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Abstract. Organic light-emitting diodes (OLEDs) are a key technology in solid state lighting. Without a long-lived phosphorescent blue emitter, a hybrid concept based on phosphorescent red and green emitters and a fluorescent blue emitter in a white OLED stack is a promising approach for pure-white emission. Several challenges such as exciton recombination on all emitters and triplet diffusion, as well as quenching, have to be overcome. To address these issues, a mixed-host phosphorescent emission layer is employed. The mixture ratio is locally varied in the emission layer. An interlayer separates the phosphorescent and fluorescent emission layer. Strategies to tune the color coordinates are presented. The lifetime and color stability versus luminance are investigated. At Commission Internationale de l'Eclairage color coordinates of 0.44/0.44, a current efficacy of 28.0 cd/A (at 1000 cd/m²), and a luminous efficacy of 20.6 lm/W can be measured. © 2011 Society of Photo-Optical Instrumentation Engineers (SPIE). [DOI: [10.1117/1.3545966](https://doi.org/10.1117/1.3545966)]

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1 Introduction

Along with a growing demand for efficient and energy-saving but nevertheless stylish illumination, organic light-emitting diodes (OLEDs) will play a major role in solid state lighting. Large in area, but nevertheless thin, light, and possibly even flexible and transparent, a whole new range of illumination designs can be realized by OLEDs. However, basic properties such as a high efficiency and a long lifetime, have to be competitive and compatible with cost-efficient high-volume production.¹ A self-evident approach to improve basic properties of OLEDs is to optimize the design of the light emitting organic layer stacks.

By combining red, green, and blue fluorescent emitters, a white light emitting organic layer stack can be realized.² The drawback of full fluorescent devices is the limitation in internal quantum efficiency (IQE) due to spin statistics to 25%.³ Their external quantum efficiency (EQE) will therefore most likely not be sufficiently competitive in the future. This restriction in IQE can be overcome with phosphorescent emitters having an IQE of up to 100% and in consequence a much higher EQE. At present, only red and green phosphorescent emitters offer an acceptably long lifetime. Until long-lived blue phosphorescent emitters are synthesized, the combination of a red and a green phosphorescent and a blue fluorescent emitter is a promising

strategy for highly efficient white OLEDs.⁴ The combination of fluorescent and phosphorescent emitters is termed hybrid.

In contrast to state-of-the-art hybrid white OLEDs processed by vacuum thermal evaporation (VTE), this work focuses on OLEDs realized by organic vapor phase deposition (OVPD).^{5,6} High-volume OVPD production offers additional degrees of freedom compared to VTE allowing novel and sophisticated device concepts regarding the emission layer (EL) design.⁷ In high-volume in-line VTE production tools, sophisticated device concepts with many layers require an increasing number of deposition chambers. This increases the cost of production. With an increasing number of materials per layer, the realization of in-line VTE tools becomes even more complicated and expensive. In OVPD tools instead, all organic materials are transported via a carrier gas and mixed prior to deposition. Thus, high-volume tools with only one deposition chamber and a high material efficiency can be realized.

Previously, phosphorescent two-color yellow OVPD OLED based on a mixed-host emission layer⁸ have been investigated in terms of efficacy and color stability. The emission color was easily tunable from red to green while the EQE was constantly high over the whole color range. A hybrid white OLED based on a single bipolar conducting host material was presented thereafter.⁹ In this work, a mixed-host yellow phosphorescent emission layer is combined with a fluorescent blue emission layer to form a mixed-host hybrid white OVPD OLED. The advantage of a mixed-host emission and exciton blocking layer will be discussed in terms of efficiency as well as exciton blocking and quenching mechanisms. Furthermore, different concepts to tune the color coordinates are presented. The color coordinate stability at increasing luminance and lifetime are investigated.

