

Process Engineered Spontaneous Orientation Polarization in Organic Light-Emitting Devices

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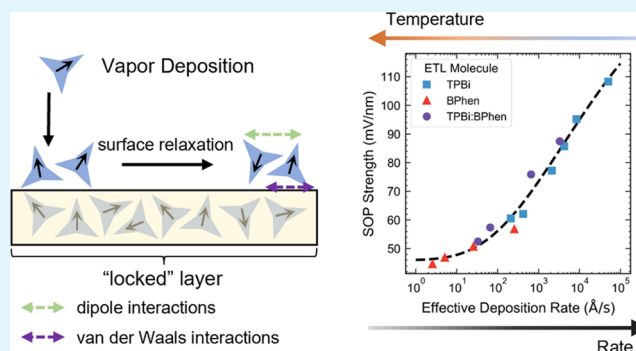
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ABSTRACT: Polar molecules with appreciable permanent dipole moments (PDMs) are widely used as the electron transport layer (ETL) in organic light-emitting devices (OLEDs). When the PDMs spontaneously align, a macroscopic polarization field can be observed, a phenomenon known as spontaneous orientation polarization (SOP). The presence of SOP in the ETL induces considerable surface potential and charge accumulation that is capable of quenching excitons and reducing device efficiency. While prior work has shown that the degree of SOP is sensitive to film processing conditions, this work considers SOP formation by quantitatively treating the vapor-deposited film as a supercooled glass, in analogy to prior work on birefringence in organic thin films. Importantly, the impact of varying thin-film deposition rate and relative temperature is unified into a single framework, providing a useful tool to predict the SOP formation efficiency for a polar material, as well as in blends of polar materials. Finally, *in situ* photoluminescence characterization and efficiency measurements reveal that SOP-induced exciton-polaron quenching can be reduced through an appropriate choice of processing conditions, leading to enhanced OLED efficiency.

KEYWORDS: organic light-emitting device, molecular orientation, spontaneous orientation polarization, excitons, exciton-polaron quenching



1. INTRODUCTION

Organic light-emitting devices (OLEDs) are widely used as displays in many state-of-the-art mobile phones, televisions, and wearable devices due to their high contrast and luminous efficiency, wide viewing angle, and mechanical flexibility.¹ While largely amorphous, the presence of collective molecular alignment makes many of these glassy organic thin films anisotropic.^{2,3} Indeed, manipulating molecular orientation is now a practical method to enhance OLED performance by aligning the emitter molecule transition dipole moment (TDM) in-plane to increase optical outcoupling.^{2,3} This favorable alignment has been realized by tuning the glass-transition temperature of the host,^{4,5} molecular shape of the emitter,^{6,7} and substrate temperature during deposition,⁸ leading to a 50% enhancement in optical outcoupling efficiency.^{9,10}

When the molecules comprising a film with preferential alignment also possess appreciable permanent dipole moment (PDM), an overall polarization field may develop, known as spontaneous orientation polarization (SOP).^{11,12} This phenomenon was first observed by Ito et al., where thin films of tris-(8-hydroxyquinolate) aluminum (Alq₃) exhibited a giant surface potential of >20 V.¹³ Past works have demonstrated the important impact of SOP on the performance of fluores-

cent,^{14–17} phosphorescent,^{18,19} and TADF OLEDs.²⁰ Our prior work has shown that when the electron transport layer (ETL) in a phosphorescent OLED exhibits SOP, the induced polarization charge leads to the accumulation of holes at the emissive layer (EML)–ETL interface. The accumulated hole density is large enough to quench 20–30% of the excitons via exciton-polaron quenching (EPQ), limiting peak device efficiency (Figure 1a).¹⁸

Prior work on birefringence in preferentially orientated organic thin films has considered the roles of deposition rate and substrate temperature in a unified rate–temperature superposition (RTS) framework, offering a useful tool to optimize processing.^{21–23} Optical birefringence originates from anisotropic molecular orientation,³ and the ability to treat its formation via RTS reflects the glassy nature of vapor-deposited thin films.²³ Since SOP also arises from anisotropy in molecular orientation,^{11,12,24} its rate and temperature depend-

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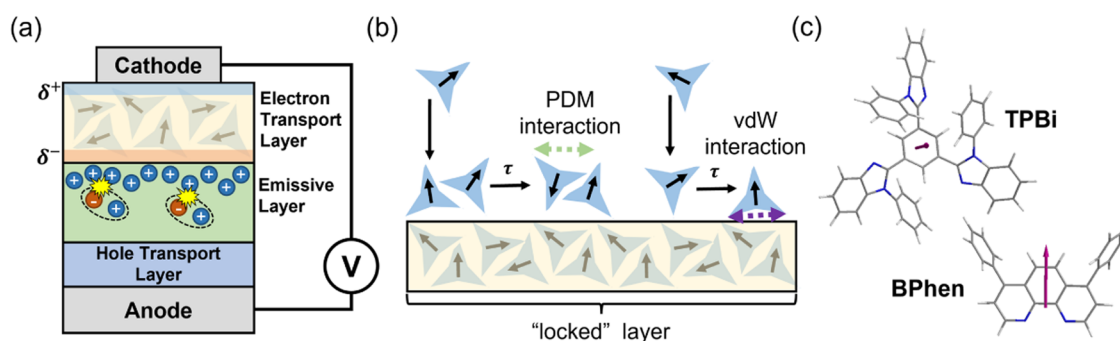


