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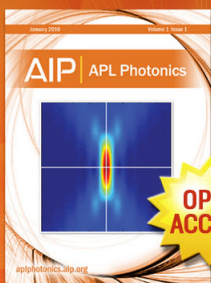
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Lithium fluoride injection layers can form quasi-Ohmic contacts for both holes and electrons

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Thin LiF interlayers are typically used in organic light-emitting diodes to enhance the electron injection. Here, we show that the effective work function of a contact with a LiF interlayer can be either raised or lowered depending on the history of the applied bias. Formation of quasi-Ohmic contacts for both electrons and holes is demonstrated by electroluminescence from symmetric LiF/polymer/LiF diodes in both bias polarities. The origin of the dynamic switching is charging of electrically induced Frenkel defects. The current density–electroluminescence–voltage characteristics can qualitatively be explained. The interpretation is corroborated by unipolar memristive switching and by bias dependent reflection measurements. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4896636>]

Organic electronic devices such as light-emitting diodes and solar cells require Ohmic contacts for their most efficient performance. Contacts of metals to organic semiconductors can often be improved by placing charge injection layers in between the semiconductor and the metal.¹ Ionic semiconductors can be used as such interfacial layers, e.g., MoO₃, V₂O₅, NiO, and CuI for hole injection^{2,3} and ZnO, Cs₂CO₃, or LiF for electron injection.⁴ LiF as electron injection layer has been studied in detail. Thin LiF interface layers lower the barrier for electron injection from Al into organic semiconductors due to a change in the effective work function of the LiF/Al contact.⁵ The mechanism by which this change in work function occurs is still under debate.^{6–10}

Here, we report that the modification of the barrier for injection of charge carriers by LiF layers is not just a static but also a *dynamic* phenomenon. The effective work function of the LiF/metal contact can either be raised or lowered depending on the applied bias voltage (“electrical conditioning”).¹¹ While thin LiF layers (≤ 2 nm) tend to give a static low workfunction contact suitable for electron injection,^{4–10} metal/LiF/organic semiconductor contacts with thicker LiF can switch from electron injecting to hole injecting and vice versa depending on the applied bias. This is demonstrated by electroluminescence (EL) under both positive and negative applied bias from poly(3-hexylthiophene) (P3HT) in metal/LiF/P3HT/LiF/metal diodes.

Efficient EL from organic diodes requires balanced injection of electrons and holes into the semiconductor. This property derives from the strong recombination regime for electrons and holes in the low dielectric organic semiconductor. EL from organic semiconductor diodes therefore

provides a highly sensitive tool to study minority carriers. In contrast, the current density reflects mainly the injection and transport of majority carriers.

We argue that depending on the charge state of defects inside the LiF layer, LiF acts either as electron or hole injection contact. Alternation of the ionization state of the defects under influence of applied bias, results in a switch of the type of charge carrier that is injected/collected by a LiF/organic semiconductor contact. We find that the various charge states of the defects are metastable under short-circuit conditions and give rise to nonvolatile memory effects.

All diodes were fabricated onto glass substrates with patterned ITO. ITO substrates were cleaned, using in order, acetone, soap scrubbing, and isopropanol. LiF (Sigma Aldrich, 99.9%) was deposited by vacuum sublimation from an alumina crucible under 10^{-6} mbar. MoO₃ was sublimed under vacuum from a baffled Mo boat under 10^{-6} mbar. ZnO layers were prepared by spin coating a sol-gel solution of zinc acetate dihydrate in methoxyethanol/ethanolamine and subsequent thermal annealing of the films at 150 °C.¹² Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) was provided by Heraeus under the reference Clevios P VP Al4083, filtered and spin cast at 3000 rpm to form layers of 40 nm. P3HT (>98% head to tail, $M_n = 54\,000$ to $75\,000$ g mol⁻¹, Plextronics, purchased from Aldrich) was dissolved in *o*-dichlorobenzene with a concentration of 15 mg/ml and cast at 800 rpm. Poly(spirofluorene) (PF) (Merck, SPB-02T) was dissolved in toluene at a concentration of 10 mg/ml and spin coated at a speed of 3500 rpm. Poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV) was obtained from American dye source, dissolved in chlorobenzene (5 mg/ml) and spin cast at 600 rpm. Ba and Al top metal contacts were sublimed under 10^{-6} mbar. The diodes with LiF bottom layers were prepared under inert atmosphere. Diodes

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were kept and characterized in N_2 atmosphere (O_2 , $H_2O < 1$ ppm).

