

Strong Electroluminescence from Polymer Films with Heavily Quenched Photoluminescence**

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Solid-state electroluminescent devices based on organic polymers have been extensively studied in recent years for potential display and lighting applications.^[1–3] Electroluminescence (EL) is the generation of light by electrical excitation (excluding incandescence). For a material to exhibit EL, a general criterion is that it must also possess photoluminescence (PL), which is an intrinsically more efficient process, as electrons and holes are always created in pairs and in close proximity, making radiative recombination a favorable process. A material that is not photoluminescent or whose PL is heavily quenched is therefore very unlikely to be a good candidate for EL.^[4] In fact, the EL quantum efficiency of a polymer light-emitting diode is ultimately limited by the PL quantum yield of the luminescent material used.^[5] Although most “conventional” polymer light-emitting diodes (PLEDs) are metal–insulator–metal (MIM) structures based on pristine luminescent polymers,^[6] EL from polymers can be achieved alternatively by the formation of a light-emitting p–n junction via in situ electrochemical doping.^[7–8] Such polymer homo-junction devices are known as polymer light-emitting electrochemical cells (LECs), and are reminiscent of traditional inorganic p–n junction LEDs. The active material of an LEC is a mixture of a luminescent polymer and a solid-state polymer electrolyte.^[9] The application of a sufficient voltage bias (typically less than 4 V for thin-sandwich devices) leads to in situ electrochemical p- and n-doping of the luminescent polymer and the formation of a light-emitting p–n junction.^[10–11]

The effects of doping on luminescent polymers are twofold. First, the electrical conductivity of the polymer is greatly increased upon doping, giving rise to a much smaller bulk and contact resistance. This, in turn, leads to more efficient and balanced charge-carrier injection. As a result, LECs are typically very efficient and insensitive to the choice of electrode material and the thickness of the active layer. Secondly, doping strongly affects both the absorption and photoluminescence of the luminescent polymer.^[8,12–13] Heavy PL quenching was first detected by scanning PL measurements^[14–15] and re-

cently by direct imaging of extremely large, planar LECs.^[10–11,16] Here, we report highly unusual PL enhancement by in situ electrochemical doping, which leads to strong EL from a polymer film whose PL is initially close to 100% quenched. The underlying mechanisms of this phenomenon and its implications for device applications are discussed.

By replacing the lithium triflate (LiTf) salt commonly used in LECs with silver triflate (AgTf), PL from the luminescent polymer poly[5-(2'-ethylhexyloxy)-2-methoxy-1,4-phenylene vinylene] (MEH-PPV) is heavily quenched even before any bias is applied. This effect is seen in Figure 1, which shows the spectrum of the AgTf-containing LEC film as well as that of the control film containing the LiTf salt. The two spectra are taken under identical conditions, so the spectrum intensity can be used to directly compare the relative PL efficiency of the polymer films. The control film displays the characteristic spectrum of MEH-PPV. A maximum PL intensity of 3340 arbitrary units (a.u.) is recorded at 595 nm. On the other hand, the spectrum of the AgTf-containing film is very weak and noisy. Approximate peak values were extracted by applying a smooth curve fit to the data, and peaks were found with intensities and wavelengths of 40 a.u. at 583 nm and 43 a.u. at 700 nm, respectively. Overall, the PL intensity of the LEC film containing AgTf is nearly 80 times weaker than that of the control film containing LiTf salt.

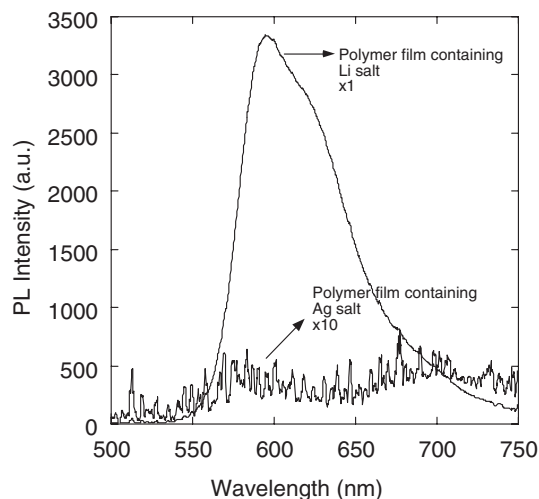


Figure 1. PL spectra of composite polymer films consisting of MEH-PPV, poly(ethylene oxide) (PEO), and either LiTf or AgTf measured at room temperature.

