Doping Evolution and Junction Formation in Stacked Cyanine Dye Light-Emitting Electrochemical Cells

Sandra Jenatsch,†,‡,* Lei Wang,†,◊ Matia Bulloni,† Anna C. Véron,† Beat Ruhstaller,§,|| Stéphane Altazin,|| Frank Nüesch,†,‡ Roland Hany,†,*

†Empa, Swiss Federal Institute for Materials Science and Technology, Laboratory for Functional Polymers, CH-8600 Dübendorf, Switzerland.
‡Institut des Matériaux, Ecole Polytechnique Fédérale de Lausanne, EPFL, Station 12, CH-1015 Lausanne, Switzerland.
§Zürich University of Applied Sciences, Institute of Computational Physics, Technikumstrasse 9, CH-8401 Winterthur, Switzerland.
||Fluxim AG, Technoparkstrasse 2, 8406 Winterthur, Switzerland.
◊Zürich University of Applied Sciences, Institute of Chemistry and Biological Chemistry, Ein-siedlerstrasse 31, CH-8820 Wädenswil, Switzerland.

*Corresponding authors.

Correspondence should be addressed to Dr. Roland Hany
Empa
Überlandstrasse 129
CH-8600 Dübendorf
Switzerland
Phone: +41 58 765 4084
e-mail: roland.hany@empa.ch
ABSTRACT: Cyanine dyes are fluorescent organic salts with intrinsic conductivity for ionic and electronic charges. Recently (JACS 2013, 135, 18008), these features have been exploited in cyanine light-emitting electrochemical cells (LECs). Here, we demonstrate that stacked, constant-voltage driven trimethine cyanine LECs with various counter anions develop a p-i-n junction that is composed of p- and n-doped zones and an intrinsic region where light-emission occurs. We introduce a method that combines spectral photocurrent response measurements with optical modelling and find that at maximum current the intrinsic region is centered at ~37% away from the anode. Transient capacitance, photoluminescence and attenuation experiments indicate a device situation with a narrow p-doped region, an undoped region that occupies ~72% of the dye layer thickness, and a n-doped region with a maximum doping concentration of 0.08 dopant/cyanine molecule. Finally, we observe that during device relaxation the parent cyanines are not reformed. We ascribe this to irreversible reactions between doped cyanine radicals. For sterically conservative cyanine dyes, this suggests that undesired radical decomposition pathways limit the LEC long-term stability in general.

1. INTRODUCTION

Two decades ago, the concept of the light-emitting electrochemical cell (LEC) has been presented.\textsuperscript{1} The particular operation mechanism arises from the presence of mobile ions, resulting in merits such as process-tolerant device fabrication, low driving voltage, or the possibility to use air-stable electrodes. Thus, LECs are receiving interest as an easy-to-fabricate and low-cost alternative to the well-known organic light-emitting diodes.\textsuperscript{2}
The basic requirement for the LEC active layer is the co-existence of ionic and electronic charge transport. In devices with conjugated polymers (pLEC) these two transport channels are decoupled, electronic charges are carried by the luminescent polymer whereas ionic charges are provided by an admixed salt. For LEC materials that consist of ionic transition metal complexes (iTMC) the ionic and electronic transport occurs on the same material. For recently, LECs using small molecules have been demonstrated, potentially offering advantages with respect to the easier chemical synthesis and their higher level of purity, as compared to polymers.

The functional principle of LECs has been intensively debated. In recent years, however, it was found that an operating LEC can best be described by an electrochemical doping (ECD) model. This model involves the formation of electric double layers by ionic charges at the electrodes which facilitate electronic charge injection. The injected charges produce p- and n-doped regions at the anode and cathode, respectively, which are locally compensated by ionic charges. A p-i-n junction (sometimes also called p-n junction) forms inside the active material and light-emission occurs from the undoped, intrinsic (i) region. Both pLECs and iTMC-LECs have been investigated in lateral and sandwich cell geometry and their operation mechanisms were found to be governed by the same fundamental processes. Findings by Tang et al. indicate that also non-ionic small molecule LECs exhibit p- and n-doping and follow the predictions from the ECD model.

