Project:

HyperOLED

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"Development of high-performance, hyperfluorescence OLEDs for use in display applications and solid state lighting"

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D5.1 Report on the performance of the reference system in optimized OLED stacks

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PU	Public	X
PP	Restricted to other program participants (including the EC Services)	
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The H2020 HyperOLED project is a three-year EC funded project entitled "Development of high-performance, hyperfluorescence OLEDs for use in display applications and solid state lighting". The project will run from January 2017 to December 2019.

The overall goal of the HyperOLED project is to develop materials and matching device architectures for high performance, hyperfluorescence organic light emitting diodes (OLEDs) for use in display applications and solid state lighting. The innovative OLEDs will be realised by combining thermally activated delayed fluorescence (TADF) molecular hosts with novel shielded fluorescence emitters, targeting saturated blue emission of very high efficiency, especially at high-brightness levels.

Further efficiency gains will be achieved through molecular alignment to enhance light outcoupling from the hyperfluorescence OLEDs. Using shielded emitters will enable simpler device structures to be used, keeping drive voltages low to be compatible with low voltage CMOS backplane electronics. This will enable demonstration of the concept's feasibility for high-brightness, full-colour OLED microdisplays as one application example.

To develop the hyperfluorescence OLEDs, the following scientific and technical objectives will be targeted:

- Objective 1: Develop shielded emitters

- Objective 2: Develop TADF hosts

- Objective 3: Photo-physically characterise the shielded emitters and TADF hosts

- Objective 4: Anisotropic molecular orientation for enhanced performance

- Objective 5: Design and test prototype hyperfluorescence OLEDs

- Objective 6: Fabricate and evaluate demonstration hyperfluorescence microdisplays

To show the project's overall goal has been achieved, multiple blue and white stack unit prototypes (2 x 2 mm² on 30x30mm glass substrates with ITO) will be integrated into a high-brightness microdisplay demonstrator (based on MICROOLED's 0.38'' WVGA CMOS backplane) and tested that demonstrate significant improvements in functionality, performance, manufacturability and reliability.

1. Motivation

The HyperOLED project's goal is the development of high performance hyperfluorescent OLEDs[1]. These devices are designed to combine the high efficiency of TADF (thermally activated delayed fluorescence) based OLEDs with the excellent color purity and stability of fluorescent emitter based ones. However, this is not a straightforward task as the details of many fundamental processes in such devices are unknown. The project consortium decided to use a "reference system" composed of literature known materials to investigate these processes. This approach has the advantage that the scientific analysis could start before the first materials developed in the project were available. Measurement and evaluation methods could thus be developed and tested in an early stage.

The reference system consists of the highly efficient green TADF material 4CzIPN[2], rubrene and a rubrene derivative were used as fluorescent emitters. The chemical structures of the materials are shown in figure 1.

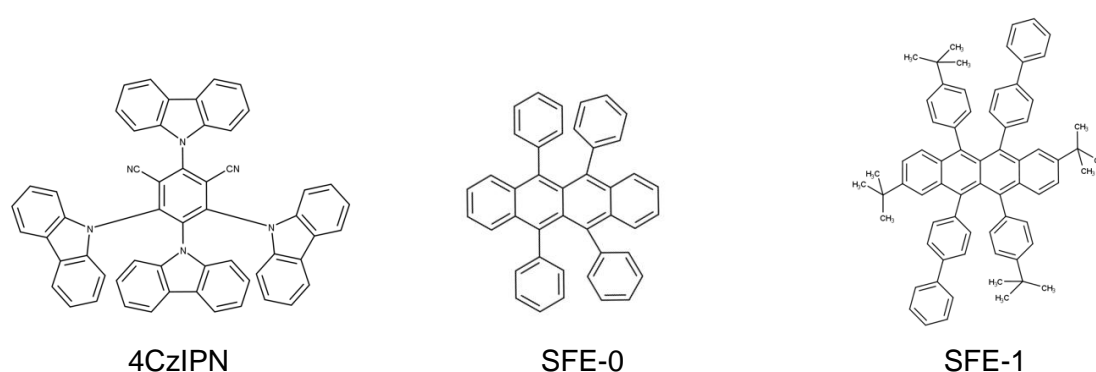

| 4CzIPN | SFE-0 | SFE-1 |

Figure 1: Reference materials used for basic investigations of hyperfluorescent OLEDs: The TADF material 4CzIPN, rubrene (named SFE-0 in the following) and a rubrene derivative called SFE-1.

