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Understanding and engineering spontaneous orientation polarization in organic light-emitting devices

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ABSTRACT

Organic light-emitting devices (OLEDs) are a ubiquitous technology for displays with growing application in a variety of other spaces. The future success of this technology depends on further improvements in device efficiency and stability. One pathway for improvement relies on engineering molecular orientation in the organic thin films comprising an OLED. This review is focused on the subsequent spontaneous alignment of molecular electric dipole moments, known as spontaneous orientation polarization (SOP), a phenomenon observed for many common OLED materials. The magnitude of polarization fields associated with SOP rival what is experienced in an OLED under high injection and can significantly impact electronic and excitonic behavior. Here, we first review current work describing the mechanism for the formation of SOP, reflecting an interplay between several factors, such as molecular shape, intermolecular interactions, and processing conditions. We also consider several strategies to tune the polarization sign and magnitude, with emphasis on connecting observations to quantitative models of SOP formation. Building on this discussion of SOP in organic thin films, we review how polarization in OLED active layers impacts key aspects of device performance, including charge injection, luminescence efficiency, and stability. Finally, this review concludes with an outlook on areas of future development needed to realize broad control over SOP for a variety of applications, highlighting gaps in our current understanding of this phenomenon.

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I. INTRODUCTION

Organic light-emitting devices (OLEDs) have seen great commercial success over the past two decades, particularly in the field of

mobile and television displays. The first report of a thin film OLED came in 1987,¹ and implementation of a single-color passive-matrix OLED display into a consumer product was realized in 1993 by Pioneer,² while a multi-color active-matrix OLED display was first implemented into a camera product by Kodak in 2003.³ Since then, a series of significant advances in this technology have enabled its growth, with OLED displays predicted to reach >50% of the global mobile display market by 2023.⁴ Attractive features of OLEDs include very high contrast, lower power consumption, wide viewing angle, slim form factor, and the potential for cost-effective roll-to-roll processing.^{2,5} These advantages can be exploited not only in display applications, but also in solid-state and automotive lighting,⁶ augmented and virtual reality,⁷ and in organic injection lasers.⁸ The future success of OLED technology in these areas relies on the ability to realize high-efficiency, longer-lived devices. This requires a deep understanding of the underlying device physics and development of methods to manipulate the key properties of materials that comprise the device. One approach to realize high-performance OLEDs that has been

increasingly explored over the past decade is molecular orientation engineering in thin film.

OLEDs are composed of ~ 10 – 100 nm thick layers of organic small molecules that are typically deposited via physical vapor deposition under high vacuum.⁹ These films are generally amorphous and do not possess long-range order. This said, molecular orientation in these materials need not be random and isotropic. This was demonstrated ~ 20 years ago by overwhelming experimental evidence for partial alignment of the molecular transition¹⁰ and permanent^{11,12} dipole moments in organic thin films. Since then, numerous small-molecule organic semiconductor materials have been shown to exhibit preferential net molecular alignment even in amorphous films.^{13–15} Nanoscale molecular alignment gives rise to certain macroscopic film properties, such as optical birefringence,^{16–20} viewing angle-dependent luminescence intensity spectra,^{21–24} or the presence of a giant surface potential (GSP).^{15,25–29} All of these phenomena vary depending on direction within the film. For example, birefringence leads to differences in the in-plane and out-of-plane refractive indices, and GSP is typically present only along the growth direction of the film. While the focus of this review is on anisotropy leading to spontaneous orientation polarization (SOP), which is the net preferential alignment of molecular permanent (electric) dipole moments (PDMs), it is instructive to introduce other types of anisotropy as their formation mechanisms are interrelated. So far, four kinds of anisotropies in glassy molecular thin films have been identified:¹⁴ (1) optical anisotropy or anisotropy of the polarizability tensor, (2) alignment of molecular transition dipole moments (TDMs), (3) molecular layering, and (4) alignment of molecular permanent dipole moments yielding SOP.

Section I will briefly cover the types of molecular anisotropy, followed by an in-depth discussion of SOP that focuses on current models developed to elucidate the role of dipole alignment in OLED physics. Having established a basic understanding of SOP, Sec. II will discuss the factors that have been shown to impact molecular permanent dipole orientation, along with explanations of the underlying physical mechanisms. Section III will focus on how an understanding of SOP in the context of device operation can be applied to enhance OLED performance, which is the emphasis of this paper. Several aspects of device performance are considered, including charge injection, luminescence efficiency, and degradation, showing how each can be engineered by manipulating the molecular permanent dipole moment alignment. Section IV will provide a perspective on future areas of research and open questions related to SOP, considering the additional advances needed to fully exploit the application of SOP in OLEDs, pathways toward better understanding of SOP formation mechanisms, and its future application in other types of organic semiconductor-based devices.

A. Molecular anisotropy in vapor-deposited organic films

For glassy organic thin films, optical anisotropy is typically measured as the difference between the out-of-plane (n_e or n_z) and in-plane (n_o or n_{xy}) components of refractive index [Fig. 1(a)], with the birefringence defined as¹⁶

$$\Delta n = n_e - n_o. \quad (1)$$

Since amorphous films frequently show in-plane isotropy (x-y plane),³⁰ there is often no distinction made between the x- and y-

directions. The physical origin of birefringence is the alignment of absorbing TDMs reflecting excitation of the molecule from the ground to excited state (conversely, emissive TDMs reflect the transition from excited to ground state).¹⁶ In this work, the impact of TDM orientation on light emission is discussed separately as it involves different characterization techniques and potential device applications. Molecular birefringence is typically probed via variable angle spectroscopic ellipsometry, which captures the changes in phase and intensity of the s- and p- components of the polarized light reflected from the sample.^{31,32} These changes are then modeled to extract anisotropic material optical constants, an example of which is shown in Fig. 1(a).

Several factors influence the strength of optical birefringence. For films vacuum deposited under typical conditions ($T_{\text{sub}} \sim 300$ K, rate ~ 0.05 – 1 nm/s), the magnitude of optical anisotropy is primarily dictated by molecular shape.^{17,33} Yokoyama *et al.* found that compact, bulky molecules [e.g., tris(8-hydroxyquinolino)aluminum (Alq_3)] are more optically isotropic, while long or planar molecules [e.g., 4,4'-bis((N-carbazole)styryl)biphenyl (BSB-Cz)] tend to lie flat, resulting in negative birefringence with its strength proportional to the length of the molecule as shown in Fig. 1(b).^{16,17,34} Optical anisotropy may also be controlled by heating the substrate during film deposition, with the molecular orientation being perturbed even when the substrate temperature is lower than the material glass transition temperature (T_g).^{18,35} This phenomenon is attributed to the enhanced mobility of molecules at the growing film surface compared to the bulk.³⁶ Generally, birefringence is reduced for high substrate temperatures ($T_{\text{sub}} > 0.8 T_g$), as shown in Fig. 1(d), although this trend also depends on the roughness of underlying substrate as it impacts molecular mobility and aggregation.³⁵ Interestingly, the orientation of some rod-shaped molecules switches from horizontal to vertical at $T_{\text{sub}} = 0.95 T_g$,^{33,37} before eventual transition to isotropic orientation at and above T_g . This is manifest as a change in the sign of birefringence as shown in Fig. 1(d). Such a behavior has been supported by theoretical calculations, where the simulated orientation of the free surface as an equilibrium liquid was linked to molecular orientation of the vapor-deposited glass, with all temperature-dependent trends being reproduced at a qualitative level.^{33,37} Birefringence has also been noted to depend on thin film deposition rate, and both temperature and rate have been considered together in a “rate-temperature superposition”^{38,39} framework that will be discussed later in this review.

Transition dipole moment orientation is also notable for its important impact on OLED performance. Electroluminescence can be modeled as radiation from an oscillating dipole in a microcavity with an oscillation direction pointing along the emissive TDM of the molecule.^{40–43} The amount of light that escapes the OLED stack to the forward viewing direction is maximized when the TDM is oriented in-plane and parallel to the substrate^{44,45} since the direction of emitted light in this case is orthogonal to the dipole moment vector and thus the substrate plane. Transition dipole orientation is quantified by the orientation factor Θ ,⁴⁶

$$\Theta = \frac{\sum_i (\vec{p}_i \cdot \hat{z})^2}{\sum_i (\vec{p}_i)^2} = \langle \cos^2 \alpha \rangle, \quad (2)$$

where α is the angle between the TDM vector and the substrate normal ($\hat{z}$). As such, $\Theta = 0, 0.33, 1.0$ correspond to completely horizontal, random/isotropic, and vertical orientations, respectively. The

