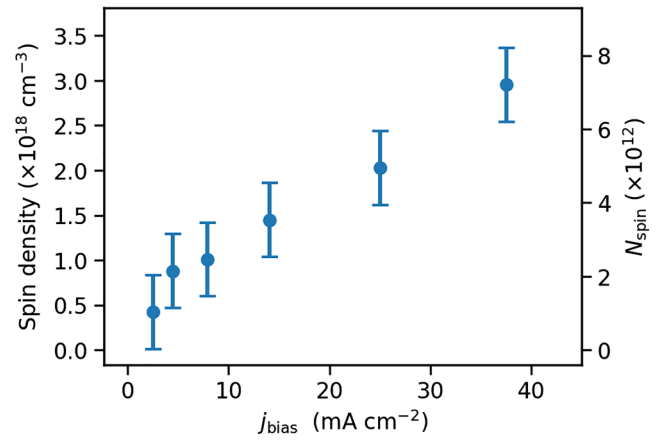


FIG. 5. Measured spin density derived from ESR spectroscopy. The measured spin density (left axis) and the total number of spins (right axis) in an LEC device as a function of the current density at the QSS. The spin density is approximately equal to the ECD density in the LEC. The error bars correspond to the minimum detectable number of spins.

[48] also used a planar LEC architecture driven by a high-voltage pulsed scheme, which differs from our study. Although we could not resolve the  $p$ -type doping and  $n$ -type doping signals in the present study (due to the low-intensity ESR signal), we argue that our system has a balanced  $p$  and  $n$  ECD, as indicated by its reported centered emission zone [14,37]. As a side note, we mention that we were unable to extract reliable data from the downward staircase bias scan due to self-heating effects that led to accelerated degradation.

Our result is somewhat surprising as it shows that only a small fraction of the available ions that are incorporated into the active layer in the form of salt are required to make our device functional and efficient. Moreover, it corroborates previous findings in other LEC systems that suggested that the actual number of *mobile* ions can be significantly lower than the number available in the active layer [20,32]. We also clarify a recurrent issue with drift-diffusion models in the literature: the required ion density in the models to replicate the experimental current densities is typically 1–3 orders of magnitude lower than the actual ion density incorporated into the experimental devices in the form of salt [1,29,32,49]. This is also true for the  $\rho_{\text{const}}$  case (see Fig. 1), where our modeled ion density corresponded to approximately 6% of the experimental ion density, aligning well with the ESR results. There, the lowering of the ion density was necessary to achieve current values of a similar order of magnitude between the model and the experiment.

### F. Modeling the $V_{\text{bias}}$ dependence of the ECD

In this section, we refine the  $\rho_{\text{const}}$  model to test whether its results are consistent with the ESR measurements by phenomenologically introducing a  $V_{\text{bias}}$ -dependent ion

density into the governing equations and creating what we refer to as the  $\rho(V_{\text{bias}})$  model or case. Figures 6(a)–6(d) show the simulated  $j$ - $V$  snapshots of the  $p$ - $i$ - $n$  structure at different  $V_{\text{bias}}$  values for the  $\rho_{\text{const}}$  [Figs. 6(a) and 6(b)] and  $\rho(V_{\text{bias}})$  [Figs. 6(c) and 6(d)] models, which can be compared with the experimental snapshots in Fig. 4. Specific details on this implementation in the simulations can be found in Appendix A.

The  $\rho_{\text{const}}$  model in Figs. 6(a) and 6(b), which assumes that all the ions in the active layer are mobile and participating in the ECD (i.e., the ECD level is independent of  $V_{\text{bias}}$ ), shows an opposite trend for both the  $j$  dependency and the CE dependency on  $V_{\text{bias}}$  compared with the experimental data (Fig. 4), as emphasized by the arrows. This is consistent with the ion reorganization process described in Figs. 1 and 2.

On the other hand, the  $\rho(V_{\text{bias}})$  model in Figs. 6(c) and 6(d), where more mobile ions are effectively “unlocked” as  $V_{\text{bias}}$  increases, shows the same trend with  $V_{\text{bias}}$  for both  $j$  and CE as the experimental data (Fig. 4). Here the number of mobile ions increases from  $2 \times 10^{17} \text{ cm}^{-3}$  at 2.75 V to  $2.5 \times 10^{19} \text{ cm}^{-3}$  at 5.00 V in a

linear manner with  $j$  (see Fig. S4 in Supplemental Material [63]). These values were qualitatively adapted to match the experimental currents. Figures 6(e) and 6(f) show the derived steady-state  $j$ - $V$  and CE- $j$  plots, further highlighting the qualitative agreement between the  $\rho(V_{\text{bias}})$  model and the experimental data.

With the  $\rho(V_{\text{bias}})$  dependency, the observed increase of the effective conductance of the  $p$ - $i$ - $n$  structure and the concurrent decrease in CE with increasing  $V_{\text{bias}}$  can be explained by the increased ECD. In this scenario, the additional ECD leads to steeper concentration gradients, which creates a higher diffusion driving force. This increased diffusion counteracts the stronger ionic drift at higher  $V_{\text{bias}}$ , which would otherwise increase  $d_i$  and reduce the device’s  $G_{\text{eff}}$  [as shown in Figs. 1(c), 8(a), and 8(b)]. The combined outcome of these two competing effects is a relatively constant  $d_i$ , as shown in Fig. 8(c). Additionally, the increased ECD also slightly reduces the space charge over the entire structure at a given voltage, reinforcing the overall increase in  $G_{\text{eff}}$ —although this effect is comparatively minor. The combined effect is a more conductive  $p$ - $i$ - $n$  junction.