The two particular tetracene derivatives were employed as reference materials because they showed different performance in preliminary work on hyperfluorescent OLEDs from one of the project partners. This was assigned to the fact that SFE-1 quenches less triplet excitons than SFE-0. Thus, less energy is lost which leads to higher efficiency in hyperfluorescent OLEDs using SFE-1. In the following, SFE-1 will be called "shielded" while SFE-0 will be called "unshielded" as SFE-1 is more "shielded" from triplet excitons.

The report summarizes the basic behavior of OLEDs using the reference materials and explains different steps to improve the device performance regarding external quantum efficiency (EQE) and lifetime (LT) in TADF only as well as hyperfluorescence devices. First, devices without fluorescent emitters were investigated and a fluorescent emitter was added only when a sufficient degree of optimization was reached.

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[1] H. Nakanotani, T. Higuchi, T. Furukawa, K. Masui, K. Morimoto, M. Numata, H. Tanaka, Y. Sagara, T. Yasuda, C. Adachi, Nature Communications, Vol. 5, Article 4016, 2014, doi: 10.1038/ncomms5016

[2] H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, Nature, Vol. 492, pp. 234, 2012, doi: 10.1038/nature11687

2. OLEDs without fluorescent emitter (TADF only devices)

TADF based OLED devices behave differently than standard OLED devices with phosphorescent emitters due to the charge-transfer character of the TADF material itself (as it consists of donor and acceptor parts). Nevertheless, the high efficiency of both device types relies on the use of triplet excitons for emission. It is thus sensible to use a stack designed for green phosphorescent emitters, for example the prototypical $Ir(ppy)_3$, as a starting point. It is shown in figure 2(a) and consists of several layers, starting with a transparent, conducting indium-tin-oxide (ITO) electrode, a p-doped hole transport material (p-doped HTM), a hole transport material (HTM), an emitting layer, a hole blocking material (HBL), an electron transporting material (ETM) and finally an aluminum electrode. The emitting layer is responsible for light generation and composed of a host material and the actual emissive material (TADF or phosphorescent emitter).

This stack was varied step by step by changing different parameters like concentration of the emissive material, by adding layers or using different host materials. This was necessary to adjust the device to work as well as possible with the TADF material instead of the phosphorescent emitter.
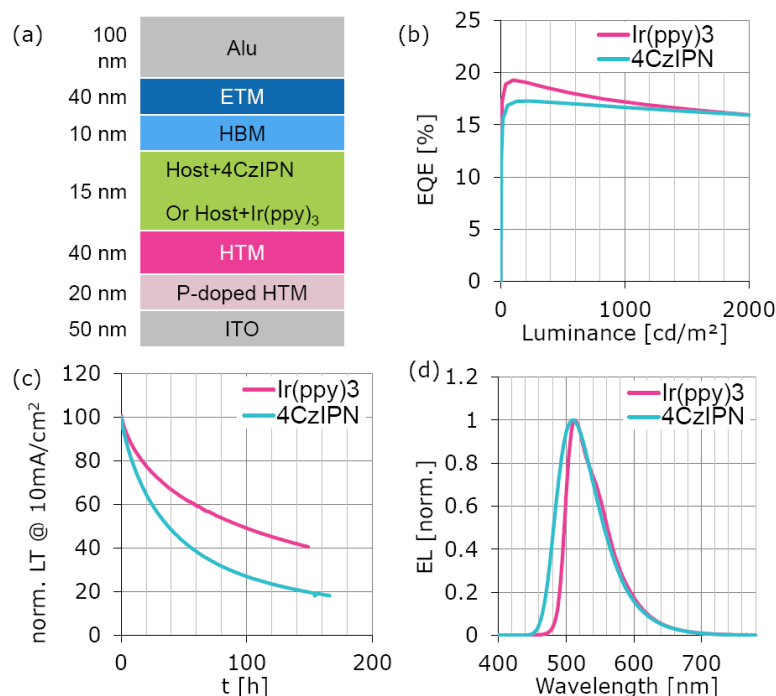