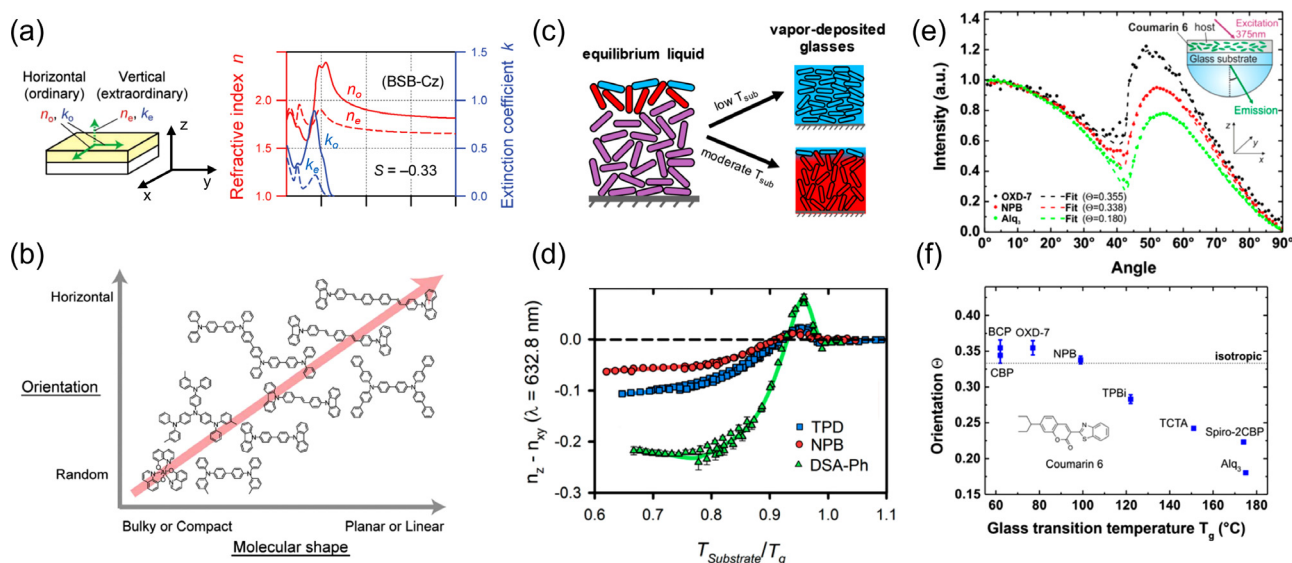


FIG. 1. Schematic illustration of thin film orientation with direction-dependent optical constants (left) and exemplary data for index of refraction/extinction coefficient of birefringent material BSB-Cz. Reproduced with permission from Yokoyama, J. Mater. Chem. **21**, 19187 (2011). Copyright 2011 the Royal Society of Chemistry. (b) Qualitative trend of the relationship between molecular shape and orientation in vapor-deposited amorphous thin films. Reproduced with permission from Yokoyama, J. Mater. Chem. **21**, 19187 (2011). Copyright 2011 the Royal Society of Chemistry. (c) Schematic representation of the impact of deposition temperature on molecular orientation of vapor-deposited glasses in connection between the structure of glasses and equilibrium liquid. Reproduced with permission from Ediger *et al.*, Acc. Chem. Res. **52**, 407 (2019). Copyright 2019 AIP Publishing. (d) Measured optical anisotropy as a function of deposition temperature for a series of rod-shaped molecules. Reproduced with permission from Dalal *et al.*, Proc. Natl. Acad. Sci. U. S. A. **112**, 4227 (2015). Copyright 2015 National Academy of Sciences. (e) p-component of the photoluminescence intensity for Coumarin 6 doped into various hosts. Orientation parameters are obtained from fitting the data by optical simulations. FIG inset shows the measurement setup. Reproduced with permission from C. Mayr and W. Brütting, Chem. Mater. **27**, 2759 (2015). Copyright 2015 American Chemical Society. (f) Orientation factors obtained from the optical modeling of angle-resolved photoluminescence spectra of Coumarin 6 doped into hosts with differing T_g . Reproduced with permission from C. Mayr and W. Brütting, Chem. Mater. **27**, 2759 (2015). Copyright 2015 American Chemical Society.

orientation factor is frequently assessed from measurements of angle-resolved photo- and electro-luminescence,^{21,44,47,48} with the former represented schematically in the inset of Fig. 1(e). Such methods rely on the fact that the relative emission intensity at higher ($>45^\circ$) angles is proportional to the fraction of vertically oriented dipoles.²¹ As such, the emission pattern represented by the green curve in Fig. 1(e) has the smallest (highest) ratio of vertically (horizontally) oriented dipoles compared to the red and black curves.

Given its application in OLEDs, TDM alignment is often probed in a host-guest film, where the goal is to orient the dilute guest species. The degree of TDM alignment is again dictated by molecular shape, with orientation preserved even when the emitter molecule is heavily diluted (1–10 vol. %) in the host matrix.^{23,49} Phosphorescent emitters, the most common of which are bulky Ir-based complexes, have been shown to adopt either isotropic or slightly horizontal ($\Theta = 0.22$ – 0.3) TDM orientations,^{50–53} although there are exceptions including the yellow-emitter 2,2,6,6-tetramethylheptane-3,5-diketone [Ir(dmpypyph)₂(tmd)] that shows a preference for even more horizontal configurations ($\Theta = 0.135$).⁵⁴ In contrast, rod-shaped fluorescent and thermally activated delayed fluorescence (TADF) emitters display a strong tendency for horizontal TDM orientation, with almost perfectly horizontal orientation ($\Theta < 0.02$) achieved in 9,10-bis(3',5''-diphenylbiphenyl-4'-yl)anthracene (TAT)⁵⁵ and 2,6-bis(4-(10Hphenoxazin-10-yl)phenyl)benzol[1,2-D:5,4-D'] bis(oxazole) (cis-BOX2).²⁴

As was the case for birefringence, guest TDM alignment can also be manipulated through appropriate choice of processing parameters.⁵⁶ In addition, this phenomenon has also been shown to depend on the T_g of the host.^{23,57,58} As illustrated by Fig. 1(f), the orientation of the fluorescent emitter 3-(2-benzothiazolyl)-7-(diethylamino)coumarin (Coumarin 6) at 2 vol. % concentration strongly depends on T_g of the host, where hosts with higher T_g (for example, Alq₃) yield more horizontal guest TDM orientation.²³ These findings are consistent with changes in surface mobility that were used to explain the temperature-dependence of birefringence.^{33,37} Higher host T_g is equivalent to reduced substrate temperature during deposition as both reduce the molecular surface mobility frustrating a full equilibration of the guest to random orientation.²³ From a practical standpoint, engineering TDM orientation increases OLED outcoupling efficiency achieving high external quantum efficiencies (EQEs) of 37–39.8%.^{59–61}

Another type of molecular anisotropy, molecular layering, has been identified for vapor-deposited molecular glasses.^{30,62–64} It refers to the tendency of molecules to form a layered structure during physical vapor deposition, as can be evidenced from a broad anisotropic grazing incidence wide-angle x-ray scattering (GIWAXS) peak at a reciprocal spacing roughly corresponding to one molecular length.^{30,62} The extent of molecular layering is proportional to the GIWAXS peak intensity and has been shown to be controlled by the substrate temperature during deposition.^{30,38,65} Similar to birefringence and TDM alignment, molecular layering tends to vanish for deposition close to

the material T_g , and analysis of the functional dependence between layering and processing conditions can reveal quantitative information on the surface dynamics of this process.^{19,39,66}

Based on the above discussion on molecular anisotropy, three key factors tend to dictate molecular orientation in vapor-deposited organic amorphous solids: molecular shape (conformation structure, aspect ratio), processing conditions (substrate temperature as it controls the surface mobility and molecular equilibration process), and molecular interactions with the substrate and other molecules (as it relates to the surface mobility). The following discussion shows what role these concepts play in the process of SOP formation.¹⁶

B. Permanent dipole moment alignment

As defined earlier, SOP is the spontaneous alignment of molecular permanent dipole moments. First observed in vapor-deposited thin films of Alq₃,¹² this phenomenon has been demonstrated for a variety of materials, including highly efficient phosphorescent and TADF emitters,^{25,67} hole- and electron- transporting molecules,^{26,68,69} and in electron donor-acceptor blends.⁷⁰ Figure 2(a) shows the degree of SOP observed in several organic semiconductor molecules,^{25–27,71} where points lying in the shadowed gray region have comparable SOP formation efficiencies.

A non-centrosymmetric molecule has the potential to possess a permanent (electric) dipole moment, and alignment of these molecular dipoles during the process of film formation results in a surface potential that scales linearly with film thickness,¹³

$$\Phi_s = - \int_0^d \vec{E} \cdot \hat{z} dz = \frac{p \langle \cos \theta \rangle n}{\epsilon_r \epsilon_0} d. \quad (3)$$

According to Eq. (3), the magnitude of this surface potential is dependent on the dipole moment magnitude p , average dipole orientation

with respect to the surface normal $\langle \cos \theta \rangle$ [see Fig. 2(b) for the angle definition], molecular density n , relative dielectric constant ϵ_r , and film thickness d . The common metric to assess the SOP strength is the GSP slope, defined as $m_{GSP} = \frac{\partial \Phi_s}{\partial d}$, which is effectively the magnitude of the electric field created within the film due to SOP. Note that only a slight net dipole orientation is needed to achieve a significant build-up of the surface potential. For example, a $\langle \cos \theta \rangle = 0.057$ is required to obtain a potential drop of 10 V for a 200-nm-thick film of Alq₃.⁷² The average orientation values for materials deposited under typical conditions (room temperature and the rate between 0.1 and 1 nm/s) ranges between 0.01 and 0.33,^{72,73} which is quite far from complete dipole alignment (i.e., $\langle \cos \theta \rangle = 1$). This is also illustrated from the simulated dipole distribution for 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi) in Fig. 2(c), which shows a wide range of dipole orientations with only slight preference toward “face up” orientation that corresponds to $\langle \cos \theta \rangle = 1$.⁷² This suggests that there is substantial room for further engineering of SOP to achieve even higher surface potential but also makes the dipole orientation harder to assess where only a small number of permanent dipoles are oriented.

In the context of OLED physics, the built-in electric field induced by SOP is comparable to what is observed in an OLED under typical operating conditions. Furthermore, the polarization charge density, defined as $\sigma_{pol} = \epsilon_r \epsilon_0 m_{GSP}$,²⁶ is formed on each side of the SOP film as shown in Fig. 2(d), where one of the transport layers in the OLED stack has positive SOP ($m_{GSP} > 0$). An initial observation of the polarization charge in OLEDs with an SOP ETL was reported by Berleb *et al.*¹¹ and Brütting *et al.*,⁷⁴ while Kondakov *et al.*⁷⁵ explored this phenomenon during device degradation. These works identified the sub-turn-on charge accumulation phenomenon, illustrated schematically in Fig. 2(d). The microscopic origin of the interface charge was linked to SOP in a later study by Noguchi *et al.*,⁷⁶ confirming that this is a polarization charge arising from electric dipole alignment. Such