For lateral structured LECs and using a combination of optical microscopy imaging and photoluminescence measurement, the movement of the p- and n-doping fronts from the electrodes towards each other and the emission originating from the contact line where they meet has been demonstrated. By scanning Kelvin probe microscopy, it has been shown that the potential profile is almost flat in the doped regions and that there is a large drop in the junction region. It is much more difficult to measure the position of the junction in sandwich cell geometry. An attempt by Leger et al. followed a procedure of simulating
experimental electroluminescence spectra.\textsuperscript{26} For the emission zone fit a certain width of the intrinsic region had to be assumed, and this value was obtained by scaling down the width from a lateral LEC. However, it has been demonstrated that the portion of the total active layer that remains intrinsic during operation is much larger in sandwich LECs compared to lateral devices. Values between 10\% and 80\% of the total active layer were reported, strongly dependent on driving voltage and ionic conductivity.\textsuperscript{15-18}

The doping concentration in the p- and n-regions and their evolution over time is an interesting, however difficult-to-measure LEC parameter. Reports by the group of Edman assessed this value for lateral LECs.\textsuperscript{5,20,21} Assuming that every injected electronic charge generates a doped species, the integrated current until the time of junction formation, together with the measured sizes of p- and n-doped regions, allows calculating individual doping concentration. Because the luminance and the current increase further after junction formation, it was proposed that electrochemical doping continues as well.\textsuperscript{22} Therefore, this method can only give an estimate of the concentration when the device starts to emit light. Recently, a quantitative p-type doping evolution during LEC operation was obtained via transient absorption measurements.\textsuperscript{27} However, data analysis required several assumptions, such as the thickness of the intrinsic region that was symmetrically placed in the middle of the active material.

Recently, cyanine dyes were introduced as active LEC components.\textsuperscript{6} Cyanine dyes possess a number of potential merits for LEC applications. Cyanines are semiconducting charged molecules that are accompanied by a counter ion. Iodide usually results from the synthesis, but I\textsuperscript{-} can be exchanged with other anions such as perchlorate or hexafluorophosphate. Thus, no additional salt is required, facilitating LEC fabrication and avoiding phase separation issues in thin multi-component films. Cyanines can be coated from polar and non-chlorinated solvents. In addition, a huge library of cyanine dyes is available for LEC testing, mainly built-
up due to their importance as sensitizers in classical silver halide photography and as fluorescent biomarkers.\textsuperscript{28,29}

Therefore, it is appropriate to study the operational mechanism of cyanine LECs in some detail, as presented in this work. For a trimethine cyanine dye and using different anions, we show that the LEC switch-on time can be adjusted and that the performance trend follows predictions from the ECD mechanism. We performed electro-, photoluminescence, attenuance measurements as well as capacitance - frequency scans at different times of constant voltage operation. This enabled to obtain the thickness of the intrinsic region as a function of time, as well as the maximum doping concentrations. To determine the junction position in the sandwich cell geometry, we introduce a method that uses a combination of photocurrent spectral response measurements and optical simulation. From consecutive LEC measurements on the same device, we find that ionic and electronic charges fully reform during device relaxation, but that parent cyanine dyes are irreversibly consumed during operation. We ascribe this to a presumed high chemical reactivity of the cyanine radicals.

