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Dynamic doping and degradation in sandwich-type light-emitting electrochemical cells

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Experimental details

Bis-2-phenylpyridine 6-phenyl-2,2'-bipyridine iridium(III) hexafluorophosphate $[Ir(ppy)_2(pbpy)][PF_6]$ was synthesized similarly according to methods described previously.[1] Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) aqueous dispersion (PEDOT:PSS) (Clevios^{TM} P VP CH8000) was purchased from Heraeus (formerly H. C. Starck). Acetonitrile (anhydrous, 99.8%) and 1-butyl-3-methylimidazolium hexafluorophosphate $[BMIM][PF_6]$ (purum, ≥97.0%) were obtained from Sigma Aldrich and were used as-received. Indium tin oxide (ITO)-coated glass substrates were patterned using conventional photolithography.

Sandwich-type solid-state light-emitting electrochemical cells were fabricated via spin-coating under ambient conditions on pre-patterned indium tin oxide (ITO)-covered glass substrates. The ITO substrates were extensively cleaned using sonication in detergent bath and subsequent oxygen plasma treatment. Prior to the coating of the active layer, a layer of 100 nm poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) PEDOT:PSS was deposited to planarize the ITO anode, increasing the yield and reproducibility of working devices. A stock solution was prepared, dissolving five percent by weight of the iridium complex and the ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate $[BMIM][PF_6]$ in a molar ratio of 3:1 in Acetonitrile. The stock solution was filtered using a 0.1 µm PTFE-filter and spin-coated on top of the PEDOT:PSS layer. Afterwards the substrate was transferred to an argon filled glovebox (O_2 and H_2O < 1 ppm) and annealed on a hotplate at 100°C for 1h resulting in a final active layer thickness of 100 nm. Finally, a 150 nm thick aluminum (Al) cathode was thermally evaporated on top under high vacuum ($< 1\cdot10^{-6}$ mbar) using a shadow mask, defining 8 pixels per substrate, each having an active lighting area of 4 mm^2. To test the devices under ambient conditions they were encapsulated under inert atmosphere by a cavity glass capping equipped with a silica getter to protect the pixel areas against penetrating oxygen and water. The capping was directly glued to the substrate without prior removal of the organic layers using a self-made UV-curable epoxy adhesive which was coated locally onto the margin of the capping. To test the functionality of the encapsulation, control devices were processed using a metallic calcium layer as a sensor. As the calcium sensor stayed metallic during the long-term study of several houndreds of hours, a possible reaction with water and oxygen to CaO or $Ca(OH)_2$ which would have changed the optical appearance and the resistivity of the transparent film, could be excluded. The device architecture and the chemical structures of the materials comprising the active layer are illustrated in Fig. S1. The thickness of the films were determined on reference samples using a KLA Tencor P·15 profilometer.

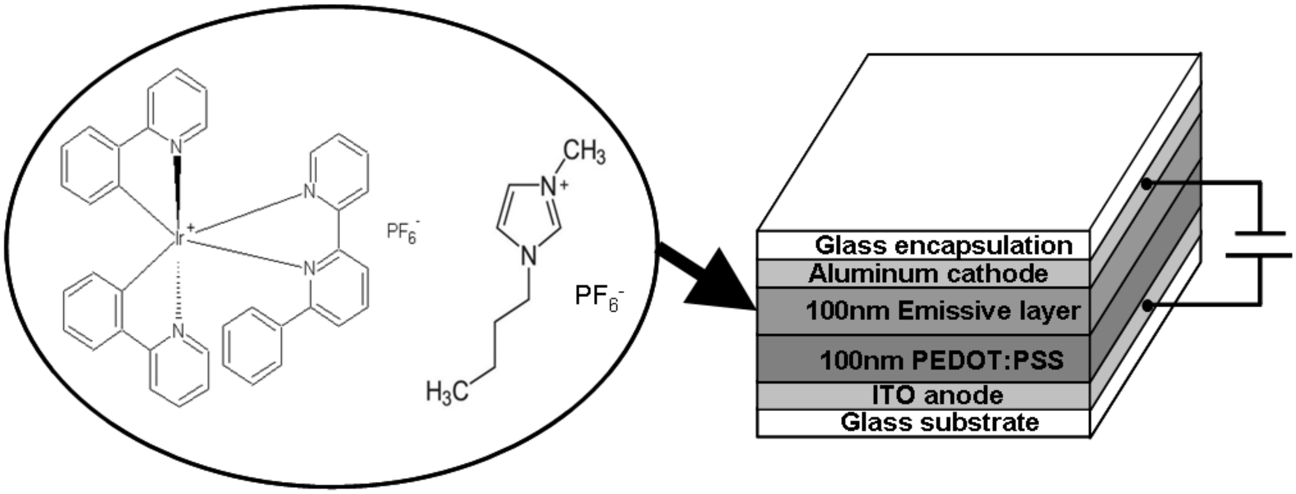

Fig. S1 Chemical structures of the iridium(III) ionic transition metal complex and the ionic liquid used in the active layer of the LEC and the corresponding architecture of the investigated device.

