Full description of dipole orientation in organic light-emitting diodes

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Considerable progress has been made in organic light-emitting diodes (OLEDs) to achieve high external quantum efficiency, among which dipole orientation has a remarkable effect. In most cases, the radiation of the dipoles in OLEDs is theoretically predicted with only one orientation parameter to match with corresponding experiments. Here, we develop a new theory with three orientation parameters to fully describe the relationship between dipole orientation and power density. Furthermore, we design an optimal test structure for measuring all three orientation parameters. All three orientation parameters could be retrieved from non-polarized spectra. Our theory provides a universal plot of dipole orientations in OLEDs, paving the way for designing more complicated OLED devices.

Keywords: organic light-emitting diodes; dipole orientation; Fourier series expansion.

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1. Introduction

Since the first reports of organic light-emitting diodes (OLEDs) in 1987$^{[1]}$, their efficiency has been improved through finding novel phosphorescent materials$^{[2-10]}$, optimizing the thickness of each layer in OLEDs$^{[11-13]}$, etc. In recent years, dipole orientation has also been drawing significant attention for enhancing light extraction from OLEDs$^{[14-21]}$.

The theory of dipole radiation in OLEDs originated from applying the theory of electrical dipoles near an interface to the problem of molecules fluorescing near a surface$^{[22-29]}$. Related researches have been proposed to enhance the external quantum efficiency$^{[30]}$, in which the theory of the dipole orientation is developed. In previous theories, dipoles in OLEDs are decomposed into vertical dipoles and horizontal dipoles. Then, the power radiated from OLEDs is formed by weighting the power radiated by vertical dipoles and horizontal dipoles in a proportion. The weight, the ratio of vertical dipoles, can be regarded as a parameter describing the vertical orientations of the dipoles in OLEDs.

Recently, along with the OLED manufacturing progress increasingly, it is pointed out that a possible research direction of OLEDs in the future is to take advantage of the dipoles with non-uniform horizontal orientations$^{[31,32]}$. Some studies point out that the carrier mobility in films using the dipoles perfectly aligning in one direction is much higher than that of films using the dipoles with uniform orientations$^{[33,34]}$. At the same time, other researchers show that OLEDs with dipoles aligning in one direction can achieve the emission of linearly-polarized light. Then, the application of OLEDs directly emitting orthogonally circularly-polarized light could be realized by letting the linearly-polarized light pass through a quarter-wave plate formed by the liquid crystal$^{[35]}$. Therefore, the non-uniform horizontal dipole orientation is of great significance for external quantum efficiency, as well as polarization. However, previous works have so far only considered the dipoles in OLEDs with non-uniform vertical orientations and lack of the description of the horizontal component.

Here, we develop a theory that fully describes the dipole orientation and its relationship with power density. Compared with the previous theory, we start from a dipole and consider an orientation distribution function, expressed as a Fourier series, to extend the power density of a dipole to the power density of the dipoles in OLEDs. Theoretically, it is the first time, to the best of
our knowledge, to strictly prove that only three orientation parameters are needed to fully describe the effect of dipole orientation on the power density and extend previous orientation parameters. Two parameters describe the ratios of the \( x \) component and \( z \) component of the dipoles. One parameter describes the coupling effect between the \( x \) component and \( z \) component of the dipoles. Finally, by using optical simulation, we design an optimal structure for extracting these three orientation parameters and present different spectra corresponding to different orientation parameters for the test structure. Then, we extract the orientation parameters for the designed optimal structure and compare them with the ground truth to verify our orientation theory.

2. Methods

2.1. Power density of a dipole in OLEDs

For the multi-layer model shown in Fig. 1(a), the emitting layer with refractive index \( n_0 \) and thickness \( h_0 \) is located between two stacks of layers. These layers have refractive indices \( n_{1,0}, n_{2,0}, \ldots \) and thicknesses \( h_{1,0}, h_{2,0}, \ldots \). The upper and lower half-infinite spaces are labeled as ±. The dipoles are located in the middle of layer 0 with a distance \( h_{0,1} \) from the interface at the ± side of the layers. OLEDs, therefore, can be simplified to multi-layer films. Energy reflection and transmission coefficients of multi-layer films are given by

\[
\begin{align*}
R_{x}^{s,p} &= |r^{s,p}_{x}|^2 \\
T_{x}^{s} &= |t^{s}_{x}|^2 \frac{k_{x}}{k_{0}} \quad \text{for all cases,} \\
T_{z}^{s} &= |t^{s}_{z}|^2 \frac{n_{z}}{n_{0}} \frac{k_{z}}{k_{0}} \quad \text{for } \text{Im}(k_{x,z}) = 0, \\
T_{z}^{p} &= 0 \quad \text{for } \text{Im}(k_{x,z}) \neq 0.
\end{align*}
\]