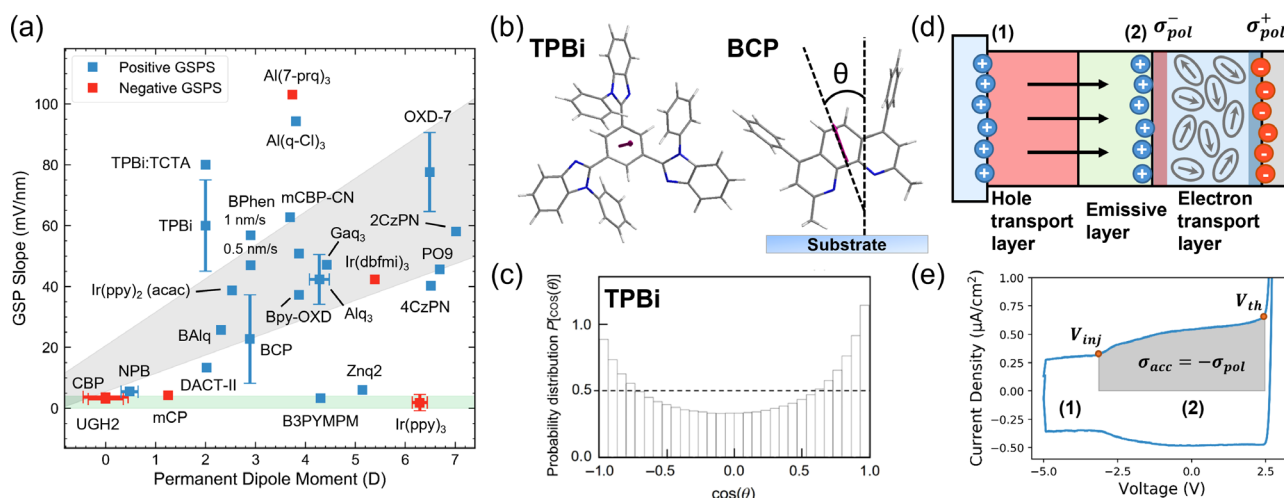


FIG. 2. (a) GSP slope values for several organic semiconductor molecules as a function of their permanent dipole moment taken from Refs. 25–27 and 71. (b) Chemical structures of electron transport molecules TPBi and BCP with directions of permanent dipole moments indicated by purple arrows. (c) Simulated distribution of the TPBi dipole moment orientation with respect to the substrate normal. Reproduced with permission from Coehoorn *et al.*, Phys. Rev. Appl. 16, 034048 (2021). Copyright 2021 American Physical Society. (d) Schematic of an OLED stack with positive SOP ($m_{GSP} > 0$) in one of the transport layers with polarization charge on each side of the layer (σ_{pol}^- and σ_{pol}^+) that leads to injection and accumulation of positive charges. (e) Displacement current measurement scan indicating injection voltage (V_{inj}) that marks a transition from (1) depletion to (2) accumulation regimes resulting in charge accumulation. Data taken from Ref. 73.

accumulation has been well characterized for OLEDs that contain an electron transport layer (ETL) that exhibits SOP,^{11,67,74,76–78} and more recent studies indicate that a similar effect is present when the device emissive (EML)^{69,79} and hole transport (HTL)^{68,69} layers exhibit SOP. Prior work has shown that polarity of the EML can also significantly modify the location and dynamics of charge accumulation.^{79,80} This phenomenon is commonly quantified via a displacement current measurement (DCM),⁸¹ which is a capacitance-voltage type measurement with displacement current being directly proportional to the apparent device capacitance. An example of the DCM scan of an archetypical tris(2-phenylpyridine)iridium (Ir(ppy)₃)-based OLED with an ETL of 1,3-Bis[2-(4-tert-butylphenyl)-1,3,4-oxadiazol-5-yl]benzene (OXD-7) that exhibits strong SOP is shown in Fig. 2(e).⁷³ The increase in displacement current corresponds to a decrease in effective dielectric thickness (and increased capacitance) and marks the transition between depletion (1) to accumulation (2) regimes. This transition is well described by the “interface charge” model,²⁶ which states that the onset voltage for charge injection (V_{inj}) occurs prior to device turn-on voltage (V_{th}), and shifts toward lower voltages for increasing SOP layer thickness (d),

$$V_{inj} = V_{th} - \frac{d}{\epsilon_r \epsilon_0} \sigma_{pol}. \quad (4)$$

Initial studies of SOP in OLEDs focused primarily on this injection/accumulation phenomenon, with only speculation on its potential impact on key device properties such as efficiency and lifetime.¹³ However, a series of recent studies have now established a quantitative link between device peak efficiency, lifetime, and SOP.^{73,82–84} These results highlight the importance of understanding and manipulating this phenomenon to maximize device performance.

II. SOP FORMATION MECHANISMS

The process of SOP formation is usually considered as an interplay between several factors reflecting intermolecular interactions and vapor processing conditions. Relevant interactions known to impact SOP include both van der Waals (vdW) interactions (between induced dipoles) and dipole–dipole interactions between PDMs [Fig. 3(a)]. As was the case for birefringence, vapor processing conditions including substrate temperature and deposition rate also strongly determine the degree of PDM alignment. These factors can be unified in a common

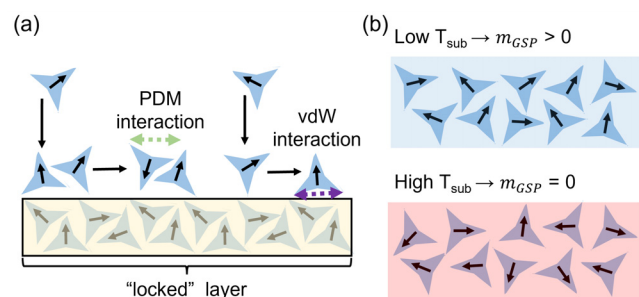


FIG. 3. (a) The role of intermolecular interactions in SOP formation during physical vapor deposition. Reproduced with permission from He *et al.*, ACS Appl. Mater. Interfaces **15**, 1652 (2023). Copyright 2023 American Chemical Society. (b) The influence of substrate temperature during processing on SOP, where increased deposition temperature reduces m_{GSP} .

“surface equilibration” framework^{20,36,37} first applied to SOP by Ediger and co-workers to explain both TDM and PDM ordering of Alq₃ molecules at a qualitative level.⁶⁵ In this framework, molecular shape and electrostatic interactions dictate the equilibrium and out-of-equilibrium states of the system, while processing conditions set the timescale for transition between these states.⁸⁵ For example, deposition at high substrate temperature T_{sub} reduces the dipole ordering as depicted in Fig. 3(b), a point which will be discussed later in this work. This section provides specific examples of how these factors impact SOP, while also connecting their role into a single coherent model of SOP formation.

A. Molecular shape

Given that molecular shape was identified as a key parameter responsible for optical anisotropy in molecular glasses,¹⁶ it is not surprising that this factor can also heavily influence SOP formation. As noted earlier, non-centrosymmetric molecular conformation is a prerequisite for a nonzero PDM; however, this alone does not guarantee the presence of surface potential due to orientation. According to the “asymmetric dice model” of SOP formation,⁷¹ the net dipole orientation is dictated by the most favorable postures a molecule can take on a surface. For example, Alq₃ has two stable postures where all three ligands touch the surface.⁷¹ Although these two postures have PDM vectors pointed in opposing directions, a nonzero net dipole moment is predicted since the vertical component of the dipoles “pointing up” is larger than for the ones “pointing down.” These postures can be altered by introducing propyl groups to Alq₃ ligands,⁷¹ which has been shown to invert the polarity of tris(7-propyl-8-hydroxyquinolinolato) aluminum(III) (Al(7-Prq)3) with its negative m_{GSP} shown in Fig. 4(a).

Based on the model described above, the change in molecular conformation can modify not only PDM magnitude and direction but also the distribution of its orientation with respect to the film growth direction. This was demonstrated through the addition of ethyl groups to TPBi,⁸⁶ a widely used organic semiconductor molecule that exhibits relatively strong SOP.^{25,29} Based on DFT calculations, the addition of these functional groups changes the conformation structure of TPBi, enhancing the z-component of its PDM.⁸⁶ While both conformers show a tendency toward the “face up” orientation, as shown in Fig. 4(b), the C₃ conformer has a permanent dipole vector nearly parallel to the central benzene ring normal, leading to a nearly twofold enhancement in SOP strength, and demonstrating a molecular conformation engineering method to manipulate the polarization.

Another molecular design method aimed toward SOP enhancement was recently proposed by Tanaka *et al.*,⁸⁷ where the dipole orientation was successfully engineered by synthesizing molecules based on trifluoromethyl (3F) units that are known to reduce the surface free energy.⁸⁸ In this way, the molecular orientation of 3F/6F units pointing upwards toward the film surface is preferred as it reduces the surface free energy. As illustrated by Fig. 4(c), the sign of SOP can be controlled by introducing either electron-donating or electron-withdrawing groups to the 3F or 6F units, which reverses the PDM vector orientation, while the SOP magnitude can be manipulated by changing the PDM direction with respect to the molecular plane, a finding that is in a good agreement with previous work.⁸⁶ Given that the majority of reported materials display a positive GSP slope [see Fig. 2(a)], molecular synthesis is a promising tool to design molecules

