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Dynamics of Charge Distribution in Sandwich-Type Light Emitting Electrochemical Cells Probed by the Stark Effect

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ABSTRACT

A sandwich-type structure composed of thin films of functional materials is the dominant architecture of organic optoelectronic devices. During device operation, injected or inside generated electrical charges arrange in a specific spatial distribution. This distribution affects the electric field profile throughout the layers and has fundamental impact on charge transport and recombination/separation processes. However, probing of the charge distribution is challenging because the hidden active layers are experimentally not directly accessible. Here, we study the temporal evolution of organic salt-based light-emitting electrochemical cells and demonstrate that electroabsorption spectroscopy in combination with electrical capacitance measurements enables the determination of the distribution of the injected, uncompensated electronic charge inside these devices. For constant-voltage operating conditions and over a period of hours, the Stark effect signal intensity and the capacitance increase steadily, but to a different extent. We demonstrate that this difference sensitively depends on the position and distribution width of injected mobile electrons. Estimates show a substantial spreading over the active layer of the injected electron density with time, screening the electric field behind the charge peak.

The magnitude of the built-in potential, the distribution of the charge density and the corresponding distribution of the built-in/applied electric field to a large extent govern the operating mode of organic electronic devices, such as light emitting electrochemical cells (LECs), light emitting diodes (LEDs) or solar cells. A simple estimate of the internal electric field by dividing the external voltage by the active layer thickness is often not justified because charges inside the device may change the field by space charge screening effects. Also, the recombination of charges nonlinearly depends on their density,¹ thus the spatial accumulation of charges leads to a stronger recombination than in the case of an even distribu-

tion over the active layer. In addition to the current originating from the drift of charges, an inhomogeneous charge density also causes a diffusion current in certain regions of the device.^{2,3}

The potential profile may be directly investigated by scanning Kelvin probe microscopy on planar devices that have a wide horizontal gap between the electrodes.⁴ However, this experimental technique is not applicable to the more relevant devices with a sandwich geometry, where sub-micrometer thin films are placed between two electrodes. Insight into the charge density distribution in operating sandwich-type devices can be obtained from modeling studies, but these results depend on the accessibility and quality of the input parameters and the direct experimental model validation is challenging.^{5,6,7}

Electroabsorption (EA) spectroscopy has been widely used to investigate internal electric fields in operating organic electronic devices. As a standard routine, an alternating (AC) electrical bias is applied on top of a constant device-driving bias (DC) and the optical response is observed using phase-sensitive lock-in detection.⁸ If the quadratic Stark effect dominates in the investigated system, the first harmonic signal is proportional to the product of the AC and DC electrical fields, while the second harmonic signal is proportional to the square of the AC field. Using this technique, Brewer et al. have demonstrated screening of the internal electric field in polymer LEDs.⁹ A similar effect was found for LEDs that utilized a polyelectrolyte electron injection / transport layer.¹⁰

A drawback when using AC bias modulation is that it has to be of the same order as the constant driving bias to yield a detectable signal. Thus, equilibrium conditions may not exist and the state of the probed device differs from the real conditions under constant bias. To solve this issue, a slow triangular shaped pulse bias was used for the detection of the EA

signal.¹¹ This study also showed that injected carriers screened the internal electric field in polymer LEDs to a great extent.

A different effect was reported for LECs, where the electric field is concentrated in the intrinsic (i) zone after p- and n-doping of the active semiconductor and the formation of a p-i-n junction.¹² The electrochemical junction formation was accompanied by an increase of the capacitance and the EA signal intensity. Here, we study the temporal evolution of a sandwich-type LECs with capacitance-frequency scans as well as optical measurements of the Stark effect using a slow ramp pulse bias. The active LEC material was a cyanine dye (Cy3-P), composed of a cationic trimethine dye chromophore and the counter anion hexafluorophosphate (PF_6^-). We have studied the doping evolution and junction formation in Cy3 LECs before¹³ and showed that the transient behavior can be adjusted by the choice of the counter anion. For PF_6^- the ionic mobility is relatively low and the device response therefore slow. The slow ionic movement, however, allows us here to measure optical and electrical parameters for a quasi-static ionic distribution. An important result from ref. 13 we use here is that the system develops a p-i-n junction with a very narrow (a few nm at most) p-doped region when operated under constant voltage. With this information, we show that differences in the evolution of the capacitance and the Stark effect intensity can be used to estimate the charge distribution of the uncompensated injected electrons over time.

