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Monolithically integrated organic resistive switches for luminance and emission color manipulation in polymer light emitting diodes

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The rising significance of organic light emitting diodes as lighting devices puts their peripheral devices into focus as well. Here, we present an organic optoelectronic device allowing for multistable luminance and emission color control. The introduced device is monolithically built up from organic resistive switching elements processed directly on top of a polymer light emitting diode (PLED). This realization, representing a serial connection, allows for precise control of the voltage drop across and thus the current density through the PLED resulting in a control of its luminance. Additionally, by using a fluorescence-phosphorescence host-guest blend as the light emitting layer, it is possible to tune the emission color in the same way. Specifically, focus was set on color temperature tuning in a white light emitting diode. Notable, for all different luminance and color states, the driving voltage is constant, enabling, e.g., a conventional battery as power supply. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4932112>]

To date, organic light emitting diodes^{1,2} (OLEDs) are without a doubt the most progressed topic in the field of organic electronics. Various applications in displays³ and lighting⁴ have been presented. However, independent of the actual application, additional peripheral electronic devices are required for addressing or controlling the luminance, the color temperature, or the switching behaviour of the OLED. Despite the rapid development of organic based transistor materials, full performance and a high dynamic range of OLEDs are only reached using selector/controlling devices (one or more transistors⁵) using polycrystalline or amorphous Si-backpanel technologies. As a consequence of the high processing temperatures of polycrystalline or amorphous Si-backpanel technologies, this certainly limits the impact of the claimed advantages of the use of π -conjugated materials with low temperature processable low cost flexible polymeric substrates.

Various different attempts were made to use memory devices not only in the sense of information storage but also as a switch to control light emission. Ferroelectric switches were employed to drive OLED devices as a passive matrix array.⁶ Also resistive switches, similar to those described here, had been used; however, the result was mostly reduced to a basic ON/OFF switching of the OLED.^{7–11} Similar attempts have also been demonstrated for inorganic systems.¹² In each of these cases, tuning of luminance (i.e., the light intensity) was only possible by changing the driving bias. Recently, it was demonstrated that resistive switches can as well be used as image information storage elements in flexible image detector arrays.¹³

Here, we present a unique optoelectronic device consisting of organic resistive switches monolithically integrated into an OLED capable of manipulating luminance or

electroluminescence emission color of an OLED. This device is fabricated in one continuous process flow combining a solution processed polymer light emitting diode (PLED) with several organic resistive switches (ORS) processed directly on top of it. The ORS are used as switches to control the voltage drop across and thus the current through the PLED. By selectively switching one or more ORS into different resistive states, the emission properties—luminance or emission color—of the PLED can be tuned at *constant* operation voltage. This fact enables for a simple circuitry and for driving the whole device with a constant voltage source, e.g., a conventional battery without having the need for any peripheral electronics.

Resistive switches and memristive devices attracted large attention throughout the past decade.^{14–17} Inorganic memristive devices are held to be capable of revolutionizing the memory market and have attracted attention from academic and industrial research alike. Resistive switching was also observed from organic devices enabling for the often claimed advantages of organic electronics, e.g., mechanical flexibility of the devices or economically and ecologically viable processing using tools like inkjet printing. ORS show remarkable properties as a high ON/OFF ratio, several years of data retention, multi-bit operation, CMOS compatible low voltage operation, inkjet-printability etc.^{18–21} In contrast to transistors, ORS are two-terminal devices, thus reducing the wiring efforts and offering a great advantage in terms of integration density reducing the area-footprint down to $4F^2$ (with F , minimum feature size). There is still an ongoing vital academic discussion about the actual switching mechanism. Different mechanisms have been suggested, including charging and discharging of metallic nanoparticles either deliberately or accidentally introduced into a matrix material,²² donor-acceptor charge transfer systems²³ or molecular conformation changes.²⁴ However, recent works strongly evidence that the unipolar switching employed here can be

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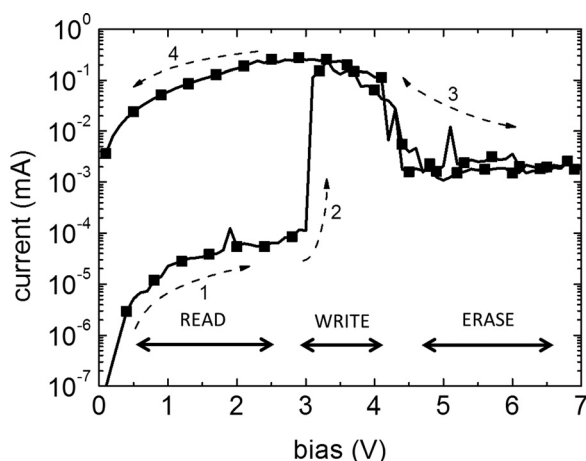