\( r^{s,p}_{x}, t^{s,p}_{x} \) are Fresnel reflection and transmission coefficients, as shown in Fig. 1(b), which could be calculated through recursive matrix algorithms\(^{[36,37]}\). These coefficients with subscripts ± represent the reflection and transmission coefficients from the emitting layer (layer 0) to the ± half-infinite space. \( k_{0} \) and \( k_{x,z} \) are the horizontal \( x \) and \( z \) component of the wave vector \( k \) in the ± half-infinite space. With the use of the superposition of plane waves, the power \( W_{z} \) radiated to the half-infinite space ± can be written as an integral:

\[
W_{z} = \int_{0}^{+\infty} K_{s} d\mathbf{k}_{1}^{z},
\]

where \( K_{s} \) is the power density of a dipole per unit \( d\mathbf{k}_{1}^{z} \). Based on the polarity, the power density \( K_{s} \) can be separated into \( s \)-polarized power density \( K_{s}^{s} \) and \( p \)-polarized power density \( K_{s}^{p} \):

\[
K_{s} = K_{s}^{s} + K_{s}^{p}. \quad (3)
\]

For a dipole in the emitting layer with orientation \((\theta, \phi)\), as shown in Fig. 1(c) upper panel, the \( s \)-polarized and \( p \)-polarized power densities radiated to the ± half-infinite space in the \( x-z \) plane per unit \( d\mathbf{k}_{1}^{z} \) have an angular dependence and are related to its dipole orientation\(^{[26,28]}\):

\[
\begin{align*}
K_{s}^{s} &= \frac{3}{8} \frac{k_{z}}{k_{0}} \left| 1 + r_{s}^{z} \right| \left( 2 j k_{z} h_{0,z} \right) \frac{T_{s}^{z}}{T_{p}^{z}} \sin^{2}(\theta) \sin^{2}(\phi), \\
K_{s}^{p} &= \frac{3}{8} \frac{k_{z}}{k_{0}} \left| 1 + r_{p}^{z} \right| \left( 2 j k_{z} h_{0,z} \right) \frac{T_{s}^{z}}{T_{p}^{z}} \cos^{2}(\theta) \\
&+ \frac{3}{8} \frac{k_{z}}{k_{0}} \left| 1 - r_{s}^{z} \right| \left( 2 j k_{z} h_{0,z} \right) \frac{T_{s}^{z}}{T_{p}^{z}} \sin^{2}(\theta) \cos^{2}(\phi) \\
&+ \frac{3}{8} \frac{k_{z}}{k_{0}} \left| 1 - r_{p}^{z} \right| \left( 2 j k_{z} h_{0,z} \right) \frac{T_{s}^{z}}{T_{p}^{z}} \sin(\theta) \sin(\phi).
\end{align*}
\]

For an emission angle \( \alpha \), the angle between the \( z \) axis and the detector (observer) in the ± half-infinite space, the power density \( K_{s} \) per unit \( d\mathbf{k}_{1}^{z} \) can be transformed to the power density \( P_{s} \) per solid angle, given by

\[
P_{s} = \frac{k_{s}^{2}}{\pi} K_{s}.
\]

2.2. Power density of the dipoles in OLEDs

For dipole orientations in OLEDs shown in Fig. 1(c) lower panel, we can use an orientation distribution function \( F(\theta, \phi) \) to describe them. Multiplied with the orientation distribution function and then integrated over the sphere with the polar angle \( \theta \) and azimuth angle \( \phi \), the power density of a dipole \( P_{s} \) can be used to describe the dipoles in OLEDs:

\[
P_{s} = \int_{0}^{\pi/2} d\phi \int_{0}^{\pi} d\theta P_{s} \times F(\theta, \phi),
\]

where \( P_{s} \) is the power density of the dipoles in OLEDs, related to the emission angle \( \alpha \) and the dipole orientations.