RESULTS

The functional principle of constant-voltage driven cyanine LECs is now firmly established.^{13,14} When initially a voltage is applied, the injection of electronic charges is hindered and the dominating process is a drift of mobile anions (PF_6^-) to the anode. This results in the formation of electric double layers^{15,16,17} at both electrodes that facilitate electronic charge

injection. As a result, the current starts to rise. The oxidized and reduced cyanine molecules are partially stabilized by opposite ionic charges. Thereby, high-conductive p- and n-doped regions are formed at the anode and cathode, respectively, which gradually grow towards the film center. The result is a p-i-n junction that allows the facile injection of electrons and holes from the electrodes into the active layer, transport via the doped regions and recombination in the intrinsic region, leading to light emission. For longer operation times, when the reduction of the intrinsic region continues, excitons in contact with the doped regions are quenched and consequently the luminance decreases.¹⁸ A decrease of the current after long operation times is usually ascribed to device degradation processes.

Figure 1 displays the reflectance spectrum and the initial EA spectrum of the cyanine LEC. Low reflectance in the range from 450 nm to 600 nm coincides with the cyanine absorption, but due to interference effects the reflectance spectrum is slightly modified when compared to a dye film absorbance spectrum (see SI, Figure S1). The reflectance spectrum is composed of contributions of cyanine monomers (at 583 nm), dimers (at 538 nm) and H-aggregates (at 453 nm).¹⁹

The inset of Figure 1 shows the temporal current and electroluminescence characteristics of the LEC. The current onset time at about 10 min indicates the formation of the electric double layers, while the points of maximum luminance (~300 min) and maximum current (~600 min) indicate the optimum p-i-n situation and the start of device degradation, respectively. Because the ionic mobility of PF_6^- is low, the transient device response of cyanine LECs is slow. For our purpose, however, this is an advantage because the constant voltage can be interrupted for various measurements without altering the p-i-n structure. For example, the ramp pulse sequence used for EA measurements has to be chosen slow enough in order to

reach equilibration of electronic charge carriers at every bias value, but ions should not redistribute when the constant voltage is interrupted.

With this functional principle at hand, the electric field inside the operated device can be qualitatively predicted. In the p- and n- regions a large number of doped molecules is present whose charges are locally compensated by ions. The conductivity of the doped regions is high compared to the intrinsic region.^{20,21} Therefore, the potential will be flat in the doped regions and drop mainly in the junction region. In order to experimentally access the transient p-i-n situation and to obtain more detailed information about the distribution of the electric field we measured the dynamics of the Stark effect intensity and of the cell capacitance.

The EA spectrum shows a pronounced feature at the monomer wavelength (583 nm) with a shape of the first attenuance derivative, calculated from the reflectance spectrum. The same holds for the dimer EA (538 nm), although the signal intensity is considerably lower. The close similarity of the EA spectrum to the first derivative of the attenuance in the range from 500 to 600 nm together with the quadratic scaling of the EA amplitude vs the electric field (see below) indicates that the quadratic Stark shift dominates the EA signal.²² A brief explanation of the mechanism is provided in the SI.

The relationship between the attenuance derivative and the EA spectrum at 453 nm in Figure 1 is less evident, where a small absorption of H-aggregates results in a large EA amplitude. This can be the result of a larger difference of polarizabilities between the ground and excited states of the H-aggregates, as compared to the cyanine monomers. It is also interesting to note that both the absorption and EA at 453 nm are active only for *p*-polarized light but they are inactive when using *s*-polarized light (see SI, Figure S2). This polarization

dependence indicates that the H-aggregates must be oriented throughout the film with transition dipole moments that are arranged perpendicular to the substrate plane.

Figure 1. Initial EA spectrum for *p*-polarized light. The reflectance of the cell (cyanine layer 30 nm) for non-polarized light is shown on the right scale. The 1st derivative of the attenuance resembles the initial EA signal. The inset shows typical transients of the current and electroluminescence for a constant voltage bias of 3 V.