The most important requirements for a hybrid white OLED suitable for general illumination are the following: The Commission Internationale de l'Eclairage (CIE) color coordinates should be situated on or close to the Planckian locus. For example, color coordinates of 0.45/0.41 match a warm-white color impression, while color coordinates of 0.38/0.38 generate a more cold-white one. The luminous efficacy should be more than 20 lm/W at 1000 cd/m² for warm-white. The lifetime at the same luminance should be longer than 10,000 h. To allow dimming of the light source, stable color coordinates with changing luminance are preferred. During the lifetime of the device, the color coordinates should not shift significantly.

2 Experimental

All OLEDs are processed by OVPD in AIXTRON tools, which allows to control all important growth parameters (substrate temperature, deposition chamber pressure, carrier gas flows) individually and most importantly guarantees stable growth rates over a long period of time. Crucial growth parameters, such as the substrate temperature and the deposition rate, have to be set carefully to achieve a smooth layer growth.¹⁰ In these experiments, the substrate temperature is kept constant at 20°C. The deposition chamber pressure is set to 0.9 mbar. Glass substrates covered with 150 nm indium tin oxide (ITO) anodes are precleaned and the ITO is oxygen plasma activated before processing.

Photometric measurements are performed by a Minolta Luminance Meter LS-110 and calibrated photodiodes, while voltages and currents are supplied and measured by a Keithley 2400 Source Meter. Spectra are recorded by an Instrument Systems CAS 140CT spectrometer. Except when stated otherwise, all efficacy figures are measured at a luminance of 1000 cd/m². Lambertian emission is assumed for photometric calculations.

All small-molecule notations are consistently abbreviated as follows. TMM004 (Ref. 11) is a prevailing electron-conducting and TCTA (4,4',4''-tris(N-carbazolyl)-triphenylamine) a prevailing hole-conducting host material. TER031 (Ref. 11) is a phosphorescent red and Irppy (tris(phenyl-pyridyl)-Ir) a phosphorescent green emitter. SMB013/SEB115 (Ref. 11) is a fluorescent blue host/guest emitter system. NPB (N,N'-diphenyl-N,N'-bis(1-naphthylphenyl)-1,1'-biphenyl-4,4'-diamine) is employed as hole transporter, whereas ETM001 is used as electron-transporting material.

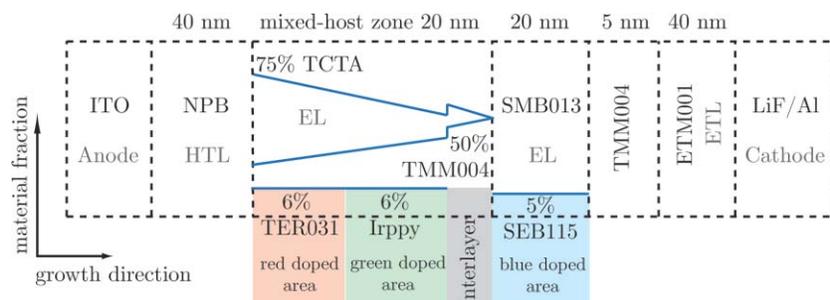


Fig. 1 Hybrid white OLED stack with a phosphorescent red and green mixed-host emission layer zone and a fluorescent blue emission layer separated by an exciton blocking interlayer.

In Fig. 1, the basic organic layer stack of the investigated hybrid white OLED can be seen. NPB is utilized as hole injection and transport material followed by the mixed-host phosphorescent emission layer. Therein, TCTA is the hole-conducting host material, whereas electrons are conducted by TMM004. One part of the phosphorescent emission layer is doped with red emitter molecules (TER031) while the other part is doped with green emitter molecules (Irppy). Between the phosphorescent and adjacent fluorescent emitting layer, an undoped interlayer consisting of a mixture of TMM004 and TCTA is inserted. The fluorescent blue emission layer consists of the electron-conducting host SMB013 and the hole-conducting emitter SEB115. Following the blue emission layer, TMM004 is deposited as an electron-blocking layer followed by an ETM001-based electron injection and transport layer (ETL).