Figure 1. (a) Illustration of SOP-induced exciton-polaron quenching in an OLED. The electron transport layer exhibits SOP leading to the formation of polarization charge (denoted as δ^- and δ^+). In balancing the polarization charge, holes are accumulated in the emissive layer leading to quenching. (b) Illustration of the surface equilibrium mechanism. The equilibrium orientation of the polar molecules is mainly dominated by the dipole interaction between adjacent surface molecules. Polar surface molecules relax toward an energy-favored antiparallel equilibrium alignment, reducing SOP. The relaxation time (τ) is the time scale of the relaxation process. (c) Molecular structures of TPBi and BPhen with their respective dipole moment directions indicated by purple arrows.

ence should be similar. The ability to engineer SOP with an appropriate choice of processing conditions is attractive in that it offers a route to minimize quenching and efficiency loss without the need to replace an otherwise promising active material. Prior reports have shown that both substrate temperature^{18,25} and deposition rate²⁶ can impact SOP. Despite this, a quantitative analysis of the impact of processing conditions on OLED efficiency, as well as the underlying physical mechanism for control over SOP remains to be elucidated.

This work quantitatively treats the impact of processing conditions on SOP using an RTS framework, considering the deposition rate dependence of SOP for a series of material glass-transition temperatures (T_g), and hence relative substrate temperatures. The experimentally measured dependence of SOP is analyzed by treating the film formation as a molecular glass relaxation process. Finally, clear tuning of exciton-polaron quenching and peak efficiency with changes in processing conditions is demonstrated for OLEDs based on SOP ETLs.

2. THEORY

Prior experimental work has shown that birefringence in glassy organic thin films is a function of substrate temperature relative to the glass-transition temperature (i.e., T_{sub}/T_g).²⁷ Subsequent work by Bishop et al. extended this study to include both substrate temperature and deposition rate,²¹ concluding that both process parameters can be considered equivalent in a common RTS framework reflecting the enhanced surface mobility during the physical vapor deposition process. Practically, an increase in the substrate temperature during deposition has an equivalent effect to depositing at a lower rate for substrate temperatures between 0.75 and 1.0 T_g .²³ This model has been presented quantitatively by unifying birefringence versus deposition rate curves collected at different substrate temperatures to an effective deposition rate (R_{eff}) at T_g .²¹ This methodology also permits consideration of rate-dependent birefringence for materials with different T_g values under a single common framework and serves as an effective tool for the predictive engineering of molecular orientation in glassy thin films.²¹

While prior work has considered an RTS analysis of molecular alignment for birefringence, application to SOP requires additional consideration. Generally, the strength of SOP in a material is defined by the giant surface potential

(GSP) slope (m_{GSP}), and it is reasonable to consider constructing a universal curve that reflects the variation of m_{GSP} with processing parameters across active materials. This however would imply a common upper bound for m_{GSP} regardless of material, which given the dependence of this parameter on molecular density and permanent dipole moment is unreasonable. Here, the RTS analysis is instead applied to the average molecular dipole orientation, defined as²⁸

$$\langle \cos \theta \rangle = \frac{m_{\text{GSP}} \epsilon_r \epsilon_0}{n p} \quad (1)$$

where $\langle \cos \theta \rangle$ is the average orientation between the dipole moment and the substrate normal, ϵ_r is the relative dielectric constant, n is the molecular density, and p is the molecular permanent dipole moment.

Underpinning the ability to collapse $\langle \cos \theta \rangle$ versus deposition rate data for several materials is the glassy nature of organic thin films, and their associated relaxation (Figure 1b).²¹ According to the “asymmetric dice model”,²⁹ molecules with asymmetric molecular shapes take stable postures, dominated by the van der Waals interaction between the molecule and the film surface,³⁰ to reduce the surface free energy during deposition, leading to SOP. However, the van der Waals force is only valid within a short range, and the dipole–dipole interaction between adjacent surface molecules plays a significant role in the relaxation process. The surface molecules near the vacuum–film interface, defined as the outermost layer, have high surface mobility, and the dipole–dipole interaction drives the surface molecules to relax toward an antiparallel dipole configuration before being trapped by the arrival of subsequent molecules,^{24,31} undermining SOP.

A lower deposition rate enables molecules in the outermost layer to have more time to reach equilibrium, favoring an antiparallel dipole alignment and reduced SOP. Correspondingly, depositing at elevated temperatures enhances the mobility of as-deposited molecules, allowing them to reach equilibrium within a shorter time, again leading to reduced SOP. The surface residence time t is the average time available for a surface molecule to move before being trapped by the arrival of additional molecules defined as²¹

$$t = \frac{d_{\text{surf}}}{R_{\text{actual}} (\text{\AA}/\text{s})} \quad (2)$$