FIG. 1. Typical IV-curve of an Ag/Alq3/Ag organic resistive switching device. Two resistance states are found at low voltages (<3 V) representing the read-out region. In the beginning of a typical sweep, the device in its LRS (1). A strong current threshold occurs at around 3 V, where the device switches from its HRS to its LRS (2). For a bias larger than 3 V, a region of negative differential resistance is found (3). A voltage at the end of the NDR leads to a reset of the resistance state to the initial HRS. If swept back from 7 V to 0 V, the device remains in its LRS (4).

ascribed to the formation and rupture of conductive pathways (filaments) through the organics established after a forming procedure.^{25,26} Although there is significant progress in the topic of organic resistive switching, a sophisticated understanding of the mechanisms of formation is still missing making an engineering of the properties of the device challenging.

For the application presented here, a simple but reliable and well characterized device based on Aluminiumtris(8-hydroxyquinolin) (Alq3) was chosen. The current-voltage (IV)-curve of this Ag/Alq3/Ag device is shown in Figure 1: Initially, this device is in its high resistance state (HRS, several 100 M Ω). A sharp current threshold is found at a typical bias of around 3 V, where the device switches from its HRS to its low resistance state (LRS, several 1–10 k Ω). It has been found that the magnitude of the LRS is largely independent of the device area, allowing for downscaling of such devices to the nanoscale.²⁷ However, certain spreading in the measured LRS current can be observed which is ascribed to a rather random formation and size of the current carrying filament. Retention times >1 year have been experimentally shown for both states in this type of device. For a voltage larger than the current threshold voltage, the device shows a rather unconventional behavior. The IV-curve exhibits a pronounced region of negative differential resistance (NDR). The device resistance can be set back to the initial HRS by

applying a voltage at the end of this NDR. Certainly, no full IV-curve has to be recorded to switch the device: After identifying the two bias levels for switching the ORS, short pulses of these values are sufficient to change the resistive state.²⁸ The state of the ORS can be read-out by measuring the resistance in the bistable region (e.g., at 0.5 V–1.5 V). The ratio between the LRS and HRS and is denoted as ON/OFF ratio and is found to be around 4 orders of magnitude for this specific device.

A highly efficient blue light emitting multilayer PLED, employing a poly(indenofluorene) based hole transport layer (HIL) and a light emitting co-polymer (LEP) with efficiencies of up to 9.7 cd/A and a luminance of up to 20 000 cd/A, was chosen and fabricated as reported elsewhere.²⁹ Its characteristics and electroluminescence spectrum can be found in the supplementary material.²⁸ IV-characterization was performed after contacting the device with tungsten tips using an Agilent B1500A Parameter Analyzer. The luminescence-voltage measurements were performed using a silicon photodiode and a computer-controlled Keithley 2612 source measurement unit. Spectral characterization was done with a LOT-ORIEL Multispec equipped with a DB 401-UV CCD camera from Andor. The characterization was performed in an argon filled glovebox (<1 ppm O₂ and <1 ppm H₂O).

Eight ORS devices, each with an individual cathode contact, were processed on top of the cathode of the PLED resulting in a ITO/PEDOT:PSS/HIL/LEP/Ca/Al/Ag/Alq3/Ag stack. Alq3 was purchased from Sigma-Aldrich and used without further purification. The material was thermally evaporated in a vacuum coating unit at a base pressure lower than 10^{-6} mbar. The silver electrodes were deposited immediately afterwards without breaking the vacuum.

The luminance of such a stack can be increased straightforwardly by switching the ORS cell-by-cell to their LRS resulting in an increase of the voltage drop across the PLED. Thus, the more ORS are in their LRS, the higher the current delivered to the PLED and the higher the obtainable luminance. This is done by selectively applying the write voltage (current threshold voltage) to a single element as indicated in Figure 2(a). Accordingly, the luminance can be decreased by switching the individual ORS back to the HRS by applying the delete voltage. After writing the desired pattern of low and high resistance states to the ORS, the whole device stack is operated at 5.5 V (Figure 2(b)).