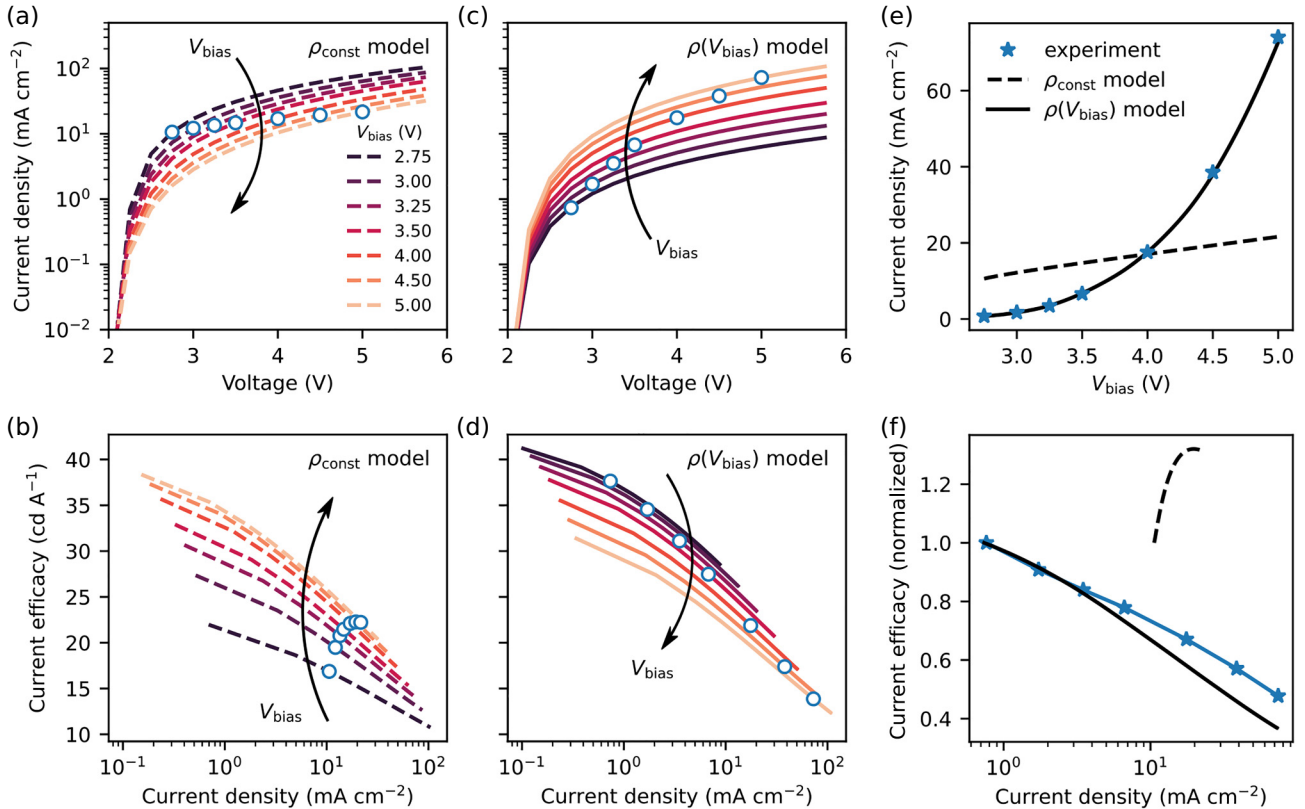


FIG. 6. Drift-diffusion simulations of the  $j$ - $V$  snapshots and steady-state characteristics for models 1 and 2. (a)–(d)  $j$ - $V$  and CE as a function of  $j$  for (a), (b) the  $\rho_{\text{const}}$  model and (c), (d) the  $\rho(V_{\text{bias}})$  model. The open circles represent the steady-state values. The arrows indicate the direction of increasing  $V_{\text{bias}}$  and ion density [for the  $\rho(V_{\text{bias}})$  case]. (e) Comparison of the steady-state  $j$ - $V$  and (f) current efficacy characteristics for the experimental LEC curve (filled stars; the blue line is a guide for the eye), the  $\rho_{\text{const}}$  model (dashed line), and the  $\rho(V_{\text{bias}})$  model (continuous black line). The CE in (f) has been normalized to its value at  $V_{\text{bias}} = 2.75$  V.

Similarly, the decrease in CE with increasing  $V_{\text{bias}}$  can be rationalized in terms of increased EPQ due to two main factors. First, the increase in ECD results in more polarons throughout the device, with those near the intrinsic region—where the excitons are created—being the most detrimental. The second factor is the higher density of excitons resulting from their confinement within a (relatively) constant intrinsic region width [19,21]. The latter contrasts with the  $\rho_{\text{const}}$  case, where  $d_i$  increases with increasing  $V_{\text{bias}}$ , causing the excitons to spread out, reducing their density and locating them further away from the quenching polarons. As a result, in the  $\rho_{\text{const}}$  case, CE increases with increasing  $V_{\text{bias}}$ , as shown in Fig. 6(b).

Although Fig. 6(e) shows good agreement between the experiment and the  $\rho(V_{\text{bias}})$  model, we emphasize that the model is intended not to provide an exact fit but rather to demonstrate qualitative agreement. Here we have chosen to keep the model simple to highlight the fundamental limitations of the  $\rho_{\text{const}}$  assumption (that is, the opposite behavior in ion rearrangement with  $V_{\text{bias}}$ ). Further improvements could include considering a field- and doping-dependent electronic mobility, the effect of doping on the dielectric constant, trapping, or additional recombination mechanisms such as Shockley-Read-Hall recombination, all of which are known to be present in SY-based devices [38,50–52]. However, despite its simplicity and when realistic material parameters are used for SY (Table I), the modeled ion densities in the  $\rho(V_{\text{bias}})$  model were found to be of the same order of magnitude as the ECD level measured by ESR spectroscopy. For example, at  $j_{\text{bias}} = 20 \text{ mA cm}^{-2}$  we obtained similar ion densities of approximately  $2 \times 10^{18} \text{ cm}^{-3}$  and approximately  $5 \times 10^{18} \text{ cm}^{-3}$  for the experimental and modeled data, respectively (see Fig. 5 and Fig. S4 in Supplemental Material [63]).