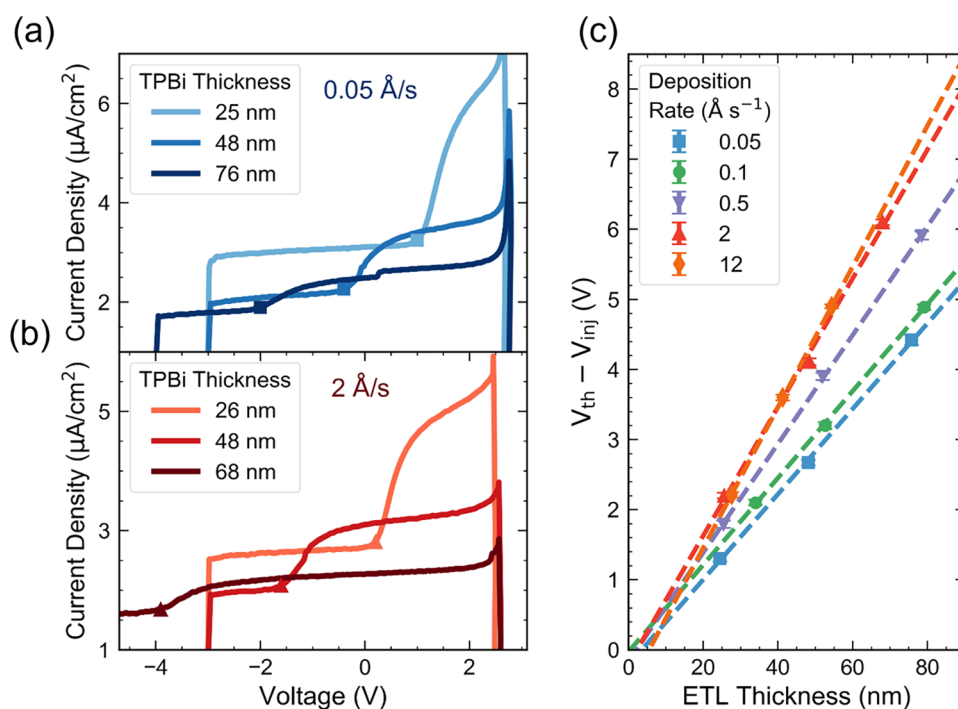


Figure 2. (a, b) Displacement current measurement (DCM) scans for devices with a TPBi ETL deposited at 2 and 0.05 Å/s, respectively, with the injection voltages (V_{inj}) marked as squares or triangles in each figure. (c) Difference of injection and device turn-on threshold voltages (V_{th}) from DCM as a function of ETL thickness ($V_{th} - V_{inj}$) under various deposition rates. The slopes of the linear fits are the GSP slopes.

where d_{surf} is the thickness of the mobile layer, which is roughly the length of one molecule ($d_{surf} \sim d_{mol}$); correspondingly, the effective surface residence time (t_{eff}) at T_g can be calculated by replacing R_{actual} in eq 2 with R_{eff} .

Glass relaxation behavior can be quantitatively described by the Kohlrausch–Williams–Watts (KWW) equation.³² The KWW equation provides a mathematical mapping for the RTS principle and reflects the glass relaxation nature of this tunability. Here, we propose that the molecular orientation responsible for SOP can also be treated using the KWW equation under various processing conditions as²¹

$$\langle \cos \theta \rangle = A \exp \left[- \left(\frac{t}{\tau} \right)^\beta \right] + C \quad (3)$$

where C represents the equilibrium average dipole orientation in the limit of infinite mobility (or infinite surface residence time), the sum of A and C represents the theoretical maximum average dipole orientation for a given SOP molecule (bounded by unity), β is the stretching parameter,³³ and τ is the surface relaxation time, effectively the time a surface molecule takes to reorient from its initial orientation to the equilibrium antiparallel alignment.^{21,33} Based on eq 3, molecular orientation, represented by the $\langle \cos \theta \rangle$ term, is defined by the ratio of surface residence and relaxation times and a set of fitting parameters (A , C , β) that are theoretically independent of processing conditions. Note that the surface residence time t is controlled by the deposition rate (see eq 2), while the relaxation time τ is controlled by the deposition temperature (higher temperature leads to higher surface mobility and a shorter relaxation time). The main idea behind the RTS is to map a given set of residence and equilibration times ($t_{actual}/\tau(T_{sub})$) to an adjusted set where the surface relaxation time corresponds to its value at T_g ($t_{eff}/\tau(T_g)$). By the definition of

this mapping procedure, time ratios must be equal to yield the same molecular orientation: $t_{actual}/\tau(T_{sub}) = t_{eff}/\tau(T_g)$.

To develop an RTS formalism for SOP, $\langle \cos \theta \rangle$ is calculated from the measured m_{GSP} for films processed as a function of deposition rate. Since the impact of deposition rate depends on the relative deposition temperature and hence material T_g , each material will exhibit a potentially different dependence. To consider extracted values of $\langle \cos \theta \rangle$ under a common framework, the actual deposition rate (R_{actual}) must be converted to an effective deposition rate (R_{eff}). Practically, this is carried out in a parametric process for the various material data sets of interest by defining a common “shift factor”, S as²¹

$$S = \frac{\log_{10}(R_{eff}/R_{actual})}{(T_g - T_{sub})} \quad (4)$$

where T_{sub} is the substrate temperature during deposition. A wide range of “shift factors” are attempted to collapse the $\langle \cos \theta \rangle$ versus actual rate data, and the curves are approximately unified into a single “master curve”. The S value that yields the minimal error between the master curve data and its KWW fitting is the optimal “shift factor” for this unification, and the resulting curve is the RTS of this study.

