Simple model-free estimation of orientation order parameters of vacuum-deposited and spin-coated amorphous films used in organic light-emitting diodes

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Supplementary Information

1. Derivation of the equations

As shown in the main text, the orientation order parameter (S) in this study is defined by Eq. (1):¹,⁷,¹⁸,¹⁹)

\[ S = \frac{3\langle \cos^2 \theta \rangle - 1}{2}, \]

(1)

where \( \langle \ldots \rangle \) indicates the ensemble average of all molecules in the film, and \( \theta \) is the angle between the transition dipole moment for light absorption of a molecule and the surface normal (the polar angle of the transition dipole moment). For a film, \( S = -0.5 \) if the transition dipole moments are completely horizontal to the substrate surface, \( S = 0 \) if...
they are randomly oriented, and $S = 1$ if they are completely vertical. It should also be noted that the absolute $S$ value can be small when molecules adopt a specific oblique angle of orientation (becomes zero at the magic angle of $\theta = 54.7^\circ$), though this is an improbable case for amorphous films.

Light absorption by a molecule is generally proportional to $\cos^2 \psi$, where $\psi$ is the angle between the transition dipole moment and the electric field of light. Thus, the absorbance of a film $A$ is proportional to $\langle \cos^2 \psi \rangle$;

$$A = A_0 \langle \cos^2 \psi \rangle,$$

where $A_0$ is the proportional constant. When we assume a hypothetical case that the transition dipole moments of all molecules are completely parallel to the electric field of the incident light ($\psi = 0^\circ$), $A$ is equal to $A_0$. Thus, the proportional constant $A_0$ represents the absorbance in this hypothetical case.

In the measurement of absorption spectra using a spectrophotometer, the electric field of the incident light is horizontal to the substrate surface. Without loss of generality, we can define its azimuthal angle as $0^\circ$. By defining the azimuthal angle of the transition dipole moment as $\varphi$ (see Fig. S1), we can represent $\cos \psi$ using $\theta$ and $\varphi$;

$$\cos \psi = \sin \theta \cos \varphi.$$
Then, we define the angular distribution of the transition dipole moment as \( f(\theta) \). Here, we assume that the angular distribution is independent of \( \phi \), which means that molecular orientation in films is two-dimensionally isotropic in the in-plane directions. Using the above equations and definitions, we can represent \( A \) as follows;

\[
A = A_0 \frac{\int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi f(\theta) \cos^2 \psi}{\int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi f(\theta)} = \frac{A_0}{2} \frac{\int_0^\pi d\theta \sin \theta \cdot f(\theta) \sin^2 \theta}{\int_0^\pi d\theta \sin \theta f(\theta)}, \quad \text{(iii)}
\]

which corresponds to Eq. (2) in the main text;

\[
A = \frac{A_0}{2} \left\langle \sin^2 \theta \right\rangle. \quad \text{(2)}
\]

When molecules are randomly oriented, which means that \( f(\theta) \) is constant, we can calculate Eq. (iii) and obtain Eq. (3);

\[
A_{iso} = \frac{A_0}{3}. \quad \text{(3)}
\]

Dividing Eq. (2) by Eq. (3), we can eliminate the unknown \( A_0 \);

\[
\frac{A}{A_{iso}} = \frac{3}{2} \left\langle \sin^2 \theta \right\rangle = \frac{3}{2} - \frac{3}{2} \left\langle \cos^2 \theta \right\rangle. \quad \text{(iv)}
\]

Finally, we can obtain Eq. (4) from Eqs. (1) and (iv) by eliminating \( \left\langle \cos^2 \theta \right\rangle \);

\[
S = 1 - \frac{A}{A_{iso}}. \quad \text{(4)}
\]

2. Transition dipole moments

We calculated the transition dipole moments of the molecules used in this study by time-dependent density functional theory (TD-DFT) calculations. After surveying stable
conformation structures by molecular mechanics calculations in free space using an MMFF94s force field, we selected one of the most stable conformation structures for each molecule. Then, we further optimized it more accurately by DFT B3LYP/6-31G(d) calculation and obtained the transition dipole moments by TD-DFT B3LYP/6-311+G(d,p) calculation using Gaussian 09.

Figure S2 shows the molecular structures and their transition dipole moments corresponding to the absorption bands used for the estimation of $S$. The transition dipole moments are nearly along the long molecular axis for TPD, $\alpha$-NPD, TPT1, and TSBF, and nearly parallel to the molecular plane of the central triphenylamine for 2-TNATA. It should be noted that these stable molecular structures are not unique for each molecule because molecules of most amorphous organic materials have various conformation structures (for example, $\alpha$-NPD have 12 conformers). Although we just selected one of the most stable structures, we can expect that the difference of conformation structures does not significantly affect the assignment of transition dipole moments.