Figure 2: (a) Standard stack for green phosphorescent emitters. (b) EQE, (c) lifetime and (d) EL spectra for devices employing either the TADF material 4CzIPN or the phosphorescent emitter $Ir(ppy)_3$. Lifetime of the devices was measured for a driving current density of 10 mA/cm². The concentration of 4CzIPN or $Ir(ppy)_3$ in the emissive layer is 10%.

2.1. Comparison of TADF to phosphorescent emitter device

In order to get a feeling for the performance of TADF based devices, we will compare them to phosphorescent OLEDs first. It should be noted that state of the art phosphorescent devices show better performance than those reported here. However, our primary goal was to establish a reference system for basic investigations, so we did not target for maximum performance to start with.

The maximum in EQE of 17.2% for the 4CzIPN based device is quite similar to the 19.2% obtained using Ir(ppy)$_3$. The EL (electroluminescence) spectrum of the TADF based device is broader (full width half maximum of 75 nm) compared to the device with the phosphorescent emitter (64 nm). This is due to the charge-transfer character of the TADF material which leads to a broad emission. The lifetime of the TADF device is not as good as that of the Ir(ppy)$_3$ one. However, the results show that the stack designed for the phosphorescent green emitter can be used as starting point to investigate TADF based devices in more detail. Further improvement achieved by optimization is shown in the next sections.

3. Stack optimization for the TADF only device

3.1. Changing the host material

The first step was to test a different host in the emitting layer of the TADF based device. The idea behind screening different host materials is to get an understanding of how 4CzIPN behaves in different environments. Furthermore, the host material has a significant influence on performance and needs to be chosen carefully for optimum results.

The results shown before in figure 2 were obtained with host 1, an electron conducting material ("e-type host"). In figure 3, results using the more hole conducting ("h-type") host material host 2 are summarized. The results when host 1 is exchanged by host 2 in the standard stack are shown as green lines in the figure. The maximum EQE is only 7% and thus significantly lower than the value obtained for host 1 (17.2%, see figure 2). At first glance it thus appears that host 2 is not suitable.

However, modifying the stack by adding a 10 nm thick electron blocking layer (EBL) between the hole transport material and the emitting layer (EML) significantly improves performance. The results of this modification are shown as blue lines in figure 3. The EQE, shown in 3(a), increases by a factor of roughly three to even better values than those obtained with host 1 and a maximum value of 22.3% is obtained. The EL spectrum (see 3(b)) is not changed significantly by the introduction of the EBL and the lifetime of the device is almost doubled as can be seen in 3(c). This shows that host 2 is actually at least as good as host 1, but an adjustment to the standard stack is required to realize the material's performance potential.
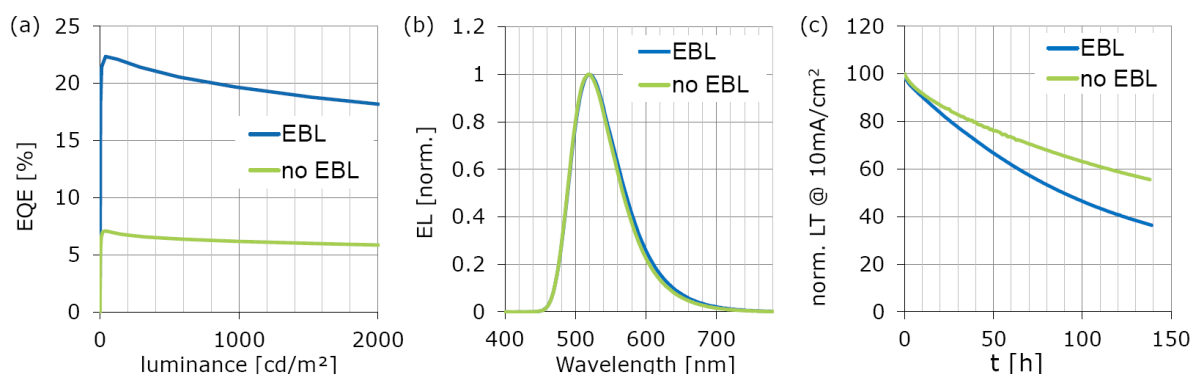