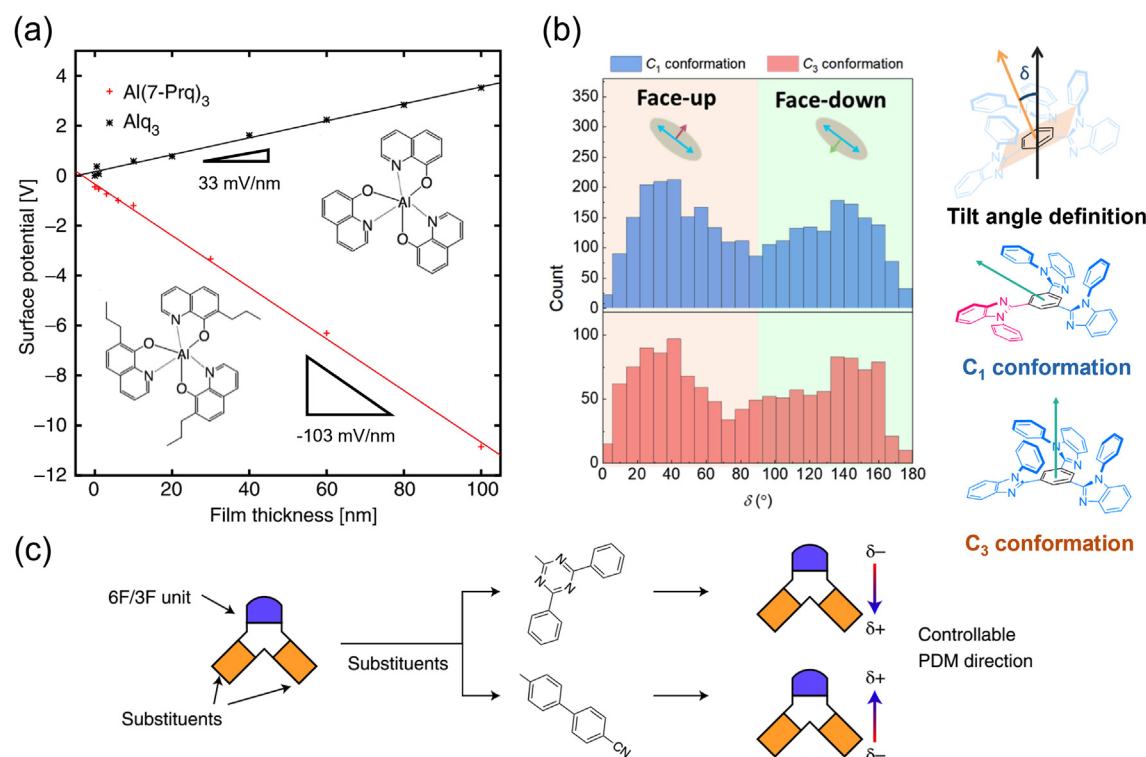


FIG. 4. (a) Surface potential as a function of film thickness for two molecules: Alq₃ (black line) and Al(7-Prq)₃ (red line), showing a difference in the m_{GSP} sign. Reproduced from Noguchi *et al.*, Appl. Phys. Lett. **102**, 203306 (2013). Copyright 2013 AIP Publishing. (b) Distributions of the tilt angles, defined as the angle between the normal to the central benzene ring (orange arrow) and the surface normal. The population of “face-up” molecules ($0^\circ < \delta < 90^\circ$) is slightly higher than the one of “face-down” molecules ($90^\circ < \delta < 180^\circ$) for both TPBi conformations. Reproduced with permission from Schmid *et al.*, ACS Appl. Mater. Interfaces **12**, 51709 (2022). Copyright 2022 American Chemical Society. (c) Control of molecular permanent dipole direction by introducing substituents that invert the dipole direction with respect to molecular symmetry axis. Reproduced with permission from Tanaka *et al.*, Nat. Mater. **21**, 819 (2022). Copyright 2022 Springer Nature.

with negative SOP that could be advantageous in several applications to be discussed later in this review.

B. Dipole-dipole interactions and substrate effects

SOP formation is commonly viewed as a competition between the molecule-surface vdW forces and intermolecular dipole-dipole interactions, with vdW forces tending to favor SOP^{25,27,72,89} and dipole-dipole interactions favoring anti-parallel dipole antialignment.^{27,29,57,90,91} As such, methods to engineer SOP have often sought to tune one or both of these interactions. For dipole-dipole interactions, some tuning can be realized through the introduction of a non-polar (zero dipole moment) molecular component in the SOP matrix, a process known as the “dipolar doping.”^{73,90,91} For example, an enhancement in TPBi PDM orientation was shown upon mixing with various nonpolar molecules, such as 4,4′-bis(N-carbazolyl)-1,1′-biphenyl (CBP), N,N′-bis(1-naphthyl)-N,N′′-diphenyl-1,1′-biphenyl-4,4′-diamine (TCTA), and 1,4-bis(triphenylsilyl)benzene (UGH2).^{27,29,84} Such enhancement is evidenced from increased surface potential values, as shown in Fig. 5(a). A maximum threefold enhancement in orientation was realized in TPBi:TCTA films with 30:70 composition, explained by the fact that nonpolar molecules act as a “spacer,”

increasing the average distance between the TPBi PDMs and thus decreasing their interaction [Fig. 5(b)]. Note that the associated decrease in dipole density tends to reduce SOP,^{29,73,90} so enhancement in orientation upon dilution does not guarantee an increase in the overall film polarization. Nevertheless, a maximum polarization enhancement of $\sim 50\%$ is reached for films with 50:50 composition and is reduced at high ($>75\%$) concentrations of the diluting species, a result consistent across several molecular pairings.^{27,90} A similar effect was observed when diluting polar Alq₃ with N,N′-di(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (NPB),⁹⁰ where the degree of Alq₃ orientation was increased in a blend, as shown in Fig. 5(c). To date, emphasis has been placed on blends where only one material shows SOP in neat film. Despite this, dipole-dipole interactions are also expected to be important for blends where both systems exhibit SOP, which have also recently been demonstrated as a means to engineer SOP.⁸⁵ In considering SOP in blends from an application standpoint, it is important to make sure that other key film properties (for example, charge transport), are not detrimentally impacted upon mixing.^{73,84}

As mentioned previously, vdW interactions with the underlying surface positively contribute to SOP formation. Strong vdW forces experienced by the molecule during vapor deposition prevent it from

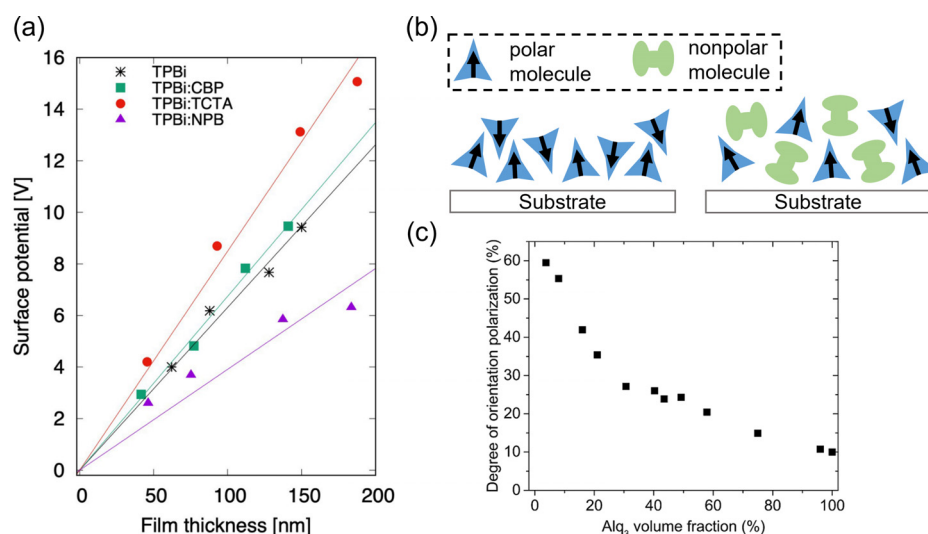


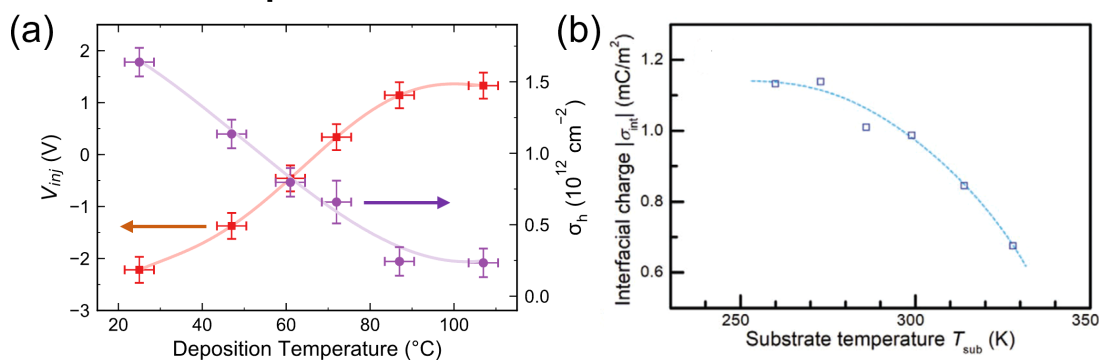
FIG. 5. (a) Surface potential as a function of film thickness for neat TPBi and TPBi codeposited with nonpolar or negligibly polar molecules (CBP, TCTA, NPB) with a 50:50 mixing ratio. Reproduced with permission from Noguchi *et al.*, J. Soc. Inf. Disp. **29**, 29 (2020). Copyright 2020 John Wiley & Sons, Inc. (b) Illustration of the “dipolar doping” principle, where introducing the nonpolar molecules increases the intermolecular distance between the polar molecules, which reduces the dipole anti-alignment thus enhancing dipole orientation. (c) Degree of Alq₃ dipole orientation as a function of its volume fraction in an NPB:Alq₃ mixture. Reproduced with permission from Jäger *et al.*, AIP Adv. **6**, 95220 (2016). Copyright 2016 AIP Publishing.

sampling numerous configurations before being immobilized by the subsequently deposited layer, frustrating a full equilibration. Note that the impact of vdW forces on SOP also depends on the direction of PDM relative to the surface normal in this “locked” state. These are very short-range forces ($U_{\text{vdW}} \propto 1/r^6$) between the molecule and its nearest neighbors, while dipole-dipole interactions are longer range ($U_{\text{d-d}} \propto 1/r^3$). An atomistic Monte Carlo-based study of SOP formation identified that the nonbonded interaction between the molecule and the surface is the key factor that drives dipole ordering in thin organic semiconductor films.⁷² This finding has been confirmed experimentally by first treating the substrate with a self-assembled-monolayer (SAM) to modify surface energy.²⁷ Films deposited on the SAM-treated substrate displayed a lower GSP slope due to reduced molecule-substrate interactions, enabling the molecules to adopt anti-parallel dipole configurations due to enhanced surface mobility. Interestingly, reduced polarization for the SAM-treated samples was observed only for the first 30 nm of the film, after which the difference in surface potential between the treated and non-treated films becomes negligible. Another study investigated the impact of the substrate on molecular packing by means of GIWAXS, concluding that the length scale over which the inorganic underlayer can perturb molecular packing is on the order of 3–8 nm,⁹² though dipole orientation was not specifically probed in this study. In an attempt to investigate the influence of underlayer SOP on dipole orientation of the subsequently deposited molecules, Okabayashi *et al.*⁹³ measured the surface potential of an Alq₃ film deposited on the backside of a separate Alq₃ film fabricated via a “peel-off” method.⁹⁴ Compared to an Alq₃ film deposited on an indium-tin-oxide (ITO)-coated glass substrate, an Alq₃ film deposited on an underlayer with opposite SOP showed practically no change in dipole orientation, concluding that the SOP sign of the underlayer has little to no effect on the subsequently deposited layers.⁹³ Currently, there has not been a systematic study on the influence of both organic and inorganic substrates on SOP formation. However, previous work suggests that the substrate effects on SOP become negligible once full coverage is realized.^{27,93}