In order to evaluate the electric field dynamics, we will now focus on the 583 nm EA band. Figure 2a shows the intensity of the 583 nm EA band vs voltage after different operation times. EA spectra at different voltage values of the ramp pulse were fitted with the characteristic line shape of the Stark feature in the range from 560 to 610 nm. The Stark signal obtained from these fits is displayed as data points in Figure 2a, and four selected EA scans at different operation times are presented. Solid lines represent parabolic approximations of the experimental points in the form of $I^S = a^S(V_{bias}^2 - 2V_{built-in} \cdot V_{bias})$. Here, the coefficient a^S indicates the steepness of the parabola and is a measure of the Stark effect intensity; $V_{built-in}$ is the argument at the parabola's minimum and corresponds to the bias value where the electric field in the cyanine film is minimal. The parabolas cross the point (0,0) by

definition because the signal at zero bias was taken as a reference when measuring EA spectra. As evidenced by the parabolas, the signal is indeed proportional to the square of the electric field, as expected for the quadratic Stark effect.

The minimum of the EA parabola shifts from -0.37 V to $+1.33$ V during operation of the cell. This shift is related to the change of the built-in field. The origin for the initial value of -0.37 V remains unclear at present. When the device is connected under short-circuit conditions, any internal electric field should be screened by moving ions and the initial minimum is expected to be at 0 V. Also for thicker (60 nm) dye layers the initial built-in field was found at a slightly negative (-0.15 V) value and we note that similar phenomena are observable in data presented in Ref. 8. During electrochemical doping, the built-in potential is determined by the chemical potential difference of the n- and p-doped regions.²³ After an operation time of 5 h, the built-in potential was at $+1.33$ V.

A p-i-n junction can also show a photovoltaic response. The principle is that excitons can be split into free charge carriers by the high electric field present in the intrinsic region and that these charges travel via the low-resistive doped regions to the electrodes. The transients of the open-circuit voltage (V_{oc}) and the short-circuit current (J_{sc}) are displayed in Figure 2b. V_{oc} increased to ~ 1 V during the first hour of operation. The value of V_{oc} is an approximation of the built-in potential and we find a good agreement between the EA ($V_{built-in} = 1.17$ V after 1 h) and photovoltaic measurement. For longer operation times V_{oc} stabilized at 0.9 V.

Figure 2. (a) Transient behavior of the intensity of the 583 nm EA band vs. voltage for a cyanine (30 nm) LEC operated at 3 V bias. The solid curves represent parabolic fits to the experimental data points. The inset shows the corresponding EA spectra at a reverse bias of -3 V. Note that the EA amplitude increases over time but the shape of the EA is not affected. (b) Transient photovoltaic response of the same device.

Simultaneously with the change of the built-in field, the intensity of the Stark effect signal also increased. This increase was more evident for cells with thicker cyanine layers. For the further quantitative analysis we have therefore chosen LECs with cyanine layers of 60 nm. For these devices we observed a better agreement between the evolving built-in potential and V_{oc} which increased up to 1.2 V during 5 h of device operation. We used the Stark band at 453 nm for the analysis of the parabolic dependence on the applied bias because of the low reflection of a thick dye layer at its absorption maximum. Figure 3a displays

the dynamics of the parabola coefficients a^S normalized to the initial value. Open squares correspond to the uncorrected values obtained from the fitting procedure and we found an increase by $\sim 40\%$ over a period of 3 h. This increase can be understood by considering that the EA signal originating from the Stark effect is proportional to the product of the optical density, i.e. the thickness of the film, and the square of the electric field. For a situation where the electric field concentrates in a shrinking intrinsic region, the resulting Stark effect intensity increases because the quadratic signal gain due to the increased electric field is higher than the linear signal decrease due to the thinner region where the signal originates:

$I^S \sim d_i \cdot E^2 = d_i \cdot \left(\frac{V}{d_i}\right)^2 = V^2/d_i$; where d_i is the thickness of the intrinsic region, E is the strength of the electric field and $V = V_{bias} - V_{built-in}$.

During device operation we observed a small but continuous decrease of the film absorption (see SI, Figure S3), meaning that in a series of consecutive EA measurements increasingly less cyanine molecules, that contribute to the Stark effect will be available. The film absorption decrease is due to the formation of doped cyanine radicals and the occurrence of chemical side reactions.¹³ To account for this, we multiplied the fitted original amplitudes by the factor by which the optical density at 453 nm had decreased after a certain time of operation. Figure 3a displays these corrected coefficients a^S as filled squares. It is clear that the way of correcting the coefficients a^S is an approximation, because the decrease of active cyanine molecules must not be homogeneous throughout the film. Possible implications of this uncertainty, however, should be considered only for long operation times, because the original and corrected coefficients differ little for times up to approximately 2 h.