Current density–electroluminescence intensity–voltage (J - EL - V) characteristics were obtained using an Agilent 4155C semiconductor parameter analyzer together with a Si-photodiode. A Keithley 2601 source-measure unit was used for pulse measurements. Current density voltage J - V sweeps were recorded with 50 mV step and 40 ms integration time. Positive bias is defined as the bottom ITO contact being charged positive. Reflection experiments were performed using a Perkin Elmer Lambda 900 UV-Vis-NIR absorbance spectrometer with a module for specular reflection measurements.

Figs. 1(a) and 1(b) show the EL intensity from an ITO/LiF (5 nm)/P3HT/LiF (5 nm)/Al diode as function of bias voltage. Both positive and negative bias voltages induce EL. Curves shown are obtained after electrical conditioning. During conditioning, the bias voltage is swept repeatedly over either the negative or positive bias voltage range (see supplementary material). This leads to an increase in the EL intensity for the particular voltage polarity chosen.¹³

Scanning the bias voltage from -14 to 0 V after conditioning (Fig. 1(a)), we note that the EL turns off around -4 V. Scanning from $+10$ to 0 V, the EL turnoff is at $+2$ V. These voltages are close to the bandgap of the polymer (1.9 eV), implying low barriers for charge injection. The observation of EL under both positive and negative polarity implies that from either LiF contact, both electrons and holes can be injected, depending on the bias applied to the diode.

The current densities under positive and negative bias voltage are almost similar, consistent with the symmetric structure of the LiF/polymer/LiF stack. The electron injecting property of LiF (top) interface layers is well documented; only few reports on hole injection via LiF are available.^{14–16} To gauge the efficiency of hole injection by the LiF interlayer, we compare the current densities and EL intensities of

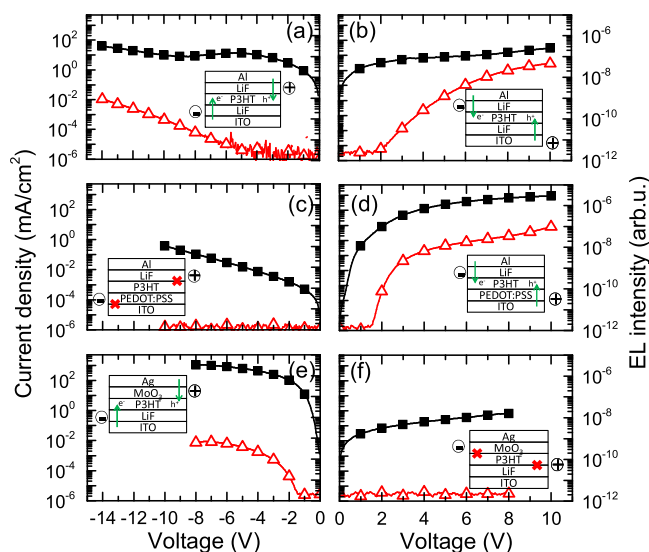


FIG. 1. Current density–electroluminescence–voltage (J - EL - V) characteristics of ((a) and (b)) ITO/LiF (5 nm)/P3HT (70 nm)/LiF (5 nm)/Al after electrical conditioning, scan directions -14 V \rightarrow 0 V or $+10$ V \rightarrow 0 V. ((c) and (d)) ITO/LiF (5 nm)/P3HT (70 nm)/LiF (5 nm)/Al. ((e) and (f)) ITO/LiF (5 nm)/P3HT (70 nm)/MoO₃ (10 nm)/Ag. Filled black squares ($-\blacksquare-$): J . Open red triangles ($-\Delta-$): EL .