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Interestingly, LECs based on AgTf salt (Ag-LECs) exhibit disproportionately strong EL as compared to regular LECs based on LiTf salt (Li-LECs). Figure 2 shows the device current and EL intensity as a function of time displayed by a Ag-LEC and a control Li-LEC, when driven by a constant voltage. The devices tested are planar LECs with an interelectrode spacing of 2 mm. Although strong EL has also been observed in sandwich LECs quenched by AgTf, the extremely

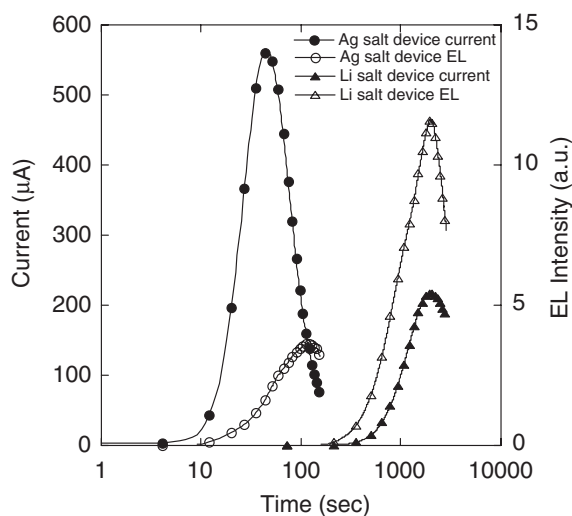


Figure 2. Current and light intensity as a function of time for two planar LECs utilizing either AgTf or LiTf salt while subjected to a constant voltage bias of 300 V at 315 K. The devices tested are planar MEH-PPV-based LECs with an interelectrode spacing of 2 mm.

large planar configuration allows easy elucidation of underlying mechanisms by spatially resolved imaging. Under a constant bias of 300 V, the device current would initially increase by 2 to 3 orders of magnitude as in situ electrochemical doping renders the device more conductive. This is accompanied by the turning-on and the increase of EL. Despite an initial PL nearly 80 times weaker than that of the control film, the Ag-LEC exhibits a maximum EL intensity approaching one-third of the Li-LEC. Moreover, since the EL in the AgTf device peaks significantly later than the current, the maximum EL is achieved at a smaller current than in the control device, suggesting an even smaller difference in EL efficiency (at peak EL intensity) between the two devices. In fact, when the EL/current ratio (efficiency) is plotted against time or current (not shown), the two devices show totally opposite trends after passing through the peak current. The sharp efficiency increase with decreasing current in the Ag-LEC eventually makes it more efficient than the Li-LEC when final efficiencies are compared. In addition, the Ag-LEC turns on more than 10 times faster than the control device, with EL being detected less than 10 s after the application of a voltage bias.

The strong EL from Ag-LECs is totally unexpected, but has been further confirmed by spatially resolved imaging of the

planar devices. Figure 3 shows a composite image consisting of photographs from two LECs identical to the ones tested in Figure 2. Each column of the composite image directly compares the two devices in PL or EL. All photographs are taken with the devices subjected to UV illumination from a 4 W UV lamp at a distance of 10 cm. The Ag-LEC (Fig. 3a) shows no visible PL because of strong quenching by AgTf, whereas the Li-LEC film (Fig. 3d) displays strong orange PL from MEH-PPV. The large difference in the PL imaged from these two films is consistent with the intensity difference shown in Figure 1. However, both devices exhibit strong EL under the same driving voltage, as seen in Figure 3b and e. Although the charge-coupled device (CCD) camera is partially saturated, there is no doubt that the orange EL imaged in both devices is from that of MEH-PPV. In addition, EL is only observed from a narrow region closer to the cathode, consistent with all previous observations in extremely large planar LECs made from MEH-PPV.^[10–11,16–17]

Figure 3c and f displays the polymer PL straight after the voltage bias is removed, and provides a direct explanation of the strong EL observed in Ag-LECs. In the control Li-LEC, in situ electrochemical doping has caused significant PL quenching throughout the polymer film, as shown in Figure 3 f. PL is 100 % quenched in the p-doped region between the EL emission zone and the anode. PL in the n-doped region is