3. RESULTS AND DISCUSSION

3.1. Control of SOP via Deposition Rate. To examine the role of deposition rate on SOP formation, OLEDs were constructed using the polar ETL material of 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl) benzene (TPBi). The device structure of interest is ITO (150 nm)/TCTA: MoO₃ (150 nm, 9 vol %)/TCTA (20 nm)/CBP: Ir(ppy)₃ (10 nm, 7 vol %)/TPBi (variable)/LiF (1 nm)/Al (100 nm). To characterize the degree of SOP via m_{GSP} , displacement current measurements (DCM) are used to track the onset of carrier

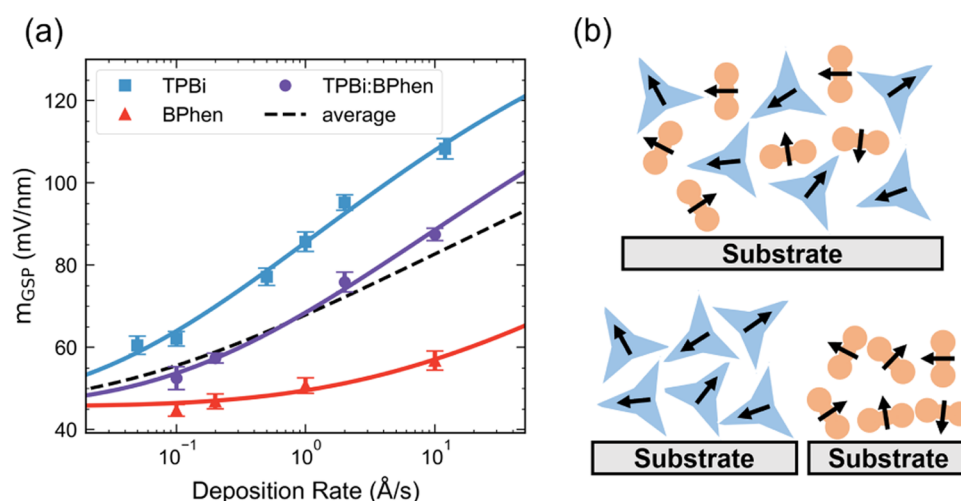


Figure 3. (a) GSP slope (m_{GSP}) versus actual deposition rate for devices based on ETLs of TPBi, BPhen, or a 1:1 blend. Solid lines are polynomial fitting for each ETL, and the dashed line represents the average of the individual data for devices based on TPBi and BPhen. (b) Schematic illustration of the polar–polar blend that maintains dipole–dipole interactions between two polar molecules present in neat films.²⁴

accumulation (V_{inj}) and device turn-on (threshold voltage, V_{th} ~ 2.4 V) as a function of ETL thickness (d_{ETL}). These voltages are related to the SOP film thicknesses by the “interfacial charge model” as^{13,34,35}

$$V_{\text{inj}} = V_{\text{th}} - m_{\text{GSP}} d_{\text{ETL}} \quad (5)$$

Since both V_{inj} and V_{th} can be extracted from DCM, a measurement of $V_{\text{inj}} - V_{\text{th}}$ as a function of ETL thickness permits the extraction of m_{GSP} .

The charge accumulation position can be probed by comparing the DCM-measured capacitance, calculated by dividing the DCM current density by the sweep rate, and the theoretical capacitance calculated based on layer thickness. For all devices at the “depletion” regime ($V < V_{\text{inj}}$), the measured capacitance values are in close agreement with the calculated theoretical capacitances including layers from the HTL to the ETL. This suggests that charges are located at the HIL/HTL interface prior to the accumulation and that the TCTA: MoO₃ layer serves as a noncapacitive HIL in the device. In the “accumulation” regime ($V_{\text{inj}} < V < V_{\text{th}}$), the measured capacitances are consistent with accumulation across the ETL, with holes accumulating at the EML/ETL interface.

Representative measurements of the displacement current density as a function of applied voltage for devices with two ETL deposition rates are shown in Figure 2a,b. All devices show the sub-turn-on accumulation of charges with distinguishable V_{inj} marked in the square (0.05 Å/s) and triangle (2 Å/s) symbols. The dependence of the voltage difference, $V_{\text{th}} - V_{\text{inj}}$, is plotted as a function of ETL thickness in Figure 2c, with the slopes of these lines corresponding to m_{GSP} . The extracted GSP slopes are shown as a function of deposition rate for devices based on TPBi ETL, ranging from 60.6 to 108.3 mV/nm for deposition rates of 0.05 to 12 Å/s, respectively (see Table S1 for the summary of calculated GSP slope values). Consistent with expectations based on the surface equilibrium mechanism,^{21,23} a higher deposition rate leads to reduced surface residence time (eq 3) for surface molecules to move to their equilibrium orientation and hence stronger SOP.