C. Surface relaxation and processing conditions

While modifications in the chemical structure or solid-state dilution with a nonpolar material can successfully tune SOP, this may also lead to undesirable changes in charge transport, molecular orbital energy levels, glass transition temperature, or other physical properties. Therefore, a less invasive method to modify SOP may be preferred, such as a change in film processing conditions. As was the case for birefringence, the two variables of interest during deposition are the substrate temperature relative to materials glass transition temperature (T_{sub}/T_g) and the deposition rate (R_{dep}). It is worth noting that earlier studies on SOP demonstrated its removal either by continuous photo-exposure^{12,95} or heating⁹⁶ after film deposition. In this section, the focus is instead on engineering SOP during the film formation process. Thin film deposition at elevated substrate temperatures has been shown to decrease the polarization charge by 40%–80% for both Alq₃ ($T_g = 175^\circ\text{C}$)⁸³ and TPBi ($T_g = 124^\circ\text{C}$)⁸² with the relative substrate temperature ranging from $0.6 T_g$ to $0.9 T_g$, as evidenced from Figs. 6(a) and 6(b). These findings stress the importance of materials T_g in the SOP formation process. For example, a difference in glass transition temperature was identified as an origin of the 10-fold difference in SOP between 6F-2TRZ and 6F-2TPA, two molecules with compatible PDM magnitudes but drastically different orientations.⁸⁷ This way, a change in materials T_g is equivalent to an indirect change in the deposition temperature, which has been used to engineer both SOP and TDM alignment.²³ Increases in deposition rate have been found to have an opposite effect on SOP, leading to a larger polarization [Figs. 6(c) and 6(d)]. In separate works, an m_{GSP} enhancement of ~50% for 6F-2BN⁸⁷ and ~80% enhancement for TPBi⁸⁵ have been observed upon an increase in the deposition rate from $0.05 \text{ \AA/s}$ to $30 \text{ \AA/s}$ and $0.05 \text{ \AA/s}$ to $12 \text{ \AA/s}$, respectively. For practical applications, SOP manipulation through the deposition rate may be preferred over variations in substrate temperature since device fabrication at elevated temperatures may lead to the degradation of other layers in the stack, although processing time must also be considered if applying slower deposition rates.

Substrate Temperature



Deposition Rate

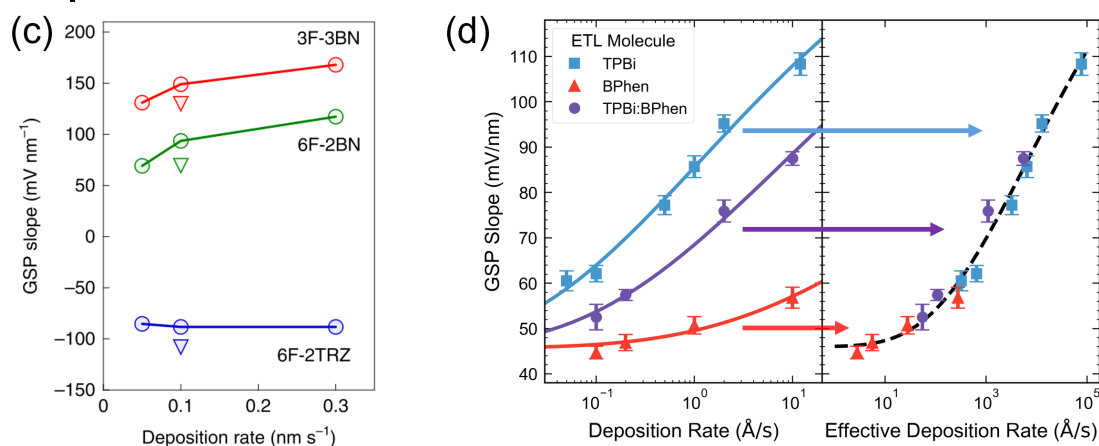


FIG. 6. (a) Hole injection voltage (red) and accumulated charge density (purple) as a function of TPBi deposition temperature for an archetypal green phosphorescent OLED. Reproduced with permission from Bangsund *et al.*, *Sci. Adv.* **6**, eabb2659 (2020). Copyright 2020 Authors, licensed under a Creative Commons Attribution (CC BY) license. (b) Interfacial charge density of NPd/Alq₃ OLED as a function of substrate temperature. Reproduced with permission from Esaki *et al.*, *Adv. Electron. Mater.* **7**, 2100486 (2021). Copyright 2021 John Wiley & Sons. (c) GSP slope as a function of actual deposition rate for molecules based on trifluoromethyl (3F) functional group (positive m_{GSP}) and hexafluoropropane (6F) functional group (6F) (negative m_{GSP}), both showing a rate dependence. Reproduced with permission from Tanaka *et al.*, *Nat. Mater.* **21**, 819 (2022). Copyright 2022 Springer Nature. (d) GSP slope for several ETLs as a function of deposition rate (left side) and as a function of a common variable of effective deposition rate (right side), which is by definition the rate that has to be used to achieve a given SOP strength if material is deposited at its glass transition temperature. Reproduced with permission from He *et al.*, *ACS Appl. Mater. Interfaces* **15**, 1652 (2023). Copyright 2023 American Chemical Society.

The processing condition dependence of molecular orientation responsible for birefringence has been previously treated using a “rate-temperature superposition” framework which includes the impact of both substrate temperature and deposition rate.^{19,38,65} The RTS principle states that in engineering molecular anisotropy, deposition at elevated substrate temperature is equivalent to a reduced deposition rate. This principle is a consequence of the “surface equilibration” mechanism^{36,37,97,98} that was successfully applied to explain the origin of both structural and optical anisotropy in vapor-deposited molecular glasses. According to this mechanism, enhanced surface mobility in the outermost layer during the process of physical vapor deposition (several orders of magnitude higher than bulk mobility) allows molecules to partially equilibrate before being “trapped” by the subsequently deposited layer. This way, both increased substrate temperature and decreased deposition rate lead to a more equilibrated film via enhanced surface mobility (and thus shorter equilibration

time) in one case and longer molecule surface residence time before trapping by the next layer in the other case.³⁸ The model of surface equilibration has to date been shown to agree quantitatively with rate- and relative temperature- dependent data on SOP in several archetypal materials.⁸⁵

Understanding the kinetics of SOP formation under a common rate-temperature framework allows for the construction of a “master curve” that provides a set of appropriate processing conditions to obtain a desirable degree of SOP, and an example is shown in the right side panel of Fig. 6(d). To construct such a curve, a common variable that incorporates both deposition temperature and rate is defined, known as the effective deposition rate at T_g ,³⁸

$$R_{eff}(T_g) = R_{act}(T_{sub}) \cdot 10^{S(T_g - T_{sub})}, \quad (5)$$

where $R_{act}(T_{sub})$ is the actual deposition rate at substrate temperature T_{sub} and S is the shift factor that is typically found empirically via the

iterative fitting process (see supplementary material in Refs. 38 and 85 for further details). Fundamentally, this relationship is based on the process of glass formation during vapor deposition with a characteristic timescale τ .³⁶ The glass relaxation time depends exponentially on the deposition temperature, with the shift factor being a fit parameter for this relaxation-temperature dependence: $\tau(T_{\text{sub}}) = \tau(T_g) \cdot 10^{S(T_g - T_{\text{sub}})}$.³⁸ Within this framework, both deposition temperature and rate are tied to the timescale of glass relaxation, making it possible to collapse these variables into one $[R_{\text{eff}}(T_g)]$. The characteristic relaxation time $[\tau(T_{\text{sub}})]$ can be extracted by fitting the rate-dependent curve for molecular orientation at T_{sub} .^{38,85} The knowledge of such timescales not only provides physical insights into the glass formation process during physical vapor deposition, but also allows predictions of the temperature ranges over which the rate dependence of molecular orientation would be the most prominent.

Notably, the rate-temperature equivalence of SOP can be used to unify already existing mechanisms of dipole alignment outlined in this section. To summarize, in the limit of low surface mobility, the molecule has a limited ability to travel along the surface, leading to an out-of-equilibrium structure with larger SOP. In contrast, the regime of high surface mobility allows the molecule to sample more configurations, making it more likely to either anti-align with its nearest neighbor or orient randomly.

III. IMPACT OF SOP ON OLED PERFORMANCE

As noted earlier, the presence of SOP in one of the active layers of an OLED alters the electric field distribution within the device leading to sub-turn-on charge injection/accumulation as in Figs. 2(d) and

2(e). This section discusses how changes in device physics due to SOP affect key OLED characteristics, such as the charge injection, efficiency, and stability.

