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Time-resolved chemical mapping in light-emitting electrochemical cells

Mohammad Javad Jafari^a, Jiang Liu^b, Isak Engquist^{b,*}, Thomas Ederth^{a,*}

^a *Division of Molecular Physics, Department of Physics, Chemistry and Biology, Linköping University, Linköping SE-581 83, Sweden*

^b *Department of Science and Technology, Campus Norrköping, Linköping University, Norrköping SE-601 74, Sweden*

Corresponding authors: isak.engquist@liu.se, ted@ifm.liu.se

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Abstract

Understanding the doping and ion distributions in light-emitting electrochemical cells (LECs) is required to approach a realistic conduction model, which can precisely explain the electrochemical reactions, p-n junction formation, and ion dynamics in the active layer, and to provide relevant information about LECs for systematic improvement of function and manufacture. Here, Fourier-transform infrared (FTIR) microscopy is used to monitor anion density profile and polymer structure *in situ*, and for time-resolved mapping of electrochemical doping in an LEC under bias. The results are in very good agreement with the electrochemical doping (ECD) model, with respect to ion redistribution and formation of a dynamic p-n junction in the active layer. We also physically slow down ions by decreasing the working temperature and study frozen-junction formation and immobilization of ions in a fixed-junction LEC device by FTIR imaging. The obtained results show irreversibility of the ion redistribution and polymer doping in a fixed-junction device. In addition, we demonstrate that infrared microscopy is a useful tool for *in situ* characterization of electroactive organic materials.

Keywords:

Light-emitting electrochemical cell, FTIR spectroscopic imaging, Electrochemical doping, Doping profile, Ion distribution, Dynamic p-n junction, Infrared microspectroscopy, Principal component analysis

Introduction

Artificial lighting is one of the most important achievements in human life. Nowadays, huge amounts of resources and effort are invested in the development of inexpensive and eco-friendly light sources and devices. Twenty years ago, Pei and co-workers applied iontronic properties of organic materials to fabricate a new generation of organic light-emitting diodes (OLEDs)¹. By focusing on electronic properties of conjugated polymers blended with an ionic material and a solid electrolyte, and moving ion carriers by electrochemical charge and discharge of conjugated polymers^{1, 2}, they successfully designed the first solid-state light-emitting electrochemical cell (LEC), which could generate light by reversible electrochemical reactions. These devices are usually constructed as two-terminal (planar or sandwich) devices with an active layer between electrodes. Under an applied bias, the anions and cations are transported through the active layer and accumulate at the electrode interfaces. Injection of charges into the semiconducting polymer, and the charge compensation provided by the ions, form p- and n-doped regions at the anode and cathode sides, respectively^{3, 4, 5, 6}. Compared to conventional OLEDs, LECs are single-layer devices with low turn-on voltage and insensitivity to the film thickness and the work function of the electrode materials^{7, 8, 9, 10}. These features make LECs flexible and low-cost artificial sources of lighting^{9, 11, 12, 13, 14}.

Ion redistribution in the LEC devices depends on different factors, such as ionic conductivity¹⁵, thickness of active material¹⁶, applied bias and working temperature, which leads to turn-on times (the time which is needed for the p- and n- doped regions to form the p-n junction¹⁷) ranging from milliseconds to hours¹⁵.

After the invention of the LEC, a debate has been ongoing regarding the operation mechanism, which is still not completely understood. Based on theoretical and experimental investigations, two operation mechanism of LECs have been proposed: the electrodynamic model (ED)^{18, 19, 20} and the electrochemical doping model (ECD)^{1, 21, 22, 23, 24}; these models explain how the active layer will be subdivided into regions with different properties under an applied bias^{5, 15}. When an external bias is applied, the external electric field forces anions and cations to migrate and redistribute, and to form two accumulated and uncompensated ion sheets close to the electrode interfaces, and the applied potential drops at these electric double layers (EDLs). The ED model predicts that the applied potential drops completely over the EDLs, and that the electric field is very weak in the bulk polymer^{5, 15}, so that the active layer is divided into three regions. The ECD model assumes that the electric field drops over the EDLs but only as much as is needed to form ohmic contacts, leading to an efficient electric

field where more charge carriers can inject into the active layer and oxidize/reduce the conjugated polymer. To compensate for the charge instability, ions migrate to electrodes of opposite sign, and when the bias voltage becomes large enough the ions eventually become completely separated and an electrical junction appears ²⁵, at which point the device reaches a steady-state. The polymer also tends to form an ohmic contact due to the generation of highly conductive p- and n-doped regions at the electrodes, and the remainder of the potential difference drops at a narrow region (p-n-junction) between the doped regions. The polymer doping increases the conductivity of the active layer by enhancing carrier density ²⁶ and light output ⁶, and it also decreases the sensitivity of LECs to the work function of electrodes and the thickness of the active layer ²⁷; these advantages open up the opportunity to fabricate wide-gap planar LECs ^{28, 29, 30}.