### III. DISCUSSION

First, it is important to address the elephant in the room: how far is the experimental LEC device from the “true” steady state at the *quasi-steady-state*. As discussed above, the hysteresis shown in Fig. 3 (see also Fig. 4 and Fig. S9 in Supplemental Material [63]) reveals an ongoing slow ECD process. Indeed, while an incomplete ECD process can (and does) explain part of the observed increase of  $G_{\text{eff}}$  of the  $p$ - $i$ - $n$  junction during the upward  $V_{\text{bias}}$  scan, it cannot account for the observed decreasing trend in the downward scan.

Hence, there are two ionic processes to consider, and they can be explained within a single framework: a heterogeneous ion and ionic mobility distribution. In this framework, the high-mobility population (which responds on timescales of seconds to minutes) is responsible for the rapid EDL formation and ECD, delivering the characteristic LEC behavior—that is,  $j$  increasing and leveling

off over time during constant-voltage driving. Meanwhile, the low-mobility population continues to rearrange over much longer timescales, resulting in continuous doping long after the QSS condition has been reached. Thus, the fast ion population determines the observed  $V_{\text{bias}}$  dependence. Moreover, before becoming *mobile*, an ion must be freed from an ion-pair configuration or from interactions with a solvent molecule. One mechanism that could regulate the availability of *free* ions is a broad distribution of salt dissociation free energy, where a field-enhancement effect modulates the dynamic equilibrium between ion pairs (salt) and *free* ions [31,53]. In such a scenario, the dynamics of the ions near the intrinsic region would be most affected due to both the higher likelihood of encountering a counterion and the faster response resulting from the stronger electric field within the intrinsic region.

The previous point highlights that our ion-transport framework in the DD model is oversimplified. While the experimental data could be well replicated by phenomenologically introducing a  $\rho(V_{\text{bias}})$  dependency, a comprehensive model that captures this behavior from first principles is still lacking. One key aspect that likely needs reconsideration is the Einstein-Smoluchowski relation assumption for the—at least—ionic charges, see Eq. (1), which inherently relies on two key assumptions: (1) independent and fully dissociated ions and (2) an ionic-liquid-like transport mechanism. These assumptions often break down in, for example, solid polymer electrolytes, where ion transport typically follows a more complex mechanism involving ion-solvent interactions, ion-ion interactions, free volume fluctuations, and incomplete ion dissociation—a behavior analogous to that of weak electrolytes [5]. These factors directly influence both the number of available ions and the relationship between diffusion and mobility. A deviation from the Einstein-Smoluchowski relation would modify the steady-state profiles and, ultimately, the dependence of the  $p$ - $i$ - $n$  junction structure on  $V_{\text{bias}}$ . Additionally, the finite size of the ions can impact the electronic transport by distorting the OSC DOS [31,41]. Therefore, a natural next step for future research is to improve our understanding of ion transport and the ECD process and to integrate these physical insights into the dynamic  $p$ - $i$ - $n$  junction model.

Finally, we address the practical implications of our findings. Our results show that only a small percentage of the total number of available ions is needed to obtain well-performing LECs, indicating that the excess of ions is not only unnecessary but may be detrimental for the LEC performance [54–56]. Therefore, one might be tempted to simply reduce the salt concentration to the small percentage that proves effective. However, typical LEC salt-optimization studies indicate that this approach is not sufficient: once the salt concentration drops below a critical threshold, the device performance—particularly the operating voltage—deteriorates quickly, for example, due

to insufficient ECD or the inability to form effective EDLs [57,58]. This highlights that reducing salt content alone is not enough; improving ion solubility—that is, transitioning from a weak electrolyte to a strong electrolyte—in the electrolyte-OSC system is crucial to address this limitation as well as to gain better control of the ion-transport mechanism. In the ideal LEC device, all ions should be dissociated and exhibit uniform mobility (e.g., exhibiting a narrow ionic mobility distribution), thereby participating in the dynamic  $p$ - $i$ - $n$  junction formation, either in the EDLs or in the ECD. We hypothesize that such an ideal LEC would follow the  $j$ - $V$  characteristics with the  $\rho_{\text{const}}$  assumption.

The higher ECD density measured in the work reported in Refs. [22,48] in ionic liquid-based LECs already hints at a different ion-transport regime. For this reason, we think it is relevant to investigate the relation between ECD and available ions in other types of LEC system, such as those comprising ionic liquids or host-guest blends, and to extend this study to other OMIEC devices. We propose the fast  $I$ - $V$  scan technique as a valuable tool for probing the formation and properties of other dynamic doping structures. Moreover, it could be worthwhile to exploit the ECD- $V_{\text{bias}}$  dependence for the optimization of the salt content for a given current density, as well as for understanding the performance gains observed in pulsed driving schemes [48].

#### IV. CONCLUSIONS

We have investigated the steady-state behavior of the dynamically formed  $p$ - $i$ - $n$  junction in a polymer LEC, focusing on its most distinctive feature: the  $j$ - $V$  characteristics. Surprisingly, and to our knowledge not previously reported, we demonstrate that as  $V_{\text{bias}}$  increases (decreases), the quasi-steady-state  $p$ - $i$ - $n$  junction structure reorganizes into a more (less) conductive state. This reorganization occurs in the opposite manner to the predictions of the  $\rho_{\text{const}}$  LEC drift-diffusion model. Importantly, this behavior is demonstrated to be reversible, ruling out the explanation that the experiments have not reached a *true* steady state. Fast  $I$ - $V$  scans, capturing “frozen” snapshots of the  $p$ - $i$ - $n$  structure as a function of  $V_{\text{bias}}$ , reveal that this behavior is consistent with an electrochemical doping density (i.e., density of mobile ions) that varies in direct correlation with  $V_{\text{bias}}$ . This hypothesis is supported by electron spin resonance spectroscopy and subsequently incorporated into a modified drift-diffusion model, which further validated it. The ESR measurements additionally show that only a fraction of the existing ions (approximately 1%–3% of the ions introduced as salt complexes during fabrication) participate in the ECD process. Our results reveal—effectively—a low and voltage-dependent ECD efficiency, with significant room for improvement. While our results provide significant insights into the LEC

operational mechanism, we also note that they could be of interest also for the wider OMIEC community. Finally, our results emphasize the need for a more realistic ion-transport model that addresses the limitations and expands the current drift-diffusion models for OMIEC devices.