the LiF/P3HT/LiF stacks with the performance of diodes with known hole injecting contacts, PEDOT:PSS (Figs. 1(c) and 1(d)) and MoO₃ (Figs. 1(e) and 1(f)). LiF/P3HT/LiF diodes reach EL efficiencies comparable to diodes with conventional electrode layout ITO/PEDOT:PSS/P3HT/LiF/Al and ITO/LiF/P3HT/MO₃/Al indicating that the two LiF interfacial layers behave as selective contacts for holes and electrons.¹¹

We note that at low bias ($|V| < 2$ V), current densities through the LiF/P3HT/LiF diode are high. The conduction at low voltage is quasi-Ohmic for both voltage polarities. The current densities do not show any indication for a built-in voltage. We conclude that at low voltage, both LiF layers form quasi-Ohmic contacts for the majority carrier.

The nature of the majority carrier can be determined by comparing with P3HT diodes featuring selective electrical contacts (Fig. 2). The current densities in the LiF/P3HT/LiF diode at low voltage is more than six orders of magnitude larger than for a diode with contacts supporting only electron current (ITO/ZnO/P3HT/Ba/Al diode, see Fig. 2) but only two orders of magnitude lower than for a diode with contacts appropriate for only hole current, ITO/PEDOT:PSS/P3HT/MoO₃/Ag diodes (Fig. 2). Thus, the majority carriers are holes, consistent with known charge transport properties of P3HT.¹⁷ Furthermore, at low bias, both LiF layers in the LiF/P3HT/LiF diode layout are selective for holes. Combined with the observation of efficient EL at high bias, it follows that one of the LiF layers in the LiF/P3HT/LiF stack switches from a hole collecting to an electron injecting contact in the voltage range from -2 V to -4 V. The switching and the nature of the charge injection by the LiF interface layers are summarized in Fig. 3.

We note that the selectivity of the LiF injection layers in the electroluminescent state can be retained if the bias voltage is lowered rapidly to zero. This is illustrated in Fig. 4, which

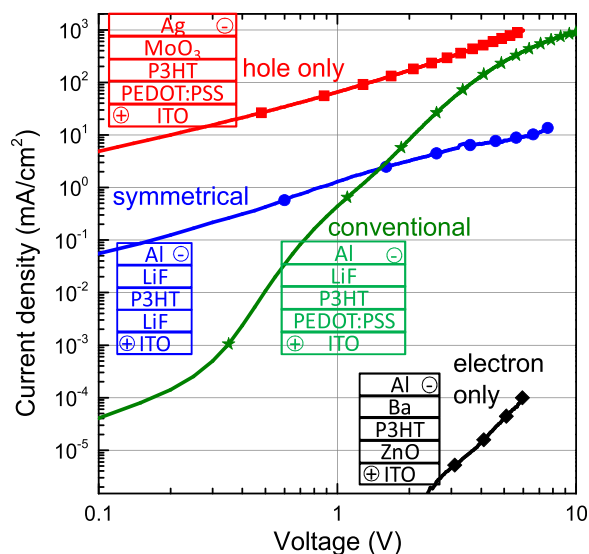


FIG. 2. J - V characteristics for P3HT diodes with different electrode configurations supporting hole-only current (ITO/PEDOT:PSS/P3HT(70 nm)/MoO₃(10 nm)/Ag, red squares), bipolar current: (ITO/LiF(5 nm)/P3HT(70 nm)/LiF(5 nm)/Al, blue circles), bipolar current (ITO/PEDOT:PSS/P3HT(70 nm)/LiF(5 nm)/Al, green stars) and electron-only current (ITO/ZnO (30 nm)/P3HT(70 nm)/Ba/Al, black diamonds).