Figure 3: Difference in (a) EQE, (b) EL spectra and (c) lifetime for 4CzIPN devices with host 2 in the emitting layer for a stack without an EBL (green lines) and with an additional 10 nm thick EBL (blue lines).

3.2. Varying the 4CzIPN concentration

Up to now, the concentration of the 4CzIPN in the EML was fixed at a value of 10%. This concentration was varied to check the influence on device performance. Tests were carried out for the two different host materials host 1 and 2. The results for host 1 are shown in figure 4. The EQE decreases continuously for increasing 4CzIPN concentration (see 4(a)). In

figure 4(b), it can be seen that the peak of the EL spectrum shifts when changing the TADF concentration. The higher the 4CzIPN concentration in the device, the more the EL is shifted towards the red region of the spectrum. An increase of the lifetime is observed for higher 4CzIPN concentrations (see figure 4(c)).
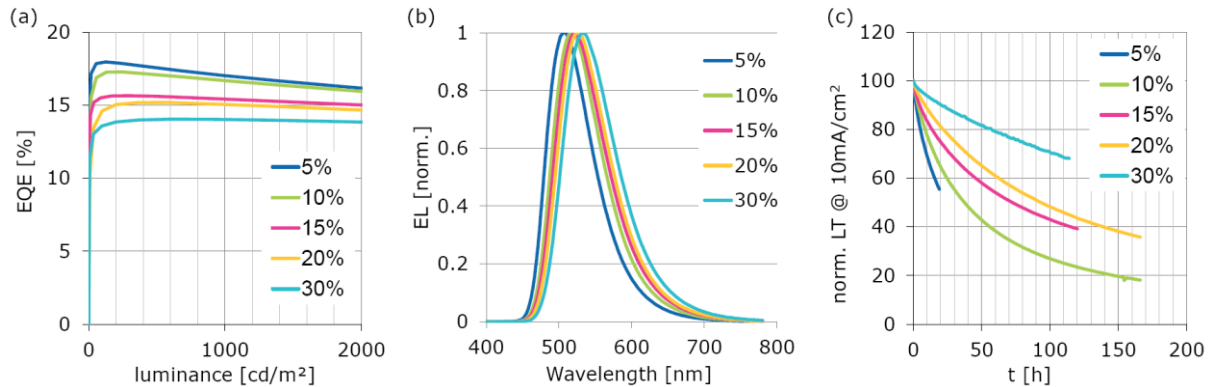

Figure 4: Results for OLEDs with different 4CzIPN concentrations in host 1: (a) EQE, (b) EL spectra and (c) lifetime.

The same experiments were also performed for host 2. Regarding EL and lifetime, the results were very similar: The EL peak shifts to higher wavelengths and lifetime increases with increasing 4CzIPN concentration. However, we observed a significant difference: The EQE **increases** with increasing 4CzIPN concentration for host 2, whereas it **decreases** for host 1.