By using the Fourier series expansion, the orientation distribution function \( F(\theta, \phi) \) could be expanded into the Fourier series:

![Fig. 1. (a) Multi-layer films for modeling OLEDs. (b) Energy reflection and transmission coefficients of multi-layer films. (c) Upper panel: the orientation of a dipole. Lower panel: dipole orientations in layer 0.](Image)
\[ F(\theta, \phi) = \sum_{l,m=1}^{\infty} \lambda_{lm} a_{lm} \cos(2l\theta) \cos(m\phi) + b_{lm} \cos(2l\theta) \sin(m\phi) + c_{lm} \sin(2l\theta) \cos(m\phi) + d_{lm} \sin(2l\theta) \sin(m\phi), \quad (7) \]

with
\[ \lambda_{lm} = \begin{cases} 1 & \text{for } l = 0, m = 0, \\ \frac{1}{2} & \text{for } l = 0, m \neq 0 \text{ or } l \neq 0, m = 0, \\ 1 & \text{for } l \neq 0, m \neq 0. \end{cases} \quad (8) \]

Coefficients \( a_{lm}, b_{lm}, c_{lm}, \) and \( d_{lm} \) are given by
\[ a_{lm} = \frac{2}{\pi^2} \int_{0}^{\pi} \int_{0}^{\pi} F(\theta, \phi) \cos(2l\theta) \cos(m\phi) \, d\theta \, d\phi, \]
\[ b_{lm} = \frac{2}{\pi^2} \int_{0}^{\pi} \int_{0}^{\pi} F(\theta, \phi) \cos(2l\theta) \sin(m\phi) \, d\theta \, d\phi, \]
\[ c_{lm} = \frac{2}{\pi^2} \int_{0}^{\pi} \int_{0}^{\pi} F(\theta, \phi) \sin(2l\theta) \cos(m\phi) \, d\theta \, d\phi, \]
\[ d_{lm} = \frac{2}{\pi^2} \int_{0}^{\pi} \int_{0}^{\pi} F(\theta, \phi) \sin(2l\theta) \sin(m\phi) \, d\theta \, d\phi. \quad (9) \]

Then, the orientation distribution function in the form of the Fourier series is substituted into Eq. (6). Due to the angular dependence relation of the power density of a dipole, as shown in Eq. (4), and also because the integral values of the product of two orthogonal trigonometric functions are all zero, only four Fourier components and coefficients are left among these integrations of the Fourier series. The orientation distribution function can be simplified to the orientation distribution function with four Fourier coefficients, given by
\[ F(\theta, \phi) = \frac{1}{2\pi^2} + \frac{1}{2} a_{1,0} \cos(2\theta) + \frac{1}{2} a_{0,2} \cos(2\phi) + c_{1,1} \sin(2\theta) \cos(\phi) + a_{1,2} \cos(2\theta) \cos(2\phi). \quad (10) \]

The power density per solid angle of the dipoles in OLEDs, for an emission angle \( a \) in the \( \pm \) half-infinite space, can be written in the form of Fourier coefficients \( a_{1,0}, a_{0,2}, c_{1,1}, \) and \( a_{1,2}, \) and different components of the power density \( \tilde{F}_1, \tilde{F}_0, \tilde{P}_1, \tilde{P}_0, \) and \( \tilde{P}_3: \)
\[ \tilde{P}_z = \tilde{P}_z \times \frac{\pi^2}{8} \left( \frac{2}{\pi^2} - a_{1,0} - (a_{0,2} - a_{1,2}) \right) \]
\[ + \tilde{P}_z \cos(a) \times \frac{3}{8} k_{\parallel} k_{\perp} |1 - r_{\parallel} r_{\perp} \exp(2j k_{\parallel} h_{\perp})|^2 T_\parallel, \]
\[ \tilde{P}_z \cos(a) \times \frac{3}{8} k_{\parallel} k_{\perp} |1 - r_{\parallel} r_{\perp} \exp(2j k_{\parallel} h_{\perp})|^2 T_\parallel, \]
\[ + \tilde{P}_z \cos(a) \times \frac{3}{8} k_{\parallel} k_{\perp} |1 - r_{\parallel} r_{\perp} \exp(2j k_{\parallel} h_{\perp})|^2 T_\parallel, \]
\[ + \frac{\pi^2}{2} c_{1,1}, \quad (11) \]

with
\[ \tilde{P}_z = \tilde{P}_z \times \frac{\pi^2}{8} \left( \frac{2}{\pi^2} - a_{1,0} - (a_{0,2} - a_{1,2}) \right) \]
\[ + \tilde{P}_z \cos(a) \times \frac{3}{8} k_{\parallel} k_{\perp} |1 - r_{\parallel} r_{\perp} \exp(2j k_{\parallel} h_{\perp})|^2 T_\parallel, \]
\[ \tilde{P}_z \cos(a) \times \frac{3}{8} k_{\parallel} k_{\perp} |1 - r_{\parallel} r_{\perp} \exp(2j k_{\parallel} h_{\perp})|^2 T_\parallel, \]
\[ + \frac{\pi^2}{8} c_{1,1}. \quad (12) \]

