Dependence of Phosphorescent Emitter Orientation on Deposition Technique in Doped Organic Films

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Supporting Information

The control of molecular orientation in emissive guest–host systems is a promising concept for efficiency enhancement in state-of-the-art organic light-emitting diodes (OLEDs). 2,3,7 Horizontal alignment of the emitting transition dipole moments increases the external quantum efficiency (EQE) of OLEDs due to reduced coupling to lossy optical modes. Hence, the outcoupling factor can be significantly increased from ca. 20% (for the isotropic case) up to 46% (when perfect horizontal alignment is achieved) 4,5 without using complex outcoupling enhancements such as nanostructured electrodes 6 or scattering particles. 6

Here, we compare two different preparation techniques for emissive guest–host layers containing phosphorescent metal–organic iridium-complexes doped in an organic matrix material. Thermal evaporation in a high vacuum is the most common fabrication process used in modern OLED materials. During this deposition process, the dye molecules assemble at an interface formed between the so far deposited material (mainly the matrix due to the low doping concentrations of approximately 5%) and vacuum. The emitting species interacts with both media at this interface until it is covered with subsequently deposited molecules, which occurs in the range of seconds for the typically used evaporation rates of 0.1 nm/s. 1,3,7 In contrast, during the solution processing, the deposition takes place in one step with the absence of such cumulative interfacial effects. Thus, if the process generating the horizontal alignment of common heteroleptic Ir-complexes is based on an interface interaction during deposition, the two preparation techniques should show significant differences in the orientation of the dye molecules and the resulting alignment of the emissive transition dipole moments.

Because the direct measurement of molecular orientation is not possible in these guest–host systems due to low doping concentrations, we followed the indirect investigation route to measure dipole alignment presented by Frischeisen et al. in 2011 8 using the angular dependent emission pattern to measure dipole alignment presented by Frischeisen et al. in 2011 8

In general, the connection between Θ and an ensemble of molecules, each having different possible orientations of the TDVs is

\[ \Theta = \frac{\sum a_i \sum b_i p_{x,y}^2}{\sum a_i \sum b_i p_{z}^2} \]  

where \( a_i \) describes the relative contribution of each dye molecule, \( b_i \) describes the relative contribution of the \( j \)-th transition dipole moment \( \vec{p}_j \) on the \( i \)-th molecule and \( p_{x,y} \) denotes the vertical component of the corresponding transition dipole moment vector. 9

The samples were prepared as 15–30 nm thick layers on glass substrates containing a doping concentration of 6–8% wt. of the investigated iridium complex. For the phosphorescent dye molecules \( \text{bis}(2\text{-methylinden} [f,h] \text{quinoxaline}) \text{(acetylacetonate)} \text{iridium(III)} \) (Ir(mqd)(acac)) and \( \text{bis}(1\text{-phenylisoquinoline}) \text{(acetylacetonate)} \text{iridium(III)} \) (Ir(ppy)(acac)), the matrix material \( \text{N},\text{N-di}(1\text{-naphthyl})\text{-N},\text{N-diphenyl}(1\text{-biphenyl})\text{-4,4-diamine} \) (NPB) was used in both evaporated and solution processed samples. For \( \text{bis}(2\text{-pyridinyl-N-phenyl-C}[(\text{acetylacetonate})\text{iridium(III)} \) (Ir(ppy)(acac)) and \( \text{tris}(2\text{-phenylpyridinato-C2,N} \text{iridium(III)} \) (Ir(ppy)_3) as dyes, two different materials, 4,4-bis(9-carbazolyl)-1,1-biphenyl,4,4-N,N-dicarbazole-1,1-biphenyl (CBP) and 2,7-bis(carbazol-9-yl)-9,9-spirobifluorene (Spiro2-CBP) have been used as hosts. Doped films of CBP were prepared by both solution processing and thermal evaporation. Spiro2-CBP was only investigated in solution processed layers. Additionally, poly(methyl methacrylate) (PMMA) was evaluated as a matrix material for spin-cast films of \( \text{Ir(ppy)}(acac) \). The solution processed emission layers were prepared by spin coating at 5000 rpm in either a chloroform solution (5 mg/mL) for the NPB, CBP and Spiro2-CBP hosts or from a toluene solution (1.25 mg/mL) for the PMMA based layers. After deposition, the samples were dried under cleanroom conditions for at least 1.5 h without further annealing treatment. The samples based on evaporated host materials were deposited at an average rate of 1.0 Å/s in a vacuum chamber with a base pressure of \( 5 \times 10^{-7} \) mbar.

The experimental setup contains a macroscopic outcoupling prism (fused silica), which is index matched to the glass substrate.
of the sample under investigation. Both are mounted on a rotary stage and excited by a laserbeam with a wavelength of 375 nm (Oxxius OXV-375). The emission passes a polarization filter and is afterward collected by a collimator lens attached via an optical fiber to a spectrometer. The outcoupling through the fused silica prism is necessary to extract the substrate modes of the sample, which actually contain the required information about the orientation of the TDVs of the emissive species in the guest—host system. Figure 1 shows an exemplary measurement of two samples prepared by each technique.