\textbf{2. EXPERIMENTAL SECTION}

LECs were fabricated with the structure ITO/PEDOT:PSS/Cy3-X/Alq3/Ag. Pre-patterned ITO substrates (Geomatec, 20 Ohms square\textsuperscript{-1}) were subsequently cleaned in acetone, isopropanol, soap and deionised water. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, Heraeus Clevios\textsuperscript{TM} P VP AI 4083) was spin coated at 1500 rpm in ambient air to give a film thickness of 80 – 95 nm. The substrates were then transferred to a nitrogen-filled glove box and heated for 10 minutes at 120 °C in order to remove residual water. The active layer with a thickness of \textasciitilde30 nm consisted of a cyanine dye with a trimethine chromophore accompanied by different charge compensating counter ions. 1-Ethyl-2-[3-(1-ethyl-3,3-dimethyl-1,3-dihydro-indol-2-ylidene)-propenyl]-3,3-dimethyl-3H-indolium hexafluorophosphate (Cy3-P) was purchased from FEW Chemicals, Cy3-ClO\textsubscript{4} (Cy3-C)\textsuperscript{30} and
Cy3-Δ-TRISPHAT (Cy3-T) were synthesized in our laboratory (for Cy3-T synthesis see supporting information, SI). Cyanine layers Cy3-P and Cy3-C were spin coated at 6000 rpm from a filtered solution using a concentration of 1 wt% in acetonitrile (ACN, Sigma-Aldrich, anhydrous, 99.8%), for Cy3-T a 1 wt% chlorobenzene (Sigma-Aldrich, 99.8%) solution was used because of its poor film formation properties from ACN. On top of the active layer a 2 nm thick tris(8-hydroxyquinolinato)aluminium (Alq₃, Sigma-Aldrich, 99.995%) was vapor deposited. Two different cell areas (3.1 and 7.1 mm²) were defined by depositing silver (Ag) through a shadow mask with a thickness of either > 65 nm or 12 nm to obtain a semitransparent top contact.

Film thicknesses of PEDOT:PSS were measured using a profilometer (Ambios XP1). For cyanine films attenuance spectra were compared to reference samples on glass with known thickness. Transient LEC operation was monitored using a Konica Minolta luminance meter LS-110 equipped with a close-up lens No. 110 and a Keithley 2400 to apply the driving voltage and to measure the current. If not specified cells were operated at a constant bias voltage of 3 V. Incident photon to current conversion efficiencies (IPCE) on pristine or biased devices were measured using a 300 W Xe light source equipped with an AM1.5G filter and a monochromator. The light intensity was determined with a calibrated Si-diode. The testing time for an IPCE measurement was 1 min. Attenuance measurements were performed on a Varian Cary 50 UV–vis spectrophotometer. Full cell spectra were recorded in transmission mode using a semitransparent Ag electrode. Transient attenuance spectra were measured without switching off the voltage during the wavelength scan. Photoluminescence spectra were recorded on a Horiba Jobin Yvon Fluorolog spectrometer. For these measurements the voltage had to be switched off during the measurement because otherwise the electroluminescence spectra would overlap with the photoluminescence spectra. The scan was started immediately after switching off the bias and the voltage was reapplied afterwards. Impedance spectroscopy before and during constant voltage LEC operation were measured.
using the PAIOS measurement platform (Fluxim). This measurement was performed without any offset voltage, using an alternating voltage of 70 mV. All measurements in this work were performed under nitrogen atmosphere. Optical simulations were carried out using the commercially available simulation software SETFOS, version 4.1 (Fluxim).

3. RESULTS AND DISCUSSION

Operating Mode

The device architecture and the chemical structure of the cyanine dyes are shown in Figure 1. We chose Ag as the metal for the top electrode instead of the more commonly used aluminum, because Ag has favorable properties for the deposition of thin semitransparent, conductive films. Further, a 2 nm thick Alq3 film was inserted between the active layer and Ag. Alq3 acts as a buffer layer to block the diffusion of cathode atoms into Cy3-P during deposition but does not display optoelectronic properties in our device configuration. First, the attenuance of a 2 nm Alq3 film is small (maximum ~1.3% at 400 nm) and does not overlap with the Cy3-P absorption. During device operation, electrons are injected via Alq3 into Cy3-P but no excitons leading to light emission (peak intensity at 550 nm) from Alq3 are formed. This is because electron-hole recombination takes place in the intrinsic region. In addition, the photoluminescence of such a thin organic film in proximity of a metal would be effectively quenched.