The mixed-host phosphorescent emission layer is based on cross-fading, e.g., the TCTA to TMM004 ratio is locally varied in the emission layer. The material curves in Fig. 1 symbolize the fraction of each material at a certain position in the organic layer.

3 Results and Discussion

In Fig. 2, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies of the described material layers can be seen.

The energy level diagram generally illustrates the advantage of a mixed-host matrix. The LUMO of TMM004 and the HOMO of TCTA enclose the emitters, resulting in a low voltage drop. Excitons are formed by carrier trapping on the phosphorescent molecules. Each host material component can be optimized in terms of mobility for a single type of charge carrier and the mixture guarantees a high mobility for both. This was confirmed by single-carrier devices consisting of pure TCTA, pure TMM004, and mixtures with a varying ratio of both.

Furthermore, by cross-fading the hole and electron-conducting host material in the phosphorescent emission layer, the charge carrier mobilities can be locally optimized. At the

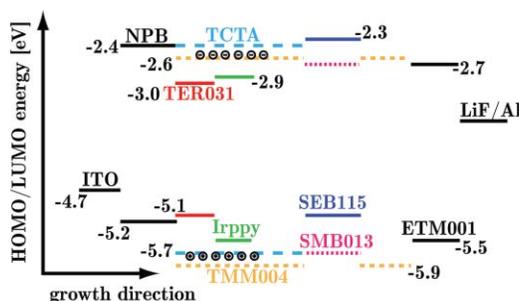


Fig. 2 HOMO and LUMO energies of the employed organic materials with TCTA as hole and TMM004 as electron conductor.

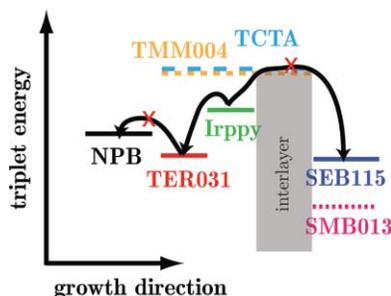


Fig. 3 Triplet energy levels of the employed organic materials and possible triplet exciton diffusion paths.

phosphorescent to fluorescent emission layer interface, the ratio between hole- and electron-conducting host and thus hole and electron mobility can be tuned to shift the exciton recombination more in the direction of the phosphorescent or fluorescent emission layer. If alternatively a constant mixture was used, the ratio of hole- to electron-conducting host would be the same over the whole phosphorescent emission layer. But obviously, close to the anode and NPB hole-transport layer, no electron-conducting host is necessary. By lowering the available states for hopping transport, this would rather reduce the hole mobility unnecessarily. Therefore, the closer to the anode, the more should the ratio between hole and electron-conducting host material be shifted to the hole conductor. Moreover, a charge-balanced device based on a constant mixture of host materials generally is very sensitive to the mixture ratio or other small process variations. This issue can be avoided with cross-faded emission layers. The following investigations will be based on cross-faded devices. Further details about cross-fading can also be found elsewhere.⁸

In Fig. 3, the triplet energy levels of the different organic materials and possible triplet exciton diffusion paths are qualitatively shown. By short range (<1 nm) Dexter transfer,¹² triplet excitons can diffuse from Irppy to TER031 molecules. Quenching at the TER031/NPB interface is prevented due to the higher triplet energy level of NPB. The triplet levels of the blue host (SMB013) and emitter (SEB115) are lower compared to that of Irppy and thus would quench the green emission drastically. To prevent exciton quenching, an exciton blocking interlayer (undoped mixed-host) is located between the phosphorescent and fluorescent emission layer.