This procedure results in a stepwise tuning of the luminance from 0 cd/m² up to 450 cd/m², back to 0 cd/m² and up again (Figure 3(a)). Importantly, the driving bias of 5.5 V of the whole device stack is not changed throughout the whole

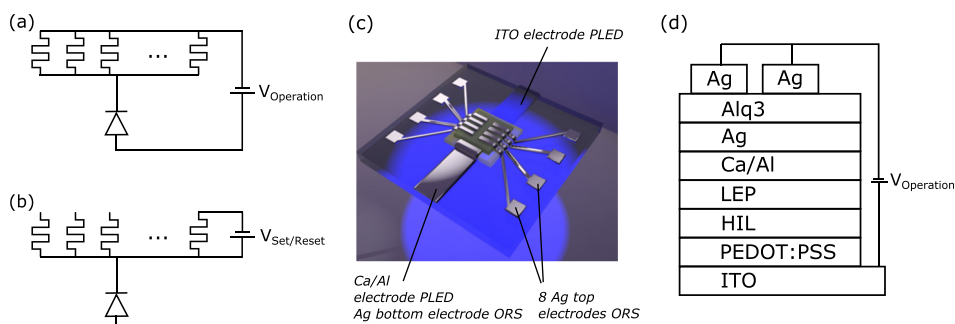


FIG. 2. Illustration and operation principle of the introduced device stack. (a) To manipulate the resistance state of an individual ORS, it is connected to the voltage supply. All other terminals are floating. (b) For the operation of the PLED, the operation voltage is applied to the whole stack. (c) 3D-sketch of the device and (d) sketch of the cross-section through the device.

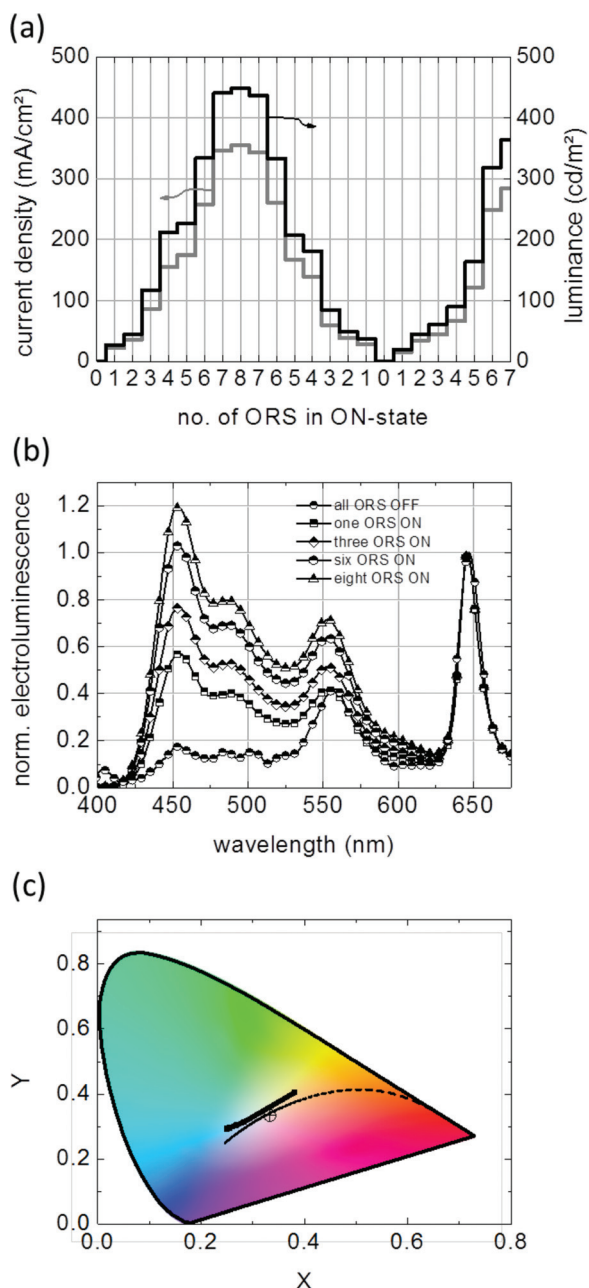


FIG. 3. Demonstration of luminance and emission color tuning of the introduced device. (a) Tuning of the luminance by selectively switching one or more individual ORS to their LRS. If all ORS are in their HRS, no light emission is observed. For eight ORS in their LRS, the maximum luminance of around 450 cd/m² is found. The operation voltage was kept constant at 5.5 V. (b) Emission color tuning of an ITO/PEDOT:PSS/PIF:MEH-PPV:PtOEP/Ca/Al device controlled by the resistive state of the ORS. If all ORS are in the HRS, strong red emission, stemming from the PtOEP dopant is found. For eight ORS in their LRS, a balanced emission between blue and red is found. (c) CIE-graph with indicated trace of the color change reported in (b) (thick line). The coordinates are close to the Planckian locus and the white point (CIE $x = 0.33$; $y = 0.33$).

sweep. It is observed that not all of the individual ORS devices contribute equal currents, which is ascribed to the aforementioned spreading of the ORS LRS most likely related to the dimensions of the filament. This distinct device-to-device variation may be addressed by a more rigorous device engineering effort to overcome this unwanted side-effect.