3.3. More on the effect of host materials

This fundamentally different behavior led us to investigate the dependence of EQE on concentration for a series of host materials. The results can be seen in figure 5. Different trends are observed for the different materials. Whereas the EQE decreases for host 1, host 4 and host 5, it increases for host 2 and host 3 with increasing 4CzIPN concentration. Hosts 2 and 3 both show h-type character while the others show e-type character. We thus conclude that the charge transporting nature of the host has a significant impact on device performance and thus should be taken in account for stack optimization.
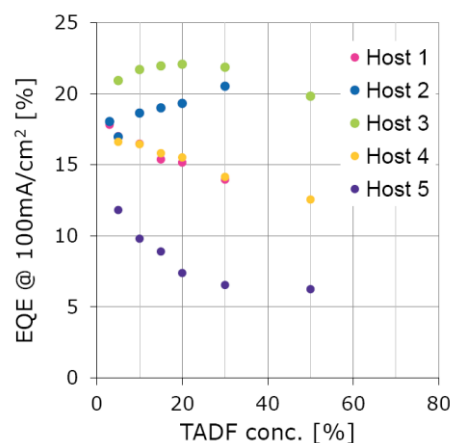

Figure 5: Dependency of EQE on 4CzIPN concentration for different host materials.

4. Hyperfluorescent devices

After some fundamental trends were investigated in TADF based OLEDs, we switched our attention to hyperfluorescent devices which, in addition to a host and a TADF material, also contain a fluorescent emitter in the emissive layer. This additional material adds a lot of complexity to the devices as the TADF and fluorescent emitter concentrations can be varied independently.

As a starting point, we compare a purely fluorescent device (without TADF) to a hyperfluorescent one. For the former we used an emitting layer with host 1 and 1% of the material SFE-0 while the latter contains an additional 10% of the TADF material 4CzIPN. The emissive layer of the hyperfluorescent OLED thus contains host 1 together with 10% 4CzIPN and 1% SFE-0. The comparison between those devices is shown in figure 6.

The device with 1% SFE-0 in the EML and no 4CzIPN shows a maximum EQE below 4% and levels off for a luminance over 100 cd/m^2 to around 2% EQE. The device with 10% 4CzIPN plus 1% SFE-0 shows a much higher EQE with a maximum slightly above 8% and better EQE for higher luminance. The principle of transferring excitation energy from the TADF to the fluorescent emitter is thus working and the EQE is improved in the hyperfluorescent device compared to the fluorescent one. But there is still a big difference compared to the TADF based devices shown before where maximum EQE values above 20% were obtained. This big difference in EQE is probably due to quenching of triplet excitons by Dexter transfer from 4CzIPN to SFE-0. This quenching is expected, as the emitter SFE-0 is not particularly adjusted to the application in a hyperfluorescent OLED.

The EL spectra for both devices are show in figure 6(b). The shape of the EL spectrum for the device with 10% 4CzIPN and 1% emitter (pink line) is similar to the EL spectrum for the device with SFE-0 alone (green line). A small emission band around 500 nm is present in the hyperfluorescent device, which results from emission of the 4CzIPN (compare 4CzIPN EL shown in figure 4(b)). Detailed analysis shows that this emission band is not responsible for the higher EQE of the hyperfluorescent device compared to the purely fluorescent one however.
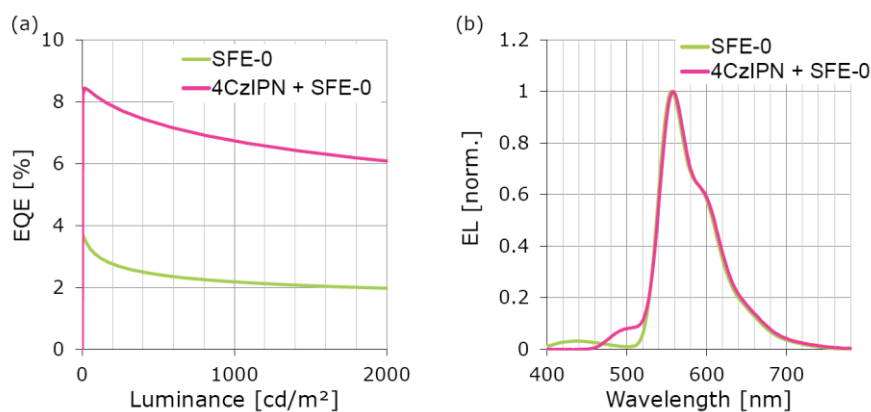