Intensive studies have been carried out to clarify the operation mechanism of LECs, and they appear to agree more with the ECD model ²¹. Most of these studies have focused on dynamic characterization of potential profiles by surface sensitive techniques such as scanning kelvin probe microscopy (SKPM) ^{21, 31, 32, 33}, electric force microscopy (EFM) ¹⁸ and contact probing in a cryogenic probe station ³⁰ on planar LEC devices. Understanding doping, ion migration, and electronic and chemical reactions of the active materials, can provide important and informative details about LEC function, and will be useful in future developments of the LEC technology. Leger's team report successful ion profile characterizations in sandwich LECs by secondary ion mass spectrometry ^{4, 34} and they demonstrate that spatial distribution of ion density could be obtained in sandwich devices, but they did not provide any information about the chemical structure and polymer doping within the active layer. Thus, techniques with the ability to characterize chemical activity and structural changes in parallel with density measurements are necessary to obtain more information about active materials in LECs and to approach a realistic model, which can explain the chemical and electrochemical reactions in LECs.

Vibrational spectroscopy is a common and useful spectroscopic method to study the material structure and follow *in situ* chemical reactions of materials in different scientific areas. Fourier transform infrared (FTIR) microscopy is a well-established method for chemical imaging and mapping of materials and it offers the possibility to provide simultaneous spectral and spatial information at different experimental conditions. This technique is widely used in bioscience and biomaterial studies ^{35, 36} and also used to monitor structural changes in

polymer science^{37, 38} and phase behavior of polymer blends and map the distribution of chemical entities^{39, 40, 41}.

The current study is based on the application of FTIR microscopy to monitor and map ion mobility and polymer doping in the active layer of LECs. The hypothesis is that under an applied bias, the ions move in the active layer and accumulate at the electrode sides, and the polymer is doped by electron/hole injection. In this paper, we use an FTIR microscope with a focal plane array (FPA) detector to obtain a deeper understanding of ion mobility and polymer doping processes in the active layer of planar LECs, with the aim of confirming which model is more accurate and gives more information about the dynamics of LECs. The device is a planar LEC with an inter-electrode gap of 300 μm , consisting an active layer of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) as the light-emitting polymer, poly(ethylene oxide) (PEO) as a solid electrolyte with potassium triflate (KCF_3SO_3 , or Ktri) salt. FTIR images were captured with a $300 \times 300 \mu\text{m}^2$ field of view of the active layer region between two planar electrodes; at zero bias and under an applied bias for 1 hour at 60°C. After that, line-averaged spectra (parallel with the electrodes) were extracted and triflate anion density profiles, as well as p- and n-doped polymer structure were characterized for different doping levels in active layer.

Experimental procedures

To study the LEC device under an FTIR microscope in reflection mode, a reflective layer is needed, and gold was selected for its good reflectivity over the used IR range. To prevent short circuit between the electrodes and the reflective gold layer, a photoresist layer was coated between the reflective layer and the electrodes; a schematic view of the fabricated LEC is shown in Scheme 1. The Au reflective layer was thermally evaporated onto a Si substrate to a thickness about 1000 Å, on top of a 400 Å Ti adhesion layer. To prepare the photoresist layer, SU-8 (2000.5 MicroChem) was spin coated onto the reflective layer at 500 rpm for 5 s and at 2000 rpm for 30 s, and then the SU-8 film was soft-baked at 95°C for 1 min and exposed to UV radiation (80 mJ/cm^2 for 15sec). After UV exposure, the sample was baked again at 95°C for 2 min, resulting in a photoresist layer of about 500 nm thickness. The Au electrodes, with an inter-electrode gap of 300 μm , were thermally evaporated through a shadow mask onto the photoresist. Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV, $M_n = 40,000\text{-}70,000$ Da, Sigma- Aldrich) was dissolved in

chloroform with a concentration of 10 mg/ml. and Poly(ethylene oxide) (PEO, $M_v = 6 \times 10^5$, Sigma-Aldrich) and potassium triflate (KCF_3SO_3 98%, Sigma-Aldrich) were dissolved in cyclohexanone to concentrations of 13.5 and 0.25 mg/ml, respectively, and the two solutions were then mixed in a ratio of 1:1, as described by Edman and co-workers⁴². This resulted in the active material solution, where the mass ratio between the three materials MEH-PPV:PEO:KCF₃SO₃ is 1:1.35:0.25. The active material was spin-coated at 1000 rpm for 45 s between the two Au electrodes on top of the photoresist substrate, and then dried at 120°C for 15 min under nitrogen atmosphere, giving a final thickness of the active layer of about 100 nm.