Figure 3a also shows how the capacitance values changed during device operation. The initial value C_0 represents the geometrical device capacitance. In the developing p-i-n

junction, the doped regions have a higher conductivity than the intrinsic region. During operation, the capacitance of the cell increases, as it is inversely proportional to the thickness of the low conductive (intrinsic) region. Accordingly, the thickness of the intrinsic region of the device can be estimated.^{20,21} Capacitance measurements showed the shrinkage of the low-conductivity region by 60% after 5 h of operation (Figure 3b). This shrinkage was significantly larger than that evaluated from the Stark signal. In our opinion, the difference originates from the step-like approximation of the p-i-n structure.

Figure 3. (a) Dynamics of the Stark effect intensity (a^s) of the 453 nm band and the capacitance for a 60 nm thick cyanine LEC operated at 4 V. The corrected a^s values account for the decrease of the parent dye absorption during device operation. (b) Relative thickness of the low conductivity intrinsic region.

DISCUSSION

In an operated LEC, the doped zones contain bound oxidized and reduced molecule radicals whose charges are compensated by counter ions. The conductivity of the doped zones is high and injected uncompensated charges can arrive with low resistance to the intrinsic region where electron-hole recombination and light emission take place. Typically, the p-i-n situation is approximated as a parallel plate capacitor, but an abrupt transition from the doped regions to the intrinsic region cannot be expected.²¹ In reality, a gradually varying doping density and conductivity throughout the doped regions are more likely. The local charge mobility and doping density profile also determines the density distribution of the injected electrical charges.

Data in Figure 3 show that during operation the capacitance increases stronger than the Stark effect intensity. In the following we explain the origin of this difference and show that it may be used as a measure for the distribution of the uncompensated electrical charge carriers inside the cyanine layer.

The distribution of the charge density inside the active layer determines both the capacitance of the cell and the Stark effect intensity. By definition, the capacitance is the ratio between the stored charge and the potential, $C = q/V$. Thus, the capacitance equals the integral

$$C \sim \frac{1}{\Delta V} \int_0^d \rho(x) dx \sim -\frac{1}{\Delta V} \int_0^d \frac{\partial^2 V(x)}{\partial x^2} dx, \quad (1)$$

where $\rho(x)$ is the charge density, d is the thickness of the layer and ΔV is the potential difference between the electrodes. Here, the interrelations between the charge density, the electric field and the potential were applied:

$$F(x) = -\frac{\partial V(x)}{\partial x} \text{ and } \rho(x) = \varepsilon_0 \frac{\partial F(x)}{\partial x} = -\varepsilon_0 \frac{\partial^2 V(x)}{\partial x^2}. \quad (2)$$

The amplitude of the Stark effect signal is proportional to the product of the optical density, *viz.* - to the thickness of the film, and the square of the electric field. Since the electric field

may vary over the thickness of the film, the Stark effect intensity can be expressed as the following integral:

$$a^S \sim \int_0^d F(x)^2 dx \sim \int_0^d \left(\frac{\partial V(x)}{\partial x} \right)^2 dx. \quad (3)$$

Equations (1) and (3) tie C and a^S via integral forms of the local distribution of the potential $V(x)$. As the electric field and charge density are interrelated to the potential (equation 2), they can be calculated once the distribution of the potential $V(x)$ is found. Note that it would be possible to extract a distribution by fitting only one parameter C or a^S , but the solution would be of little relevance since completely different distributions may give the same integral result of C or a^S . However, if the capacitance and the Stark effect intensities are fitted simultaneously by equations (1) and (3), the correspondence between the resulting and actual distributions is qualitatively much higher.