The stack design of Fig. 1 shows a current efficacy of 28.0 cd/A and a luminous efficacy of 20.6 lm/W at CIE color coordinates of 0.44/0.44. A hybrid white OLED⁹ based on a single bipolar conducting phosphorescent host and interlayer material (without a mixed-host), shows at color coordinates of 0.42/0.43 a current efficacy of 18.9 cd/A. This is 33% less compared to the mixed-host/cross-faded OLED. The increase in current efficacy is assumed to be mainly caused by less exciton quenching in the interlayer. Through the interlayer, holes and electrons are interchanged between the yellow and blue emission layer. If a single species of molecules has to transport these holes and electrons, it is much more likely that excited states (e.g., excitons) are created. The nonradiative decay of these states will reduce the current efficacy of the device significantly. In the mixed-host interlayer, holes and electrons are transported by two different species of molecules, each with a high mobility, so that the probability of unwanted recombination is significantly reduced.

To tune the color coordinates between warm-white and cold-white, different concepts can be applied. The amount of red to green emission can simply be controlled by the red to green doped area (see Fig. 1). At arrow A in Fig. 4, the change in color coordinates can be seen. The red to green doped area is varied by only 1 nm to tune the color coordinates effectively toward green or red. This indicates a recombination zone which is situated in the middle of the phosphorescent emission layer.

By changing the ratio between the hole- and electron-conducting host materials at the phosphorescent to fluorescent emission layer interface and thereby the material fraction slopes

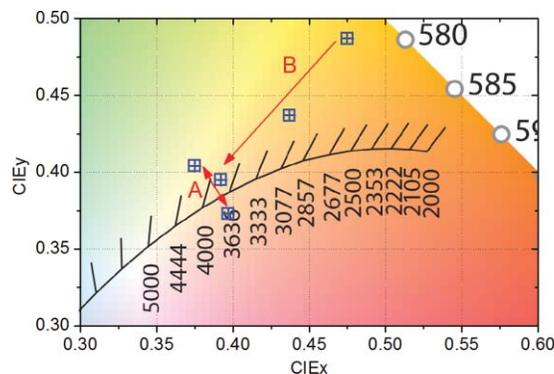


Fig. 4 Change in color coordinates if the red to green doped area is changed (arrow A) and if the TMM004 to TCTA ratio is varied at the phosphorescent to fluorescent emission layer interface (arrow B).

in the phosphorescent emission layer and interlayer, the distribution of holes and electrons between the emission layers can be controlled effectively. Arrow B in Fig. 4 illustrates how the color coordinates change if the ratio TCTA:TMM004 is varied from 1:3 over 1:1 to 3:1. At pure-white color coordinates of 0.39/0.40, a current efficacy of 22.8 cd/A, a luminous efficacy of 16.1 lm/W, and an EQE of 10.3% can be measured.

To further tune the color coordinates toward cold-white, the electron-blocking layer thickness between blue emission layer and electron-transport layer, as well as the blue emission layer thickness can be varied. In Fig. 5 at arrow C, the TMM004 electron-blocking layer thickness is varied from 0 to 3 nm, 5 nm, 7 nm, and 9 nm. SMB013, TMM004, and ETM001 are good electron conductors and the energetic difference between the LUMO of SMB013, TMM004, and ETM001 is small. But nevertheless, surprisingly the combination of the three materials creates a strong electron barrier. Otherwise, the extreme blueshift in color coordinates with increasing TMM004 layer thickness could not be explained. Independent investigations of monochrome blue devices showed a driving voltage increase of 1.5 V upon introduction of a 5 nm TMM004 layer sandwiched between the EL and the ETL. TMM004 does not act as a hole blocker, which was confirmed by monochrome blue devices as well. The same electron-blocking effect can be observed if ETM001 is replaced by tris-(8-hydroxyquinoline) aluminum (Alq_3), which is a common electron conductor. In conclusion, it is assumed that an electron-blocking dipole layer is created at the SMB013/TMM004 interface. Due to the accumulation of negative charges, holes