Scheme 1. Schematic representation of the LEC device for FTIR imaging.

FTIR spectra of MEH-PPV, PEO, Ktri, and the active material were obtained with a Bruker Vertex 70 spectrometer using the KBr pellet method; the system was continuously purged with nitrogen before and during the measurements. All spectra were acquired at 2 cm^{-1} resolution with a total of 200 scans, and over a wavenumber range between 4000 and 800 cm^{-1} .

The FTIR imaging measurements were carried out with a Bruker Hyperion 3000 microscope coupled to a Bruker Tensor 27 spectrometer as the light source. The FTIR microscope was equipped with a focal plane array (FPA) detector with an array of 128×128 pixels. The system was continuously purged with nitrogen before and during the measurements. The sample stage was equipped with a heater plate to control the device temperature. The FTIR

images were captured with a 15x reflection objective, giving a field of view of $300 \times 300 \mu\text{m}^2$ and a pixel size of $2.3 \times 2.3 \mu\text{m}^2$. Spectra were acquired at 4 cm^{-1} spectral resolution between $4000\text{-}1000 \text{ cm}^{-1}$ and by summing 64 scans. Background images were obtained on the photoresist-coated gold substrate to minimize the SU8 contribution to the spectra of the active layer. A rubber-band baseline correction was used for all data, and data analysis was performed using Bruker OPUS software (v. 7.2).

Principal Component Analysis (PCA) was performed for identification of spectral variations between data sets to follow polymer doping and ion distribution under an applied bias, and to estimate the LECs' turn-on time at the specific spectral ranges. Three principal components were chosen for data analysis and a 2D score and loading plots were used to demonstrate data variation.

Results and discussion

Experiments were conducted as follows. First, transmission FTIR spectra of components and pristine active material were captured to characterize the chemical structure of the materials; then, an FTIR image of the pristine LEC device at zero bias was recorded to monitor initial ion distribution and polymer structure. After that, a 4 V forward bias was applied for 1 hour, and FTIR images were recorded every 5 minutes during this 1 h period, to follow the dynamics of ion migration and polymer doping under forward bias. Experiments were conducted with a 4 V bias since higher applied voltages caused faster degradation of the exposed active layer, due to the remaining small amount of oxygen in the purged measurement chamber. PEO needs to have an operational temperature above the melting temperature (T_m) in order to conduct ions effectively^{43, 44}. In this study we have used PEO with large molecular weight (average M_v 600,000), which has a T_m above room temperature; therefore, the measurements were carried out at 60°C . 20 line-averaged spectra (parallel to the electrodes) were extracted from each FTIR image to characterize chemical structure changes at different positions between the electrodes. Ion density and polymer structure profiles were generated from the data by integration of the area under specific absorption bands. Time-resolved maps were assembled for the triflate anion and the p-doped MEH-PPV density profiles, to study anion redistribution and polymer structural changes and doping in the active layer of the LEC, under the influence of an external electric field. (It is not possible to follow the distribution of the atomic cation K^+ by FTIR, but future studies of polymer LECs with

ionic liquids may reveal also the cation distribution). Finally, bias was switched off for 20 hours and the LEC was kept at room temperature under nitrogen atmosphere to characterize our LEC sample as a fixed-junction device ⁴⁵, then an FTIR image of the open-circuit LEC was taken to compare the chemical structure and ion distribution in the active layer after relaxation, with those under bias.

The FTIR spectra of pure Ktri, MEH-PPV, PEO and a mixture of the three (the active material) in the wavenumber range 1600-800 cm^{-1} are shown in Figure 1, with band assignments in Table 1. In Figure 1, the averaged reflection spectrum of the pristine active material extracted from an FTIR microscopy image is also compared to the KBr pellet transmission spectrum. The potassium triflate (KCF_3SO_3) spectrum presents asymmetric SO_3^- vibration bands near 1291 cm^{-1} and 1263 cm^{-1} . The shoulder at 1231 and the peak at 1179 cm^{-1} are due to symmetric stretching of CF_3 , and asymmetric stretch of CF_2 , respectively. The bands at 1038, 1033 and 1029 cm^{-1} correspond to SO_3^- symmetric stretching of the aggregated triflate potassium salt, a pair coordinating the same counterion, and free triflate anion, respectively ^{46,47}. The pure MEH-PPV bands at 1591, 1505, 1413 and 1352 cm^{-1} are due to C=C and C-C ring vibrations of phenyl groups ^{48,49}, peaks at 1463 and 1378 cm^{-1} correspond to asymmetric and symmetric alkyl CH_2 vibration, respectively ⁴⁹. The bands at 1255, 1204 and 1186 and 1080 cm^{-1} are attributed to aryl-alkyl ether (C-O-C) vibrations and the peaks at 965 and 853 indicate vinylene and phenyl C-H wagging, respectively ^{49,50}. The FTIR spectrum of PEO can also be identified: asymmetric (1468 cm^{-1}) and symmetric (1455 cm^{-1}) CH bending ⁴⁷, C-C (1360 and 1150 cm^{-1}) and C-O-C (1150-1060 cm^{-1}) stretching ⁵¹, and the other bands are related to CH_2 wagging (1344 and 842 cm^{-1}), twisting (1281 and 1243 cm^{-1}) and rocking (964 and 947 cm^{-1}) ⁵¹. The FTIR transmission spectrum of the active material composite shows contributions from all of the three components. The bands located between 1550-1320 cm^{-1} and 1000-800 cm^{-1} are formed through overlapping of structural vibrations in MEH-PPV and PEO and suggest that there is no chemical reaction between MEH-PPV and PEO. The broad band at 1278 cm^{-1} with an intense shoulder at 1267 cm^{-1} represents the contribution of triflate salt in the composite spectrum, and shifts could be related to the sensitivity of the triflate ion to ionic co-ordination in different environments ⁵². The band at 1030 cm^{-1} is due to the SO_3^- symmetric stretch of the triflate ion, and comparison between potassium triflate and the active material spectra demonstrates an increase of free and pair ion density and a decrease of aggregated ion density in the mixture. The averaged spectrum of the active material was also obtained with FTIR microscopy in reflection mode, showing similar