In-situ photoluminescence (PL) spectra of the LEC active layer at fixed time intervals during device operation at a constant voltage of 5 V and after switch-off (relaxation period) were collected in the wavelength range from 400 to 800 nm using a Perkin Elmer LS-50B spectrometer equipped with a xenon lamp at an excitation wavelength of 330 nm and with a scan speed of 1500 nm/min, which results in a scan time of 16 s. The excitation light beam enters the device through the glass substrate, crosses the ITO/PEDOT:PSS anode and eventually reaches the emissive layer. Excited light from the emissive layer leaves the device in a similar manner and is detected by a photomultiplier. A schematic of the measurement setup is illustrated in Fig. S2.

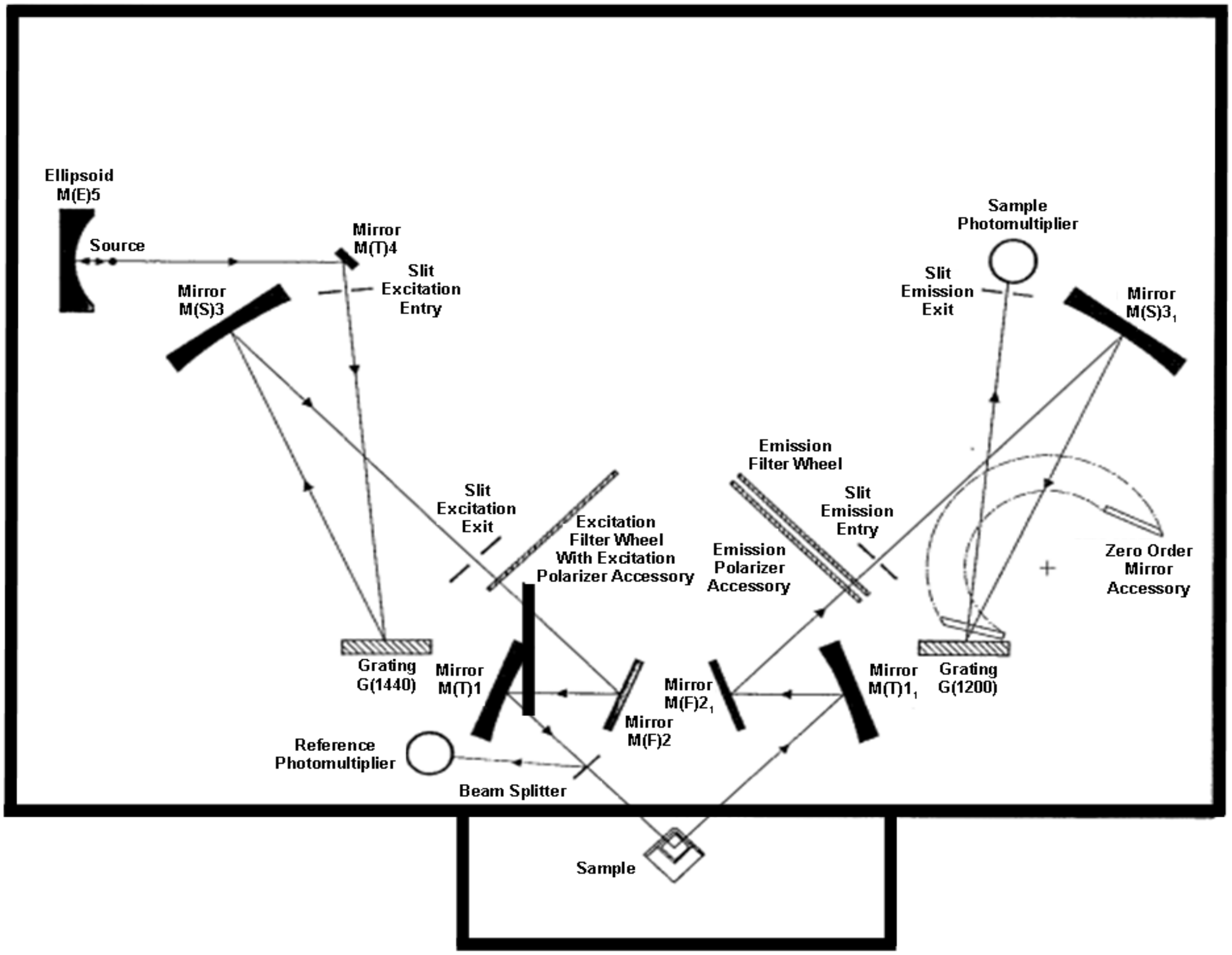

Fig. S2 Schematic of the Perkin Elmer LS-50B spectrometer which has been used to measure the PL of the LEC active layer during operation and after switch-off.

The electro-optical characterization (luminance over time) was carried out in a Botest OLED Lifetime Test System (OLT) under a constant voltage of 5 V at a constant temperature of 20 °C. The photo diodes were calibrated using a Photo Research PR-650 SpectraScan® Colorimeter.

Study of PL/EL interference

To examine a possible interference of the PL measurement of the LEC active layer by the electroluminescence (EL) of the device in the spectrometer, the relative PL spectra of three monochromatic organic light-emitting diodes (OLEDs) at various EL intensities ranging from 20 cd/m² to more than 1700 cd/m² have been compared among each other with the results depicted in Fig. S3 a) - c).