3. Results

3.1 Orientation parameters

The power density \( \tilde{P}_z \) in Eq. (11) is adjusted by three independent parameters \( a_{1,0}, a_{0,2} - a_{1,2}, c_{1,1}, \) indicating that only three orientation parameters are needed for a full description of dipole orientations in OLEDs. Therefore, three orientation parameters should be defined based on four Fourier coefficients \( a_{1,0}, a_{0,2}, a_{1,2}, \) and \( c_{1,1}. \)

Here, we define the orientation parameters \( v_x, v_z, \) and \( v_{xz}, \) where \( v_x \) represents the ratio of the \( x \) component of the emitting dipoles, \( v_z \) represents the ratio of the \( z \) component of the emitting dipoles, and \( v_{xz} \) represents the coupling effect between the \( x \) component and \( z \) component of the emitting dipoles, given by
\[ v_x = \frac{\pi^2}{8} \left( \frac{2}{\pi^2} - a_{1,0} + (a_{0,2} - a_{1,2}) \right), \]
\[ v_z = \frac{\pi^2}{4} \left( \frac{2}{\pi^2} + a_{1,0} \right), \]
\[ v_{xz} = \frac{\pi^2}{2} c_{1,1}. \quad (13) \]

Thus, the power density of the dipoles in OLEDs could be written in a form of orientation parameters \( v_x, v_z, \) and \( v_{xz}, \) and different components of the power density \( \tilde{P}_z, \tilde{P}_0, \tilde{P}_0, \) and \( \tilde{P}_3: \)
\[ \tilde{P}_z = \tilde{P}_z \times (1 - v_x - v_z) + \tilde{P}_z \times v_x + \tilde{P}_z \times v_z + \tilde{P}_3 \times v_{xz}, \quad (14) \]
where $1 - v_x - v_z$ represents the ratio of the $y$ component of the emitting dipoles.

In the case that there are $N$ possible dipole orientations in OLEDs represented by $(\theta, \phi)$ and the corresponding dipole vectors are $\mathbf{v}_i$, the orientation distribution function reads

$$F(\theta, \phi) = \frac{1}{N} \sum_{i=1}^{N} \delta(\mathbf{v} - \mathbf{v}_i) \sin(\theta) = \frac{1}{N} \sum_{i=1}^{N} \delta(\theta - \theta_i) \delta(\phi - \phi_i). \quad (15)$$

Considering Eqs. (13) and (9), the orientation parameters $v_x$, $v_z$, $v_{xz}$ of $N$ dipoles could be obtained:

$$v_x = \frac{1}{N} \sum_{i=1}^{N} \sin^2(\theta_i) \cos^2(\phi_i),$$
$$v_z = \frac{1}{N} \sum_{i=1}^{N} \cos^2(\theta_i),$$
$$v_{xz} = \frac{1}{N} \sum_{i=1}^{N} \sin(2\theta_i) \cos(\phi_i). \quad (16)$$

Equation (16) verifies the physical meaning of the orientation parameters $v_x$, $v_z$, and $v_{xz}$. As shown in Figs. 1(c) and 2, dipoles are decomposed along the $x$, $y$, and $z$ axes. $\sin(\theta_i) \cos(\phi_i)$ represents the ratio of the $x$ component of the emitting dipoles, ranging from 0 to 1, $\cos(\theta_i) \cos(\phi_i)$ represents the ratio of the $y$ component of the emitting dipoles, ranging from 0 to 1, and $\sin(\theta_i) \cos(\phi_i)$ represents the coupling effect between the $x$ component and $y$ component of the emitting dipoles ranging from $-1$ to 1. Also, Eq. (16) provides a simple form for calculating the orientation parameters.