#### ACKNOWLEDGMENTS

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J.R.-R. and C.L. conceptualized the original idea. X.Z. contributed early  $j$ - $V$  measurements. J.R.-R. developed the method, conducted the experiments and simulations, data analysis, and data curation and wrote the original draft. X.Z. measured the preliminary data. J.R.-R., A.S., and K.M. performed and analyzed the ESR measurements. C.L., A.K., and S.J. participated in the analysis of the different datasets. L.E. acquired the financial support for the project. All authors participated in the revision of the final manuscript.

#### DATA AVAILABILITY

The data that support the findings of this article are openly available [64].

#### APPENDIX A: METHODS

##### 1. Device fabrication

The structure of the fabricated devices was ITO/active layer/Al (see Fig. 7). The active layer consisted of a blend of the fluorescent, phenyl-substituted, poly(*para*-phenylene vinylene) conjugated copolymer Super Yellow (Merck, Germany), the salt  $\text{KCF}_3\text{SO}_3$  (Sigma-Aldrich, USA), and the ion transporter TMPE-OH (Sigma-Aldrich, USA;  $M = 450 \text{ g mol}^{-1}$ ). Super Yellow was used as received; the salt and the ion transporter were dried in a vacuum oven at 190 and 50 °C, respectively, for 12 h before use.

The components of the active layer were individually dissolved in cyclohexanone (Sigma-Aldrich, USA) at the

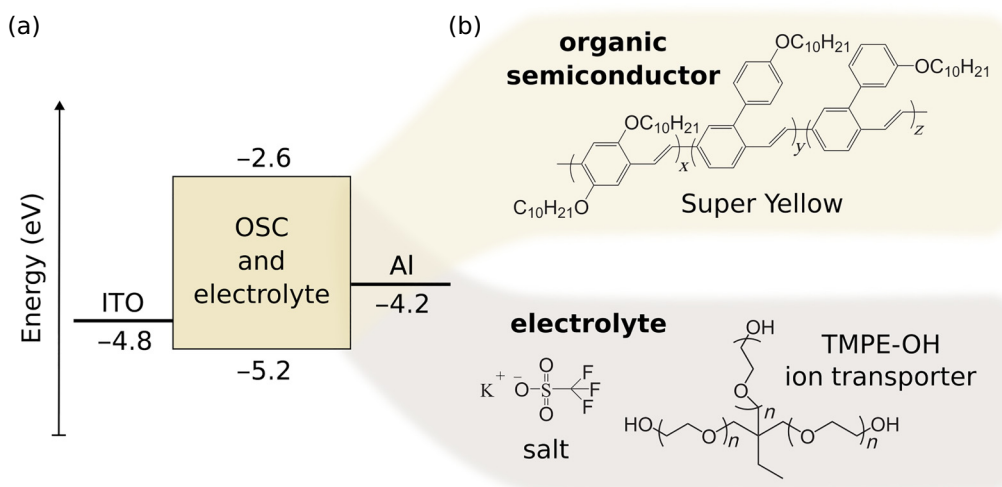


FIG. 7. Device structure, energy-level diagram, and chemical structures of the components. (a) Device structure and energy-level diagram of the LEC. (b) Chemical structure of the active-layer components: the OSC and the electrolyte (and its constituents).

following concentrations: 9.6 mg ml<sup>-1</sup> (SY) and 10 mg ml<sup>-1</sup> (KCF<sub>3</sub>SO<sub>3</sub> and TMPE-OH). The active-material ink was prepared by first mixing the individual inks in an SY:TMPE-OH:KCF<sub>3</sub>SO<sub>3</sub> solute mass ratio of 1:0.10:0.03, and thereafter diluting this blend with cyclohexanone to obtain a final concentration of SY in cyclohexanone of 8.5 g l<sup>-1</sup>. The entire ink fabrication was done under an inert N<sub>2</sub> atmosphere (O<sub>2</sub> concentration less than 1 ppm, H<sub>2</sub>O concentration less than 1 ppm).

The devices were fabricated on ITO-coated glass substrates (ITO thickness 145 nm,  $R_s = 15 \, \Omega \square^{-1}$ , Kintec, Hong Kong). The substrates were cleaned by sequential ultrasonication in detergent (Extran MA 01, Merck), deionized water, acetone, and 2-propanol. The active-material ink was spin-coated on top of the ITO at 3000 rpm for 60 s and subsequently dried at 70 °C for 2 h. The measured dry thickness of the active layer  $d_{AL}$  of the different devices ranged between 125 and 140 nm, as measured with a stylus profilometer (DektakXT, Bruker). The reflective Al top electrodes of thickness 100 nm were deposited by thermal evaporation under a high vacuum (pressure less than  $8 \times 10^{-6}$  mbar) at a rate of less than  $3 \, \text{\AA s}^{-1}$  with the use of a shadow mask. The overlap between the bottom ITO electrodes and the top Al electrodes defined four independent  $2.0 \times 2.0 \, \text{mm}^2$  LEC devices on each substrate. A glass lid was attached on top of the Al electrodes by means of a UV-curable epoxy (Ossila, United Kingdom) to protect the devices from ambient air.

The devices for the ESR spectroscopy measurements were fabricated on a  $3 \times 20 \, \text{mm}^2$  ITO-coated quartz substrate. The active-material ink was spin-coated at 3000–4000 rpm for 60 s, and the rest of the fabrication process was the same as described above. The two devices

measured by ESR spectroscopy had a dry active material thickness of  $122 \pm 3 \, \text{nm}$  and  $113 \pm 3 \, \text{nm}$ , respectively. The overlap between the ITO electrode and the Al electrode defined an active area of  $2.0 \times 10.0 \, \text{mm}^2$ , which ensured a larger area necessary to increase the ESR signal.