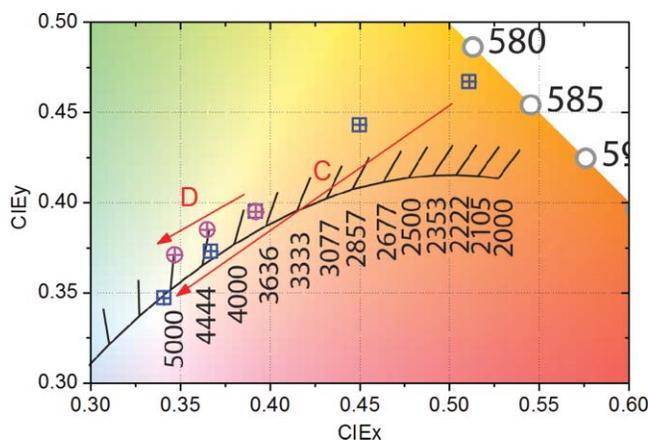


Fig. 5 Change in color coordinates if the electron-blocking layer thickness is increased (arrow C) and if the blue emission layer thickness is decreased (arrow D).

Table 1 CIE color coordinates at increasing luminance.

Luminance [cd/m ²]	CIE _x	CIE _y
1,000	0.371	0.363
2,000	0.378	0.368
5,000	0.381	0.372
10,000	0.378	0.372

are attracted and forced to penetrate deeper in the blue emission layer increasing the amount of blue emission. The color coordinates can be tuned over a wide range. Nevertheless, the effect seems to saturate. This is an expected behavior, because the effect of charge accumulation should not be thickness-dependent, but rather saturating as soon as a closed interface is formed. At color coordinates of 0.34/0.35, a current efficacy of 16.1 cd/A and a luminous efficacy of 10.5 lm/W can be measured.

Another possibility to tune the color toward colder-white color coordinates is to decrease the blue emission layer thickness. The TMM004 electron-blocking layer thickness is kept constant at 5 nm. In Fig. 5 at arrow D, the change in color coordinates can be seen. The emission layer thickness was varied from an initial 20 to 10 nm and 5 nm. Thus, a decrease in emission layer thickness increases the amount of blue emission. More holes must enter the blue emission layer to increase the amount of blue emission. Monochrome blue devices were investigated for comparison, but the reason for this effect remained unclear.

The described mechanisms allow to tune the color coordinates over a wide range close to the Planckian locus. Based on the stack design of Fig. 1, pure-white color coordinates can be realized if the TCTA:TMM004 ratio is changed to 3:1 at the phosphorescent to fluorescent emission layer interface. To measure the color coordinate stability versus luminance, the luminance is increased from 1000 to 10000 cd/m². The color coordinates change only slightly from 0.37/0.36 to 0.38/0.37 as shown in Table 1. This indicates an extreme stability and a well charge-balanced device.

For lifetime measurements and to identify possible degradation mechanisms, an OLED with color coordinates of 0.39/0.40 was stressed at 4.2 mA/cm². This equals an initial 1000 cd/m². In Fig. 6, spectra taken after increasing duration of stress can be seen. Already after about 8 h of device stressing, an intense blueshift of color coordinates can be observed. This is a result

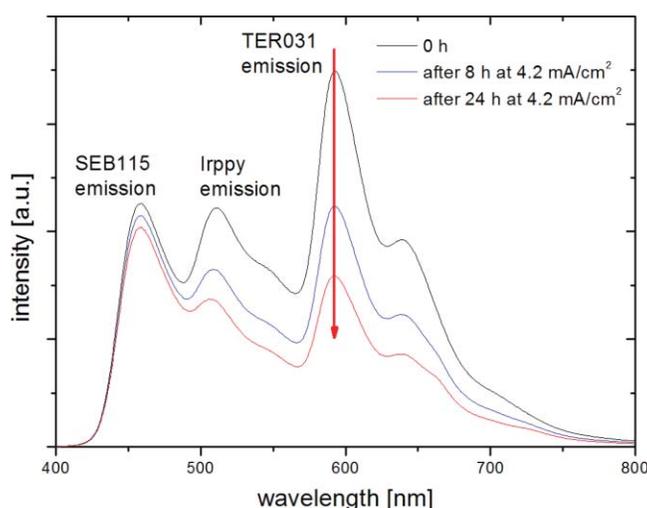


Fig. 6 OLED spectra taken at 0, 8 and 24 h after device stressing with 4.2 mA/cm² (initial 1000 cd/m²).