We chose a Gaussian distribution of uncompensated electrical charges as a simple model and calculated the peak positions and widths which result in the measured (Figure 3) increase of the capacitance and the Stark signal at different times of device operation. It was assumed that before application of the bias the intrinsic region spans the whole thickness of the cyanine film, there are no injected charges and that the electric field is homogenous when the bias is being applied. This situation corresponds to the initial capacitance and the Stark effect intensity, C_0 and a_0^S . As a further assumption, the p-doped zone was considered as very thin, *i.e.* only the n-doped zone grows with operation time and only injected electrons are distributed in the cyanine layer.¹³ We note that in reality a certain thickness of the p-doped zone must be present. First, the p-doped zone comprises an electric double layer of anions to compensate for the anodic injection barrier. In addition, charge conservation requires the existence of a p-type doping region (that should approximately match the n-type

doping number) and the non-compensated hole space charge (that should approximately match the electronic space charge).

A series of uncompensated injected electron distributions and the electric fields are shown in Figure 4. These results show that there is little accumulation of electrons near the silver cathode. The electronic charge is concentrated closer to the intrinsic zone and screens the electric field behind it – in a considerable volume of the n-doped zone. Most probably, the doping concentration in this charge and field free volume is high, resulting in a high conductivity. Thus, the current of injected electrons passes this area driven by a small electric field. The peak of the electron density progresses further from the cathode into the cyanine layer and the electric field concentrates in a thinner volume of the intrinsic region as the operation of the cell continues. C and a^S values increase when the electronic charge is localized closer to the anode and the electric field concentrates in a thinner region of the film. The capacitance is determined by the center position of the distribution, whereas the Stark signal depends on both the position and the width of the distribution. The widths of the distributions shown in Figure 4 are determined by the different increase of C and a^S at a certain time of cell operation. A larger difference results in a wider distribution, and *vice versa*.

Figure 4. Gaussian distributions of the uncompensated electron charge densities and electric fields at different operation times (min) for a 60 nm thick cyanine LEC operated at 4 V. The p-doped zone is assumed to be very thin and not growing over time.

Figure 5 illustrates the effect of the width of the distribution on the Stark signal. The situation depicted in Figure 5 corresponds to a twofold increase of C and different increases of a^S , with respect to the initial values. If the concentration of the uncompensated charge were characterized by a delta function localized in the middle of the cyanine layer—a plane capacitor model, both C and a^S would be two times larger. Broader charge distributions result in weaker Stark signals approaching the limit of $a^S/a_0^S = 1.33$ for a flat distribution. It is not possible to reveal more details of the charge distribution relying on the integral relations of equations (1) and (3). Examples would be skewed charge distributions or multiple peak scenarios which, although unlikely, could not be captured. The essential outcome of our analysis is that (i) the magnitude of the capacitance and the Stark effect intensity yield information about the thickness of the intrinsic region, and that (ii) the different dynamics of C and a^S is a measure for the sharpness of the charge distribution and the electric field.

Figure 5. Gaussian distributions of the uncompensated electron charge and the electric field distribution for an increase of the capacitance by a factor of $C/C_0 = 2$ and different changes of the Stark effect intensities $a^S/a_0^S = 2, 1.8, 1.6, 1.4$ and 1.33 . These curves correspond to the Gaussian widths (standard deviations) of $0, 0.09, 0.18, 0.38$ and infinity.

CONCLUSIONS

Electroabsorption spectroscopy in combination with electrical capacitance measurements enables the evaluation of the electric field distribution in light emitting electrochemical cells, and its changes during the cell operation time. The EA spectra of the investigated cyanine LECs are the result of the quadratic Stark effect. The parabolic dependence of the Stark effect intensity on the applied voltage shifts with operation time of the cell due to a change of the built-in potential. We reconstructed the dynamics of the built-in field from temporal EA and capacitance data. In addition to the well-known fact that the capacitance of the operating cell increases with time because of the shrinkage of the intrinsic region in favor of the doped zones, the Stark signal also increases, however, by a smaller factor. From these experimental data it is possible to determine the width and the position of the uncompensated injected charges. We have found that electrons injected into the cyanine layer are not homogeneously spread over the n-doped region, but they concentrate at a distance from the cathode, substantially screening the electric field in the n-doped zone behind. A similar experimental approach can be applied to other sandwich-type devices, where accumulation of charges inside the active layers occurs.