To extract the orientation parameter $\Theta$ from the measured angular dependent photoluminescence spectra, a cross section at the peak wavelength was analyzed by optical simulation. To improve the quality, measured values were averaged over a small...
Figure 3. Sketch of the model, which explains the different orientation in the evaporated and solution processed layers, using CBP (a) and Ir(ppy)$_2$(acac) (b) as an exemplary guest–host system. (c) Orientation process during thermal evaporation, where the molecules are deposited step-by-step. The aliphatic acetylacetonate group is highlighted in red together with the symmetry axis (C$_2$) pointing from the Iridium central atom to this group. The C$_2$ axis orients perpendicular to the aromatic surface in the direction of the vacuum. (d) Sample preparation from solution by spin coating. The molecules (i.e., the C$_2$ symmetry axis) do not align in a predominant direction in the solvent. This random behavior is conserved during the film drying process and thereby the deposited film shows isotropic orientation.

wavelength range (±3 nm to the peak intensity) and 1−3 different samples. The resulting angular dependent emission pattern was used for fitting, the standard deviation of these values was used as measurement error. Figure 1c shows the simulated angular dependent emission spectra for selected orientations of the TDVs together with measurements and the corresponding fits.

Note that the simulation of isotropic host materials is based on the model by Barnes et al.$^{10}$ whereas the calculation taking into account the presence of anisotropic media was performed following the approach by Penninck et al.$^{11}$ A detailed description of the optical models behind the numerical simulation tool used for the following investigations is given in refs 12 and 13. The calculation of the emitted light intensity depends on the outcoupling angle and therefore uses the layer thickness, optical constants, wavelength and dipole orientation of the emitting molecules as input parameters.

Four different emissive Ir-complexes were doped into a variety of host materials and were deposited by evaporation and from solution. The materials NPB and CBP were chosen as common host materials for the investigated phosphors. PMMA and Spiro2-CBP were selected due to their higher glass transition temperatures to suppress crystallization in the films deposited by spin coating. All investigated heteroleptic emissive dopants (Ir(mdq)$_2$(acac), Ir(piq)$_2$(acac) and Ir(ppy)$_2$(acac)) contain one acetylacetonate (acac) ligand and show net horizontal alignment of the TDVs in evaporated films.$^{1,5,7,9}$ Ir(ppy)$_3$ shows no preferred alignment in evaporated systems.$^{7,14}$ The results for all analyzed guest–host systems are summarized in Figure 2. Full orientation fits can be found in the Supporting Information.

All investigated Ir-complexes show the orientation expected from literature in samples fabricated by thermal evaporation.$^{1,5,7,14}$ The emissive molecules containing an acetylacetonate (acac) group exhibit predominantly horizontal alignment, whereas the homoleptic complex Ir(ppy)$_3$ shows no preferred orientation. The comparison between the different host materials indicates no dependency of the anisotropy factor Θ on the higher glass transition temperature of Spiro2-CBP. Earlier reported mechanisms for the orientation process of guest molecules propose increased alignment of the TDVs for high glass transition temperatures of the matrix material, if the guest and host molecules have comparable masses. This would lead to more horizontal orientation in films using Spiro2-CBP as the host material.$^{12}$ However, in the investigated films the mass of the Ir-complex is much higher compared to the matrix material and this model cannot be applied.

The horizontal alignment of the heteroleptic complexes is governed by the deposition process, as none of the samples fabricated from solution developed this kind of preferred orientation. Comparison of the equivalent values measured for solution processed films of the normally horizontally oriented Ir(ppy)$_2$(acac) and the always isotropic Ir(ppy)$_3$ species demonstrates that orientation in solution processed films is not influenced by molecular symmetry of the phosphorescent dopant. A similar effect has been observed for the orientation of differently shaped fluorescent molecules in neat layers.$^{7,11}$

Furthermore, the orientation for solution processed samples is slightly influenced by the host material. Films of CBP as matrix material doped with either Ir(ppy)$_3$ or Ir(ppy)$_2$(acac) show slightly vertical alignment. This kind of orientation is not favorable, as it would decrease the outcoupling efficiency in OLEDs.

Because of the absence of this effect in PMMA and Spiro2-CBP, it can be connected to crystallization processes. Such effects have been reported for CBP at room temperature and for NPB based layers at 50 °C.$^{17,18}$ Furthermore, the crystallization could be enhanced by solvent residues in the layer after the spin coating process, which could cause “solvent vapor annealing”. This effect is known to activate or increase the crystallinity in other organic thin films.$^{20}$ Although the influence of these effects on the orientation of TDVs is not yet clarified, the investigated samples show a trend to vertical alignment in the presence of crystallization processes. This could possibly be enhanced by post annealing treatments below the glass transition temperature of the host material, which were not investigated in this work.

The significant dependency of the horizontal alignment of the heteroleptic phosphors on the fabrication process can be
explained by the formation of an interface between the aromatic matrix and vacuum during the sample preparation by evaporation. This interface is not present during the spin coating process, thus the alignment of the emissive Ir-complexes is disabled in these samples. Figure 3 illustrates this process.

**CONCLUSION**

In summary, the orientation of four different iridium complexes doped into a range of host materials was compared in solution processed and evaporated layers. All of the evaporated heteroleptic iridium complexes develop predominantly horizontal orientation in the matrix material, whereas the solution processed layers show nearly isotropic or slightly vertical orientation. The isotropic orientation of the TDVs is explained due to the missing interface between the aromatic matrix material and vacuum during the liquid-phase fabrication process. However, the slightly vertical orientation in some emission layers still needs further investigation, but could be tentatively assumed to originate from a matrix effect. Having High Quantum Yield and Horizontal Orientation of Transition Dipole Moments. Adv. Funct. Mater. 2013, 23, 3896–3900.

**ASSOCIATED CONTENT**

1. Supporting Information
   The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.1b04607.

   Measured angular dependent emission patterns for all phosphorescent guest–host systems together with fits and error margins of the extracted orientation parameters (PDF).

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**REFERENCES**


