OLLA Project Report

White pin-OLED with improved polymer injection layer and efficiency above 10 lm/W

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Executive summary

In this deliverable, a new polymeric anode made from PEDOT:PSS is used to demonstrate a white OLED with a power efficiency of 10 lm/W, based on an anode layout free of TCO (transparent conducting oxide). Starting from a previous (non-public) deliverable a further development had to be carried out to reach a significant increase in device efficiency.

To reach this, we used a three colour white OLED stack developed in WP2, which had to be adapted to the special needs of a polymeric anode. This three colour approach is based on a phosphorescent green emission layer (EML) consisting of TCTA:Ir(ppy)$_3$, a red emission layer from NPD:ADS_RE76, and a fluorescent blue EML of Spiro-DPVBi.

To avoid a nonradiative decay of triplet excitons in the blue EML by nonradiative transitions from triplet excitons, an exciton blocking layer consisting of TCTA:TPBi was implemented between fluorescent and phosphorescent EML. To achieve the value of 10 lm/W, the thickness of the emission layer as well as the doping concentrations were designed to achieve CIE coordinates near to the so-called colour point “A”, the warm white point at (0.45/ 0.41). Using an anode of Baytron PH 500 + 5 % DMSO we demonstrate a white OLED with a power performance of 10 lm/W at CIE co-ordinates of (0.44/0.38).

This three colour OLED stack requires high stability and reproducibility of the OLED evaporation tool. Due to the very thin exciton blocking layer this is a challenging aspect of this approach in view of going to larger scale lighting areas. Further on, the impact of the PEDOT-OLED interface will be discussed briefly in terms of sample preparation and loss mechanisms of the complete device.

1 Technical Summary

In the first part of deliverable 4.3a in month 12 a, we demonstrated a first white small-molecule OLED using in-situ PEDOT as an anode. Due to the high particle content of in-situ PEDOT and thus a rather rough anode surface, this device was facing high leakage currents, resulting in a lower power efficiency as compared to similar devices on ITO anodes. To circumvent this issue and to increase the device performance, a new formulation of PEDOT:PSS - so-called Baytron PH 500 + 5 % DMSO - from HC-Starck was used to reach this deliverable. This new PEDOT shows a conductivity of 500 S/cm and a lower surface roughness due to the small particle size of the dispersion. Further, a new approach of HC-Starck for structuring the cathode side of the spin-coated sample was introduced. This leads to significantly lower leakage currents. These shunts could be decreased at least by an order of magnitude. Now, for the cathode side dip coating is used to prepare an isolating area such that the anode (PEDOT:PSS) and the cathode (Al) can’t be shortened by cathode deposition.

The three colour white consists of red (NPD:ADS_RE76), blue (Spiro-DPVBI) and green (TCTA:Ir(ppy)$_3$) emission layers. Due to the fact that the green and the red dopants are phosphorescent emitters and the blue one is fluorescent, a separating layer was inserted in between to prevent from exciton quenching by nonradiative transitions via the triplet states of the blue emitter. By controlling the doping concentration of the green and red emitters, as well as the thickness of the individual emission layers, the emission spectra of the OLED could be modified. The intermediate layer consists of co-evaporated TCTA and TPBI. Whereas TCTA is a more hole conductive material, TPBI is preferentially electron conducting. The ratio of both materials was chosen to 2:1 for TCTA: TPBI to provide a separating layer with mobility for both electrons and holes. Further on, the impact of layer thickness variations for the red, blue and green EML shows a very sensitive dependence of the spectra especially if the green EML is varied. Due to the fact that both the green EML and the separation layer are very thin, the spectra are very sensitive to small variations of both.

Additionally, it turns out that the PEDOT - small molecule interface is a critical aspect for understanding and controlling the performance of such OLEDs. Better OLED performance and increased lifetimes should be reached by decreasing possible loss paths at this interface.

2 Introduction

2.1 White – OLED stack

In Figure 1 we show the OLED stack for the device discussed in this Deliverable, achieving a power efficiency of 10 lm/W. On top of a glass substrate, a polymeric anode is deposited, followed by a small molecule white OLED stack and metal cathode.

