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Orientation of emissive dipoles in OLEDs: Quantitative *in situ* analysis

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ABSTRACT

The orientation of the emissive dipole moments in organic light-emitting diodes (OLEDs) has a major impact on the optical outcoupling efficiency and, consequently, on the device performance as well as on possible optimization strategies. In this study we propose and demonstrate a general method to quantify the amounts of parallel and perpendicular emissive sites in OLEDs. The presented *in situ*-method is based on measurements of the far-field emission of an electrically operating device and corresponding optical reverse simulations. A well adapted OLED stack is utilized, where the contribution of perpendicularly oriented dipoles to the radiation pattern in air is optically enhanced. Additionally, for the reverse simulation we take advantage of the fact that perpendicular dipoles do contribute to transverse-magnetic polarized light emission only. We apply the method to a polymeric OLED and show that the radiation pattern is generated by 93.5% parallel and 6.5 % perpendicular dipoles. Assuming a Gaussian distribution of dipole orientations, the dipoles stagger around the preferred parallel direction with an 1/e-angle of ±22°.

1. Introduction

Optical modeling and optimization of organic light-emitting diodes (OLEDs) require a general understanding of the emission and propagation of light within multilayer systems. Besides the *passive* optical properties of the layered system (material refractive indices and layer thicknesses), the *active* optical properties of the emissive material (like internal electroluminescence (EL) spectrum, profile of the emission zone and orientation of the transition dipole moments) strongly affect the radiation pattern (i.e. the angular distribution, the polarization, and the spectrum of the emission) as well as the overall device efficiency. While material dispersions and thin film thicknesses can be measured by e.g. standard spectroscopic methods [1], the *active* properties of the light-emitting material are difficult to access. However, our aim is to determine the optical features of the internal emission *in situ* by measurements of the far-field emission pattern generated by active OLEDs (i.e. in electrical operation) and corresponding reverse simulations. Recently, we presented methods to investigate the profile of the emission zone [2] and the internal luminescence quantum efficiency q [3] in electrically operated devices. In the current study, we introduce and demonstrate a method to determine the orientation of the emissive sites, in order to take a further step towards complete optical *in situ* characterization of OLEDs.

In OLEDs, the electroluminescent emissive process can be considered as a dipole transition from an excited molecular state into the ground state, where the emissive dipole transition moment has a certain orientation with respect to the surrounding layered system [4]. For the purpose of optical analysis, the classical emission pattern of an arbitrarily oriented dipole can be decomposed into contributions of three orthogonal dipoles (||TE, ||TM, ⊥TM) [5], as illustrated in Fig. 1. These orthogonal dipoles are specified according to their orientation with respect to the interfaces of the layered system (parallel "||", perpendicular "⊥") and

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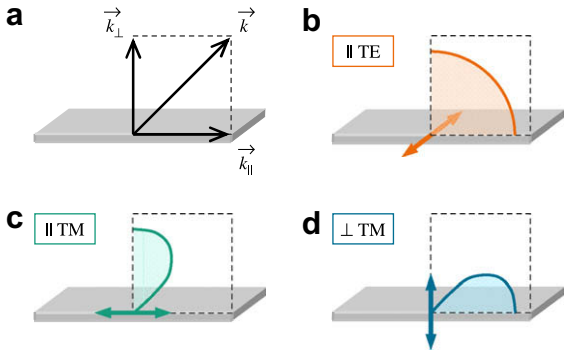

Fig. 1. (a) The wave-vector k (representing the direction of observation or measurement) and its two components in the directions parallel ($k_{||}$) and perpendicular ($k_{\perp}$) to the interfaces of the layered system are shown. The orientations of the dipole transition moments (arrows) of the three orthogonal dipoles ||TE (b), ||TM (c), and ⊥TM (d), with respect to the layered system are also illustrated. The indicated schematics of the internal radiation patterns of the dipoles correspond to those in the homogenous, infinite emissive material and are distorted in the presence of the interfaces of the layered system.

the corresponding polarization of the emitted radiation (transverse-electric "TE", transverse-magnetic "TM"); the direction of measurement or observation is represented by the wave-vector k [see Fig. 1 (a)].