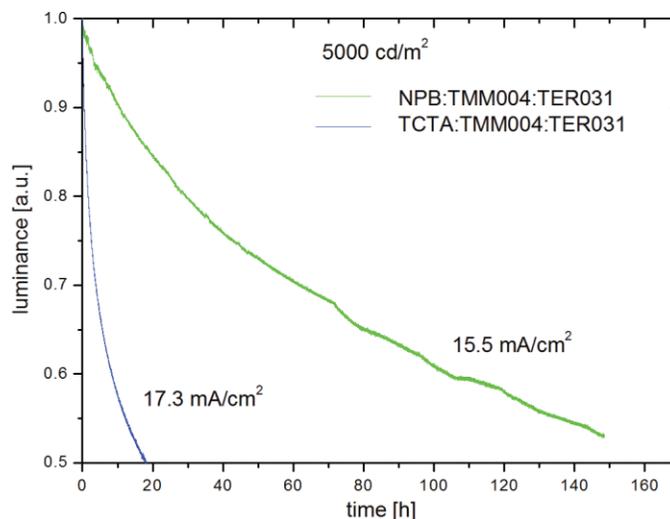


Fig. 7 Luminance of different monochrome TER031 red OLED versus time of stressing at 5000 cd/m².

of the decreasing TER031 red emission peak. Apart from a degradation of the red emitter, this could also be caused by a shift of the recombination zone to the cathode side of the device or the creation of nonradiative recombination centers. To further investigate these possibilities, the lifetime of red monochrome TER031 devices with different hole-conducting host materials was investigated separately.

In Fig. 7, the luminance of different TER031 devices versus time can be seen. The decrease in luminance is by the order of 1 magnitude higher if TER031 is doped into TCTA as a hole-conducting host instead of NPB. It is therefore concluded that TCTA and TER031 are an unsuitable combination regarding device lifetime. Due to the triplet energy level of NPB between those of TER031 and Irppy (see Fig. 3), TCTA cannot be replaced simply by NPB. In Ref. 13, chemical transformations of the hole transport materials NPB and TCTA in phosphorescent blue OLED were investigated. It was found that radical anions of TCTA can dissociate. It is proposed that the reduction of TCTA molecules inside the mixed-host emission layer leads to instable anionic TCTA species. Degradation fragments can react and products can act as phosphorescence quenchers reducing the red emission. Whether TCTA fragments react with TER031 molecules or only act as phosphorescence quenchers, cannot be answered. Compared to the green emission the red emission decreases slightly faster, so that an additional degradation of the red emitter is probable. Currently, it is investigated if a different high triplet energy host can replace TCTA and if the combination TCTA:TER031 can be stabilized by preventing the reduction of TCTA.

4 Summary and Outlook

In summary, hybrid white OVPD OLEDs with a mixed-host interlayer and an EQE of 12.1% (28.0 cd/A, 20.6 lm/W) have been realized at color coordinates of 0.44/0.44 by employing a mixed-host/cross-faded phosphorescent emission layer and exciton blocking interlayer. Compared to an OLED based on a single bipolar conducting host material, the current efficacy could be increased by 48%. Different concepts to tune the color coordinates on a wide range near the Planckian locus were presented. The investigated devices are extremely color-stable with rising luminance. Due to an unsuitable combination of the red emitter and the hole-conducting host material, the lifetime was shown to be limited.

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Biographies and photographs of the authors not available.