Baytron PH 500 + 5% DMSO

MeO-TPD:F4-TCNQ

SpiroTAD

NPD:RE76

TCTA:Ir(ppy)$_3$

TCTA:TPBI

Spiro-DPVBI

TPBI

BPhen:Cs

Al

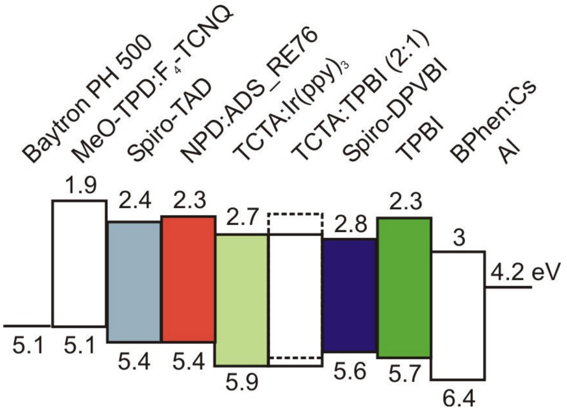


Figure 1: *Small molecule stack of a white OLED based on a polymeric anode, the HOMO / LUMO energy levels of the materials in this stack are shown at the right side.*

IAPP reached a high efficacy at warm white colour co-ordinates using a quite similar OLED stack on top of the well-established ITO anode. However, due to different optical properties of the polymer anode the stack had to be modified in view of layer thickness. As the outcome of micro-optical calculations revealed, the polymeric anode calls for a thicker p-MeO-TPD layer due to other optical properties than ITO. The p-MeO-TPD layer was chosen to be optimised for highest emission efficiency of the blue luminescence due to the fact that the blue emission has the lowest efficiency of the three emission colours. Further on, the Spiro-DPVBi, TCTA:Ir(ppy)3 and TCTA:TPBi layers were varied to come close to the warm white point. The following picture shows the operating white OLED.

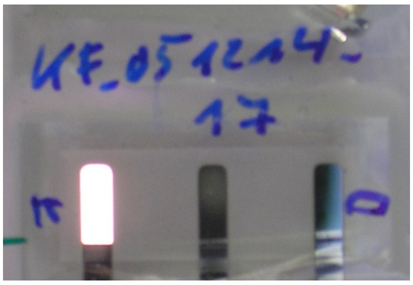


Figure 2: *The photo shows the WOLED at 5 V with CIE coordinates of (0.44/ 0.38).*

In Figure 3, an overview is presented that shows the change of the electroluminescence spectra upon variation of the layer thickness of the green, red or blue emission layers. The strongest change in the device spectra is observed upon changes in the thickness of the green emission layer (Figure 3A and B). There, already slight changes in the green EML thickness can result in a very intense green emission (B). In contrast, the influence of the red (C) and blue (D) emission layer variations is significantly less pronounced and results in minor spectral changes only.

The spectrum of the white OLED sample with CIE (0.44/ 0.38) is presented in graph E (Figure 3).