band characteristics as the transmission spectrum. Small differences between the KBr bulk and microscope reflection spectra would be expected due to partial alignment of the polymer chains during spin-coating, with associated reorientation of transition dipole moments.

Band position (cm ⁻¹)	Band assignment		
	KCF ₃ SO ₃	MEH-PPV	PEO
1591		$\nu(\text{C}=\text{C})_{\text{phenyl}}$	
1505		$\nu(\text{C}-\text{C})_{\text{phenyl}}$	
1468			$\delta_{\text{as}}(\text{CH}_2)$
1463		$\nu_{\text{as}}(\text{CH}_2)_{\text{alkyl}}$	
1455			$\delta_{\text{s}}(\text{CH}_2)$
1413		$\nu(\text{CC})_{\text{Semicircular phenyl}}$	
1378		$\nu_{\text{s}}(\text{CH}_2)_{\text{alkyl}}$	
1359			$\nu(\text{CC}) + \omega_{\text{s}}(\text{CH}_2)$
1352		$\nu(\text{CC})_{\text{phenyl}} + \gamma(\text{CH}_2)$	$\omega_{\text{as}}(\text{CH}_2)$
1291, 1263	$\nu_{\text{as}}(\text{SO}_3^-)$		
1281			$\tau_{\text{as}}(\text{CH}_2) + \tau_{\text{s}}(\text{CH}_2)$
1255, 1204		$\nu_{\text{as}}(\text{COC})_{\text{aryl-alkyl ether}}$	
1243			$\tau_{\text{as}}(\text{CH}_2)$
1231 ^{sh}	$\nu_{\text{s}}(\text{CF}_3)$		
1186, 1080		$\nu_{\text{s}}(\text{COC})_{\text{aryl-alkyl ether}}$	
1179	$\nu_{\text{as}}(\text{CF}_2)$		
1150			$\nu(\text{CC}) + \nu(\text{COC})$
1060			$\rho(\text{COC})$
1038, 1033, 1029	$\nu_{\text{s}}(\text{SO}_3^-)$		
964, 947			$\rho(\text{CH}_2)$
956, 853		$\omega(\text{CH})_{\text{vinylene, phenyl}}$	
842			$\rho_{\text{as}}(\text{CH}_2)$

Table 1. Infrared band assignments for KCF₃SO₃, MEH-PPV and PEO. (Note: δ bending; ω wagging; ν stretching; ρ rocking; τ twisting; γ deformation; as asymmetric; s symmetric; and sh shoulder.)

Figure 1. FTIR transmission spectra of potassium triflate (Ktri; black), MEH-PPV (red), PEO (blue) and the active material (brown), as well as an averaged spectrum of the active material obtained from an FTIR image (green).

FTIR microscopy enables lateral monitoring of chemical composition, such as ion density and chemical structure. We captured FTIR images before and after applying 4 V bias, the measurements have been done at 60°C, and line-averaged spectra in parallel with the electrodes were extracted from the FTIR images. Figure 2b shows an optical micrograph of the LEC device; line-averaged FTIR spectra at the anode side (I), in the middle (II) and at the cathode side (III) of the LEC at zero bias, and under applied bias after 1 hour, are shown in Figures 2a and c, respectively. From Figure 2a it is seen that the spectra at zero bias are similar across the device, and do not show any significant differences with respect to the lateral position. These results confirm that the active material is distributed homogeneously between the electrodes. The spectra of the sample under an applied bias (Figure 2c and Figure S1 in the supporting information) exhibit the effect of potential on the ion distribution, and changes in the structure of the active material; the intensities and positions of several bands in Figure 2c have changed after applying bias.