The lines in Figure 2c have negative y-intercepts. One explanation is that the devices turn on before reaching the “flat band” device condition ($V_{\text{th}} > V_{\text{turn-on}}$). The current theory of

SOP-induced charge accumulation is based on the bilayer OLED structure with no electron injection layer,¹⁴ which assumes that the turn-on voltage corresponds to the “flat band” condition ($V_{\text{th}} = V_{\text{turn-on}}$). However, in this study, a LiF layer is used between the cathode and ETL to facilitate the electron injection, slightly lowering $V_{\text{turn-on}}$ and making the DCM-extracted turn-on voltage a less accurate proxy for the “flat band” voltage. Meanwhile, this underestimation of V_{th} can lead to a lower charge accumulation compared with what would be expected based on the corresponding m_{GSP} . Especially for thin ETL devices ($d_{\text{ETL}} \sim 30$ nm) since their injection voltages (V_{inj}) are close to V_{th} , and thus reduced device turn-on prominently decreases the charge accumulation density. However, for devices with thicker ETLs, this phenomenon becomes less significant.

3.2. Role of Glass-Transition Temperature. While varying substrate temperature has been previously demonstrated as a viable means to engineer SOP in the thin film,¹⁸ processing OLEDs at high temperatures complicates fabrication and can lead to the degradation of other layers in the stack. Here, the relevance of an RTS approach for SOP was instead considered by fixing the substrate temperature at room temperature and varying ETL T_g to adjust the relative substrate temperature effectively. Bathophenanthroline (BPhen) was selected as a low T_g ETL ($T_g = 63$ °C)³⁶ relative to TPBi ($T_g = 127$ °C),³⁷ meaning the relative substrate temperature for BPhen is increased relative to TPBi for deposition at room temperature. In addition, devices were also constructed using an ETL consisting of an equal mixture of the materials to tune T_g and SOP. While there is previous work examining SOP in a mixture of polar and nonpolar molecular materials, there is limited characterization for mixtures of two polar materials.^{24,38,39}

The extracted GSP slopes for devices based on BPhen show a less pronounced dependence on deposition rate than those based on TPBi (Figure 3). DCM curves used to extract the GSP slope for BPhen in the same manner used for TPBi are shown in Figures S1–S3. The reduced sensitivity to rate exhibited by BPhen is consistent with the surface equilibration mechanism described earlier. Molecules of BPhen are deposited at a higher relative substrate temperature such that surface molecules have higher surface mobility that weakens

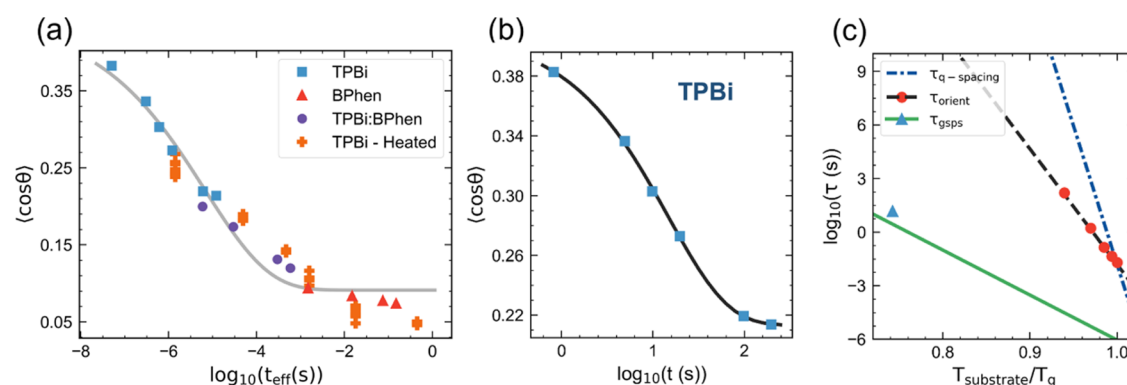


Figure 4. (a) Rate–temperature superposition for the average dipole orientation; data for each material are shifted by a shift factor of 0.075 decade/K. The KWW fit (gray line) is used to obtain the relaxation time (τ) at T_g . The data for TPBi deposited at elevated substrate temperature (orange crosses) is taken from Bangsund et al.¹⁸ (b) KWW fit (black line) of the unshifted TPBi ETL data leading to $\tau = 14.8$ s. (c) Relaxation time (τ) as a function of relative substrate temperature obtained from KWW fits of the dipole orientation data (τ_{gsp} , blue triangle) from this study, birefringence data (τ_{orient} , red circles), and GIWAX peak data (blue dashed line) reported by Bishop et al.²¹

the effect of the time scale induced by changing deposition rate. While a monotonic rise of the SOP with the deposition rate is observed for all of the systems and rates employed in this study, it is worth considering whether such a dependence on rate will be observed universally. Prior work considering the rate dependence of other types of molecular anisotropy at elevated temperatures, such as birefringence and molecular layering, has shown that molecular orientation switches from horizontal to slightly vertical at small deposition rates before becoming completely random in the limit of extremely small rates.⁴⁰ Although a similar effect may potentially occur in the systems presented here, the analysis discussed in the next section suggests that such a “switch” in orientation will require extremely small rates (<0.001 nm/s).

Devices with an ETL consisting of an equal mixture of TPBi and BPhen were also constructed to realize an intermediate value for T_g . The blend T_g can be predicted using the Gordon–Taylor equation (see Section 2 in the Supporting Information (SI)),⁴¹ a widely used model to describe the glass-transition temperature of mixtures, to be ~ 98 °C (relative $T \sim 0.80 T_g$). The dependence of the GSP slope on rate shows an intermediate dependence compared to devices based on neat ETLs, consistent with the estimate of T_g and the surface equilibration mechanism.