The density of ions (anions or cations) in the active layer was calculated with the following formula:

$$\rho_{\text{total}} (\text{cm}^{-3}) = \frac{\rho_{\text{film}} w_{\text{salt}} N_A}{M_{\text{salt}}},$$

where the film density  $\rho_{\text{film}} = 1.0 \, \text{g cm}^{-3}$ , the weight ratio of salt relative to the total weight  $w_{\text{salt}} = 0.027$ ,  $N_A$  is Avogadro's constant, and the molar mass of the salt  $M_{\text{salt}} = 188.17 \, \text{g mol}^{-1}$ . This number yields a total density anions/cations of  $8.5 \times 10^{19} \, \text{cm}^{-3}$ .

## 2. Current-voltage-luminance characteristics

The optoelectronic characterization was performed by placing the devices on a temperature stage, with the encapsulation glass facing the stage surface. A thermally conductive paste was applied between the stage and the glass to ensure good thermal contact. The temperature stage consisted of a Peltier element and a Pt100 sensor, and its temperature was software-controlled with a Raspberry Pi400 and a proportional-integral-derivative algorithm. The temperature of the devices was maintained at either 21 °C or 25 °C with a variation of less than 0.1 °C. Details on the suppression of self-heating are further discussed in Appendix D.

The electrical curves were obtained with the use of a source meter (Keithley 2400) in a standard two-wire configuration. For the luminance measurements, a second

source meter (Keithley 2400) was synchronized with the first one to obtain the photocurrent generated in a photodiode (BPW21, Osram, equipped with an eye-response filter), which was later calibrated with a luminance meter (Konica Minolta LS-110). All the devices were initially prebiased at a constant  $j = 12.5 \text{ mA cm}^{-2}$  (and a compliance voltage set to 21 V) for 20–30 min to ensure characterization began with an already developed  $p$ - $i$ - $n$  structure. Thereafter, the driving mode was switched to constant voltage and the staircase  $V_{\text{bias}}$  scan started. Only  $V_{\text{bias}}$  values above the nominal energy gap (2.6 V) were scanned since it was not a goal of this work to study the doping process.

The scan consisted of application of a constant bias voltage until the quasi-steady-state condition was met before changing to the next  $V_{\text{bias}}$  step. The quasi-steady-state condition was defined as the point at which the current density change over time ( $dj/dt$ ) was sufficiently small, in an effort to mimic the “true” steady state, where  $dj/dt = 0$ . In this work, that was quantified as the relative rate of change ( $r$ ) for the current density as

$$r = \frac{dj/dt}{j}, \quad (\text{A1})$$

which ensured a comparable rate of change across the different order-of-magnitude current densities obtained. An  $r$  of less than  $9 \times 10^{-5} \text{ s}^{-1}$  was chosen as the proxy for the quasi-steady-state. In practice, the time at each  $V_{\text{bias}}$  step was fixed and adjusted to ensure that the condition was met and to account for the longer transients at lower  $V_{\text{bias}}$ , e.g., 45 min for 2.75 V and 30 min for 5.00 V.

The fast  $I$ - $V$  scans were taken at the end of each  $V_{\text{bias}}$  step once the experimental steady state was reached. The total duration of the scans was kept below 2 s, ensuring that the ion reorganization was minimal (see the main text for discussion and Fig. S9 in Supplemental Material [63]). The sweep rate was determined by the number of acquired points, which translated into an effective scanning rate of approximately  $4 \text{ V s}^{-1}$ , except for the injection regime [see region 2 in Fig. 4(a)], where it was approximately  $2 \text{ V s}^{-1}$  to resolve more accurately the exponential behavior. The choice of these scanning rates was a compromise between speed and good signal-to-noise ratio for both the electrical current and the photocurrent signal from the photodiode.

### 3. Electron spin resonance spectroscopy

ESR measurements were performed with an X-band ESR spectrometer (JES-FA200, JEOL). The fabricated devices were sealed in ESR sample tubes (inner diameter 3.5 mm, total length 270 mm), together with a desiccant, in a  $\text{N}_2$ -filled glovebox ( $\text{O}_2$  concentration less than 0.2 ppm,  $\text{H}_2\text{O}$  concentration less than 0.5 ppm). The devices were connected with the use of copper wires and silver paste.

The devices were operated at different constant currents with the use of a source meter (Keithley 2612A) controlled by SweepMe! [59], while the luminance was recorded manually with a luminance meter (BM-9M, TOPCON). The choice of constant current ( $I_{\text{bias}}$ ), instead of constant voltage ( $V_{\text{bias}}$ ), was deliberately made to suppress thermal runaway of the devices. The free-standing geometry of the devices inside the ESR tube resulted in very poor heat dissipation, hindering the suppression of self-heating. In this case, a constant-voltage driving of the LEC induces a current transient that increases with time: simultaneously, the delivered power also rises and, consequently, so does the device temperature. As temperature rises, conductivity also increases, allowing more current to flow and, therefore, more power and a subsequent temperature rise. This positive feedback loop ultimately leads to device failure. On the other hand, constant-current driving shows the opposite behavior: as the device becomes more conductive (doping increases over time) the voltage decreases and so does the power. In this scenario, a temperature increase coincides with a power decrease, which, in turn, self-limits the temperature rise.

The ESR signals were measured as a function of  $I_{\text{bias}}$  by averaging between 10 and 20 ESR spectra over 20–30 min per  $I_{\text{bias}}$  step. The  $g$  factor and the linewidth of the ESR signals were calibrated with the use of  $\text{Mn}^{2+}$  marker standards. The number of spins  $N_{\text{spin}}$  was evaluated by double integration of the ESR spectra and comparison of the result with the  $\text{Mn}^{2+}$  marker signal, which was calibrated with the use of a standard consisting of a 220  $\mu\text{l}$  solution of 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl. The spin density was calculated by dividing the  $N_{\text{spin}}$  by the volume of the active layer in the device.