**Fig. S2.** Molecular structures optimized by DFT B3LYP/6-31G(d) calculation and their transition dipole moments corresponding to the absorption bands used for the estimation of $S$ obtained by TD-DFT B3LYP/6-311+G(d,p) calculation.
3. Comparison with VASE

Figure S3 shows the anisotropic refractive indices and extinction coefficients of the 100-nm-thick vacuum-deposited films before annealing, which were obtained by VASE analysis using the films on Si(100) substrates. From these results, we can estimate the $S$ values using the following equation,$^{1,7,18,19}$

$$S = \frac{k_e - k_o}{k_e + 2k_o},$$

where $k_o$ and $k_e$ are the extinction coefficients in the horizontal and vertical directions, respectively. The obtained $S$ values are summarized in Table I in the main text.

![Graph](image)

**Fig. S3.** Anisotropic refractive indices and extinction coefficients of the 100-nm-thick as-prepared vacuum-deposited films before annealing obtained by VASE analysis. The red solid and dashed lines show the refractive indices in the horizontal and vertical directions ($n_o$ and $n_e$), respectively. The blue solid and dashed lines show the extinction coefficients in the horizontal and vertical directions ($k_o$ and $k_e$), respectively.

It should be mentioned that the $S$ values obtained by VASE in Table I are somewhat different from those reported in a past study.$^{25}$ This is because fused silica substrates were used for VASE analysis in that past report. For high accuracy of VASE analysis,
the choice of substrate is important because the errors of the optical constants of the underlying substrate affect the results of the analysis of the overlaying organic film. The optical constants of fused silica substrates depend on the fabrication process, and their transparency causes unwanted back-side reflection. Thus, it is much better to use Si(100) substrates for high accuracy of VASE analysis. Because the optical constants of single crystals of Si is unique, the results shown in Table I are more accurate than those in the past report.

In addition, to confirm the validity of our new method, we calculated $k_o$ and $k_e$ from the obtained absorbances $A$ and $A_{iso}$. The process of this calculation is as follows. First, $A_{iso}$ can be regarded as the average of the absorbances of an as-prepared film for horizontally and vertically polarized light;

$$A_{iso} = \frac{2A + A_{vert}}{3}, \quad (vi)$$

where $A_{vert}$ is the absorbance of the as-prepared film for vertically polarized light, which is hard to be measured experimentally. We also used the Lambert-Beer equation and the equation between absorption coefficient and extinction coefficient, which are shown below, respectively;

$$\frac{I}{I_0} = 10^{-A} = \exp(-\alpha_o d) \quad \quad \quad (vii)$$

$$\alpha_o = \frac{4\pi k_o}{\lambda}, \quad \quad \quad (viii)$$

where $I_0$ is the intensity of the incident light in the measurement of absorbance, $I$ is the intensity of its transmitted light, $\alpha_o$ is the absorption coefficient for horizontally polarized light, $d$ is the film thickness, and $\lambda$ is the wavelength of the incident light. The
similar equations can be used for vertically polarized light;

\[ 10^{-A_{\text{vert}}} = \exp(-\alpha_v d), \quad (ix) \]

\[ \alpha_v = \frac{4\pi k_v}{\lambda}, \quad (x) \]

where \( \alpha_v \) is the absorption coefficient for vertically polarized light. From Eqs. (vi)–(x), we can obtain the following two equations;

\[ k_v = \frac{\ln 10 \cdot \lambda}{4\pi d} A, \quad (xi) \]

\[ k_v = \frac{\ln 10 \cdot \lambda}{4\pi d} (3A_{\text{iso}} - 2A). \quad (xii) \]

Using Eqs. (xi) and (xii), we converted \( A \) and \( A_{\text{iso}} \) of 100-nm-thick vacuum-deposited films into \( k_v \) and \( k_v \). The obtained \( k_v \) and \( k_v \) values are shown in Fig. S4. They are qualitatively similar to those obtained by VASE shown in Fig. S3, demonstrating the validity of our new method.

**Fig. S4.** Anisotropic extinction coefficients of the 100-nm-thick as-prepared vacuum-deposited films before annealing calculated from the absorbances \( A \) and \( A_{\text{iso}} \) using Eqs. (xi) and (xii). The solid and dashed lines show the extinction coefficients in the horizontal and vertical directions (\( k_v \) and \( k_v \)), respectively.
Additional references for Supplementary Information

23) T. A. Halgren, J. Comput. Chem. 17, 490 (1996).

24) M. J. Frisch et al., Gaussian 09, Revision D.01 (Gaussian, Inc., Wallingford CT, 2009).

25) D. Yokoyama, A. Sakaguchi, M. Suzuki, and C. Adachi, Appl. Phys. Lett. 93, 173302 (2008).