Recent studies have shown that the SOP can be engineered by diluting the average molecular PDM strength via the mixing of nonpolar molecules in a polar matrix.^{38,39} Noguchi et al. have further demonstrated that the nonpolar dopant can spatially separate polar host molecules, leading to a disruption of the dipole–dipole interaction.²⁴ Interestingly, the relative agreement in Figure 3a between the measured behavior of the blend and the predicted average behavior based on the neat ETL results suggests a different behavior. Here, there appears to be no change in the PDM interaction between molecules in the blend relative to the case of the neat ETL, leaving the behavior akin to two noninteracting dipolar lattices. This may reflect the relative similarity of the PDMs for TPBi and BPhen.^{14,28} This result suggests that polar–polar mixtures may also offer a means to tune SOP in organic thin films. However, additional insight is needed for the generality of this conclusion. First, the TPBi and BPhen molecules have relatively similar PDMs, and how the dipole moment mismatches between the materials needs further investigation. Second, the difference in PDM direction relative to the

molecular shape may play a role in the behavior of SOP in blends. This factor appears insignificant for BPhen and TPBi blends probably due to the non-disk shape of the two molecules.

3.3. SOP and Rate–Temperature Superposition. To demonstrate the equivalence of rate and temperature for SOP, the individual curves from Figure 3a are shifted in accordance with eq 4 to create a master curve with a common variable of effective deposition rate (R_{eff}) or, equivalently, effective surface residence time (t_{eff}). Here, the average dipole orientation for each ETL is calculated using the data from Figure 3a, and eq 1 and is successfully fit to an RTS model with a “shift factor” of $S = 0.075$ decade/K, as shown in Figure 4a (see Section 3.1 in the SI for additional details). The same “shifting” procedure can be applied to the temperature-dependent SOP data for TPBi reported by Bangsund et al.,¹⁸ where the average orientation was calculated from the GSP slope obtained from a two-point estimation based on DCM data. Although extra care should be taken in the analysis of the samples fabricated at elevated temperatures due to potential changes in the film morphology^{42–44} and impurity incorporation,^{45,46} the temperature-dependent data for TPBi appear to follow the same general trend as shown in Figure 4a. The extracted shift factor value of 0.075 decade/K means that for the SOP effect under investigation, raising the substrate temperature by 13.3 K is equivalent to depositing 10 times more slowly ($1/\text{S.F.} = 13.3$ K/decade). The KWW fitting of the resulting master curve yields a common τ -value of ~ 1 μs , corresponding to the surface relaxation time for each ETL deposited at their T_g . This is several orders of magnitude shorter than the surface residence time, which is on the order of seconds. Such a short time scale for surface relaxation at T_g may reflect enhanced mobility at the surface during the physical vapor deposition process, which is in agreement with the previous reports of a surface equilibration mechanism responsible for anisotropy in small-molecule organic semiconductors.^{40,47}

Separately, an unconstrained KWW fit of experimental data collected for TPBi was performed since it offers the most data points and highest variability across the experimentally probed deposition rates (or surface residence times). Analysis of such unshifted data can reveal the relaxation properties corresponding to one specific substrate temperature. This fit (Figure 4b) yields a surface relaxation time of ~ 15 s. Note that this value is several orders of magnitude higher than the surface relaxation

time at T_g , since when the substrate temperature is much smaller than the glass-transition temperature ($T_{\text{sub}} = 0.75T_g$), the surface mobility decreases (and equilibration time increases) exponentially.

The extracted relaxation times can be compared to those previously reported by Bishop et al. for itraconazole, which is a glass-forming liquid crystal.²¹ This prior work probed glass relaxation via both optical anisotropy and molecular packing as evidenced by birefringence and grazing incidence (GIWAX) X-ray measurements, respectively. The solid and dashed lines in Figure 4c represent the exponential variation of relaxation times with the substrate temperature, which can be calculated from eq 4 and the definition of the RTS mapping procedure. τ_{gsps} , $\tau_{\text{q-spacing}}$, and τ_{orient} refer to the surface relaxation times extracted from KWW fitting of average dipole orientation in this study, GIWAX-measured molecular layering, and birefringence under different deposition conditions,²¹ respectively. As shown in Figure 4c, the theoretical prediction of the relaxation times that reflect the process of SOP formation (solid green line) agree well with the time extracted for TPBi (blue triangle). Relaxation times for the materials reported here are much lower than ones for itraconazole as evidenced by Figure 4c, meaning that the surface dynamics of SOP formation are faster than those for birefringence in a glass-forming liquid crystal. The most likely sources of this difference are variations in molecular size, shape, and the strength of intermolecular interactions in these systems. Furthermore, there is no universal one-to-one correlation between the TDM and PDM alignment,⁴⁸ so the timescales for SOP and birefringence are not necessarily expected to be on the same order of magnitude even for similar systems.