### 4. Drift-diffusion and optical modeling

The electrical modeling was performed with the drift-diffusion package of the software SETFOS (version 5.4, Fluxim AG, Switzerland), which uses the implicit Euler method to solve the continuity, current drift-diffusion, and Poisson equations. While extensive details of the model can be found in the SETFOS manual [60], we provide a minimal description of the governing equations of the model in Sec. A of Supplemental Material [63] for convenience. The injection through the formed EDLs is not captured by SETFOS since more advanced injection models are not implemented. To compensate for that, a symmetric and Ohmic injection of 0.1 eV was used for both electrodes. This choice is motivated by two reasons: (1) the good quality of the experimentally observed EDLs, as demonstrated in Fig. 4(a) (and the corresponding text), and (2) previous drift-diffusion numerical studies by van Reenen *et al.* [11,30], which have shown Ohmic injection through the EDLs with the use of an *ad hoc* injection model and numerical strategies. The general selection of the model

parameters, which was inspired by Refs. [14,21], is given in Table I. Figure S1(a) in Supplemental Material [63] shows the simulated energy diagrams for the  $\rho_{\text{const}}$  model at three different values of  $V_{\text{bias}}$ .

Except for the transient simulations shown in Fig. 2(a), the equations were solved only for the steady state with a constant-voltage driving scheme and for different values of  $V_{\text{bias}}$ , as indicated in the corresponding figures. At the steady state, ionic mobility does not play a role. The  $j$ - $V$  snapshots from Fig. 6 were modeled by setting a precondition voltage (analogous to  $V_{\text{bias}}$ ) and locking the ion profiles in place before simulating an  $I$ - $V$  scan. Figure S1(b) in Supplemental Material [63] shows the simulated energy diagrams of the *frozen*  $p$ - $i$ - $n$  junction for the  $\rho_{\text{const}}$  model at three different voltages when  $V_{\text{bias}} = 3$  V.

For the transient simulations, a transient signal corresponding to the constant-voltage scheme shown in Fig. 2(a) was applied, and the current transient was obtained. The duration of each  $V_{\text{bias}}$  step was chosen to be sufficiently long for the system to reach a steady state. For this study, the choice of an ionic mobility of  $10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and a duration of 50 ms per  $V_{\text{bias}}$  step ensured that the system reached the steady state. However, we emphasize that the choice of ion mobility affects only the timescale of the transients—either speeding them up or slowing them down—but does not alter the observed behavior. For this reason, the time axis is presented in arbitrary units in Fig. 2(a).

The  $\rho_{\text{const}}$  model was obtained by solving the governing equations and boundary conditions using a fixed total ion concentration  $\rho$  (see Sec. A of Supplemental Material [63]). In contrast, the  $\rho(V_{\text{bias}})$  model was implemented by assigning a different value of  $\rho$  for each applied  $V_{\text{bias}}$  when solving the same set of equations. Lacking a comprehensive model describing the  $\rho(V_{\text{bias}})$  dependency, we introduced the variation phenomenologically: the total ion density was scaled with  $V_{\text{bias}}$  on the basis of a qualitative fit to the experimental data. The resulting empirical dependency is shown in Fig. S4 in Supplemental Material [63] and incorporated into the equations presented.

In all cases, only bimolecular Langevin recombination of holes and electrons was included in the model, with the aim to keep it as simple as possible. The rate equation for the resulting excitons included a generation efficiency of 25% (to account for a fluorescent emitter), diffusion, radiative, and nonradiative decay, and exciton-polaron quenching (see Appendix C for detailed parameter values). To calculate the luminance and current efficacy, the DD output exciton profile was coupled to the transfer-matrix optical model from SETFOS, which accounts for the light propagation through the layered structure. The optical structure also included a glass substrate layer (0.70 mm) and its interface with air. The wavelength-dependent optical properties for each layer were used, and are reported elsewhere [61].

## APPENDIX B: EFFECTS OF $V_{\text{bias}}$ AND TOTAL ION DENSITY ON THE $p$ - $i$ - $n$ STRUCTURE

Figure 8 shows the simulated effect of  $V_{\text{bias}}$  and total ion density (i.e., ions available for ECD), defined as  $\rho_{\text{const}}$ ,