The bands corresponding to asymmetric and symmetric SO_3^- stretching of the triflate anion, with peak maxima at 1265 and 1027 cm^{-1} in the pure Ktri sample (Figure 1), were approximately constant all over the LEC at zero bias (Figure 2a), showing that the triflate

anions were distributed homogeneously. FTIR images of the asymmetric (Figure 2d) and symmetric (Figure 2f) SO_3^- stretching bands in the pristine sample also confirm homogeneous distribution of the triflate anion in the active layer. After applying 4 V bias for 1 hour, Figure 2c shows that the intensities of the asymmetric (1265 cm^{-1}) and symmetric (1027 cm^{-1}) SO_3^- bands increase at the anode side, while decreasing at the cathode side. The FTIR images in Figures 2e and g (obtained by integrating the total area in the band regions $1290\text{--}1218\text{ cm}^{-1}$ for $\nu_{\text{as}}(\text{SO}_3^-)$ and $1055\text{--}1007\text{ cm}^{-1}$ for $\nu_{\text{s}}(\text{SO}_3^-)$) confirm that a significant ion density change and ion separation near the middle of the LEC appeared under the external field, with accumulation of triflate at the anode side, and depletion at the cathode side, confirming the formation of an electrical junction in between the two electrodes, with anions (and presumably also cations) spatially separated across the junction and the appearance of two doped regions. During electrical junction formation, anions and cations are blocked by the electrodes and EDL formation occurs, which will reduce the electrical field in the active layer. Results however do not show any evidence of high ion density near the electrodes, which we interpret in accordance with the scanning Kelvin probe measurements by van Reenen et al.⁵ showing that two narrow EDLs have formed near the electrodes to overcome the injection barriers, and that the device is operating in the non-injection-limited ECD regime. All of these results are compatible with the ECD model for LECs at steady-state^{25, 53}.

Comparing the band positions in Figures 2a and 2c (also see Figure S1 in the supporting information), the pristine bands at 1503 cm^{-1} (C-C ring vibration) and 1413 cm^{-1} (ring stretch and C-H deformation) are shifted to 1489 and 1432 cm^{-1} , respectively, at the anode side under forward bias. These shifts could be caused by structural and electronic modification in the MEH-PPV backbone and ring conversion during polymer doping, and are consistent with polaron injection and formation of quinoid structure upon polymer oxidation (p-doping) (see Scheme 2)⁵⁴. Figures 2h-k were obtained by integrating the area over a line connecting the spectrum points at the band edges ($1441\text{--}1406\text{ cm}^{-1}$ for 2h-i and $1503\text{--}1475\text{ cm}^{-1}$ for 2j-k). Data in figures 2i and 2k are relative intensities, with h and j as references. As shown in the FTIR images, the bands corresponding to quinoid structure (1489 and 1432 cm^{-1}) are absent from the pristine sample (Figures 2h and j) but appear on the anode side after applying bias (Figures 2i and k). The bands corresponding to MEH-PPV backbone and ring vibrations in the spectra at the cathode side were not changed by the applied bias; the peak positions of the bands corresponding to neutral and n-doped MEH-PPV in spectrum III in both Figures 2a and 2c are the same, while spectrum I in Figures 2a and 2c differ considerably. Comparing these

results with Scheme 2, formation of quinoid structure in MEH-PPV as a consequence of oxidation (p-doping) near the anode follows from the data, but since the reduced state is similar to pristine MEH-PPV, reduction (n-doping) of MEH-PPV and formation of benzoid structure at the cathode side is not immediately evident from Figures 2h-k. However, from the distribution of p-doped MEH-PPV it is clear that the MEH-PPV remains in the reduced state on the cathode side, but from the ion distributions and overall charge neutrality, we infer that charges are injected from the cathode, and that n-doping takes place at that electrode. Thus, there is electrical charge carrier injection into the bulk material and p- and n- doped region formation based on polaron migration, which is in very good agreement with the ECD model. Results from triflate ion density redistribution and polymer doping confirm that polymer doping is followed by counterion migration to maintain charge neutrality in the bulk⁵⁵ and formation of a *p-n* junction at steady-state in the active layer of the LEC. Light emission from the device is very weak, because of its long inter-electrode distance, small thickness and low sourcing current ($< 1 \mu\text{A}$). With our current setup, we observe light emission from the same type of device only with thicker active layers (observed with $5 \mu\text{m}$ active layer thickness, but these are not suitable for IR mapping). A high-sensitivity camera will most likely be needed to capture the light emission.