Based on eq 3, the largest variation in SOP and birefringence will be observed when the relaxation time lies close to or within the range of experimentally achievable surface residence times, which typically vary between 0.1 and 200 s. This is why the relaxation times from Bishop et al.²¹ (red circles) and this study (blue triangle) lie close to this range. This way, it is possible to predict whether the variation in SOP with the deposition rate will be observed based on the knowledge of τ as a function of temperature. For example, no variation in SOP with rate is expected when $T_{\text{sub}}/T_g > 0.9$ since this temperature range corresponds to relaxation times that are several orders of magnitude smaller than the shortest achievable residence time. Due to the limited temperature- and rate-dependent SOP data available in the literature, it is not currently possible to further test the generality of this conclusion. However, it is worth noting that birefringence in itraconazole has a pronounced dependence on deposition rate in the temperature regime of $0.9 T_g < T < 0.97 T_g$.²¹ So the possibility of observing a dependence of SOP on rate even at high deposition temperatures cannot be entirely ruled out.

3.4. Impact on Exciton Quenching and OLED Efficiency. Prior work has shown that SOP-induced exciton-polaron quenching (EPQ) can significantly limit OLED efficiency.¹⁸ With the dependence in Figure 3 of m_{GSP} on deposition rate, we also investigated the impact of processing conditions on exciton quenching and OLED efficiency. Here, SOP-induced quenching is quantified by a previously reported technique^{18,49} that relies on a lock-in measurement of device photoluminescence (PL) as a function of applied voltage in a working device. This *in situ* lock-in PL characterization can isolate exciton quenching induced via relative PL changes while excluding any background electroluminescence (EL)

allowing the detection of PL even at biases above the turn-on voltage. The device's internal quantum efficiency (IQE) is compared with its corresponding lock-in PL measurement to assess the role that PL losses play in determining overall device efficiency. Prior work has shown that OLEDs with ETLs exhibiting SOP show minimal charge balance loss and that IQE is limited instead by SOP-induced EPQ. Here, the IQE is calculated by dividing the measured external quantum efficiency by the optical outcoupling efficiency calculated with Setfos 5.2 (Fluxium AG) (Figures S5 and S6). Overlays of IQE and lock-in PL versus voltage for OLEDs based on three different ETLs deposited at different deposition rates are shown in Figure 5. In all cases, good agreement is observed between lock-in PL and IQE at the voltages close to the device

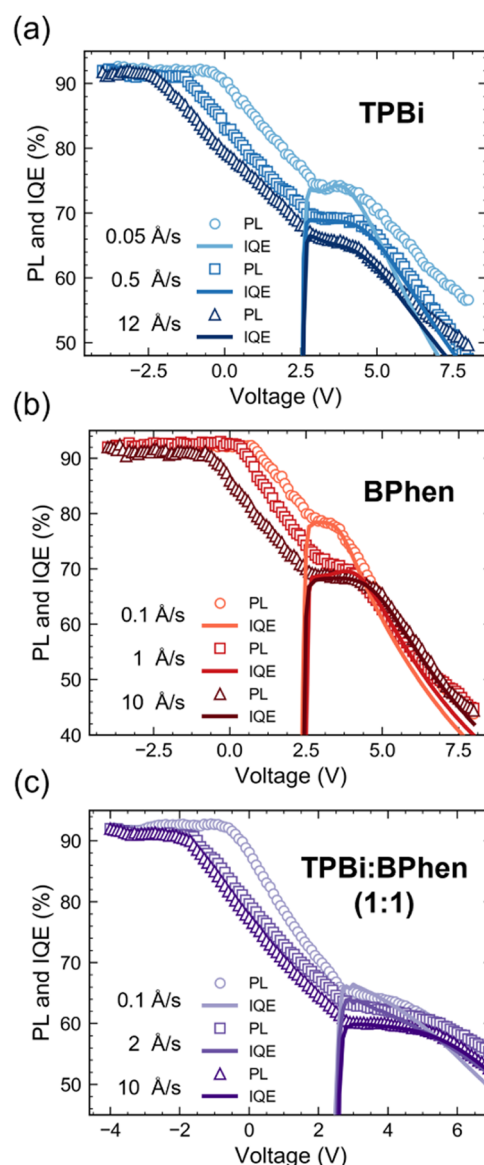


Figure 5. Overlays of device photoluminescence (PL) and internal quantum efficiency (IQE) as a function of voltage and deposition rate for devices based on (a) TPBi with thicknesses of 48 nm (0.05 Å/s), 52 nm (0.5 Å/s), and 54 nm (12 Å/s); (b) BPhen with thicknesses of 46 nm (0.1 Å/s), 45 nm (1 Å/s), and 46 nm (10 Å/s); and (c) 1:1 TPBi: BPhen blends with thicknesses of 51 nm (0.1 Å/s), 52 nm (2 Å/s), and 48 nm (10 Å/s).

turn-on. Deviations between PL and IQE are observed at a high bias ($V_{\text{applied}} > 5.5$ V), likely reflecting carrier leakage and reduced charge balance. This hypothesis is supported by prior work simulating the charge carrier density in OLEDs with similar structures, showing an excess hole density at the EML/ETL interface and hole leakage into the ETL at high bias.⁵⁰ The degree of PL quenching is found to increase with deposition rate, leading to a corresponding reduction in device IQE, consistent with the observed increase in m_{GSP} with deposition rate in Figure 2. Correlating the rate-engineered device performance and the previous temperature-dependent study,¹⁸ we can conclude that the SOP-induced EPQ can be suppressed by tuning the processing conditions, resulting in enhancing the device efficiency. The quantitative connection between the peak efficiency, degree of PL quenching, and SOP strength was established previously,¹⁹ and the results of this work support this quantitative picture of the impact of SOP on OLED efficiency.