The obtained maximum luminance of 450 cd/m² can be further increased by using an even more efficient PLED stack

or by simply increasing the number of ORS processed on top, as compared to the proof-of-principle device presented here. Increasing the number of ORS also leads to a more homogeneous distribution of current (the dispersion of the low resistive state current through the ORS cancels out) and a more continuous functionality as compared to Figure 3(a).

The same functional principle can also be used to tune the emission color of a PLED. Here, the focus was set on tuning the color temperature of white-light emitting diodes, yet the underlying idea can also be used for bistable color emitting devices.

A commonly applied concept to achieve white light is to blend two or more different luminophores into one emissive layer^{30,31} (either as multi-component blends or as copolymer with different on-chain emitters³²) utilizing excitation energy transfer between the luminophores and charge carrier trapping to attain white light by additive color mixing. For this study, a single layer white light emitting diode using a blue emitting poly(indenofluorene) at a concentration of 4 mg/ml, a red/orange emitter poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) (0.5 wt. %), and phosphorescent platinum octaethylporphyrin (PtOEP) (0.4 wt. %) was blended and prepared into a device.³³ Unlike in other blend systems, the used configuration exhibits significant bias dependent emission spectra, which usually undesired, can be exploited for exact color temperature tuning in the white light emitting diode in the vicinity of the white point. The voltage dependent emission spectrum is caused by the saturation of the dopant at higher current densities^{33–35} due to the strong imbalance of excited state lifetimes between fluorescent (\sim ns) and phosphorescent (\sim μ s-ms) materials.

The PIF:MEH-PPV blend doped with PtOEP³⁶ was processed in an monolithic device stack: ITO/PEDOT:PSS/PIF:MEH-PPV:PtOEP/Ca/Al/Ag/Alq3/Ag. If all ORS are switched to their HRS, strong red emission is found with slight contributions from the blue region (Figure 3(b)). By gradually increasing the number of ORS in their LRS, the blue spectral components start to emerge due to the increasing excitation of the fluorescent components. Also here, the driving voltage of the stack was constant at any time of the experiment at 5.5 V. This process ends up with a balanced emission (CIE $x = 0.25$; $y = 0.29$) between red and blue when each ORS is in its LRS. The corresponding CIE 1931 coordinates are indicated in Figure 3(c). The emission spectra were found to be close to the Planckian locus. Also, the luminance changes with changing emission color similar to the data presented in Figure 3(a). This implies that for the more reddish emission (warm white light, colortemperature \sim 4000 K), a low luminance is found. For bluish emission (cold white light, colortemperature \sim 12 000 K similar to a clear blue sky), a high luminance is obtained.

Such special emission characteristics matches with the daylight cycle where also a low luminance and warm white light is observed during the morning and evening hours, and a high luminance and cold white light at midday. Apparently, such low cost lighting devices may be applied in buildings and areas where daylight is not accessible as subways or airports.

In conclusion, we have presented a monolithically fabricated optoelectronic device allowing for multi-stable

luminance or emission color control. The serial connection of several parallel ORS with a PLED device enables for precise control of the voltage drop across—and thus of the current through—the PLED at a constant overall operation voltage. As more ORS are switched to their low resistance state, the voltage drop across the PLED increases leading to higher luminance. If the light generating layers were to be changed from a monochromatic emitter to a fluorescent—phosphorescent host—guest system, the same principle could be used to additionally tune the emission color of the device. Notably, the driving voltage of the device stack is not changed during operation. With the stacked buildup, the footprint of the PLED is not significantly altered.

Future development will focus on the implementation of the presented single devices into crossbar matrix structures, e.g., for structured lighting panels. For proper addressing of single elements in a matrix, an additional selector element is required. This selector device can be an (organic) rectifier for ORS.^{37–39} The appealing point on the approach presented here is that the OLED can possibly be used as a rectifying element, similar to that presented in Ref. 13 as it also exhibits a strong nonlinearity in its IV characteristics.

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