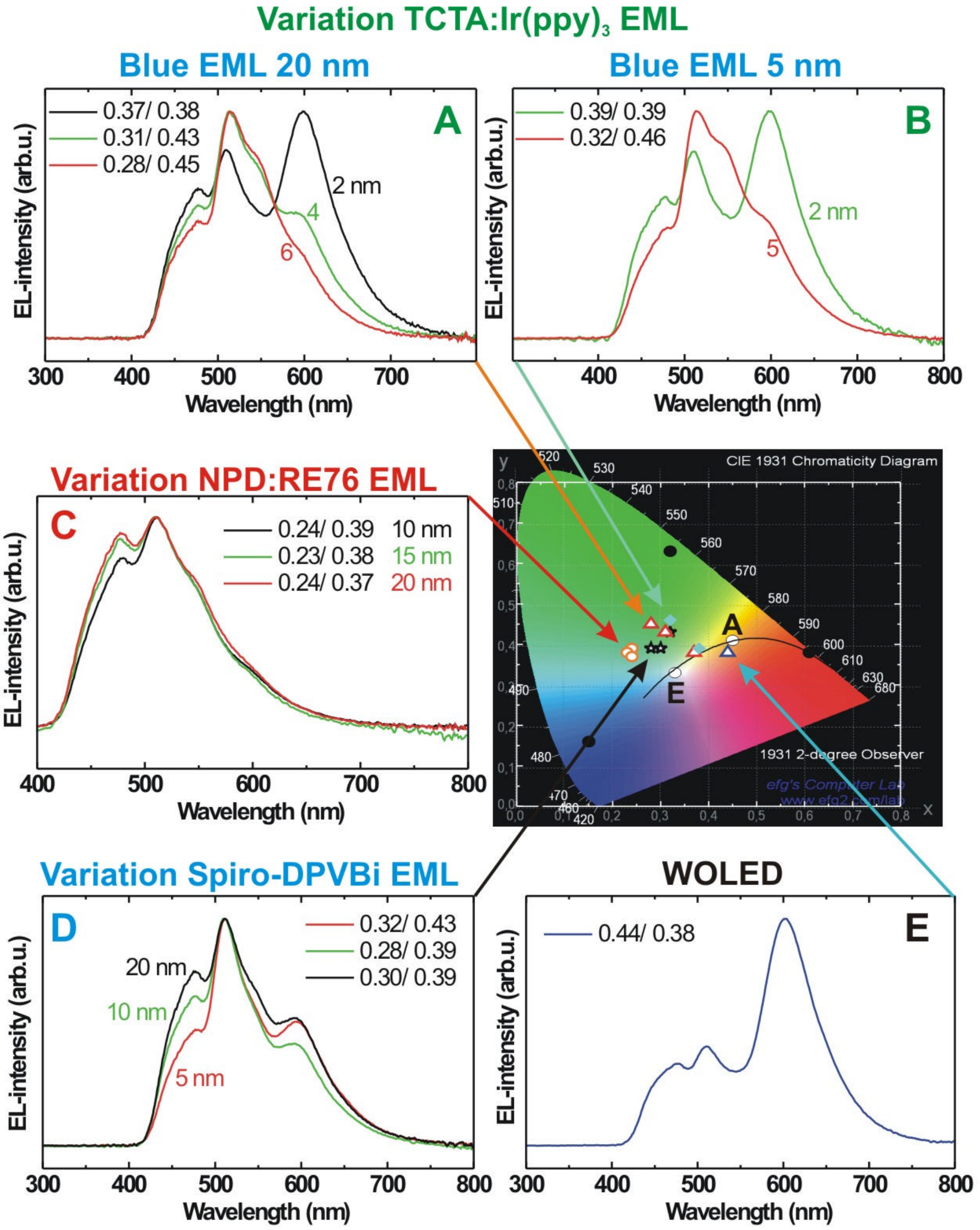


Figure 3: *EL-spectra of different samples upon variation of EML thickness. In all cases, the contribution of one colour was varied, while all other layer thicknesses remained constant. Further, the CIE co-ordinates of all samples and their position in the CIE plot are shown. The black dots in the CIE graph represent the single colour red, green, and blue OLEDs. Additionally, the white points A and E are plotted within the CIE graph.*

The overview of the spectral change in dependence of EML thickness as shown in Figure 3 reveals that it is of eminent importance to control the exact layer thickness and doping concentration. This is a challenging aspect for every OLED deposition tool. While the blue and red emission layers are 20 nm thick and thus well-controllable, making layers of 2 – 3 nm thickness for green EML are quite challenging, especially since the final emission colour depends strongly just on this colour. This resulted in the need of test samples for this 3 EML white system. By knowing the influence of all these layers on the resulting white OLED spectrum the system may be further optimised to reach the desired CIE points even closer.

If one neglects the (mainly technical) aspect of aligning the spectra of the OLED stack, a second fact becomes important: The loss mechanisms in the PEDOT:PSS-OLED interface are not yet understood and can lead to inefficient devices. The following Figure 4 demonstrates quite drastically what can happen to such OLEDs, even when evaporated onto the same substrate.

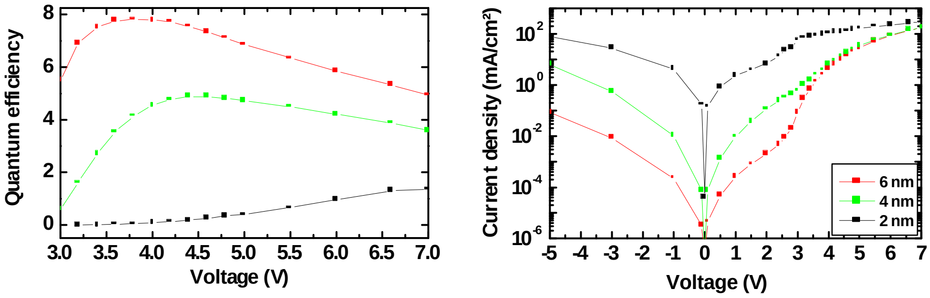


Figure 4: *As to be seen in the backward current direction, the current density shows leakage currents differing by 3 orders of magnitude for these three OLEDs, which were made on the same substrate. Consequently, the quantum efficiency decreased strongly for samples with the higher leakage currents. These plots correspond to the samples shown in figure 2.1.3 (A), where the TCTA:Ir(ppy)3 layer has been varied.*