### 3.2. Structure design

To extract the orientation parameters of the dipoles in OLEDs, non-polarized spectra should be used, and different components of the power density $\widetilde{P}_x$, $\widetilde{P}_y$, $\widetilde{P}_z$, and $\widetilde{P}_{xy}$ are supposed to be adjusted in different shapes but in the same order of magnitude, as suggested by Eq. (14). Therefore, an optimal test structure should be carefully designed for extracting the orientation parameters $v_x$, $v_z$, and $v_{xz}$. We consider a test structure, as shown in Fig. 3 (left panel). An organic thin film is evaporated on the glass substrate, whose thickness is $h_0$. ($h_0$ should be chosen for adjusting different components of the power density.) The dipoles are doped in the middle of the emitting layer. The refractive indices of the glass substrate and organic thin film are 1.524 and 1.72, respectively, and the emission wavelength is 500 nm. By using a hemispherical prism along the glass substrate side and measuring the power density radiated into the glass substrate at different angles, the intensity changing with respect to the emission angle could be obtained. Then, the intensity of the spectra at normal direction (0 deg) is normalized to one.

Without selecting the appropriate thickness of the organic layer, the spectra with different orientations only have a slight difference, as shown in Fig. 3 (right panel). It is hard to extract all of the orientation parameters from them.

By adjusting the thickness of organic thin film $h_0$, different components of the power density $\widetilde{P}_x$, $\widetilde{P}_y$, $\widetilde{P}_z$, and $\widetilde{P}_{xy}$ could be balanced in the same order of magnitude but in different shapes with the help of the interference effect of the micro-cavity, as shown in Fig. 4. When the thickness of organic layer $h_0$ is nearly 160 nm, all four components have a significant impact on the power density $\widetilde{P}_z$, compared with the component $\widetilde{P}_{xy}$ being much stronger than others when thickness $h_0 = 20$ nm. Note that extracting orientation parameters of the structure with $h_0$ = 20 nm is also possible, but the $s$-polarized spectrum and $p$-polarized spectrum should be measured separately, and a high dynamic range detector should be used. Finally, we design an optical test structure with the thickness of organic layer $h_0$ = 160 nm, in which three orientation parameters could be measured precisely.

Non-polarized spectra with different orientation parameters, when the thickness of the organic layer is 160 nm, are shown in Fig. 5. These simulated results show that the orientation parameters proposed in our theory do cause significant difference on the spectra and could be used for extracting orientation parameters from the spectra. Here, we further explain these differences of each orientation parameter from the perspective of the dipole radiation pattern, showing the consistence with our dipole orientation theory. For an electric dipole, it hardly radiates along the direction of its dipole vector, as the orientation of the dipole vector tends to be parallel to the $z$ axis ($v_z$ increases), and its intensity along the $z$ axis 0 deg emission angle becomes weak. Thus, the normalized non-polarized spectra have stronger intensities at large emission angles, as illustrated in Fig. 5 (red lines). When the orientation of the dipole vector is parallel to the $x$ axis ($v_x$ increases), the normalized non-polarized spectra have weaker intensities at large emission angles, shown in Fig. 5 (yellow lines). When the total internal reflection occurs at the interface between the air layer and the emitting layer, the distribution parameter $v_{xz}$, describing the coupling effect, has no
effect on the power density, as shown in Eq. (12). The distribution parameter $v_x$, $v_z$, only affects intensities where the emission angle is smaller than the total internal reflection angle, as illustrated in Fig. 5 (blue lines).

### 3.3. Parameter retrieval

We simulated radiation of 1000 dipoles with different orientations in the test structure ($h_0 = 160$ nm), obtained their radiation spectrum, and calculated their four Fourier components and orientation parameters, as shown in Fig. 6(a). Then, Gaussian noise is added into the radiation spectrum to imitate the experimental noise in reality. We retrieve the parameters from the radiation spectra, whose orientation parameters are already known as ground truth to validate the parameter extraction of our theory. In the retrieval process, random orientation parameters are chosen as an initial guess, as shown in Fig. 6(b) (gray line). The least squares algorithm (Levenberg–Marquardt algorithm) is used for fitting and extracting. The final fitting
4. Conclusions

By introducing an orientation distribution function to extend the power density of a dipole to the power density of the dipoles in OLEDs, it is the first time, to the best of our knowledge, to strictly prove that only three orientation parameters are needed to fully describe the relationship between the dipole orientations and the power density. These three orientation parameters could adjust the ratio of different components of the power density. Therefore, the orientation parameter can be extracted from the power density of the dipoles in OLEDs.

We design a test structure with the thickness of organic layer $h_0 = 160$ nm for extracting the three orientation parameters. Then, we retrieve the orientation parameters from the non-polarized spectrum to verify the capability and experimental feasibility. With the improvement of OLED manufacturing technology, more precise control of the dipole orientations in OLEDs is required. Our method, fully describing the dipole orientations in OLEDs, thereby provides guidance for OLED manufacturing technology.

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