Figure 2. FTIR line-averaged spectra of (a) the pristine sample and (c) the sample under 4V applied bias after 1 hour, obtained from the lines I, II and III in the reflection image (b) of the LEC device. The chemical intensity maps in (d)-(k) were obtained over the same field of view as (b), and show integrated intensities over specific bands. For each pair of images, the left was obtained under zero bias (pristine sample) and the right under applied bias. (d, e) correspond to asymmetric and (f, g) symmetric SO_3^- vibration of the triflate anion; (h, i) C-C stretching and (j, k) ring stretching of MEH-PPV. The bands are as follows: asymmetric SO_3^- : $1290\text{--}1218\text{ cm}^{-1}$; symmetric SO_3^- : $1055\text{--}1007\text{ cm}^{-1}$; C-C stretch: $1441\text{--}1406\text{ cm}^{-1}$; ring vibration: $1503\text{--}1475\text{ cm}^{-1}$. The field of view is $300 \times 300\text{ }\mu\text{m}^2$ in all images.

Scheme 2. p- and n- doping reaction schemes for MEH-PPV

The LEC device was operated under 4 V forward bias at 60°C for 1 hour, with the current-time curve shown in Figure S2 in the supporting information. In order to map and understand both the anion distribution and polymer doping dynamics in the device under the applied bias, FTIR images of the active material between the electrodes were recorded every 5 minutes. 20 line-averaged spectra (parallel with the electrodes and spaced apart by 15 μm) of the active material were obtained from each FTIR image, to map the density profiles of triflate anion and p-doped MEH-PPV. For each spectrum, the areas under specific bands due to the anion (asymmetric SO_3^- : 1290-1218 cm^{-1} ; symmetric SO_3^- : 1055-1007 cm^{-1}) and p-doped polymer (quinoid structure ring vibration: 1503-1475 cm^{-1} ; C-C stretch: 1441-1406 cm^{-1}) were integrated, and profiles of these intensities were mapped versus time. Figures 3a and b show the time-resolved density maps of asymmetric and symmetric SO_3^- , respectively, which represent the change in triflate anion density distribution under 4V bias at 60°C. For the device at zero bias, the anion density is almost homogenous all over the LEC between the electrodes (zero time), but after applying bias the density increases at the anode side (bottom of the figure), and decreases at cathode side (top of the figure). The rate of formation of a *p-n* junction depends on the ionic conductivity of the solid electrolyte⁵⁶, and the switch-on time in LECs is directly related to the time that an ion needs to cross approximately half the device⁵⁵. This can be controlled via several factors, such as applied bias voltage, thickness of the active layer⁵⁵, position of the *p-n* junction in the interelectrode gap⁵⁷ and working temperature. After applying bias, counterions start to move inside the active layers and an EDL is immediately formed. After that, counterions continue to migrate inside the bulk until

the device reaches the steady-state. To get a more detailed picture of the changes in the active layer under applied potential and p - n junction formation, distribution maps of C-C and quinoid ring vibrations, corresponding to p-doped MEH-PPV, are shown in Figures 3c and d. There is no evidence of doping before applying potential, but after applying bias and EDL formation, initial holes (polarons) inject into the active material and a p-doped zone (red color in the figure) appears, and continues to grow with operating time until the LEC device reaches a steady-state. Electrons presumably form the n-doped zone but no direct spectral evidence is available to confirm this. These results are in agreement with the ECD model, confirming EDL formation, polymer doping, ion migration and p - n junction formation under an applied bias.

Figure 3. Time-resolved intensity maps, which represent density profiles of (a, b) triflate anion and (c,d) p-doped MEH-PPV. (a) is asymmetric and (b) symmetric SO_3^- vibration of the triflate anion; (c) C-C and (d) ring stretch of p-doped MEH-PPV. The density profiles are

drawn with respect to fractional inter-electrode gap, where 0 corresponds to the anode interface and 1 corresponds to the cathode interface.