In the sample discussed above (see Figure 3A and Figure 4), the green EML thickness was varied. The resulting efficiency decrease to thinner green EML cannot only be attributed to this fact. The performance of the 2 nm TCTA:Ir(ppy)$_3$ sample (with red and blue EML) is worse than a single blue emission OLED. The high leakage current is responsible for the strong efficiency difference between these OLEDs. Though using a new dip coating process to provide smoother interface of PEDOT:PSS-isolating layer we still observe high leakage currents for some polymer samples.

2.2 PEDOT development

In deliverable 4.3a in month 12, we demonstrated a first white small-molecule OLED using in-situ PEDOT as an anode. The particles in this material hindered the preparation of smooth surfaces. A new material, Baytron PH 500, was developed at H.C.Starck, which could be homogenised and filtered several times in order to remove particles. The average particle in this material is ca 30 as measured on swollen gel particles in the dispersion. The particle size of the particles in the dried film will be even smaller than 30 nm. Baytron PH 500 with 5% Dimethylsulfoxide shows a similar conductivity to in-situ Baytron in the dried film. It is furthermore available as a ready to use PEDOT:PSS dispersion which allows easy handling.

Table 1: *Comparison of properties of in-situ Baytron and Baytron PH 500.*

	in-situ Baytron	**Baytron PH 500**
Preparation method	Prepared by mixing Monomer and Oxidant	Ready to use aqueous dispersion
Composition	PEDOT with Tosylate as counterion	PEDT:PSS 1:2.5 (w/w)
Treatment after polymerisation	None	Homogenisation + Blending with 5% Dimethylsulfoxid
Filtration	0.45µm filter	0.20µm filter
Conductivity	500 - 700 S/cm	Ca 500 S/cm
Surface resistance at 90% transmittance	150 Ohm/sq	100 Ohm/sq
Average particle size	Unknown	Ca 30 nm

As shown in Table 1, both materials show a similar conductivity. Due to the lower absorption of Baytron PH 500, the surface resistance at 90% transmittance is better for Baytron PH 500 than for in-situ Baytron. The conductivity of 500 S/cm is sufficient for replace ITO in small area OLEDs.

Overall we concluded that Baytron PH 500 is the preferred PEDOT-type for ITO replacement by a polymeric anode within the OLLA project. This material will be used as a standard in all further developments.

The former discussed white OLED stack shows the following performance:

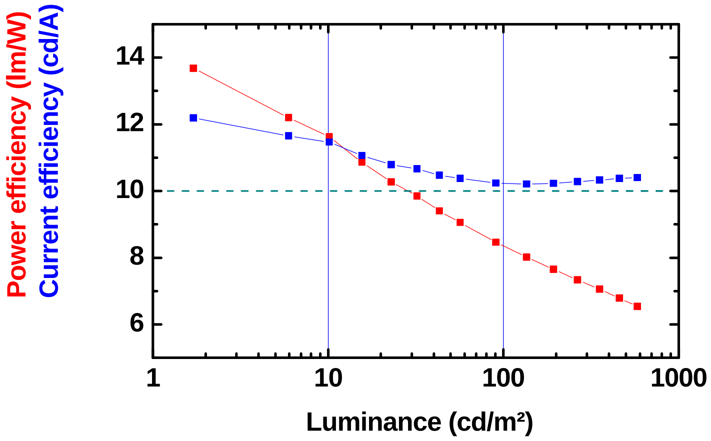


Figure 5: *Performance of a white OLED with three emission layers on a polymer anode.*

Power efficiencies above 10 lm/W are achieved for a luminance up to 30 cd/m². Upon further increase of current density, we observe a roll-off process, which is due to internal loss mechanisms. The I-V-characteristics of this sample (Figure 5) reveals low leakage currents for this polymer anode OLED. In initial samples we observed up to two orders of magnitude higher leakage currents. We attribute this decrease in leakage currents to a new dip coating method for the PEDOT samples, which was introduced recently.