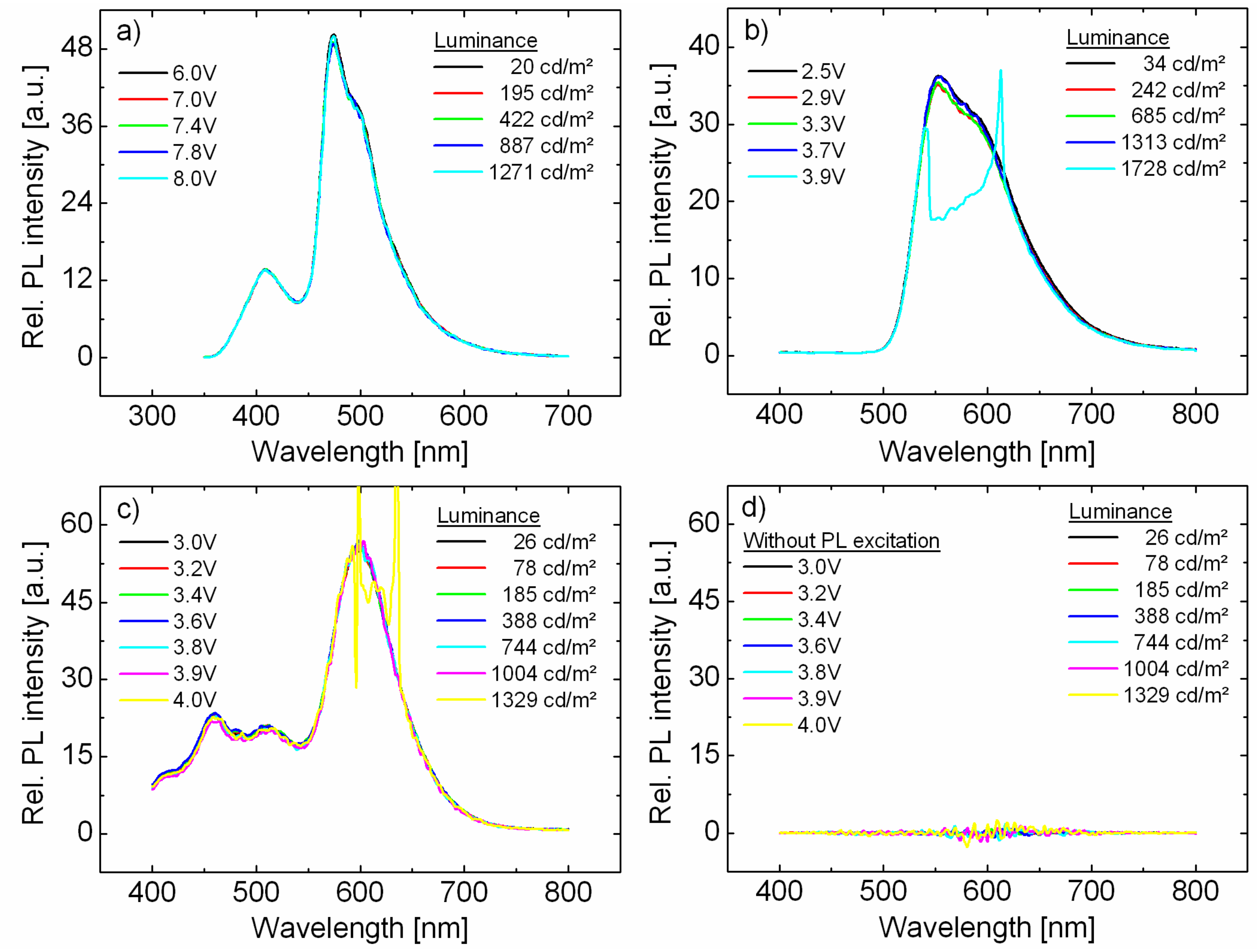

Fig. S3 Relative PL spectra as a function of EL intensity of a) an evaporated blue organic light-emitting diode (OLED), b) a spin-coated yellow polymer OLED and c) an evaporated red OLED. d) illustrates the measured EL signal of the photodetector of the spectrometer from the red OLED without PL excitation.

No significant differences could be detected for moderate luminance levels (1000 cd/m² - 1300 cd/m²) for which reason an interaction of EL and PL up to the investigated luminous intensities is excluded. It was only for the yellow and red OLED beyond the latter limits, that a disturbance of the PL signal by the EL of the diode was observed. However, the latter feature has not been observed for the LEC driven at 5 V even at its maximum brightness of 1200 cd/m². To have further proof that the EL of the devices is not detected by the spectrometer, the intensity signal measured by the spectrometer has been analyzed as a function of the EL intensity for the red OLED without an optical excitation of the latter with the results illustrated in Fig. S3 d). The study clearly reveals that independent of the OLED's brightness, there is no measurable rise in the detected signal of the spectrometer. On the basis of the latter results, any changes in the PL spectra of the LEC during operation can be exclusively attributed to an alteration of the active layer itself.

PL investigation as a function of ionic liquid (IL) concentration

In addition to the described ratio iTMC:IL = 3:1 (25 mol.-% of IL in the film) we performed additional experiments with ratios of iTMC:IL = 1:1 (50 mol.-%) and iTMC:IL = 9:1 (10 mol.-%). Fig. S4 shows the reduction and recovery of the photoluminescence (PL) signal for devices with the corresponding iTMC:IL ratios. The LECs were driven for 35 h at a constant voltage of 5 V and had time to recover afterwards for a period of 25 h. Moreover in Fig. S5, the evolution of the recovered versus non-recovered peak PL intensity as a function of IL concentration is shown. The PL is reduced faster for films with a high IL concentration and its recovery is highest for the film with the lowest IL concentration.