Figure 2 shows a long-term luminance and current transient of a Cy3-P LEC. This transient is characteristic for an LEC operated at constant voltage driving. First, the current is dominated by ions drifting to their respective electrodes. When the ions reach the electrodes charge injection is facilitated, which enables oxidation and reduction of the cyanine molecules to start at the anode and cathode, respectively. The doped cyanines are stabilized by the opposite ionic charge. Injected holes and electrons recombine in the intrinsic region leading to light emission. Further growth of the doped regions leads to an increase of both the current
and the luminance in phase 1. In phase 2, the reduction of the intrinsic region continues such that more and more excitons undergo non-radiative recombination in the doped regions and consequently the luminance decreases.\textsuperscript{2,37} Finally, also the current starts to decrease which is generally attributed to irreversible device degradation (phase 3).\textsuperscript{12,38} 

**Figure 1.** Chemical structure of the cyanine dye Cy3\(^+\) and the device configuration under operation.

**Figure 2.** Current density (filled symbols) and luminance (open symbols) transients for a Cy3\(^+\)-PF\(_6\) (Cy3-P) cell operated at 3 V. The three regimes of operation are indicated.
The switch-on time or more generally the transient LEC behavior is directly governed by the ionic mobility.\textsuperscript{12,39} To study the ion-transport-limited junction growth we used different cyanine counter anions and monitored the LEC transient luminance and current (see Figure 3). We define the switch-on time as the time when the luminance reaches a value of 0.1 cd m\textsuperscript{-2} for the first time. This parameter exhibits a difference of one order of magnitude between ClO$_4$\textsuperscript{-} and PF$_6$\textsuperscript{-} based devices. Such behavior is in agreement with their large difference in ionic conductivity.\textsuperscript{40} For a very bulky anion such as Δ-TRISPHAT\textsuperscript{-} no increase in current and consequently no light-emission were observed for an operation time of more than 16 hours. This indicates the inability of both Δ-TRISPHAT\textsuperscript{-} and Cy3\textsuperscript{+} ions to drift to their respective electrodes. Consequently, for Cy3-P and Cy3-C, the mobile ions are solely PF$_6$\textsuperscript{-} and ClO$_4$\textsuperscript{-}.

For all further experiments we focused on PF$_6$\textsuperscript{-} as counter ion, as the relatively slow movement allowed us to measure optical and electrical parameters for a quasi-steady-state ionic distribution. Another typical feature of LECs is the decrease of switch-on time with increasing amount of an ion-transporting material, such as poly(ethylene oxide), PEO.\textsuperscript{41,42} A decrease from ~18 min to < 3 s could indeed be observed for Cy3-P LECs when adding PEO up to 30 wt\% (see SI).
Figure 3. Current density (filled symbols) and luminance (open symbols) transients for cyanine LECs with different counter ions: PF$_6^-$ (black squares), ClO$_4^-$ (blue circles), Δ-TRISPHAT$^-$ (red triangles).

Our LECs display a modest luminance of 20–50 cd m$^{-2}$ at a high current density. This is primarily due to the low (< 1%) photoluminescence quantum yield of single Cy3 films. Excitons are able to hop between neighboring cyanine molecules and encounter quenching sites that leads to a reduction of the exciton-to-photon conversion efficiency. The photoluminescence quantum yield can be increased by dispersing a smaller bandgap cyanine dye emitter in a host material with a wider bandgap. This host-guest concept has successfully been used in organic light-emitting diodes and leads also to efficient cyanine dye LECs. By using cyanines both as guest and host materials, near-infrared emitting LECs were demonstrated with an external quantum efficiency (EQE) of roughly one-third of the theoretical maximum. EQEs of 0.8% and 1.24% were reported for two near-infrared cyanine guests dispersed in a iTMC host matrix. Recently, LECs containing Cy3-P as guest and a charged carbazoyldicyanobenzene derivative host with an EQE of 2.0% were fabricated, which was close to the theoretical maximum for that material system.

There are several reasons why for the purpose of this study we worked with single-layer Cy3 LECs and omitted the host-guest concept. The method to determine the p-i-n junction (see below) is based on a photovoltaic response from the intrinsic region. For guest excitons that are formed via energy transfer from photo-excited host molecules the charge generation efficiency is expected to be reduced because of the energy gaps that must be overcome to reach the charge transport levels of the host. In addition, doping-induced charge trapping effects can occur. The method is finally applicable when the number of photo-generated excitons is proportional to the amount of light that is absorbed in the intrinsic region, but does not depend on the position where that region is located across the film. When using a host-guest
material system, this would imply the difficult to provide proof that the guest is indeed homogeneously dispersed in the host matrix.