A. Charge injection

The presence of SOP in the transport layer of an OLED can affect charge injection in two ways. First, SOP alters the field distribution within the device resulting in charge injection at sub-threshold voltages, an effect that scales with SOP layer thickness according to Eq. (4). The implications of such charge injection and accumulation are discussed further in Sec. III B. Second, if the SOP layer is adjacent to one of the electrodes, the polarization charge at the organic/electrode interface will Coulombically interact with charges injected from the respective electrode. The influence of the polarization charge sign on electron injection has been investigated by comparing OLEDs with ETLs of differing polarities but otherwise similar molecular orbital energy levels: Alq_3 ($m_{\text{GSP}} = 33\text{--}55\text{ mV/nm}$ ^{12,25,71,99}) and $\text{Al}(7\text{-Prq})_3$ [$m_{\text{GSP}} = -(118\text{--}103)\text{ mV/nm}$ ^{28,71}]. By tracking the electron injection/extraction processes via DCM, a frustration in electron injection was observed for the samples with an ETL of $\text{Al}(7\text{-Prq})_3$, a finding further reflected in a much higher turn-on voltage as evidenced from the current-luminance-voltage characteristics shown in Fig. 7(a).²⁸ Such a decrease in electron injection was attributed to the repulsion between electrons and negative polarization charges at the $\text{Al}(7\text{-Prq})_3/\text{Ca}$ interface. The physical mechanisms behind SOP and charge injection were further evaluated by the means of high-sensitivity photoelectron spectroscopy (HS-PES) and photoelectron yield spectroscopy (HS-PYS),

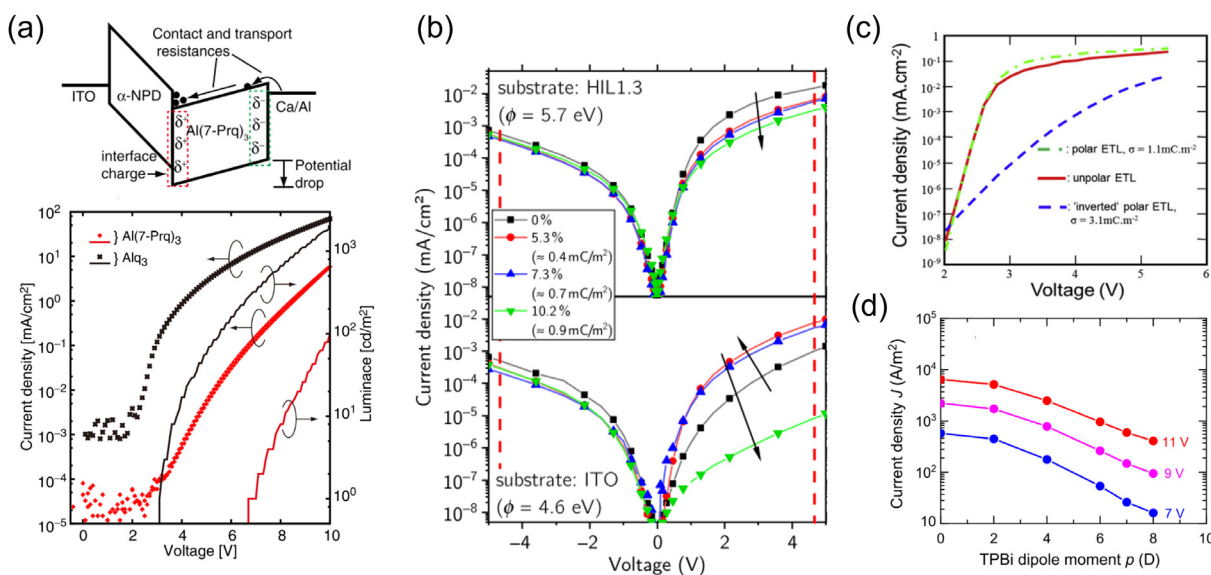


FIG. 7. (a) Energy diagram for a bilayer OLED with an ETL having negative m_{GSP} , illustrating the process of electron injection (top) and current-voltage-luminance characteristics for OLEDs with positive (black) and negative (red) polarity ETLs (bottom). Reproduced with permission from Noguchi *et al.*, Appl. Phys. Lett. **102**, 203306 (2013). Copyright 2013 AIP Publishing. (b) Current-voltage measurements of hole-only devices based on an NPB:Alq₃ mixture for various doping concentrations of Alq₃. Unipolar samples with HIL substrate serve as a benchmark for low hole injection barrier (top), while ITO substrate samples initially display poor hole injection at positive bias that improves at moderate doping levels. Reproduced with permission from Hofmann *et al.*, Phys. Rev. Appl. **12**, 06452 (2019). Copyright 2019 American Physical Society. (c) Drift-diffusion simulation of OLED current density-voltage characteristics for ETL with positive (green), zero (red), and negative (blue) polarities. Reproduced with permission from Altazin *et al.*, Org. Electron. **39**, 244 (2016). Copyright 2016 Elsevier. (d) Current density of an archetypical green phosphorescent OLED at various voltages as a function of ETL dipole moment magnitude simulated by the 3D-KMC model. Reproduced with permission from Coehoorn *et al.*, Phys. Rev. Appl. **16**, 034048 (2021). Copyright 2021 American Physical Society.

techniques commonly used to evaluate the electronic structure at metal-organic^{100–103} and organic-organic^{104,105} interfaces. This study provided experimental evidence of the Coulombic interaction between the injected electrons (anion states of Alq₃) and the bound polarization charges, showing that the charge injection from the electrode to transport layer can be either enhanced or frustrated depending on the polarization sign.¹⁰⁶

Similar results have been observed in attempts to modify hole injection into the HTL with positive SOP, where the negative polarization charge at the anode (or HIL)/HTL interface reduces the hole injection barrier. Indeed, Hofmann *et al.* achieved an improvement in hole injection by moderately (1–10 vol. %) doping the negligibly polar hole transporter NPB with SOP-exhibiting Alq₃.⁹¹ Unipolar samples with the layer stack of ITO/NPB:Alq₃/1,4,5,8,9,11-hexaazatriphenylene-hexacarbonitrile (HATCN)/Au showed an improvement in hole injection with an optimum at a doping level of 5–7 vol. % as evidenced from an increase in hole current and a reduced injection barrier shown in the bottom panel of Fig. 7(b).⁹¹

The experimental findings described above are in good agreement with drift-diffusion simulations of carrier behavior, which suggest an enhancement in current density for a given voltage above turn-on when positive SOP is introduced to the ETL, and a drastic (>2 orders of magnitude) reduction in the case of an ETL with negative SOP [Fig. 7(c)].¹⁰⁷ Such a difference arises due to the change in electron injection/transport, which was confirmed by simulating the electron concentrations as a function of SOP sign, showing an enhanced electron concentration at the ETL/cathode interface when the SOP is positive in excellent agreement with the experimental findings.¹⁰⁷ The change in current density may reflect not only the drop/rise in the charge injection barrier but also the change in mobility. As pointed out by multiple studies, it is thus important to understand the behavior of hole- and electron-mobilities with SOP.^{28,91,108} It is known that the presence of a significant electric dipole moment widens the frontier orbital density of states (DOS) and, therefore, decreases the hopping probability and consequently carrier mobility.^{109–111} Such a behavior has been captured by the 3D kinetic Monte Carlo (KMC) simulations, where the calculated OLED current density was reduced upon an increase in the ETL dipole moment as shown in Fig. 7(d).¹⁰⁸ A similar behavior was observed experimentally in the NPD:Alq₃ films, where the increase in Alq₃ concentration resulted in lower hole mobility of the film, as shown in the top panel of Fig. 7(b).⁹¹

B. Efficiency

It is well-known that excess polarons present in the emissive layer of an OLED can act as exciton quenchers,^{112–117} and exciton-polaron quenching (EPQ) has been previously identified to be a contributing factor to efficiency roll-off.^{118–121} The severity of bimolecular processes like EPQ *prior* to device turn-on, and even close to the onset of efficiency roll-off, has been regarded as negligible, given the assumed small charge density in this regime.^{122,123} However, this assumption is not valid in the presence of SOP due to the significant *sub-turn-on* charge accumulation. Although it has been speculated that accumulated charges may quench excitons and lead to efficiency reduction,¹³ a direct measurement of such quenching was reported only recently.⁸² In an archetypical green phosphorescent OLED, the amount of peak internal efficiency reduction was found to scale directly with the amount of SOP-induced quenching, ranging from 20% to 50%,^{73,82}

depending on the SOP strength (an equivalent of up to 9% reduction in peak external quantum efficiency). While the focus of this review is on the impact of SOP on OLED efficiency, it is important to note that the PDM alignment is not the only efficiency limiting factor, and a complete analysis requires consideration of the full device structure. Emissive layer structures discussed in this section include (1) phosphorescent iridium-based complexes in a host-guest system with 7–8 vol. % emitter doping concentrations^{73,82,124} [CBP:Ir(ppy)₃ and TPBi:Ir(ppy)₃], (2) archetypical Alq₃-based fluorescent bilayer OLEDs,^{26,83} and a (3) blue-emitting fluorescent host-guest system with 4 wt. % emitter doping concentration.⁸⁴ Generally, the degree of SOP-induced EPQ (and, thus, the efficiency reduction) should reflect the choice of EML, where more diffusive excited states might experience increased quenching. Ideally, the magnitude of quenching and peak efficiency should be measured independently and compared to identify whether SOP is the key efficiency limiting source. In such an analysis, it is crucial to properly account for other sources of efficiency losses, especially if they are also impacted by activities directed at tuning SOP. These might include (1) the light outcoupling efficiency (η_{oc} , can be simulated using the classical emission model with the knowledge of the transition dipole orientation^{42,43}), (2) the charge balance or exciton formation efficiency (η_{eff} , can be influenced by changes in the charge mobilities of the transport layers¹²⁵), and (3) the photoluminescence quantum yield of the emitter (η_{PL} , which depends strongly on the emitter concentration¹²⁶ and can also be impacted by the processing temperature^{124,127}). When a direct measurement of EPQ is not available, it is still possible to assess the impact of SOP on device efficiency by accurately measuring the factors (1)–(3) and ascribing remaining efficiency losses to EPQ, a procedure demonstrated in Ref. 83.

The methods to tune SOP outlined in Sec. II have been successfully applied to engineer charge accumulation and enhance OLED efficiency. Raising the substrate temperature during TPBi deposition from 25 °C (0.75 T_g) to 80 °C (0.9 T_g) increases the external quantum efficiency by 30% in phosphorescent OLEDs based on an EML of TPBi:Ir(ppy)₃,^{82,124} which can be fully explained by the reduction in TPBi SOP and therefore reduction in deleterious exciton-polaron quenching. Deposition at higher temperatures also improves the photostability of TPBi due to an “ultrastable glass” effect.¹²⁴ A similar enhancement has been observed for the bilayer N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-2,2'-dimethylbenzidine (α -NPD)/Alq₃ fluorescent OLED, where ~40% efficiency enhancement was observed between the samples deposited at –13 °C (0.58 T_g) and 55 °C (0.73 T_g),⁸³ a result of improvement in several factors: PL quantum yield (3.7%), outcoupling efficiency increase due to more horizontal TDM alignment (10.5%),¹²⁷ and reduction in SOP-induced singlet-polaron quenching (~25%). As such, reduction in SOP is the primary factor contributing to the efficiency enhancement in these devices.