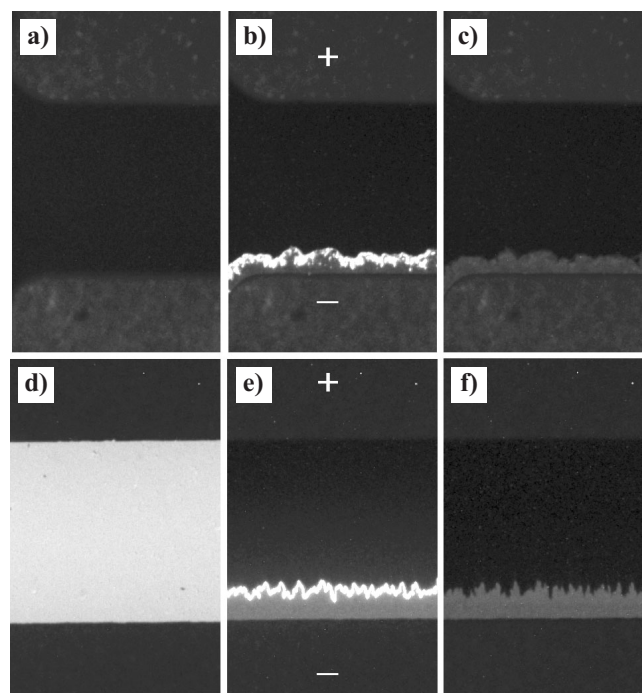


Figure 3. Photographs of AgTf (top row) and LiTf (bottom row) based planar LECs under UV illumination. a,d) PL before bias; b,e) EL under a constant bias of 300 V; c,f) PL immediately after the voltage bias was removed. The devices were kept at a constant temperature of 315 K. The distance between the 4 W UV lamp and the device is approximately 10 cm. A shutter speed of 4 s and an aperture of f/14 have been used for all images. The input level of the composite image has been adjusted to improve the contrast.

less quenched, but nevertheless much weaker than in the undoped film (Fig. 3d). Strikingly, the Ag-LEC also exhibits a similar PL profile and weak but clearly visible orange PL close to the cathode. Since MEH-PPV PL is initially heavily quenched in the Ag-LEC (Figure 3a), the PL observed after the bias is much stronger than that observed before the bias. The greatly enhanced PL allows for much stronger EL than one would expect from a heavily PL-quenched film.

From above observations, it is obvious that the PL criterion for EL generation still holds. The strong EL from an apparently non-photoluminescent polymer film is possible simply because PL is enhanced/recovered in the same region where EL originates. Time-elapsing fluorescence imaging reveals that PL recovery occurs gradually in the same region and in a propagating fashion as in electrochemical n-doping. We, therefore, conclude that the latter is responsible for the observed PL enhancement. More specifically, two competing quenching mechanisms are involved, with electrochemical n-doping overcoming the effect of initial quenching by Ag^{I} ions as the device is turned on. The weaker quenching by electrochemical n-doping gives rise to the apparent effect of PL recovery. However, the PL of the polymer film is never completely recovered, as the luminescent polymer is still electrochemically doped. This can be clearly seen by comparing Figure 3c and d. On the other hand, the effect of electrochemical p-doping on the initial PL quenching by Ag^{I} ions cannot be directly observed by imaging because of the 100% PL quenching caused by electrochemical p-doping itself.

Although fluorescence quenching/enhancement is very commonly used in molecular sensors for the detection of ions and molecules,^[18] the quenching of luminescent conjugated-polymer PL by Ag^{I} ions and subsequent PL recovery by in situ electrochemical doping has never been reported. More work is needed to achieve a better understanding of the underlying mechanisms involved. However, our preliminary study does offer some insight into the mechanisms of PL quenching by Ag^{I} ions. We have also fabricated LECs containing other cations (Cu^{II} , Eu^{III} , and Tb^{III}) using the same anion, CF_3SO_3^- . Similar PL quenching/recovery effects were observed in Cu^{II} devices, but not in Eu^{III} and Tb^{III} devices. The absence of PL quenching by rare earth metal ions is probably because of better shielding of 4f electrons from the donor polymer, whereas transition metal ions are well known to quench fluorescence via various electron and energy transfer mechanisms.^[19–20] The quenching of the luminescent-polymer PL by Ag^{I} ions is most likely results from charge transfer, because there is no overlap between the emission spectrum of MEH-PPV and the absorption spectrum of Ag^{I} ions.^[19] In addition, the charge transfer likely occurs in the ground state because the Ag-LEC film is at least 20 times more conductive than the Li-LEC film, as measured by the initial device current under identical driving voltage and temperature. Although it is also possible that Li-LEC and Ag-LEC films have different ionic conductivity, the difference is likely to be small as the films contain the same molar amounts of salt and there is no evidence that the Ag ion is more mobile than Li ion. The

increased initial conductivity allows a larger redox current flow, and is responsible for the much faster turn on of the Ag-LEC, as seen in Figure 2.

The above discoveries have some interesting implications. PL enhancement by in situ electrochemical doping suggests that the active material used in polymer EL need not be initially photoluminescent. This expands the class of EL materials available and the flexibility in EL polymer synthesis, which typically involves the use of PL quenching metallic catalysts.^[21] Heavy quenching by metal ions and the associated increase in conductivity may also find applications in polymer photovoltaics, where radiative recombination of photogenerated charge carriers and series resistance are two major factors affecting the device efficiency.^[22]

In summary, we have demonstrated heavy quenching of luminescent-polymer PL by Ag^{I} ions in the solid state. LECs made with the heavily quenched polymer film exhibit unusually strong EL, comparable to regular LECs made with the unquenched films. Spatially resolved fluorescence imaging during the operation of planar LECs containing Ag^{I} ions reveals significant PL recovery in the EL emission zone, which can be attributed to in situ electrochemical n-doping.