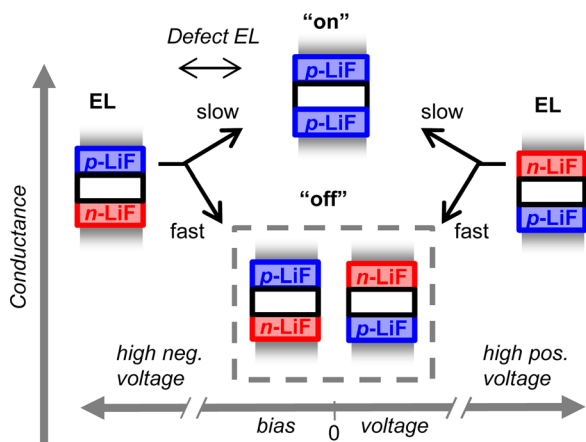


FIG. 3. Selectivity of the LiF interface layers in ITO/LiF/P3HT/LiF/Al diodes. *p*-LiF denotes selectivity for positive charge carriers, *n*-LiF for negative carriers. The electroluminescence at high bias implies the presence of a *p*-type and *n*-type contact. A high conduction at low bias implies two quasi-Ohmic *p*-type contacts forming an “on” state. LiF layers of opposite type give rise to a low conductivity, “off” state.

shows two *J-V* characteristics recorded by sweeping the voltage for 0 V to -14 V. The black curve ($-\blacksquare-$) is obtained by preparing the diode first in the EL state at -14 V and then slowly lowering the applied bias before starting the sweep illustrated in Fig. 4. In contrast, the red trace was recorded by putting the diode first in the EL state at -14 V, followed by immediate removal of the applied bias voltage before starting the sweep shown. The red trace shows a much lower current density at low bias, indicating that one of the contacts is blocking the majority carriers. At around 4 V, the bias voltage exceeds the built-in potential of the *p*-LiF/P3HT/*n*-LiF diode and the current density and EL intensity rise rapidly with

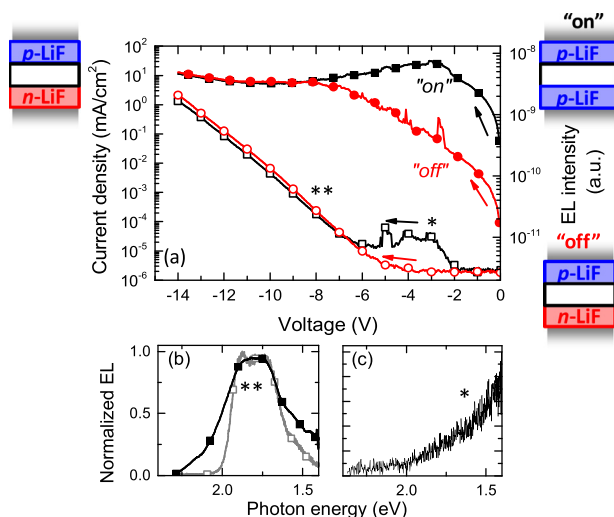


FIG. 4. (a) *J-EL-V* characteristics of an ITO/LiF(5 nm)/P3HT/LiF(5 nm)/Al diode. Current density *J* ($-\blacksquare-$) and electroluminescence intensity *EL* ($-\square-$) directly after a -14 V \rightarrow 0 V sweep, i.e., programmed in the high conduction state with the top LiF contact set to hole collection. *J* ($-\bullet-$) and *EL* ($-\circ-$) for the same diode after a 0 V \rightarrow -14 V sweep followed by immediate lowering of the bias voltage to 0 V, i.e., programmed in the low conduction state with the top LiF contact set to electron injection. (b) Normalized EL spectra of a ITO/LiF(5 nm)/P3HT/LiF(5 nm)/Al diode at -8 V (closed symbol) and of a ITO/PEDOT:PSS/P3HT/LiF(5 nm)/Al at $+4$ V (open symbol). (c) Normalized EL spectra of a ITO/LiF(5 nm)/P3HT/LiF(5 nm)/Al diode at -3 V.

increasing bias. Below -4 V, the current density and EL starting from the “off” state coincide with current and intensity measured starting in the “on” state. By resolving the EL at -8 V spectrally, it can be proven that the EL originates from excitons in the polymeric semiconductor (Fig. 4(b)). Curiously, when starting in the “on” state, we notice irregular electroluminescence in the voltage range -2 – -4 V. Spectral measurements show that this erratic emission is due to defects featuring a broad emission band with maximum below 1.5 eV (Fig. 4(c)). Because the defect emission is not observed in the “off” state, we argue that it is associated with the switch of one of the LiF layers from *p*-type to the *n*-type charge injection configuration. Measurements of the conductivity of the diode applying alternating voltage pulses of 4 and 8 V to put the diode in, respectively, the “on” and “off” states confirm the nonvolatile memory effect^{18,19} (see supplementary material).

