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Employing exciton transfer molecules to increase the lifetime of phosphorescent red organic light emitting diodes

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The lifetime of phosphorescent red organic light emitting diodes (OLEDs) is investigated employing either N,N'-diphenyl-N,N'-bis(1-naphthylphenyl)-1,1'-biphenyl-4,4'-diamine (NPB), TMM117, or 4,4',4''-tris(N-carbazolyl)-triphenylamine (TCTA) as hole-conducting host material (mixed with an electron conductor). All OLED (organic vapor phase deposition-processed) show similar efficiencies around 30 lm/W but strongly different lifetimes. Quickly degrading OLED based on TCTA can be stabilized by doping exciton transfer molecules [tris-(phenyl-pyridyl)-Ir (Ir(ppy)₃)] to the emission layer. At a current density of 50 mA/cm² (12 800 cd/m²), a lifetime of 387 h can be achieved. Employing exciton transfer molecules is suggested to prevent the degradation of the red emission layer in phosphorescent white OLED. © 2011 American Institute of Physics.

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Commercialization of organic light emitting diodes (OLEDs) for general lighting applications can only be successful if key parameters like efficiency, lifetime and cost of high-volume production are comparable to competing technologies.¹ While by employing phosphorescent² instead of fluorescent emitters, efficiencies of white OLED at 1000 cd/m² exceeded even the ones of fluorescent tubes,³ the OLED lifetime is still limited. To be cost-competitive in terms of lumen output, the luminance has to be as high as possible at an acceptable lifetime. Even though phosphorescent red OLED with a long lifetime have been realized, in three-emitter hybrid⁴ white OLED and high triplet energy hosts, the lifetime of the phosphorescent red emitter can be shorter⁵ depending on the employed organic layer stack. This causes an unwanted shift in color coordinates toward green and blue. If it was possible to extend the lifetime of the red emitter in host materials employed in white OLED, their lifetime would be significantly enhanced. In general, lifetime limiting factors include the instability of the host and emitter molecules against charge carriers and excitons, as well as changes in the morphology of the organic layers (thermal degradation).^{6,7} Furthermore, a lack of energetic stability of the indium tin oxide (ITO)/organic interface and the diffusion of metal quencher atoms from the electrodes into the active layers can limit the lifetime.^{8,9} At high luminance of around 10 000 cd/m², lifetimes well below 1000 h can be found^{10,11} for phosphorescent red OLED with different emitter molecules. Our goal is to achieve a comparable long lifetime in host materials employed in white OLED suitable for phosphorescent high triplet energy green and blue emitters. In future, it would be possible to realize a full-phosphorescent OLED with one emission layer (EL).

In the following, hole-conducting host materials with different highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels as well

as low and high triplet energy states will be investigated and it will be shown that the choice of host material dramatically influences the lifetime of phosphorescent red OLED. Furthermore, it is investigated if OLED with an initially short lifetime can be improved by employing exciton transfer molecules to prevent the degradation of the host and red emitter. For fluorescent OLED it is known that the lifetime can be increased by employing exciton transfer molecules¹² and recent investigations¹³ revealed that a similar effect probably is true for phosphorescent OLED as well.

All OLED are processed by organic vapor phase deposition^{14,15} 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. A smooth layer growth is obtained by choosing optimized values for crucial growth parameters like the substrate temperature and the deposition rate.¹⁶ 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 ITO anodes are pre-cleaned (particle removal) and the ITO is oxygen plasma activated before processing.

Photometric measurements are carried out 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. In-house developed constant current supplies drive the OLED during lifetime measurements while photodiodes monitor their luminous decay. Lambertian emission is assumed for photometric calculations.

All small-molecule notations are consistently abbreviated as follows: TMM004 (Refs. 17–20) is a predominantly electron-conducting host material and 4,4',4''-tris(N-carbazolyl)-triphenylamine (TCTA) as well as TMM117 (Refs. 17–20) are predominantly hole-conducting host materials. Ir(MDQ)₂(acac) [Ir(III)bis(2-methyldibenzo[f,h]

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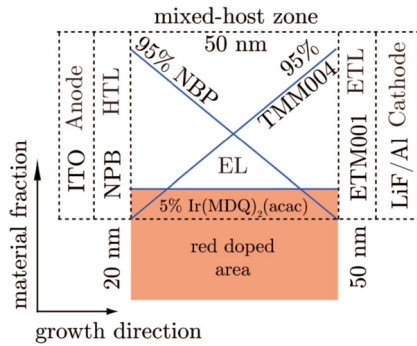


FIG. 1. (Color online) Basic layer stack of investigated OLED with a mixed-host EL (cross-faded). The solid material curves symbolize the fraction of each material in the EL.

quinoxaline)(acetylacetonate)] is a phosphorescent red and Ir(ppy)₃ (tris-(phenyl-pyridyl)-Ir) a phosphorescent green emitter. NPB (N,N'-diphenyl-N,N'-bis(1-naphthylphenyl)-1,1'-biphenyl-4,4'-diamine) is employed as hole transporter, whereas ETM001 (supplied by Philips) is used as electron-transporting material.