Figure 6: Comparison between a fluorescent (green lines) and hyperfluorescent device (pink lines). (a) EQE, (b) EL spectra.

5. Effect of the fluorescent emitter

The next point was to investigate the influence of the fluorescent emitter material on the performance of the devices. In order to do so, devices with the two materials SFE-0 and SFE-1 were fabricated. The corresponding data is shown in figure 7 for an EML with 10% 4CzIPN and 1% fluorescent emitter. The host material used was host 2.
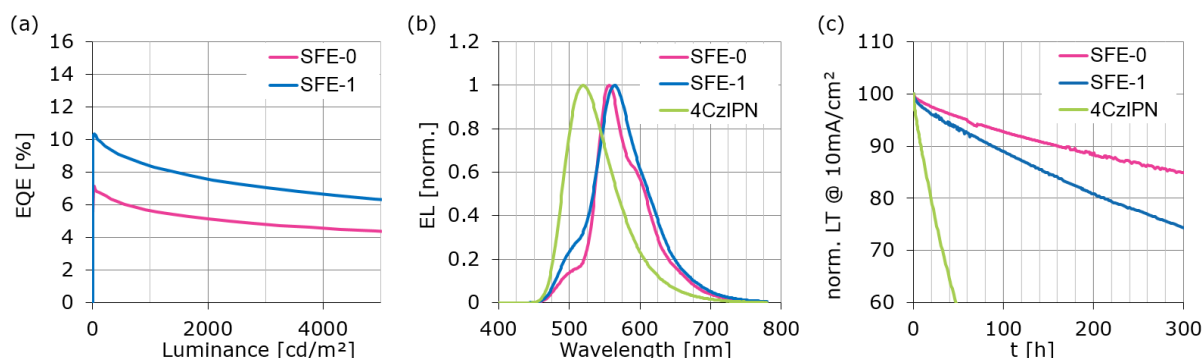

Figure 7: Comparison of hyperfluorescent OLEDs using the two fluorescent emitters SFE-0 and SFE-1. (a) The more shielded emitter SFE-1 shows an improved EQE. (b) EL spectra and (c) lifetime are shown together with results from a pure TADF device with 10% 4CzIPN but no fluorescent emitter (green lines).

The EQE is shown for the two emitters in figure 7(a). It shows higher values for the shielded emitter SFE-1 (blue lines) in comparison to the unshielded version SFE-0 (pink lines). The explanation is that the Dexter transfer from the TADF to the fluorescent emitter is suppressed by the additional substituents and therefore triplet quenching is reduced. The lifetime of the devices, shown in figure 7(c), is significantly increased by adding a fluorescent emitter into the system (blue and pink vs green).

The EL spectra for the devices are shown in figure 7(b) together with that of the pure TADF device with 10% 4CzIPN (green lines). Even at a low concentration of 1% fluorescent emitter, the electroluminescence is dominated by the emission from the fluorescent emitter. However, a small emission band is visible around 500 nm which corresponds to the EL of the 4CzIPN. In the following, the intensity of this residual TADF emission serves as an estimate for how well the energy transfer from the TADF to the fluorescent emitter works. The less of this TADF emission is visible in the EL spectrum, the better is the energy transfer.