EXPERIMENTAL SECTION

Figure 6a shows a scheme of the setup to measure the Stark effect of cyanine LECs. Measurements were carried out in ambient atmosphere. Experimentally, the spectrally resolved reflected light intensity is measured over time with and without a voltage applied to the cell. The applied bias causes the build-up of an electric field in the cyanine layer. This field modifies the absorption of the cyanine via the Stark effect and the intensity of the reflection changes with respect to the zero bias condition. Although the reflected light is detected, the signal is due to electric field induced changes of the dye absorption. Therefore, we use the term electroabsorption (EA) when referring to this signal.

A halogen lamp was used as the probe light source. The long wavelength range was filtered in order to increase the dynamic range of the CCD camera in the visible and to minimize the heat load on the sample when measuring the Stark effect. The light polarization was adjusted to *s* or *p* with a Glan prism. Mostly, we used *p*-polarized light because this polarization has the electric field component parallel to the applied DC electric field. As a consequence, *p*-polarized light is more sensitive to the molecular dipole moment changes induced by the external electric field. The collimated beam hits the sandwich-type device through the glass substrate and the ITO electrode at an incidence angle of 45 degrees. The light, transmitted through the cyanine layer and reflected from the silver electrode, was directed into the input slit of an Andor Shamrock 500i spectrometer equipped with an Andor Newton DU970 CCD camera (1600 x 200 pixels). A diffraction grating (150 lines/mm) was centered at 560 nm on the spectrometer output that allowed detection of the spectral window from 390 to 730 nm by the CCD. The electrical part of the setup includes a Tektronix AFG3101 function generator and an Agilent DSO5054A oscilloscope. The generator was used to apply a constant bias and ramp pulses when recording the Stark effect scans, respectively. The current for both bias modes was monitored and recorded with the oscilloscope. Camera

reads, operation of the function generator and the oscilloscope were synchronized via TTL trigger outputs from the generator. All three devices were connected to and controlled by a PC.

The measurement was started by applying a constant voltage bias to the cell. The constant bias was interrupted by a ramp-like voltage pulse during which the voltage dependence and spectral information of the Stark effect were detected. During the 1 s duration of the ramp pulse 283 camera scans of 3.5 ms duration were taken. Thereby, a single scan corresponded to a certain voltage applied to the cell, providing the data for the voltage dependence of the spectral changes induced by the applied bias. For every ramp sequence during the device life cycle, the light intensity at zero bias was used as reference for the calculation of the bias-induced changes of the reflected light intensity. In order to accumulate statistical data for the noise reduction, one interruption of 1 min duration contained 60 ramp pulses.

During constant voltage driving, the probe light was blocked by a computer-controlled mechanical shutter. With the shutter closed, the spectrometer and camera were used for measuring the spectrally resolved electroluminescence (EL) of the cell. EL scans were continuously repeated providing the EL dynamics and confirming the device functionality. The reflectance spectrum was measured on a home-built setup consisting of an Avantes AvaSpec-2048-SPU fiber spectrometer and using a silver mirror as reference.

The capacitance was measured using the Paios measurement system (Fluxim AG, www.fluxim.com) during short interruptions of the constant voltage bias. For capacitance acquisition zero offset voltage and 70 mV oscillating voltage with a frequency of 1 kHz were applied to the cell. During the same interruption a current-voltage (J-V) scan was performed using a white LED (Cree® XLamp® XP-G) with a nominal intensity of 72 mW/cm² to

determine the open circuit voltage (V_{oc}) and the short circuit current (J_{sc}) of the LEC operated in photovoltaic mode. The device fabrication procedure is described in ref. 13. We used cyanine layers (Figure 6b) with thicknesses of 30 nm or 60 nm. These were prepared by spin-coating a 1 wt% or 2 wt% acetonitrile solution at 6000 rpm, respectively.

Figure 6. (a) Experimental setup for the measurement of the EA and timing of the ramp pulse applied to the cell during the EA scan. During the yellow time interval light irradiates the sample. (b) Chemical structure of the cyanine dye (Cy3-P) and schematic of the device.

ASSOCIATED CONTENT

Supporting Information

Absorbance vs reflectance spectra, absorption spectra for polarized light, absorption changes during device operation, explanation of the Stark effect.

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Notes

The authors declare no competing financial interest.

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Dynamics of Charge Distribution in Sandwich-Type Light Emitting Electrochemical Cells Probed by the Stark Effect

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The graph schematically depicts the LEC device as a capacitor. Gaussian distributions of injected, uncompensated electronic charge are displayed between the electrodes.