As noted previously, SOP can be engineered via solid-state dilution with a second material. This approach has been used to tune the SOP-induced exciton-polaron quenching in OLEDs and improve efficiency. For example, a 3.5% absolute improvement in the external quantum efficiency of a green phosphorescent OLED was realized by dilution of a TPBi ETL with nonpolar UGH2.⁷³ Device efficiency showed a non-monotonic trend with mixture composition due to the poor electron transporting properties of UGH2, further emphasizing the need to consider potential changes in electrical performance when

using this approach to tune SOP.^{73,84} Noguchi *et al.*⁶⁹ realized a full compensation of the polarization charge density by diluting a non-SOP HTL with a polar dopant, which removed the accumulation charge almost entirely. However, a corresponding efficiency enhancement was prevented by dilution-induced deterioration in charge balance.⁶⁹ In a separate study, a 30% efficiency improvement in device external quantum efficiency (from 5% to 6.5%) was observed in a blue fluorescent OLED by co-depositing TPBi with medium-density polyethylene (MDPE).⁸⁴ Interestingly, a drastic (>50%) reduction in SOP was achieved even for low (10%) MDPE concentrations, which may reflect non-uniform composition and the specifics of the polymer-small molecule mixture.⁸⁴ Such findings are in contrast with small molecule mixtures that typically show modest changes in SOP for low dilution levels^{73,90} and merits further investigation.

Building off the work of Sec. II C describing the ability to tune SOP with thin film processing conditions, similar methods have been used to reduce SOP-induced exciton-polaron quenching and increase OLED efficiency. For example, deposition of TPBi at substrate temperatures of 0.9T_g leads to significant reduction in sub-turn on carrier accumulation and low-bias exciton quenching in phosphorescent OLEDs.⁸² Similarly, the preparation of OLEDs based on several ETLs at low deposition rates has been shown to reduce SOP and the degree of exciton-polaron quenching, leading to an increase in device efficiency. Specifically, deposition of the ETL at low rates (0.05–0.1 Å/s) resulted in 10%–15% absolute enhancement in device internal quantum efficiency, with no further changes in layers electrical properties observed for the range of deposition rates under investigation.⁸⁵ For devices employed in these temperature- and rate-dependent studies,^{82,85} SOP was found to be the dominating factor reducing peak efficiency, and internal quantum efficiencies close to 100% were realized by reducing SOP via processing condition optimization.⁸²

Since the deleterious exciton quenching caused by SOP is directly proportional to the amount of efficiency reduction in an OLED,^{73,82,84} it is crucial to understand the device parameters that contribute to exciton-polaron quenching. One way to quantify EPQ is by measuring the change in OLED photoluminescence (PL) as a function of the SOP-induced accumulated charge density.^{69,82,84} To fully capture the impact of EPQ in an OLED, this measurement should be carried in the regime of device operation.^{69,128} Since the accumulated charge density depends on voltage according to Eq. (4), measuring PL as a function of voltage reveals the SOP-induced exciton dynamics, as illustrated by Fig. 8(a) where PL scans are compared between devices containing ETLs of either the polar TPBi or non-polar 4,6-bis(3,5-di(pyridin-3-yl)phenyl)-2-methylpyrimidine (B3PYMPM).⁸² Notably, a reduction in the PL signal at voltages below the device turn-on voltage (luminance-voltage curves reflect device turn on) is only present for OLEDs with a polar ETL, a phenomenon ascribed to exciton-polaron quenching with SOP-induced charges.^{73,82} This quenching significantly impacts peak device efficiency, as illustrated by the strong correlation between the PL intensity and the peak internal quantum efficiency (IQE) in Fig. 8(b), a result consistent across OLEDs constructed using a variety of ETL molecules⁷³ and processing conditions.⁸² SOP-driven reductions in peak efficiency or PL can be understood as a reduction in the steady-state exciton density under continuous optical or electrical excitation, respectively. The exciton density can be modeled by choosing an appropriate rate equation.^{73,82}

$$\frac{\partial n_{\text{ex}}(x)}{\partial t} = G(x) + D \frac{\partial^2 n_{\text{ex}}(x)}{\partial x^2} - n_{\text{ex}}(x) \left(\frac{1}{\tau_{\text{ex}}} + k_{\text{tp}} n_{\text{h}}(x) \right), \quad (6)$$

where x is the out-of-plane spatial coordinate, $n_{\text{ex}}(x)$ is the exciton density as a function of the position within the emissive layer, $G(x)$ is the optical or electrical exciton generation rate, D is the exciton diffusivity, τ_{ex} is the exciton lifetime, k_{tp} is the quenching rate constant, and $n_{\text{h}}(x)$ is the spatially dependent polaron density (hole density in the case of positive ETL SOP). The severity of EPQ and efficiency reductions depend on the spatial overlap between excitons and polarons, which is influenced by the exciton diffusivity D and the spatial profiles of $n_{\text{ex}}(x)$ and $n_{\text{h}}(x)$, along with the ability to effectively quench excitons set by k_{tp} and the polaron sheet density $\int_0^{d_{\text{EML}}} n_{\text{h}}(x) dx$. While the injected polaron density can be calculated from DCM⁸¹ and varies linearly with SOP strength,^{26,73} accurately establishing the spatial overlap between the exciton and polaron populations is challenging as it requires knowledge of the spatial profiles for each species. Nevertheless, by using Eq. (5) along with a common set of kinetic simulation parameters separately extracted from the literature for the relevant EML,^{129–131} the magnitude of quenching can be predicted across several ETL materials, compositions, and deposition temperatures, as shown by Fig. 8(c) with the blue line representing the simulation results. Note that this model assumes that the spatial distribution of accumulated polarons decays exponentially away from the EML/ETL interface. This is in qualitative agreement with the previous assessment of the charge distribution in α -NPD/Alq₃ OLEDs¹³² via the Mott-Schottky analysis.^{133,134} Note that the magnitude of EPQ is a strong function of the assumed charge distribution, as illustrated by Fig. 8(d). Based on the kinetic population modeling of PL, the estimated carrier accumulation length scale is in the range of 2–7 nm.^{73,82} However, new methods to quantitatively probe the spatial distribution of polarons are critical for accurate modeling of this phenomenon in OLEDs, especially those with thicker (>10 nm) emissive layers and multiple layers exhibiting SOP.

More broadly, the phenomenon of SOP in OLEDs has been successfully modeled from first principles using the well-established drift-diffusion formalism that utilizes continuity equations for electrons and holes combined with the Poisson equation.^{107,135} In a drift-diffusion simulation, SOP is considered by introducing a sheet charge density at each side of the polar layer. This method is able to quantitatively predict the device capacitance-voltage characteristics and also captures the key qualitative features of the current-voltage data.¹⁰⁷ This approach also qualitatively reproduces SOP-induced EPQ⁸⁴ with a predicted exponential decay of the accumulated charge from the interface adjacent to the SOP layer. As such, both charge injection and exciton quenching phenomena induced by the polarization in OLEDs are predicted theoretically within the drift-diffusion formalism. However, this method may not fully capture the dipole-induced energetic disorder that is known to impact charge injection¹³⁶ and transport.¹³⁷ These effects are accounted for in three-dimensional KMC simulations of archetypal green phosphorescent OLEDs.¹⁰⁸ Such KMC simulations rigorously include dipole-induced energetic disorder, along with the magnitude and angular distribution of molecular dipoles. Notably, the best agreement between the modeled and experimental efficiency and current-voltage data is achieved when SOP is included in the model, supporting the fact that polarization has a major impact on OLED operation. Device efficiency was found to be sensitive to the

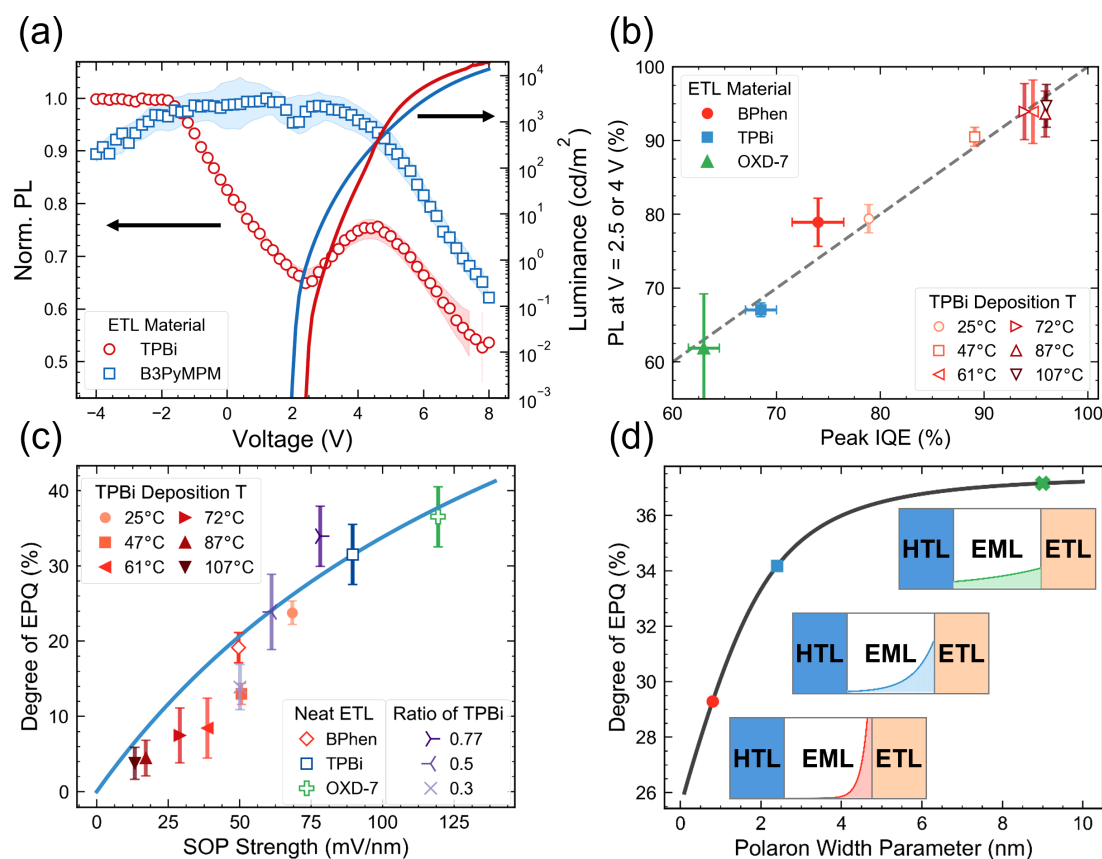


FIG. 8. (a) Normalized photoluminescence as a function of applied voltage for OLEDs with TPBi and B3PYMPM ETLs. Bangsund *et al.*, *Sci. Adv.* 6, eabb2659 (2020). Copyright 2020 Author(s), licensed under a Creative Commons Attribution (CC BY) license. (b) Comparison between the peak internal efficiency and normalized PL for archetypical green phosphorescent OLEDs with several SOP ETLs and several ETL deposition temperatures. Data taken from Refs. 73 and 82. (c) Magnitude of the exciton-polaron quenching (EPQ) as a function of SOP strength, represented by the m_{GSP} magnitude. The model prediction (solid line) is in quantitative agreement with the experimentally measured EPQ for OLEDs with different deposition temperatures (solid symbols), ETL materials (hollow symbols), and ETL compositions (line symbols). For the compositional ETL data, TPBi is diluted with non-polar UGH2. Data taken from Refs. 73 and 82. (d) Simulated degree of quenching as a function of polaron width. Figure insets illustrate the polaron distribution within the emissive layer.