Multivariate data analysis methods are valuable tools to test hypotheses from vast amounts of data. In this work, principal component analysis (PCA) modeling has been used to estimate the turn-on time of the LECs, and to determine when the device reaches steady-state under an applied bias. To obtain comparable data sets, three different fixed positions (anode, middle and cathode sides, as shown in Figure 2b) were chosen and eleven difference spectra (ΔS_n) for each position have been obtained based on 300 s time intervals between measurements (i.e., the first difference spectrum is the difference between spectra at $t = 300$ s and $t = 0$ s, $\Delta S_1 = S_{300s} - S_{0s}$). After that, PCA was performed on data sets at the specific spectral ranges related to MEH-PPV and triflate ion vibrations, and two-dimensional score plots from PCA modeling are shown in Figure 4. Figure 4a is obtained from asymmetric (1290 - 1218 cm^{-1}) and symmetric (1055 - 1007 cm^{-1}) SO_3^- vibrations of the triflate anion. The PCA plot shows that the difference spectra related to the position in the middle of the LEC are centered around zero of the first principal component (F1), and also that the anion density is almost unchanged at the middle of device under an applied bias for 1 hour. Points related to the anode and cathode sides are initially far from the F1 zero, but after six time intervals (~ 1800 s), they have centered around the F1 zero. This pattern indicates that the ion density is changing during the first six time intervals (~ 1800 s), and that the LEC reaches a steady state where ions are spatially separated after 1800 s. To have a more clarified view about the conduction mechanism and junction formation in LECs, PCA plots of the MEH-PPV vibration are shown in Figure 4b, where the PCA modeling is based on quinoid (1503 - 1475 cm^{-1}) and C-C (1441 - 1406 cm^{-1}) vibrations of MEH-PPV under a 4V applied bias. Results show that the difference spectra points from both the middle position and the cathode side in the device are centered around zero of the first principal component, F1. This behavior indicates similarity in the MEH-PPV ring vibration (benzoid structure) at neutral and n-doped states. At the anode side, spectral points are far from the F1 zero at the first 4-5 time intervals, after which they center around the F1 zero, which can be interpreted as p-doping proceeding during the first 5 time intervals (~ 1500 s) and that MEH-PPV needs this time to reach a steady-state. We note that this time is shorter than the time needed to reach steady-state for the triflate anion distribution. It is important to note that electronic charge carriers such as polarons inject into the active layer immediately after EDL formation, and the PCA plots in Figures 4a and b indicate that

the MEH-PPV is partially doped already in the first time intervals. As a result of the electrical charge injection (polarons and electrons) and charge polarization in the bulk, counterions redistribute and migrate to neutralize the charge polarization in the active layer, and the device will reach a steady-state.

Figure 4. PCA score plots of FTIR spectral ranges related to (a) triflate anion and (b) MEH-PPV vibrations.

Ion redistribution and polymer de-doping of LECs after removing the external potential demonstrate material reversibility under an electrochemical reaction, and hence the capability of long-term use and polarization change of the LECs. This reversible nature is one of the advantages of using LECs in comparison with light-emitting diodes (LED). However, after removing the external potential, the p-n junction disappears, and when potential is applied again, the same turn-on time is needed to grow the p-n junction, and to reach the chemical and physical steady-state. Physical methods are applicable to shorten the turn-on time by focusing

on temperature-dependent ion conductivity and design of fixed-junction systems. To form a fixed-junction system, the working temperature is decreased below T_m to slow down and immobilize ions in the active layer when the LEC has reached steady-state and ions are separated along the electrode under an applied bias^{45, 58}. To investigate the ion dynamics and polymer structure in a fixed-junction system, FTIR images of LECs were recorded at zero bias, and under a 4V bias after 1 hour at 60°C. After that, temperature was decreased to 21°C and the LEC switched off, and when FTIR images were captured again after 20 hours, the position-dependent intensity profiles of the triflate anion and quinoid MEH-PPV were obtained, characteristic of a fixed-junction LEC.

The intensity profiles of asymmetric and symmetric SO_3^- vibrations of the triflate anion are shown in Figures 5a and b, respectively. Results show that the distribution of anions is homogenous at zero bias (red lines). After applying potential (blue lines), the intensity of the anion profile is changed and increased/decreased dramatically at the anode/cathode side, which demonstrates counterion accumulation and p-n junction formation under the external potential. When the bias is switched off at 21°C, the anion intensity profile after 20 h is almost unchanged in comparison with the anion profile under applied bias, which means that the migration rate of ions is really slow, presumably due to the temperature-dependence of the ion migration. This is a consequence of using a high- T_m polymer electrolyte (large molecular weight PEO), which is able to transport ions at high temperature but shows limited ionic motion at room temperature^{59, 60}. That anions did not redistribute, but are relatively immobilized confirms the p-n junction fixation and prevention of reversibility of the device after being switched off for 20 hours. Figure 5c represents the intensity profiles of the bands corresponding to C-C vibrations of MEH-PPV. For the pristine sample, the intensity profile of the band related to benzoid ring vibrations at 1503 cm^{-1} (solid red line) is almost constant across the sample, demonstrating that the polymer is not doped and distributed homogeneously. After applying bias, the intensity profile of the band at 1503 cm^{-1} (solid blue line) decreases at the anode side and a new band related to quinoid structure appears at 1489 cm^{-1} (dashed blue line) at the anode side. It is important to mention that the position of the band at 1503 cm^{-1} corresponding to undoped and n-doped benzoid structure of MEH-PPV is the same, and when the new band appears under an applied bias at the anode side we can infer that the polymer is p-doped at the anode side and we also have n-doped polymer at the cathode side, and a p-n junction is formed. These results clarify the benzoid-quinoid reaction and polymer doping in LECs under an external electric field. When the bias that generates the