5.1. Influence of the fluorescent emitter concentration

Apart from the TADF concentration, the fluorescent emitter concentration can be adjusted in hyperfluorescent OLEDs. This is a good way to study the influence of shielding the emitter in more detail. Thus, a series of devices with different fluorescent emitter concentrations at a fixed 4CzIPN concentration of 10% was investigated. The EQE measured at a luminance of 100 cd/m^2 is plotted vs the emitter concentration in figure 8(a) for the unshielded emitter SFE-0 in comparison to the more shielded variant SFE-1. The shielded emitter consistently shows higher EQE than the unshielded one. As mentioned before, this is probably due to the better suppression of Dexter transfer from the TADF to the fluorescent emitter in the case of SFE-1. However, the EQE drops off for increasing emitter concentrations in both cases. For concentrations above 7%, the EQE is similar to a purely fluorescent device without TADF. An important goal of the project is to suppress this drop in efficiency by developing suitable fluorescent emitters. The reasoning is that at higher fluorescent emitter concentrations, the emission band from the TADF will disappear which improves the color purity of the devices (see section 6).
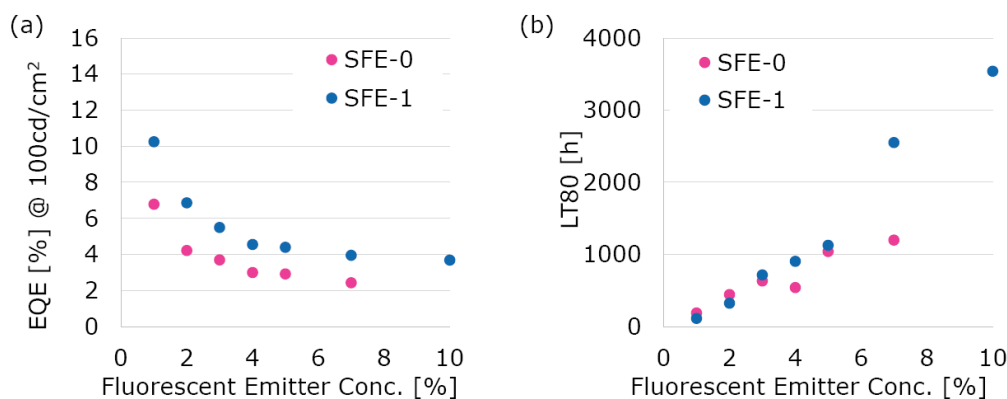
Figure 8: (a) EQE versus fluorescent emitter concentration for the unshielded emitter SFE-0 and the shielded emitter SFE-1 in an EML with 10% 4CzIPN in host 2 and (b) resulting lifetime values LT80 for the two different emitters. LT80 is the time at which the luminance has dropped to 80% of its initial value when the device is driven with a current density of 10 mA/cm².

The LT80 value is plotted in figure 8(b) against the emitter concentration. This is the time at which the luminance has dropped to 80% of its initial value when the device is driven with a current density of 10 mA/cm². The higher the fluorescent emitter concentration, the better the lifetime of the device. Both fluorescent emitters show nearly the same LT80 for a given concentration. This means that the shielding has a positive effect on the device performance as the lifetime is better for a given EQE when the material SFE-1 is used as emitter.

It should be noted that though we did not target best performance but understanding of the hyperfluorescent system, more thorough device optimization was carried out. We obtained devices with good overall performance showing 17% EQE and an LT80 of 350h using the reference material system in hyperfluorescent OLEDs.

6. Analysis of the energy transfer

As mentioned above, the residual TADF emission is a measure for the efficiency of the (desired) energy transfer from the TADF to the fluorescent emitter. The understanding of this energy transfer is crucial to design good materials for hyperfluorescent OLEDs. Thus, the EL spectra for the different emitter concentrations were investigated in more detail. As an example, we show the spectra for SFE-1 in host 2 together with 10% 4CzIPN in figure 9(a). As shown before, a residual emission band around 500 nm arising from the 4CzIPN is visible besides the EL of the fluorescent emitter. This emission band decreases for increasing fluorescent emitter concentration. The same decrease in the TADF emission is also observed for other hyperfluorescent systems we investigated (not shown). This shows that energy transfer becomes stronger with increasing fluorescent emitter concentration as expected, because in the Förster model of energy transfer the fluorescent emitter represents an energy acceptor and increasing its concentration increases the probability of energy transfer.