**Determination of the p-i-n junction position**

Within the ECD model it is anticipated that the potential drops predominantly across the thin intrinsic region. Consequently, the electric field in this region is high and excitons that are formed after light absorption can potentially be split into free charges, resulting in a photovoltaic response.\textsuperscript{47-49} In addition to the weak electric field in the doped regions, reduced and oxidized cyanine molecules also efficiently quench excitons, meaning that the extracted current originates from the intrinsic region only; we confirmed this statement via photoluminescence quenching experiments (see SI).

IPCE spectra for an unbiased and an operating Cy3-P LEC are shown in Figure 4a for illumination through either the transparent ITO or the semi-transparent Ag contact. Almost identical spectra were obtained when measuring immediately after turning off the voltage or after a waiting time of 10 min. This means that the established p-i-n situation can be probed without the need to fix the junction, e.g. by lowering the temperature. Firstly, no photovoltaic response was observed for a pristine device. Only when applying a voltage an electric field arises across the intrinsic region where charges can be photo-generated and transported via the low-resistive doped regions out of the device.
**Figure 4.** (a) Experimental incident photon to current conversion efficiencies (IPCE) before (black squares) and after LEC turn-on at the point of maximum current when irradiating the device through ITO (blue circles) or semitransparent Ag (red triangle). The dashed lines indicate the simulated intrinsic layer absorbance for illumination through ITO (blue) and Ag (magenta), respectively. (b) Ratio of the absorbances for ITO and Ag illumination for different junction thicknesses and positions. The vertical lines indicate the active layer thickness. Experimental results of three different cells are marked by orange stars.

IPCE curves follow the typical cyanine absorption spectrum with a maximum at ~575 nm which confirms that the extracted charges are generated inside the Cy3-P layer. As excitons are quenched in the doped regions, the IPCE intensity is proportional to the amount of light
that is absorbed in the intrinsic region and therefore depends on the junction position inside the cyanine layer. We modelled this situation by considering the full cell stack (including the semitransparent top electrode, see Figure 1) and dividing the active layer into three regions (p-i-n) with a constant total thickness. In a first step, a fixed thickness for the intrinsic region was chosen and was swept through the active layer to mimic different junction positions inside the device. For every position the intrinsic layer absorbance was calculated for both illuminations sides. As a characteristic number, the ratio between the maximum absorbance values was evaluated. This procedure was repeated for different intrinsic layer thicknesses. Simulated results were compared with the experimental ratio of the IPCE intensities (see Figure 4b). Independent of the chosen intrinsic layer thickness, the intensity ratio vs. position collapsed on the same trend chart. Thus, it can clearly be determined that the junction is situated at 37 ± 5 % of the total active layer thickness away from the anode. The modelled intrinsic layer absorbance for this junction position is included in Figure 4a. The good spectral agreement of experimental IPCE and simulated absorbance supports the proposed p-i-n structure situation. In principle, there is a slight difference in the shape of the simulated intrinsic layer absorbance spectra for junctions with different thicknesses but centered at the same position. However, in our case these small differences can experimentally not be resolved; consequently, it is not possible to extract the intrinsic layer thickness from these measurements. A potential issue in the analysis relates to light scattering which is not included in the optical simulation. Light scattering, e.g. at the top electrode or due to a changing microstructure under the influence of moving anions, can result in absorbance contributions others than the differences in path lengths to the intrinsic region. We determined the angle dependence of the light scattering. Samples were illuminated at a wavelength of 572 nm and the intensity of the transmitted light was measured at variable angles using a silicon photodiode. Both for as-prepared samples and after biasing to the maximum current, light was transmitted within an aperture angle of ± 2° which corresponds to the resolution of the measurement setup (data not shown). Therefore, in
our case light scattering effects can be excluded. Details on the optical simulation can be found in the SI.

**Dynamic doping and junction formation**

To investigate the junction formation dynamics we performed different experiments during LEC operation. Figure 5 presents luminance (a), Δattenuance (b), capacitance (c) and photoluminescence intensity (d) data of Cy3-P LECs as a function of bias time. For all measurements the current was monitored in parallel. Because we focus on the junction formation process, measurements were terminated after the current started to decrease slightly and device degradation begins. To allow for a direct comparison among these experiments and to account for slight differences between measurement setups and cell to cell variations, bias times were scaled in such a way that the transient current always shows the same trend over time.
Figure 5. Transient behavior of luminance (a), Δattenuance at 572 nm (b), normalized capacitance (c) and (d) normalized photoluminescence together with the individual current densities (open squares). The dashed lines indicate the position of the switch-on time and the maximum luminance, respectively.