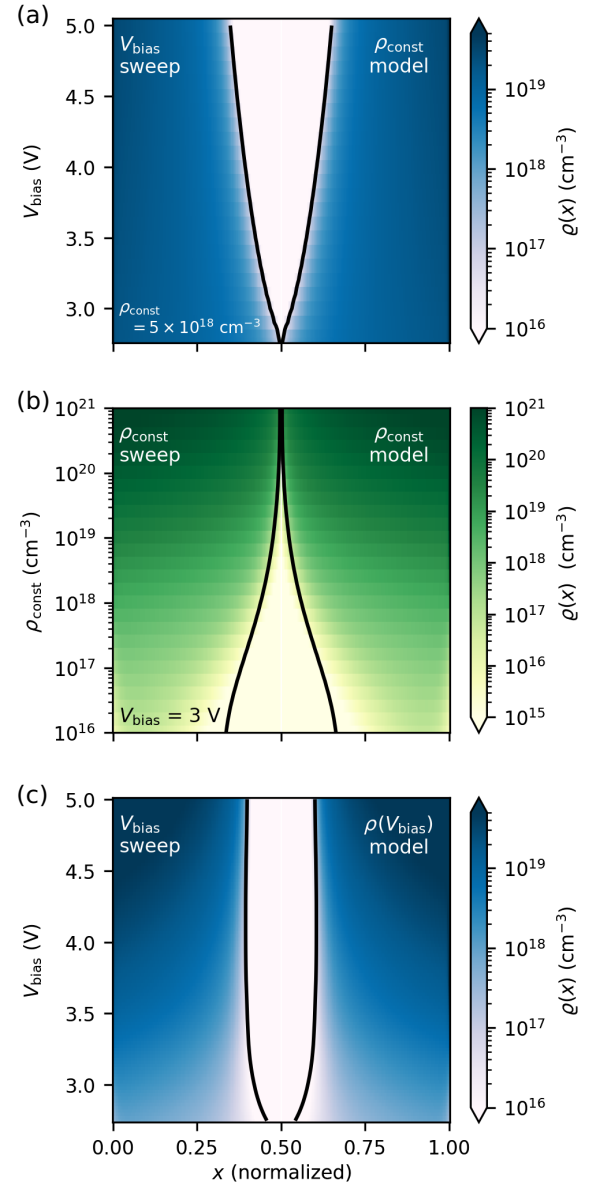


FIG. 8. Simulated effects of  $V_{\text{bias}}$  and total ion density on the local ion distribution profiles across the active layer. The color map represents the local ion density [as the absolute difference between anions and cations,  $|\rho_a(x) - \rho_c(x)|$ ]. The continuous black lines enclose the region where the local ion density  $\rho(x)$  is less than 1% of the total ion density ( $\rho_{\text{const}}$ ), which is defined as the intrinsic region. The ion distribution across the active-layer position is presented as a function of (a) bias voltage at a fixed constant total ion density of  $5 \times 10^{18} \text{ cm}^{-3}$  and equivalent to the  $\rho_{\text{const}}$  model presented in Fig. 1(c), and (b) the total ion density at a fixed voltage of 3 V. (c) Ion distribution for the  $\rho(V_{\text{bias}})$  model, in which the total ion density increases with voltage.

on the dynamic  $p$ - $i$ - $n$  structure at the steady state. The  $x$  axis represents the relative position within the active layer, and the color map represents the local ion density (as the sum of anions and cations),  $\varrho(x)$ , with  $x$  being the position across the active layer. Figure 8(a) shows the effect of  $V_{\text{bias}}$  for a constant  $\rho_{\text{const}} = 5 \times 10^{18} \text{ cm}^{-3}$ , and Fig. 8(b) shows the effect of varying the total ion density at a fixed  $V_{\text{bias}} = 3 \text{ V}$ . In both cases, the assumption is that all the ions are mobile and participating in the ECD ( $\rho_{\text{const}}$  model, see the main text). The continuous black lines enclose the region where  $\varrho(x) \leq 0.01\rho_{\text{const}}$ , which determines the intrinsic region,  $d_i$  (see the main text).

Figure 8(a) shows that  $d_i$  increases with increasing  $V_{\text{bias}}$  (see the main text for further discussion). Figure 8(b) shows a reduction of  $d_i$  with increasing  $\rho_{\text{const}}$  up to the point where it vanishes at around  $2 \times 10^{20} \text{ cm}^{-3}$ , effectively leaving a  $p$ - $n$  junction. A similar effect is seen for  $V_{\text{bias}} < 2.8 \text{ V}$  in Fig. 8(a). Obviously, the transition from  $p$ - $i$ - $n$  to  $p$ - $n$  is not fundamental, and it relies entirely on our definition of the intrinsic region. As shown in Fig. 9(a), the lack of sharp boundaries that classical  $p$ - $n$  and  $p$ - $i$ - $n$  junctions would exhibit makes our choice somewhat more arbitrary since there is no region free from ions (i.e., ECD). Our definition of the intrinsic region highlights the region of the device with significantly fewer charges than the doped regions, with  $\rho_{\text{const}}$  as a reference for definition. However, we emphasize that the choice of  $\varrho(x) \leq 0.01\rho_{\text{const}}$  or  $\varrho(x) \leq 10^{-4}\rho_{\text{const}}$  does not alter the analysis or the naming choice ( $p$ - $n$  vs  $p$ - $i$ - $n$ ), as shown in Fig. 9(b).

Figure 8(c) shows the  $p$ - $i$ - $n$  junction structure under the  $\rho(V_{\text{bias}})$  assumption (see the main text); that is, with increasing  $\rho$  along with  $V_{\text{bias}}$ . In this case, the two opposing

effects of  $V_{\text{bias}}$  ( $d_i$  increase) and  $\rho$  ( $d_i$  reduction) cancel out, giving rise to a more conductive  $p$ - $i$ - $n$  structure—in agreement with the experimental results. Additionally, although not necessarily an inherent outcome, these two competing effects yield a relatively constant  $d_i$  for the case presented. See the main text for further details.

### APPENDIX C: DRIFT-DIFFUSION MODELING PARAMETERS

Table I provides all the parameter inputs necessary to replicate the simulations presented in this study.

### APPENDIX D: VALIDATION OF SELF-HEATING SUPPRESSION IN THE EXPERIMENTAL THERMAL STAGE

To validate that self-heating was effectively suppressed during the operation of the device, we conducted the following experiment. An OLED device, fabricated on the same type of substrate and with the same active area as the LEC devices presented, was placed on the temperature-controlled stage (as described in Appendix A). The device was then subjected to an electrical power sweep ranging from 0.3 to 30 mW, with each step lasting 20 s. During this sweep, the temperature increase of the device's upper surface (measured through the glass substrate) was monitored with a thermal camera positioned 15 cm from the device. A description of the setup can be found in Ref. [46]. The temperature increase is referenced to the baseline temperature of the device before application of any power.