Two major effects need to be pointed out when discussing the relevance of the emitter orientation in OLEDs: First, perpendicularly oriented active sites emit most power in the direction parallel to the interfaces [see Fig. 1(d)], and not in the desired perpendicular direction. Second, different interference conditions with the surrounding multilayer system apply to the fields of the three basic orthogonal dipoles. Consequently, the orientation of the emissive sites in the light-emitting material has a major impact on the device performance and overall efficiency [6,7]. Most common and optimized OLEDs stacks are designed in order to enhance the emission of parallel dipoles as this allows extracting most power to the outside medium air. This optimized stack architecture tends to trap almost all light generated by perpendicularly oriented dipoles inside the layered system or the substrate glass. As s result, the optical outcoupling efficiency for emitters with isotropic orientation is ~1/3 lower than for exclusively parallel oriented emitters. In the past, the external quantum efficiency (EQE) of devices was frequently used as a starting point to estimate internal properties of OLEDs such as the singlet-triplet generation ratio in the emissive material or the internal luminescence quantum efficiency q [6,8,9]. Because the orientation of the emissive sites strongly affects the optical outcoupling efficiency, it has to be known precisely for such estimates to be meaningful.

The orientation of the emissive sites in spontaneously emitting materials utilized in OLEDs is determined by the molecular morphology of the particular material. Considering *polymeric* materials deposited from solution by spin-coating, the polymer chains usually align in the plane of the film and the emissive sites tend to adopt this preferential orientation, as indicated by various photoluminescence (PL) and Raman studies [4,9–11]. Still, the chromophore could be attached to a polymer side-chain rather than to the backbone, which would cancel any orientation-correlation suggested from the spin-coating process. For a long time, vacuum deposited *small-molecule* materials were believed to have no preferred emitter orientation due to their rather isotropic, small molecular structure. Only recently, strong birefringence accompanied by a preferred parallel orientation of the transition dipole moments in vacuum deposited small molecular films was observed in PL investigations and attributed to the increased molecular length of the molecules [12].

In general, PL experiments suffer from the fact that the initially photo-generated excited states are not necessarily equal to those in EL operation [9]. Furthermore, the molecular orientation might depend on the exact deposition conditions and post-processing techniques [13]. Consequently, an *in situ* investigation of the orientation of the dipole transition moment in electrical operation is desirable.

In this study we propose and demonstrate a general method to determine the orientation of the emissive dipole moments in OLEDs *in situ* via optical characterization. The method is based on two main ideas. First, a special OLED stack is utilized, where the distance between the emissive sites and the metallic cathode is well adapted. Due to constructive interference, the contribution of perpendicularly oriented dipoles to the radiation pattern in air is optically enhanced. Second, these perpendicular dipoles contribute to TM polarized light emission only. Consequently, the TE polarized emission can be utilized to investigate the profile of the emission zone and the internal electroluminescence spectrum independent of the emitter orientation. Subsequently analyzing the radiation pattern with TM polarization allows quantifying the contributions form parallel and perpendicular emitters. In general, the method can be applied to all classes of emissive materials for OLEDs, including *small-molecule* and *dendrimer* materials. However, in the present study we apply it to a *polymeric* emitter material and show that the actual orientation of the emissive sites must be described by a superposition of both, parallel and perpendicular components.

2. Method

2.1. Optical modeling

The angular (θ, angle to the layered system normal) and spectral (λ, wavelength) radiation pattern of an emitter inside the OLED stack is simulated assuming a continuously oscillating dipole source [5]. The dipoles electromagnetic fields in the system are evaluated using a transfer-matrix formulation of the well known Green's function model by Chance et al. [14]. For further details on the generation of the dipole fields see Ref. [15] and references therein. In order to ensure normalization of the power emitted from the dipole in the layered system, we utilize the equivalence between the probability for spontaneous emission of a photon via a dipole transition and the radiated power of a classical dipole source in the corresponding layered system [5]. By this means, the so-called microcavity effect or rather the influence of OLED stack on the rate of emission can be regarded [3].