As explained above, the luminance reached its maximum before the current was maximized, due to a decrease of the intrinsic region width with associated exciton quenching (see Figure 5a). The Δattenuance spectrum contains the attenuance difference between the scan before applying the voltage and the spectrum at a certain operation time. By its
definition, a negative value corresponds to a decrease of the attenuance during LEC operation.

Figure 5b presents the time evolution of this quantity for the maximum of the Cy3-P monomer absorption at 572 nm. The decrease of the monomer attenuance is due to doping and the formation of oxidized cyanine radical dications (absorbing at 460 - 540 nm\textsuperscript{50}) and reduced cyanine radicals (420 – 470 nm\textsuperscript{51}). Because of their lower extinction coefficients\textsuperscript{50,52} and the overlap with the monomer absorption, these doped species could not be clearly identified. In the absence of side reactions and decomposition of the doped species, the reduction of parent dye molecules is equal to the sum of oxidized and reduced cyanine molecules. At 572 nm the attenuance of p- and n-doped cyanines is negligible. Thus, the decrease in attenuance at the peak absorption can be used to calculate a maximum doping fraction. We find a reduction of 2.6 ± 0.6% and 4.4 ± 1.7% (averages of 5 cells) of parent Cy3-P molecules until the points of the maximum luminance and current, respectively.

Figure 5c shows the time evolution of the capacitance measured at 1 kHz. The capacitance-frequency scan did not show a second plateau down to 10 Hz indicating that the ion mobility is slow and the measurement itself does not modify the ionic distribution. The initial value ($C_0$) represents the geometrical device capacitance. As soon as charges are injected from the electrodes and the doped regions form, the intrinsic region will shrink. Consequently, the capacitance which is dominated by the reduced intrinsic region will increase with time. Assuming an unmodified permittivity the upper limit of the thickness of the intrinsic region can be calculated as $d_{int} = C_0/C \cdot d_{total}$. More precisely this thickness represents the low conductivity part of the device which is not necessarily equal to the region where recombination takes place as reported by van Reenen et al.\textsuperscript{17} Notice that the capacitance stays at its initial value until the current and the luminance show a steep increase. This period is followed by a distinct increase until the point where the luminance peaks and the current levels off. After that, the capacitance is only slightly increasing, indicating a relatively constant intrinsic region that only further shrinks marginally. From this data the size of the
intrinsic region is calculated to be ~80% and ~72% (average of 4 cells) of the total active layer thickness at the points of maximal luminance and current, respectively. Literature values for this quantity during steady state operation vary between 10 – 80 % depending on the used material, the operating voltage and the conductivity of mobile ions.\cite{15-18} The values for our system are therefore in the upper range of this spectrum.

In Figure 5d, the normalized PL intensity at the Cy3-P monomer peak emission (595 nm) is plotted as a function of bias time. PL is constant until electronic charges are injected, doped regions are formed and the cell starts to emit light. This is different to data presented by Meier et al.\cite{12} using iTMC-LECs, where the PL decreased immediately after applying the voltage. Until to the point of maximum luminance, the PL decreased by only ~15%. We found for chemically p-doped Cy3-P films that doping concentrations above ~20% induced almost complete quenching of the PL signal (see SI). With the calculated dopant concentrations in the n- and p-type regions (see below), we can estimate that the remaining PL in our LEC originates mainly from the undoped, intrinsic region. For this situation, the remaining PL directly probes the intrinsic junction width. For the two positions in time that are indicated by a dashed line in Figure 5, this width obtained from PL is 100% and 85%, respectively, in excellent agreement with the junction width obtained from capacitance measurement, namely 99% and 83%.