In Fig. 1, the basic organic layer stack of the investigated phosphorescent red OLED is shown. The EL is sandwiched by a 20 nm NPB hole transport layer and a 50 nm ETM001 electron transport layer. The EL consists of a mixture of a predominantly hole- and a predominantly electron-conducting host material (e.g., NPB:TMM004) doped with constant 5% vol. of the phosphorescent red emitter Ir(MDQ)₂(acac). To investigate the impact of different hole-conducting host materials, NPB is replaced in the EL by either TMM117 or TCTA.

The mixture ratio of the host materials is locally varied versus the EL position to achieve locally optimized mobilities for holes and electrons (Fig. 1). The solid material curves in Fig. 1 symbolize the fraction of the host materials at a certain position in the EL. The concept of a locally varied host material ratio is termed cross-fading and advantages for yellow and white OLED are described elsewhere in detail.^{5,21} Because of the different hole mobilities of the investigated hole-conducting host materials, it is advantageous to choose a cross-faded EL instead of a mixed-host with constant ratio versus EL position. A constant ratio would require the adjustment of the mixture ratio depending on the hole mobility of the chosen host material to achieve a charge balanced high-efficiency OLED. Cross-fading guarantees a high-efficiency and comparable devices without any tuning.

In Fig. 2, HOMO and LUMO energies of the basic layer stack are shown. HOMO energies are based on cyclic voltammetry data. LUMO energies are calculated from HOMO energies plus energy gap. The optical absorption edge deter-

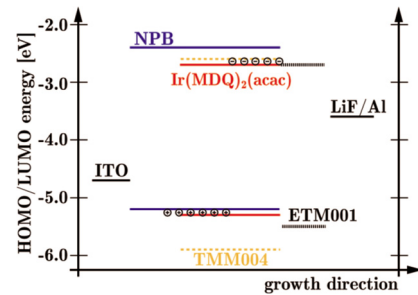


FIG. 2. (Color online) HOMO and LUMO energies of the employed organic materials of the basic layer stack.

mines the energy gap. The HOMO of NPB and the LUMO of TMM004 enclose the emitter leading to low energy losses when charge carriers are trapped on emitter molecules.

In Table I, the current and luminous efficacy at 1000 cd/m² of all investigated devices can be found. The hole-conducting host material of the EL of OLED-1-NPB, OLED-2-TMM117 and OLED-3-TCTA is based on NPB, TMM117, and TCTA, respectively. The three samples OLED-4,5,6-Ir(ppy)₃ are based on OLED-3-TCTA plus an additional fraction of Ir(ppy)₃ as explained later. The current efficacy for all devices is in the range between 26.6 and 31.9 cd/A at a voltage between 3.0 and 4.2 V. The CIE color coordinates of all devices are 0.62/0.38. TMM117 and TCTA as hole-conducting host alternatives have HOMO energies of -5.5 and -5.3 eV and LUMO energies of -2.2 and -2.0 eV.

The lifetime in Table I is defined as the time until the luminance has decreased to 50% of its initial value (12–14 kcd/m²). To achieve reasonably low measurement times, such high initial luminance was chosen. Nevertheless, to avoid thermal degradation of the hole-transporting NPB layers, it was taken care that the initial electrical power did not exceed 320 mW/cm², which could otherwise result in a different lifetime limiting mechanism. The OLED temperature during measurement was below 65 °C. Extrapolations are not applied, because necessary acceleration factors are always a source of uncertainty and a small change in boundary conditions (e.g., ITO surface preparation) can have a large impact on them. For literature comparison the lifetime of OLED-6-Ir(ppy)₃ can be extrapolated to more than 60 000 h (at 1000 cd/m²) applying an acceleration factor of 1.9 (estimated from lifetime measurements at different high current densities) using the Coffin–Manson model.²²

Comparing Table I (part A), OLED-1-NPB has the longest lifetime of 149 h, whereas the TCTA-based OLED-3-TCTA already degrades in 15 h. 51 h can be measured employing TMM117. Regarding TCTA, an internal organic

TABLE I. Comparison of OLED with EL based on different hole-conducting host materials [NPB, TMM117, TCTA, and TCTA:Ir(ppy)₃]. Efficacy and voltage at 1000 cd/m² and lifetime data at a current density of 50 mA/cm².