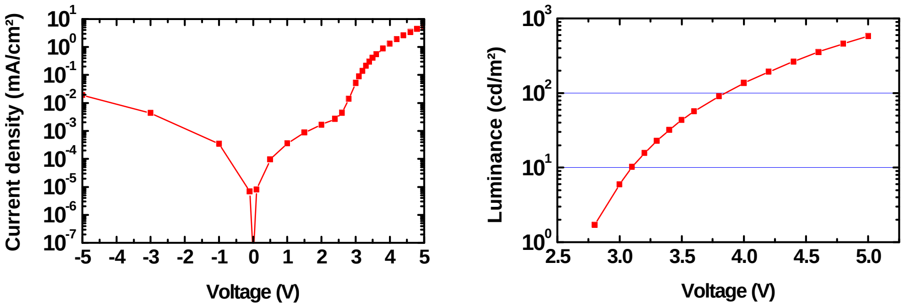


Figure 6: *I-V characteristics and luminance depending on the voltage show slightly (approx. 1 V) higher voltages for white OLED as compared to similar devices on ITO.*

Parallel to the work on the current deliverable, quite some work was dedicated to deliverable 4.3b, a 1cm² OLED on a polymer anode. This work lead to successful results based on an idea of HC-Starck to simplify the cathode structuring: Up to this point, glue was used to provide an isolating area to which the cathode could be deposited without coming into contact with the spin coated PEDOT underneath. The new approach uses polystyrene, which is dissolved in toluene. After storing this mixture over night, the PEDOT covered samples were dipped into this liquid and were slowly pulled out. By decreasing the dipping depth of the sample from the first to the fifth dipping, a smooth border, with probably lower height step between the PEDOT surface and the isolating layer (ISL) could be achieved. Such a smooth transition prevents from problems of shorts: The loss mechanisms occurring at the PEDOT-OLED interface and by the structuring of the sample will be further investigated in the next deliverable.

Next, we demonstrate another sample having CIE coordinates of (0.39/0.39), and thus, almost perfectly matching the black body curve. This sample possesses a better performance at higher luminance compared to the sample discussed above. The roll-off in power efficiency starts at a luminance above 240 cd/m². By shifting the spectra to the warm white point (0.45/0.41), the higher efficient green and red EML would enhance their contribution to the device performance resulting in a higher OLED efficiency.