p-n junction is removed, the intensity of the de-doped MEH-PPV structure band at 1503 cm^{-1} increases again (Fig 5c, solid blue and green lines), while the intensity of the p-doped band at 1489 cm^{-1} decreases at the anode side (Fig 5c, dashed blue and green lines). The results indicate that the polymer starts to de-dope after switching off the external electrical field, but the profile density still shows that some level of polymer doping remains in the active layer, and doping reversibility is slowed down by immobilization of ions in the fixed-junction device. Figure 5d demonstrates that the same characteristic behavior is exhibited by the semicircular phenyl stretching of MEH-PPV. The band position is shifted from 1413 cm^{-1} (pristine) to 1432 cm^{-1} (p-doped) at the anode side under an applied bias and formation of a *p-n* junction. After switching off the applied bias, the intensity of the p-doped structure at 1432 cm^{-1} decreased, but did not disappear completely, again indicating slow de-doping, after fixed-junction formation.

The ion and doping distributions in Figures 2, 3 and 5 do not exactly coincide spatially. However, the triflate ion concentration drops faster from about 0.4 (fractional length), which coincides with the end of the p-doped region; this is particularly clear from a comparison of the distributions in Figure 5. Hence, the triflate ion concentration is high in the p-doped region, which seems reasonable by virtue of charge compensation by the polymer, and the ion concentration then decreases further away from this region. From the PCA analysis it also appears that MEH-PPV doping is saturated before the triflate ion distribution reaches a steady-state (at approximately 1200-1500, and 1800 s, respectively). We believe that this is related to differences in charge carrier mobilities, where the triflate ion migration is slower than electron/hole migration due to the steric constraints on the triflate molecule. Also, the device current (see Figure S2) does not saturate until about 2500 s, which is considerably longer than the saturation of the doping but comparable to the saturation time for triflate ion redistribution (cf. Figure 3a and 3b).

Figure 5. Integrated IR intensity profiles of (a) asymmetric (1265 cm^{-1}) and (b) symmetric (1027 cm^{-1}) SO_3^- vibrations of the triflate anion, and (c) C-C vibrations, where 1503 cm^{-1} is due to benzioid structure (solid line) and 1489 cm^{-1} due to quinoid structure (dashed line); and (d) typical ring vibrations of MEH-PPV, where 1413 cm^{-1} is due to benzioid structure (solid line) and 1432 cm^{-1} due to quinoid structure (dashed line). For all graphs, data are shown for zero bias (red, $T=60^\circ\text{C}$), under applied bias (blue, $T=60^\circ\text{C}$) and as open circuit LEC (green, $T=21^\circ\text{C}$). The intensity profiles are drawn versus fractional inter-electrode gap, where 0 corresponds to the anode interface, and 1 is the cathode interface.

Conclusions

We used FTIR imaging for *in situ* characterization of organic materials in an organic electronic device. We successfully monitor and map ion redistribution and polymer doping in LECs under an applied bias (4 V at 60°C). We demonstrate that triflate anions migrate from the cathode side to the anode side under an applied bias, accumulating at the anode side to reach a steady-state after around 1800 seconds, and the bands corresponding to structural vibrations of the MEH-PPV conducting polymer clearly show p-doping at the anode side. The n-doped state is structurally similar to the undoped (neutral) state and hence cannot be explicitly identified. The FTIR microscopy results show that the conduction mechanism in our LEC is in good agreement with the electrochemical doping (ECD) model. We also characterized a fixed-junction LEC, for this purpose we decreased the working temperature and removed the bias, and successfully slowed down and immobilized ions, and the results show low reversibility of the formed junction after 20 hours, indicating that the device works as a fixed-junction LEC.

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Supporting Information

Detailed spectra from the device after 4V bias applied for 1h, and the involved structures in the active layer molecules. An *I-t* diagram for the LEC under applied bias.

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TOC graphic

Supporting information for

**Time-resolved chemical mapping in light-emitting
electrochemical cells**

Mohammad Javad Jafari^a, Jiang Liu^b, Isak Engquist^{b,*}, Thomas Ederth^{a,*}

^a *Division of Molecular Physics, Department of Physics, Chemistry and Biology, Linköping University, Linköping SE-581 83, Sweden*

^b *Department of Science and Technology, Campus Norrköping, Linköping University, Norrköping SE-601 74, Sweden*

Corresponding authors: isak.engquist@liu.se, ted@ifm.liu.se

Figure S1. (a) FTIR line-averaged spectra of the sample under 4V applied bias after 1 hour. Redox band changes are highlighted and numbered, and (b) shows the corresponding chemical bonds related to the numbered vibration bands.

Figure S2. Current versus time for the LEC under applied bias.