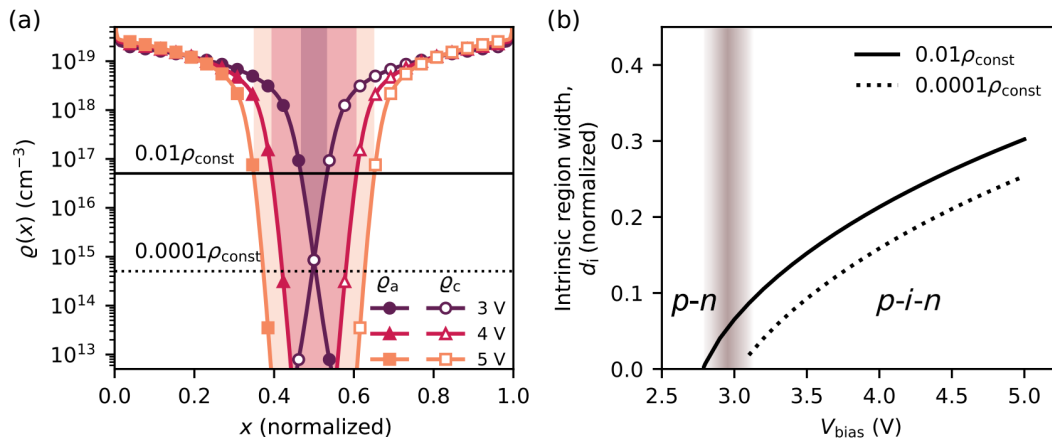


FIG. 9. Intrinsic region width determination for the  $\rho_{\text{const}}$  case. (a) Logarithmic-linear plot of the simulated ion density profiles across the active layer and at the three different steady-state voltages indicated by the corresponding symbols and colors [equivalent to Fig. 1(c)]. The color-coded rectangles in the center represent the width of the intrinsic region starting with our main definition of  $0.01\rho_{\text{const}}$  and a more restrictive definition of  $10^{-4}\rho_{\text{const}}$  ( $\rho_{\text{const}} = 5 \times 10^{18} \text{ cm}^{-3}$ ). (b) Intrinsic region width vs applied bias according to the two definitions of  $d_i$ . The dark shaded region qualitatively highlights the transition from a  $p$ - $n$  to a  $p$ - $i$ - $n$  junction “regime”.

TABLE I. Parameter selection for the drift-diffusion simulation.

| Parameter                                     | Value or type              | Unit abbreviation                         |
|-----------------------------------------------|----------------------------|-------------------------------------------|
| Active-layer thickness $d_{AL}$               | 130                        | nm                                        |
| Relative permittivity                         | 3.0                        |                                           |
| Temperature                                   | 300                        | K                                         |
| Electronic mobility model                     | Constant                   |                                           |
| Electronic mobility $\mu_n, \mu_p$            | $4 \times 10^{-7}$         | $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ |
| Ionic mobility model <sup>a</sup>             | Constant                   |                                           |
| Ionic mobility $\mu_a, \mu_c$ <sup>a</sup>    | $10^{-8}$                  | $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ |
| HOMO level (SY)                               | 5.2                        | eV                                        |
| LUMO level (SY)                               | 2.6                        | eV                                        |
| Injection type                                | Ohmic                      |                                           |
| Injection barrier                             | 0.1                        | eV                                        |
| Density of states (SY) [52]                   | $2.44 \times 10^{20}$      | $\text{cm}^{-3}$                          |
| Ion density $\rho_a, \rho_c$                  | $10^{16}$ – $10^{21}$      | $\text{cm}^{-3}$                          |
| Recombination model                           | Langevin (efficiency of 1) |                                           |
| Singlet-triplet ratio                         | 0.25                       |                                           |
| Singlet diffusion coefficient [62]            | $3 \times 10^{-8}$         | $\text{m}^2 \text{s}^{-1}$                |
| Singlet radiative decay rate constant [62]    | $5.6 \times 10^8$          | $\text{s}^{-1}$                           |
| Singlet nonradiative decay rate constant [62] | $1.6 \times 10^8$          | $\text{s}^{-1}$                           |
| Single-polaron quenching rate constant [44]   | $9 \times 10^{-10}$        | $\text{cm}^3 \text{s}^{-1}$               |
| Electrical circuit                            |                            |                                           |
| Device area                                   | 4                          | $\text{mm}^2$                             |
| Parallel resistance                           | 0.5                        | G $\Omega$                                |

<sup>a</sup>While provided, we emphasize that the choice of ion mobility affects only the timescale of the transients, but it does not alter the observed behavior or the attained steady state, and that is not a relevant factor for this study.

Figure 10 shows the power delivered to the device over time (black line, left axis, logarithmic scale) and the corresponding temperature increase (dashed red line, right axis). In this study (see the main text), the maximum power delivered was approximately 15 mW, corresponding to the highest operating voltage. Figure 10 demonstrates that even under this upper-limit condition, the device temperature increased by less than 0.8 °C. For most of the study, the devices operated below 6 mW, keeping the self-heating-induced temperature rise below 0.5 °C.

Additionally, Fig. 10 shows that the characteristic timescale for temperature equilibration following a change in delivered power is only a few seconds. This behavior contrasts with the much longer characteristic timescales—on the order of tens of minutes—associated with the effect observed in Fig. 3, providing further evidence that these are distinct phenomena. In summary, the results in Fig. 10 confirm that self-heating is—for our practical purposes—effectively suppressed under the

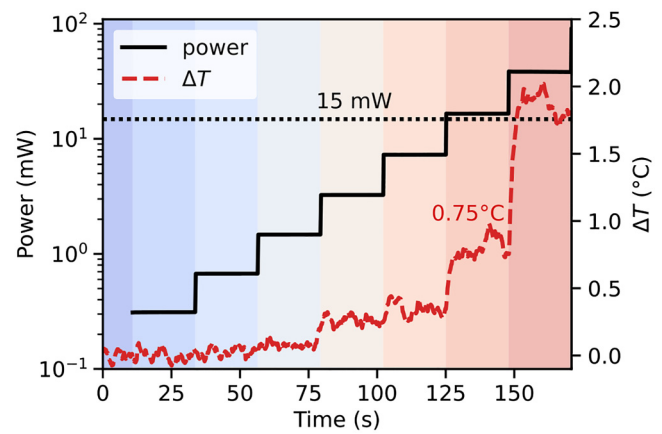


FIG. 10. Self-heating suppression validation of the experimental thermal stage. The left axis (black line) represents the power staircase sweep delivered to the OLED device as a function of time. The right axis (dashed red line) shows the temperature increase of the device's active area, monitored by a thermal camera through the transparent glass substrate. The temperature increase is referenced to the baseline temperature of the device with no applied power (time less than 10 s). The color-coded values indicate the maximum power applied to the devices in this study (also highlighted by the dotted black line) and the corresponding measured temperature rise.

electrical power levels used in this study (except for the ESR measurements, as discussed in the main text).

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