Data in Figure 5 support the picture of the device working according to the ECD mechanism. This includes continued p- and n-doping, seen indirectly in the reduction of the monomer attenuance and shrinkage of the intrinsic region observed both in transient capacitance and PL measurements. That the doping concentration in the doped regions increases in phase 2 is also supported by capacitance-frequency scans on thicker devices during operation (see SI). For the luminance, capacitance and PL data an initialization time is noticed during which these parameter show almost no change. This is attributed to the relatively slow motion of PF$_6^-$ anions which have to reach the electrode before charge
injection is facilitated at the contacts and the doped regions can grow. A similar observation was reported for capacitance transients in ionic transition metal complex LECs. We note that for the UV-vis experiment no such initialization time was found and the Cy3-P attenuation started to decrease immediately when applying the voltage (see Figure 5b). We cannot clearly explain this observation at this moment. One explanation relates to a slightly changing dye attenuation due to rearrangement of the cyanine molecules when the PF$_6^-$ anions drift through the film. In preliminary experiments we indeed observed similar initial Δattenuance changes for LECs operated at 1 V, well below the threshold value for bipolar electronic charge injection (see SI).

At maximum current, the decrease of parent dye molecules was 4.4% over the whole Cy3-P layer, as determined from Δattenuance measurements. At this point, the thickness of the intrinsic layer from capacitance measurements was ~72%. With the assumption that no electrochemical reactions other than balanced p- and n-doping of Cy3$^+$ are taking place, an estimation of the actual dopant concentrations is possible. This requires knowledge of the widths of the p- and n-type doped regions. With the junction centered at ~37% of the total dye layer thickness away from the ITO anode (see Figure 4), the width of the n-doped region is ~8.1 nm and the concentration is ~0.08 dopant / Cy3-P. On the other hand, the p-type doped region is very small compared to the n-type doped region. Consequently, the p-type concentration is much higher. It is proposed that the reason for the off-centered junction position and the small width of the p-doped region is because it is only the small PF$_6^-$ anion that is mobile whereas the Cy3$^+$ cation is immobile. During the initial device operation anions will drift to the ITO electrode and accumulate within a thin electric double layer, the thickness of which has been approximated to ~ 0.26 nm. For thicknesses of the p-type region below 1 nm, the concentration is above 0.6 dopant / Cy3-P molecule.

It is important to emphasize that the accuracy of the doping-concentration calculation depends on the assumption that the Cy3-P Δattenuance decrease is only due to the formation
of p- and n-doped cyanine radicals, that no other decomposition channels for the parent molecule exist and that the doped species are stable. We find below that these assumptions are not entirely justified in our case; therefore, stated doping concentration must be considered as the upper limit value. In general, the determination of doping concentrations in operating LECs is difficult and few studies have been reported so far. For pLECs in lateral structures, concentrations of 0.1 and 0.15-1 dopants / polymer-repeating unit for p- and n-type doping were found, strongly depending on the used salt.\textsuperscript{20,21} Using the same method for small molecule LECs an n-type doping concentration of 0.8 dopant / molecule was found.\textsuperscript{5} For LECs in sandwich geometry, p-type doping values of 0.1 and 0.4 were reported for operation until to the maximum luminance and to the saturation value, respectively.\textsuperscript{27}

Device relaxation

When no degradation is occurring during LEC operation and after turning off the voltage, the ions redistribute throughout the film and de-doping occurs, establishing the original situation. When the LEC is then operated for a second time, the same kinetics for the transient luminance and current should be measured. Such behavior was indeed observed for our Cy3-P LEC when the voltage was turned off at the point of maximum current (end of phase 2). Because of the slow PF\textsubscript{6}⁻ mobility the time required for a full device relaxation was more than 60 hours (see Figure 6). Identical times to the points of maximum luminance and current were measured for the first and second run. In contrast to similar reported measurements, however,\textsuperscript{38} both luminance and current stayed below the values measured at the end of the first run.
Figure 6. Current density (filled squares) and luminance (open squares) transients for a cyanine LEC operated twice with a relaxation period of 65 h between the two measurements.