Experimental

The luminescent polymer used in this study is poly[5-(2'-ethylhexyloxy)-2-methoxy-1,4-phenylene vinylene] (MEH-PPV). The polymer electrolyte consists of ion-solvating poly(ethylene oxide) (PEO) and a molecular salt, being either lithium trifluoromethanesulfonate (LiTf) or silver trifluoromethanesulfonate (AgTf). The cyclohexanone solution of MEH-PPV, mixed with the polymer electrolyte, was spin-cast onto a 15 mm × 15 mm sapphire substrate to form a polymer film of approximately 600 nm in thickness. The weight ratio of MEH-PPV/PEO/salt in the composite films is either 5:5:1 when LiTf is used, or 5:5:1.6 when AgTf is used. This ensures the same molar concentrations of salt (or ions when fully solvated) exist in the two types of polymer films. After drying at 50 °C for 12 h, 50 nm thick aluminum strips were deposited 2 mm apart on top of the polymer layer to serve as contact electrodes. All device fabrication procedures were carried out in a glove-box/evaporator system filled with dry nitrogen. The spectra were taken with an OceanOptics (HR2000) spectrometer inside the glove-box by illuminating the polymer films with a 4 W UV lamp. The spectra were not corrected for system response. Device current and light intensity were tested in an optical cryostat under a vacuum of 10^{-5} Torr (1 Torr ≈ 133.3 Pa). A Nikon digital camera (D100) was used to take images of the devices directly, without the use of a microscope.

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- [1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, A. B. Holmes, *Nature* **1990**, 347, 539.
- [2] D. Braun, A. J. Heeger, *Appl. Phys. Lett.* **1991**, 58, 1982.
- [3] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund, W. R. Salaneck, *Nature* **1999**, 397, 121.
- [4] A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem. Int. Ed.* **1998**, 37, 402.
- [5] Y. Cao, I. D. Parker, G. Yu, C. Zhang, A. J. Heeger, *Nature* **1999**, 397, 414.

- [6] I. D. Parker, *J. Appl. Phys.* **1994**, *75*, 1656.
- [7] Q. B. Pei, G. Yu, C. Zhang, Y. Yang, A. J. Heeger, *Science* **1995**, *269*, 1086.
- [8] Q. B. Pei, Y. Yang, G. Yu, C. Zhang, A. J. Heeger, *J. Am. Chem. Soc.* **1996**, *118*, 3922.
- [9] F. P. Wenzl, C. Suess, P. Pachler, A. Haase, E. J. W. List, P. Poelt, D. Somitsch, P. Knoll, U. Scherf, G. Leising, *Solid State Ionics* **2004**, *169*, 161.
- [10] J. Gao, J. Dane, *Appl. Phys. Lett.* **2004**, *84*, 2778.
- [11] J. Gao, J. Dane, *J. Appl. Phys.* **2005**, *98*, 063513.
- [12] T. Johansson, W. Mammo, M. R. Andersson, O. Inganäs, *Chem. Mat.* **1999**, *11*, 3133.
- [13] A. L. Holt, J. M. Leger, S. A. Carter, *J. Chem. Phys.* **2005**, *123*, 044704.
- [14] D. J. Dick, A. J. Heeger, Y. Yang, Q. B. Pei, *Adv. Mater.* **1996**, *8*, 985.
- [15] L. Edman, M. A. Summers, S. K. Buratto, A. J. Heeger, *Phys. Rev. B: Condens. Matter Mater. Phys.* **2004**, *70*, 115212.
- [16] J. Gao, J. Dane, *Appl. Phys. Lett.* **2003**, *83*, 3027.
- [17] L. Edman, J. H. Shin, S. Xiao, *Adv. Funct. Mater.* **2006**, *16*, 949.
- [18] B. Valeur, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, Weinheim, Germany **2002**.
- [19] J. A. Kemlo, T. M. Shepherd, *Chem. Phys. Lett.* **1977**, *47*, 158.
- [20] A. W. Varnes, E. L. Wehry, R. B. Dodson, *J. Am. Chem. Soc.* **1972**, *94*, 946.
- [21] D. B. Romero, M. Schaer, L. Zuppiroli, B. Cesar, B. Francois, *Appl. Phys. Lett.* **1995**, *67*, 1659.
- [22] H. Hoppe, N. S. Sariciftci, *J. Mater. Res.* **2004**, *19*, 1924.