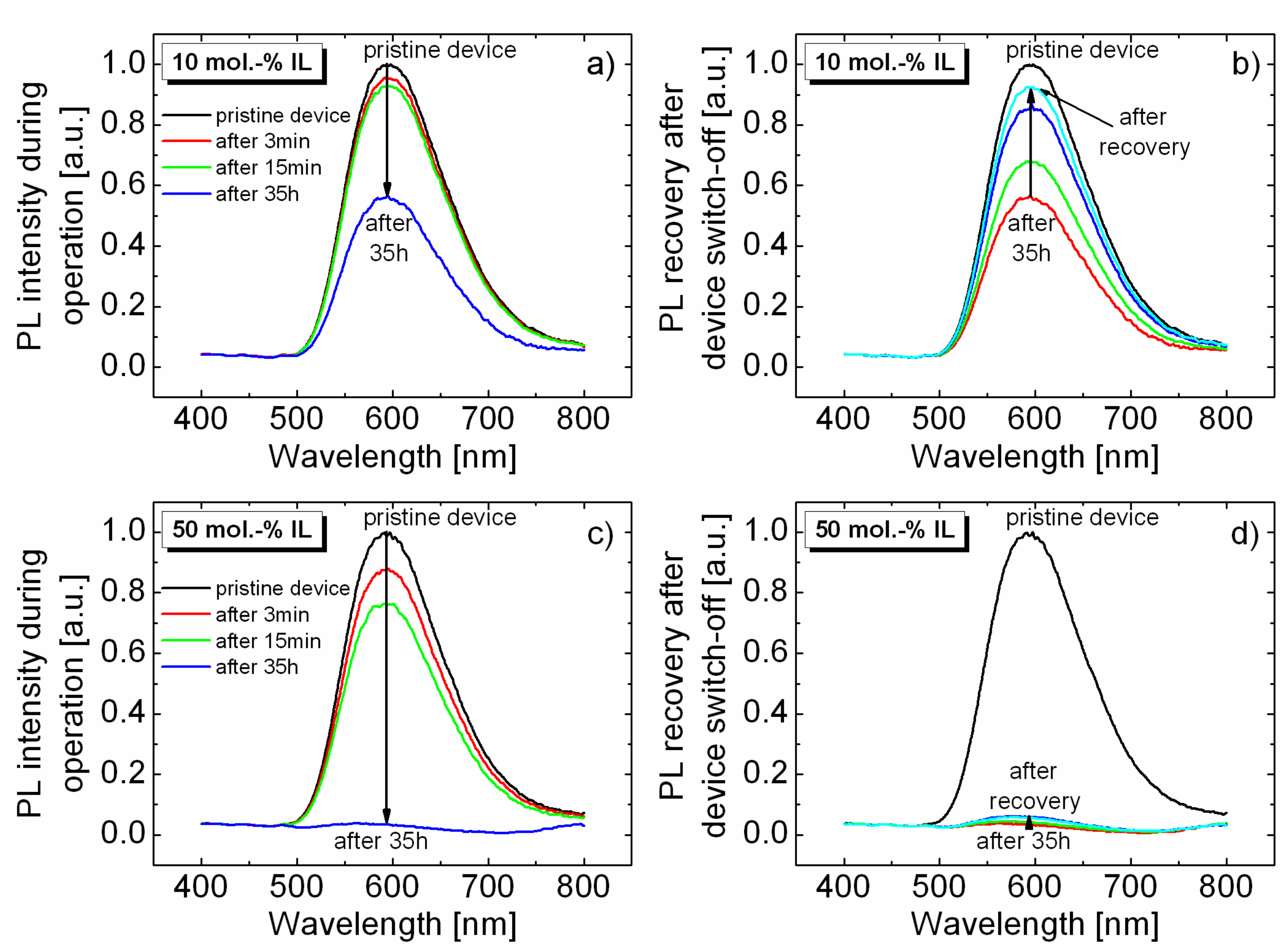

Fig. S4 A) and c): PL spectra of the LEC active layer during operation at a constant voltage of 5 V for IL concentrations of a) 10 mol.-% and c) 50 mol.-%. The arrow denotes the direction of proceeding operating time up to 35 h. B) and d): PL spectra during a recovery period after operation for 35 h for IL concentrations of b) 10 mol.-% and d) 50 mol.-%. The arrow denotes the direction of proceeding recovery time up to 25 h.

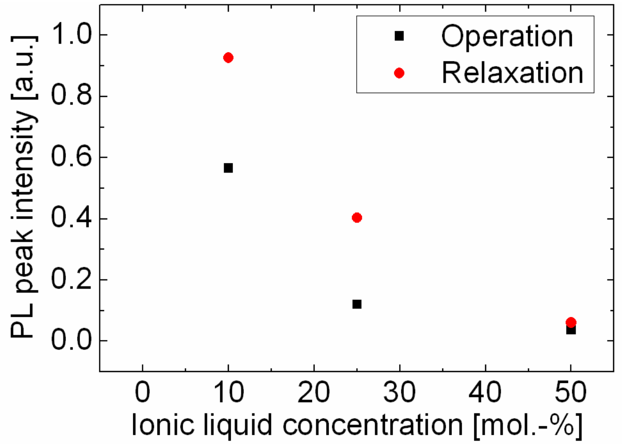

Fig. S5 Evolution of the non-recovered (black squares) and recovered (red circles) peak PL intensity of the LEC as a function of ionic liquid concentration. Devices were operated at 5 V for 35 h and had time to relax for 25 h after switch-off.

Current density as a function of operation time at a constant voltage of 5 V

Fig. S6 represents the current density as a function of operation time for the investigated LEC device at a constant voltage of 5 V. A decrease in current is observed after 30 h of operation.