4. CONCLUSIONS

This study demonstrates that as an anisotropic molecular orientation property, spontaneous orientation polarization in a vapor-deposited organic thin film can be engineered by two processing parameters, deposition rate and relative temperature. This processing tunability is consistent with the surface equilibrium mechanism that has been previously used to explain birefringence resulting from anisotropic molecular orientation in vapor-deposited organic thin films and their mixtures. Experimental results were fitted using an empirical glass relaxation model, providing a quantitative understanding of how the processing parameters separately impact SOP formation. The blending of two types of polar molecules is shown to preserve the intrinsic dipole orientation and thus can serve as a predictable method to engineer SOP, although consideration of additional polar systems is needed to generalize this conclusion. More importantly, we successfully combine the effects of deposition rate and relative temperature in a single rate–temperature superposition, which can facilitate the predictive engineering of SOP. Finally, these findings were used to guide device processing conditions for enhanced efficiency, demonstrating a straightforward approach to minimizing SOP-induced exciton–polaron quenching.

5. EXPERIMENTAL SECTION

5.1. Device Fabrication. Organic light-emitting devices were fabricated on glass substrates precoated with a 130 nm thick layer of indium tin oxide (ITO; Kintec) with a sheet resistance of 15 Ω/cm^2 . Substrates were cleaned with deionized water, acetone, and isopropanol, followed by UV ozone treatment for 15 min before usage. Organic layers were deposited by high-vacuum thermal evaporation at a base pressure of $<10^{-7}$ Torr and a rate of 1–2 $\text{\AA}/\text{s}$. LiF and Al were deposited at 0.5 and 2.5 $\text{\AA}/\text{s}$, respectively, through a shadow mask, defining an active area of 4 mm^2 . Devices were encapsulated with epoxy and cover glass in an N_2 glovebox. Organic active materials (4,4',4''-tris(*N*-carbazolyl) triphenylamine (TCTA), fac-tris(2-phenylpyridine) iridium (III) ($\text{Ir}(\text{ppy})_3$), 2,2',2''-(1,3,5-benzenetriyl) tris-(1-phenyl-1*H*-benzimidazole) (TPBi), and bathophenanthroline (BPhen)) were purchased from Luminescence Technology Corporation.

5.2. Characterization. Current–voltage (J – V) measurements were conducted using an Agilent 4155C parameter analyzer, and luminance measurements were performed using a calibrated Hamamatsu S3585-08 large-area photodiode, with a Lambertian emission profile being assumed for luminance calculations. Electroluminescence spectra were collected using a Teledyne Princeton

Instruments FERGIE spectrograph. Voltage-dependent photoluminescence measurements used a Keithley 2636B as a voltage source. Voltage sweeps were taken from -5 to 8 V with a step size of 0.1 V, a settling time of 0.25 s, and an integration time of ~ 1 s per step. The emissive layer of the device was optically pumped with a $\lambda = 405$ nm laser (Coherent OBIS 405LX) at a power of 100 mW, which was attenuated with a neutral density filter (1.0 O.D.) to the intensity of ~ 320 mW/cm^2 , chopped at 2 kHz. It expanded with a Thorlabs GBE05-A 5x achromatic Galilean beam expander to a $1/e^2$ diameter of ~ 2 mm. The laser incidence angle was $\sim 45^\circ$. Devices were masked to prevent excitation outside the active device area. The PL signal was passed through a 450 nm long-pass filter to exclude reflected laser light from the measurement, collected by Si photodetector (Thorlabs PDA36A), and measured with a lock-in amplifier (Stanford Research Systems SR810). The highest observed PL intensity for a given voltage sweep is normalized to the maximum efficiency of the CBP: $\text{Ir}(\text{ppy})_3$ system in the absence of bimolecular quenching, previously reported to be 92% for a dopant molar concentration of 7%.⁵¹ Displacement current was measured as a function of voltage with a Pine Research WaveDriver 10 potentiostat system. The sweep rate for all scans was kept at 50 V/s with a step of 5 mV. Triangular voltage sweeps were performed from -5 V (or -3 V) to $+3$ V both in positive and negative directions.

5.3. Calculation of Average Dipole Orientation. The average dipole orientation is calculated using eq 3. The material relative dielectric constants (ϵ_r) and dipole moments (p) are taken from ref 14, and the molecular density values are taken from ref 30.

5.4. Optical Outcoupling Calculations. Light outcoupling efficiencies (η_{oc}) for OLEDs of interest were calculated using the simulation results obtained from Setfos 5.2 (Fluxim AG). During the simulation, an isotropic dipole orientation was assumed, and optical constants measured via spectroscopic ellipsometry were used. The IQE for each device is calculated by dividing its η_{EQE} by its corresponding η_{oc} .

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.2c17960>.

Raw data used to extract GSP slopes, details on shift factor determination and KWW fitting, and OLED performance data (PDF)

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Notes

The authors declare no competing financial interest.

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