A rather unexpected result is seen when the TADF concentration is varied while the fluorescent emitter concentration is fixed at a value of 1%, see figure 9(b). The 4CzIPN emission decreases when increasing its concentration. This behavior is not expected at first glance as it means that the **more** of the TADF material we put in the device, the **less** emission we get from it.
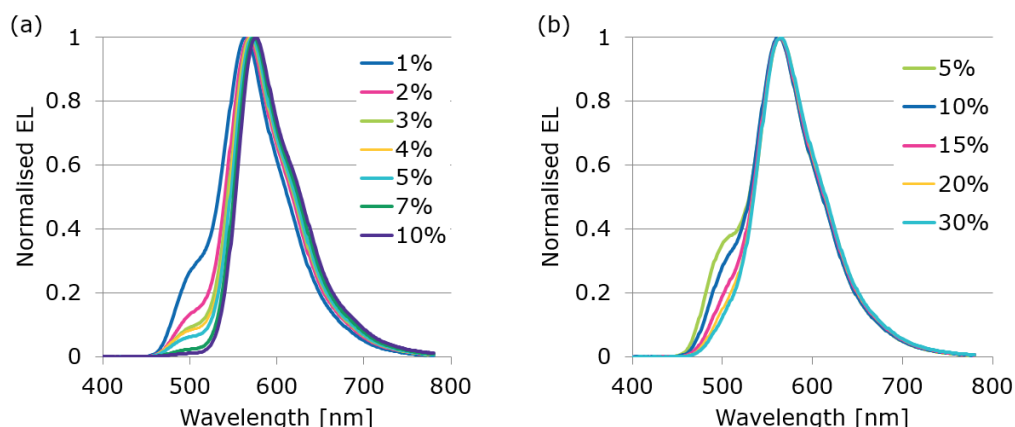
Figure 9: (a) EL spectra for a fixed 4CzIPN concentration of 10% and different concentrations of SFE-1. (b) EL spectra for a fixed SFE-1 concentration of 1% and different 4CzIPN concentrations. The host in both cases was host 2.

The unexpected decrease of the TADF emission can be explained by looking at the EL spectra in figure 4(b), where pure 4CzIPN devices were investigated. The peak in the EL for an increasing 4CzIPN concentration shifts to higher wavelengths with increasing 4CzIPN concentration. This shift in the 4CzIPN peak emission also occurs in the hyperfluorescent devices which means that the 4CzIPN emission is covered more and more by the spectrum of the fluorescent emitter when the TADF concentration increases. A more detailed investigation shows that this effect completely explains the decrease in the TADF emission band.

7. Summary and outlook

We successfully established a stack for the reference material system. The stack was first optimized for a TADF based emission layer and then transformed into a hyperfluorescent device by adding a fluorescent emitter. This stack is suitable as a starting point for the evaluation of the materials developed within the project.

The dependence of device performance on different parameters was investigated in detail using the reference materials defined by the project consortium. The results for the hyperfluorescent devices show that high efficiency is obtained for low fluorescent emitter concentrations. However, a stable device with high color purity requires high concentrations. This shows that though we can optimize the hyperfluorescent devices regarding one performance parameter, it is not possible to obtain very good overall performance yet. Furthermore, we could show that the choice of the host for the TADF material is of crucial importance not only for the overall performance, but also influences the basic behavior of the devices.

The next step is to design fluorescent emitters with suitable chemical structure in order to reduce the drop-off in EQE for increasing concentration. This will allow to find a good trade of between efficiency, stability and color purity. The results from photo physical investigations on the energy transfer and quenching processes in the emissive layer using different host materials together with the reference materials will be exploited in order to reach this goal.