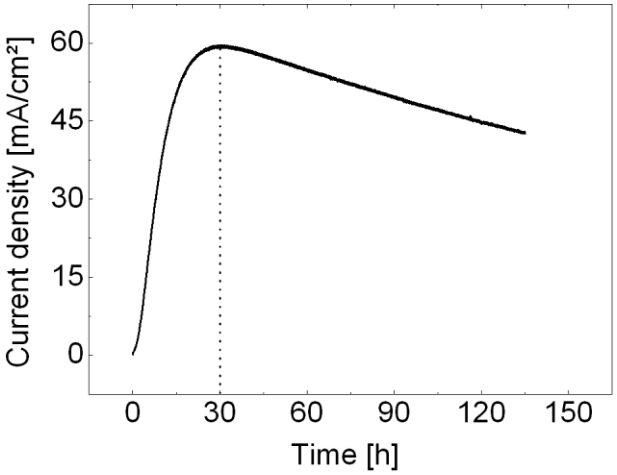

Fig. S6 Current density as a function of operation time at a constant voltage of 5 V.

Extended analysis of PL recovery after switch-off as a function of operation time

Fig. S7 illustrates the PL spectra of several identical LEC devices driven at a constant voltage of 5 V for various time intervals after a relaxation period of 25 h after the device was switched off. The experiments were performed to examine the point in time when the PL intensity of the LEC device as a function of operating time is no longer fully recoverable after the relaxation period. Up to an operation time of 3 h a complete recovery of PL intensity can be observed, whereas beyond an increasing decline in PL can be detected which is dependent on the former operating time.

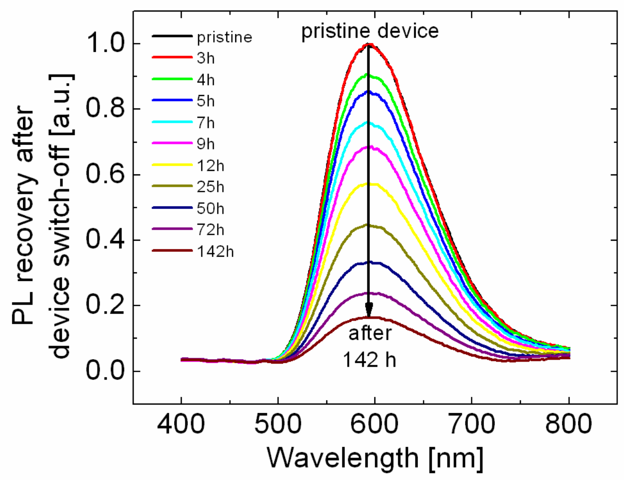

Fig. S7 Photoluminescence spectra of the LEC active layer after a relaxation period of at least 25 h after the device was switched off as a function of the operating time for several identical devices driven at a constant bias of 5 V. The arrow denotes the direction of proceeding driving time up to 142 h.

Fig. S8 displays the PL recovery of a LEC driven for 142 h after the device was turned off. Even after this prolonged operation time, there can still some relaxation of the PL intensity be detected, which can be attributed to a depletion of electrochemical doping.

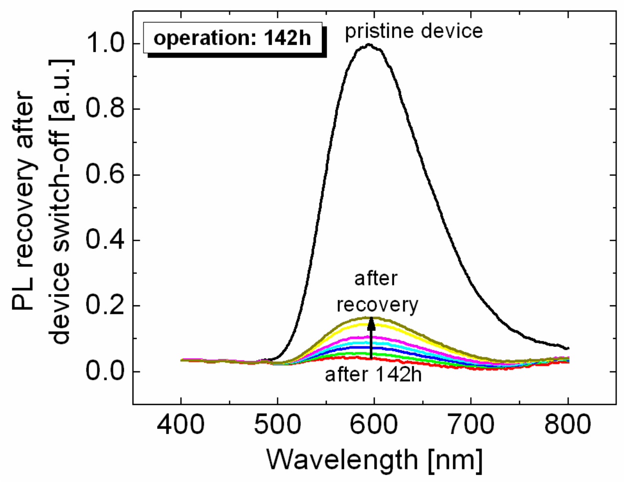

Fig. S8 Photoluminescence recovery in the LEC active layer during a relaxation period of at least 25 h after the device has been switched off. The operating time was 142 h at a constant bias of 5 V. The arrow denotes the direction of proceeding relaxation time.

References

1 H. J. Bolink, E. Coronado, R. D. Costa, E. Ortí, M. Sessolo, S. Graber, K. Doyle, M. Neuburger, C. E. Housecroft, E. C. Constable, *Adv. Mater.* 2008, **20**, 3910