Schlaf *et al.*⁷ have suggested that the change in effective work function of a metal covered with a LiF interface layer results from charged Frenkel defects in the LiF. Here, we follow this suggestion and argue that the dynamic changes in effective work function of the metal/LiF contact leading to the switching between electron and hole selective contacts is due to changes in the ionization state of the Frenkel defects.

Defects in alkali halides can form when an exciton becomes self-trapped and subsequently dissociated into a Frenkel defect pair consisting of an anion vacancy and a halide interstitial. Defect formation can be induced by direct optical excitation of electrons across the bandgap.^{20–24} Here, we propose that recombination of holes and electrons in the alkali halide, injected under high bias conditions, may also lead to formation of defects. Ionization of the defects in the LiF²⁵ can dramatically lower the barrier for charge carrier injection resulting in efficient EL.

Direct experimental evidence for voltage induced defect formation can be obtained from spectrally resolved measurements of the reflection of light by ITO/LiF/organic semiconductor/Ba/Al diodes (Fig. 5). The wide bandgap organic semiconductor poly(spirofluorene) allows a large spectra window for measurement of absorption by voltage induced defects. LiF/poly(spirofluorene)/LiF and LiF/poly(*para*-phenylene vinylene)/LiF diodes also show efficient EL after electrical conditioning.¹¹

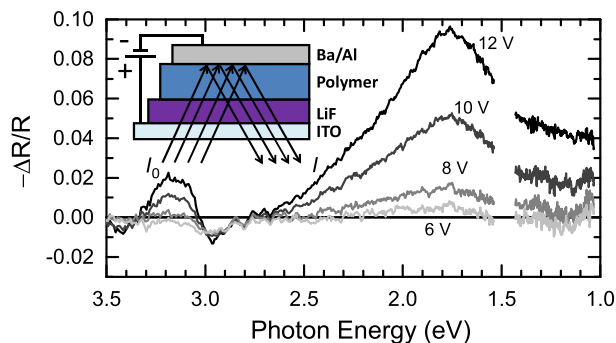


FIG. 5. Relative change in reflectance $-\Delta R/R$ of an ITO/LiF(100 nm) poly(spirofluorene)/Ba/Al diode induced by bias voltage *V* for 6 to 12 V. The inset shows the diode structure with specular reflection traces onto the Ba/Al electrode. Spectral reflection occurring at other interfaces is omitted for clarity.

By plotting the relative, voltage-induced change in the intensity of light reflected by the back Ba/Al reflecting contact ($-\Delta R/R$) we find a broad voltage induced absorption band with maximum around 1.7 eV. The absence of significant bleaching of the absorption band due to the neutral polymer at 3 eV in the ($-\Delta R/R$) spectrum indicates that the voltage-induced absorption at 1.7 eV is probably not due to charge carriers in the polymer.¹³ We tentatively assign it therefore to defects in the alkali halide. Defect formation requires voltages exceeding 6 V.

In conclusion, we have shown that LiF interface layers in between metal and organic semiconductor can form quasi-Ohmic contacts for both holes and electrons, depending on the voltage history of the diode. The occurrence of electroluminescence from defects during the switching of a LiF layer from the hole to electron injecting configuration, provides direct evidence for charge recombination at the defect during switching and indicates that the ionization state of the defects is crucial in determining the selectivity of the LiF charge injection layers.

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¹³See supplemental material at <http://dx.doi.org/10.1063/1.4896636> for electrical conditioning, electroluminescence efficiency of LiF/P3HT/LiF diodes, electronic memory effects, and J - EL - V characteristics for LiF/P3HT/LiF diodes with different LiF thickness and for LiF/MDMO-PPV/LiF and LiF/PF/LiF diodes.

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