Part	OLED	Curr. eff. (cd/A)	Voltage (V)	Lum. eff. (m/W)	Initial lum. (kcd/m ²)	Lifetime (h)
A	1-NPB	31.6	3.0	33.6	13.6	149
	2-TMM117	27.5	4.2	20.5	11.9	51
	3-TCTA	26.6	3.4	24.7	11.5	15
B (based on 3-TCTA)	4-Ir(ppy) ₃ (5%)	31.9	3.3	30.1	13.2	66
	5-Ir(ppy) ₃ (15%)	31.6	3.4	29.3	13.4	216
	6-Ir(ppy) ₃ (25%)	30.0	3.4	27.5	12.8	387

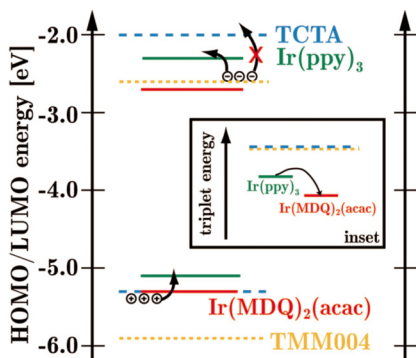


FIG. 3. (Color online) HOMO and LUMO energies employing TCTA and Ir(ppy)₃ in the EL. Triplet energy transfer from Ir(ppy)₃ to Ir(MDQ)₂(acac) (inset).

degradation mechanism must exist reducing the luminescence. Investigations about chemical transformations of the hole transport materials NPB and TCTA in phosphorescent blue OLED revealed that radical anions of TCTA can dissociate.²³ It is therefore proposed that the chemical reduction of TCTA molecules inside the mixed-host EL leads to instable anionic TCTA species. Degradation fragments can furthermore react and products can act as phosphorescence quenchers reducing luminescence. A similar behavior has also been found for the common and long-lasting electron conductor tris-(8-hydroxyquinoline) aluminum (Alq₃).^{6,7} Cationic Alq₃ species are instable and their degradation products act as fluorescence quenchers and nonradiative charge carrier recombination centers.

To validate the assumption of instable anionic TCTA species, it is investigated if the lifetime of OLED-3-TCTA can be increased if another molecule with a LUMO between the one of TMM004 and the one of TCTA is added to OLED-3-TCTA. Respectively, the EL of OLED-4,5,6-Ir(ppy)₃ contain additional 5% vol., 15% vol., and 25% vol. Ir(ppy)₃ [Table I (part B)]. In Fig. 3, HOMO and LUMO energy levels of such an EL are plotted. Compared to the pure TCTA-based OLED-3-TCTA, the lifetime increases from initial 15 h to 66 h, 216 h, and 387 h. This is longer than that of the TMM117-based OLED-2-TMM117 and also longer than that of the NPB-based OLED-1-NPB.

It is concluded that the LUMO of Ir(ppy)₃ forms a protection level for TCTA, so that electrons do no longer reduce and degrade TCTA molecules (Fig. 3). If by electron transfer, excited triplet states are created on Ir(ppy)₃, these states will diffuse via Dexter²⁴ transfer to Ir(MDQ)₂(acac) (Fig. 3 inset). The triplet energy state of Ir(MDQ)₂(acac) is lower than the triplet energy state of Ir(ppy)₃. OLED-4,5,6-Ir(ppy)₃ show no emission from Ir(ppy)₃, so that the Dexter transfer from Ir(ppy)₃ to Ir(MDQ)₂(acac) has to be very fast. Ir(ppy)₃ acts as a fast exciton transfer molecule and protects TCTA from reduction.

Furthermore, this exciton transfer mechanism can be the reason for the lifetime of OLED-6-Ir(ppy)₃ being even higher compared to OLED-1-NPB. In case of a TCTA:Ir(MDQ)₂(acac):Ir(ppy)₃ mixture in the EL, holes preferentially oxidize Ir(ppy)₃ instead of Ir(MDQ)₂(acac). It is proposed that this indirect mechanism stresses Ir(MDQ)₂(acac) emitter molecules less than direct exciton generation by charge carrier trapping on Ir(MDQ)₂(acac)

like in OLED-1-NPB, explaining the surprisingly even higher lifetime.

In summary, it was shown that the lifetime of phosphorescent red OLED is strongly dependent on the choice of hole-conducting host material. However, the introduction of exciton transfer molecules increased the lifetime dramatically even in combination with an unstable high triplet energy host material. The maximum lifetime without transfer molecules but with a more stable low triplet energy state host was 149 h at a high luminance of over 10 000 cd/m², while the lifetime of 15 h with a high triplet energy host could be increased to even 387 h using transfer molecules. Future investigations will focus on different electron-conducting host materials and their impact on OLED lifetime. The results allow the usage of high triplet energy host materials like TCTA for phosphorescent red emitter molecules in white OLED without the drawback of a preterm decrease of the red emission.

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