We followed the device relaxation by monitoring Δattenuance and PL spectra over time. For devices operated to the point of maximum current, almost complete (~90%) recovery of the PL intensity was measured over 65 h (see SI). When operated into phase 3 where irreversible degradation occurs, the PL signal decreased by more than 70% and recovered only marginally (see SI). These finding are in agreement with literature results, where the complete recovery of the PL signal during device relaxation was attributed to de-doping without degradation of the active material.

Δattenuance spectra during relaxation revealed a different situation. During the same time that allowed for a full ionic relaxation and de-doping with an almost complete PL recovery, Cy3-P molecules were not reformed and only a negligibly small recovery of the parent dye signal was measured (data not shown). This implies that when operating the device for the second time, the number of cyanine molecules will be smaller compared to the first run and consequently the luminance and current are smaller.

We tentatively ascribe this observation to the high reactivity of oxidized and reduced cyanine molecules. It is well known that these species are susceptible to radical-radical
reactions at the polymethine chain, and that the rate of dimerization and stability of the dimer depend on the nature of the heterocyclic unit and the type of alkyl substituent at the methine carbons.52-55

In general, the improvement of the operational stability of LECs presents a significant challenge. The lifetime can be influenced by the way the device is operated. To retard the ongoing detrimental, but partly reversible, doping process a pulsed driving protocol was found to be favorable over constant voltage or current driving operation.56,57 LECs are also susceptible to chemical and electrochemical side reactions, for example of the electrolyte or at the cathode material.21,38 In our case, the sign of irreversible chemical reactions between doped cyanine species limits the operational Cy3-P LEC stability. However, it is likely that other lifetime-restricting effects are taking place in parallel and these are studied in ongoing work. For example, data for the two measurements in Figure 6 show the same kinetics for the transient luminance and current, but the efficacy (cd A⁻¹) after relaxation decreased. Together with the observation that the PL is largely recovering during relaxation, this points to degradation processes in the emission zone. It was demonstrated that photoinduced reactions in the light-emitting junction lead to device degradation, and that these processes are pronounced due to the increased temperature in the intrinsic region.58

4. CONCLUSION
The reliable determination of the intrinsic junction position via spectral photocurrent response experiments requires that the device is tested in quasi steady-state and that the ions do not relax during the measurement. In our case this was possible by the proper choice of the PF₆⁻ anion that is sufficiently mobile to allow for device operation but for which relaxation occurs over many hours. In the general case, we propose that the required ionic mobility can be adjusted via temperature. Together with capacitance measurements, the widths and positions of the p-i-n regions can be obtained for every point in time and the LEC device performance
can then be studied as a function of these parameters. The procedure is not limited to cyanine LECs. For example, the best-performing LECs use iTMCs as triplet emitters. Also iTMCs perform the dual role of emitter and charge transporter and the transient turn-on and relaxation LEC behavior can be adjusted by changing the counter anion.\(^{43}\) An estimation of the actual doping concentrations via transient attenuance measurements was possible in our case because the absorption spectra of oxidized and reduced cyanines are hypsochromically shifted relative to, and do not overlap with the parent dye absorption. This shift to smaller wavelengths upon doping presents a potential advantage compared to pLECs where the doped species absorptions often arise at longer wavelengths, resulting in undesired doping-induced self-absorption of emitted light. From a chemical point of view, our initial findings suggest that the high reactivity of doped cyanines leads to undesired side-reactions that limit the long-term device operational stability. In ongoing work, we introduce sterically demanding groups on the heterocyclic unit and the methine carbons, such that the dominant cyanine radical-radical dimerization decay pathways are hindered.

**ASSOCIATED CONTENT**

**Supporting Information.** Synthesis of Cy3-Δ-TRISPHAT, effect of PEO addition on the switch-on time, simulation of intrinsic layer absorbance, effect of chemical p-type doping on PL intensity, below bandgap operation, capacitance-frequency spectra of a thicker Cy3-P LEC during operation, photoluminescence evolution during LEC relaxation time. This material is available free of charge via the Internet at [http://pubs.acs.org](http://pubs.acs.org).

**AUTHOR INFORMATION**

**Corresponding Author**

* E-mail: sandra.jenatsch@empa.ch; roland.hany@empa.ch
Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support from the Swiss National Science Foundation is acknowledged (grant number 200021_144120).

REFERENCES