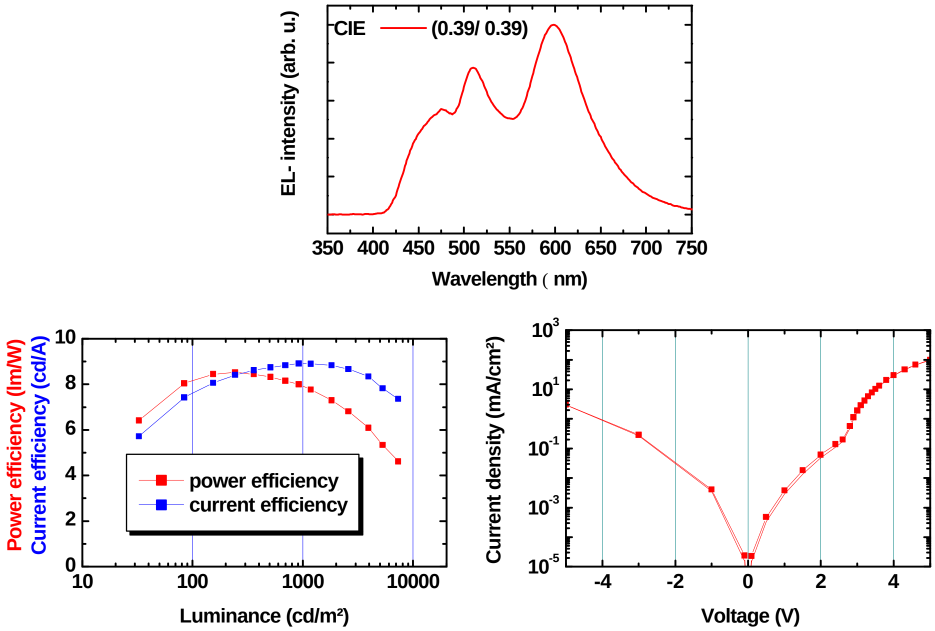


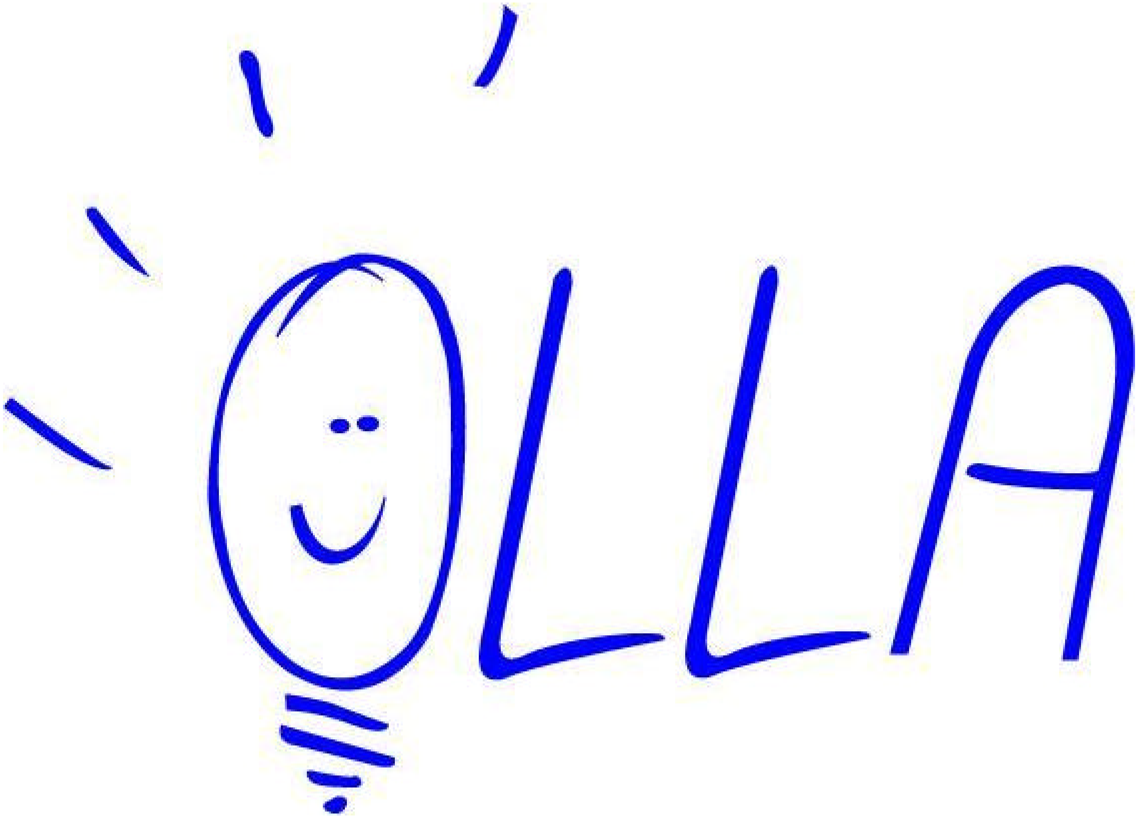
Figure 7: *Performance data of a similar OLED as shown in Figure 3E. The sample spectrum shows white light with CIE coordinates almost on the black body curve. In contrast to the former sample, this one has a lower roll-off in power efficiency, but its peak power efficiency is somewhat below the goal of 10 lm/W.*

4 Summary and outlook

A white OLED with a TCO-free polymer anode (Baytron PH 500 + 5% DMSO) is demonstrated that reaches 10 lm/W with a CIE colour co-ordinate of (0.44/0.38).

The improved sample preparation technique indicates that the loss mechanism can be decreased. Still, the OLED suffers from leakage currents. With the work on the next deliverable (degradation/ interface/ lifetime) this white approach will be repeated to improve the performance of this white OLED.

This work relies on an OLED layer stack from WP2, which was slightly modified with respect to the polymer anode. The device performance depends critically on suitable OLED stacks from WP2, as it turned out that the emission spectrum depends very strongly on the exact EML thickness.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