magnitude and order parameter of the TPBi dipole moment, which is in agreement with the experimental studies on the role of SOP strength in OLED efficiency.^{79,82}

C. Lifetime

Exciton-polaron interactions have been previously identified as an important degradation pathway for phosphorescent,^{121,138,139} fluorescent,^{138,140} and TADF¹²⁰ OLEDs. It is, therefore, important to consider whether the presence of additional polarons, especially in the EML, due to SOP impacts OLED lifetime. One challenge is decoupling polarization-induced effects from other changes that may occur with changes in processing conditions or material of choice. For instance, heating the substrate during the deposition has been shown to reduce the interfacial charge density, reduce device degradation, and increase the operational lifetime of an archetypical α -NPD/Alq₃ fluorescent OLED.⁸³ While a clear decrease in the accumulated charge density with substrate temperature (T_{sub}) is observed, the device lifetime exhibits a more complicated functional form as can be seen in Figs. 9(a) and 9(b).

A convex functional dependence of lifetime on T_{sub} with a peak at ~ 300 K is attributed to an interplay across several temperature-dependent factors, including the presence of impurities for depositions at lower T_{sub} , imbalance between the hole- and electron- currents for higher T_{sub} , and changes in injected charge density.⁸³ Another identified mechanism of the lifetime enhancement with an increase in T_{sub} is the formation of an “ultrastable glass,”^{37,97} where the deposition of a phosphorescent TPBi:Ir(ppy)₃(acac) OLED at elevated temperatures has been shown to improve the kinetic stability of the TPBi host.¹²⁴ To summarize, a commonly observed lifetime enhancement for the SOP emissive layer deposition temperatures around 0.8–0.85 T_g has been attributed to multiple factors, including reduction in polarization charge,^{82–84} enhancement in glass kinetic stability,¹²⁴ and impurity elimination.⁸³

To fully isolate the role of polarization changes from other factors impacting OLED lifetime, Afolayan *et al.* employed the concept of dipolar doping as described in Sec. II B to reduce the SOP of the TPBi ETL in a fluorescent blue OLED via dilution with MDPE.⁸⁴ A reduction in polarization charge was quantitatively linked to enhancements

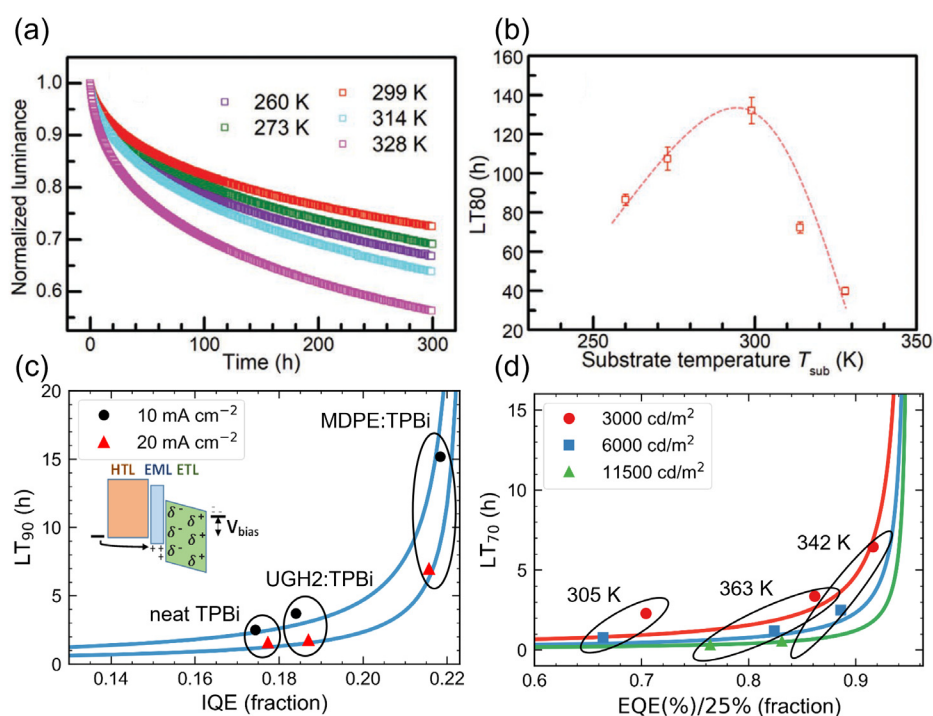


FIG. 9. (a) Time evolution of the normalized electroluminescence in fluorescent Alq₃-based OLEDs with different Alq₃ deposition temperatures T_{sub} and (b) time to 80% of initial luminance (LT_{80}) as a function of T_{sub} . Reproduced with permission from Esaki *et al.*, Adv. Electron. Mater. 7, 2100486 (2021). Copyright 2021 John Wiley & Sons. (c) Time to 90% of initial luminance (LT_{90}) as a function of pristine device IQE. Solid lines are the fits obtained from the scaling relationship between efficiency and lifetime. Reproduced with permission from Afolayan *et al.*, Phys. Rev. Appl. 17, 51002 (2022). Copyright 2022 American Physical Society. (d) Time to 70% of initial luminance (LT_{70}) as a function of external quantum efficiency (EQE) divided by the approximated outcoupling efficiency of 25%, showing a trend between device lifetime and efficiency similar to one in panel (c). Lifetime data for the Ir(ppy)₃ (acac)-based OLEDs fabricated at different deposition temperatures (305, 363, and 342 K) are taken from Ref. 124

in both efficiency and lifetime. An exciton kinetic model proposed in this study gives a functional relationship between the efficiency and lifetime enhancements, assuming that exciton-polaron quenching is the primary degradation mechanism. As can be seen in Fig. 9(c), this model is in good agreement with the experimental data.⁸⁴ Additionally, we have applied this model to fit the efficiency and lifetime data for TPBi:Ir(ppy)₃(acac) OLEDs fabricated at elevated temperatures,¹²⁴ and the results of this analysis are shown in Fig. 9(d). Since the model assumes that both efficiency and lifetime are primarily limited by SOP-induced EPQ, increases in efficiency are expected to come with an enhancement in lifetime as both are driven by reduced EPQ. While this holds for a certain temperature range [i.e., 305, 342, and 363 K as depicted in Fig. 9(d)], there are temperature regimes where lifetime and efficiency have opposite trends with temperature. Such instances imply that other, non-SOP factors, contribute to the observed changes in device operating parameters, which cannot be captured by the current model. Similarly, a decrease in Alq₃-based OLED stability has been observed for substrate temperatures above 300 K despite a positive trend in device efficiency due to reduction in SOP.⁸³ These inconsistencies arise from the fact that other temperature-dependent factors discussed earlier come into play, such as the changes in Alq₃ charge transport properties,^{83,141} glass density, and thermodynamic stability.^{37,124}

Tracking the amount of SOP-induced accumulated charges can reveal additional information on OLED degradation for various device architectures.^{67,75,78,132} Changes in the amount of accumulated charges and the onset of accumulation with device degradation were first observed by Kondakov *et al.* for an OLED based on NPD/Alq₃.⁷⁵ It was suggested that the formation of hole traps during device degradation compensates for the negative

polarization charges of Alq₃ thus reducing the amount of injected holes, although the randomization of dipole moments with aging cannot be excluded, as has been pointed out in later studies.^{132,142}

Interestingly, the reduction in accumulated charge density scales directly with the luminance loss suggesting a close relationship between the two quantities.^{75,132} Tracking SOP during degradation was used to identify the governing degradation mechanism in a TADF OLED with the emissive host-guest pair of CBP:4CzIPN.⁶⁷ Observed changes in the injected charge density with device degradation were used to identify hole trap formation in the CBP host as a mechanism responsible for the degradation, which has been reported previously for a different layer stack.¹⁴³ In a similar fashion, Schmidt *et al.* employed the combination of optical (time-resolved electroluminescence spectroscopy) and electrical (impedance spectroscopy, DCM) measurements to develop a kinetic model that is able to fit the degradation data of an archetypical CBP:Ir(ppy)₃ green phosphorescent OLED.⁷⁸ Notably, the exciton-polaron quenching with the degradation-induced CBP trapped holes can only explain the 50% of the observed reduction in luminance, and the remaining 50% were attributed to the change in charge balance that arises due to the trap-assisted non-radiative charge recombination.⁷⁸

IV. CONCLUSION AND FUTURE OUTLOOK

While it may appear that the presence of SOP mainly deteriorates OLED performance by reducing its efficiency^{73,82,84} and lifetime,^{83,84} this phenomenon can be advantageous in improving the charge injection.^{28,91,106} It may not be a coincidence that several common electron transport molecules exhibit positive SOP,²⁵ because electron injection is an important parameter for an optimal ETL. Furthermore,

polarization-induced charge accumulation can be used as a tool to determine degradation pathways in OLEDs.⁶⁷ To use SOP to its full advantage in OLEDs while also minimizing potentially negative impact of accumulated charges on excitons, a better understanding of several aspects of SOP must be realized. While the “surface equilibration” model has been successfully applied to explain the process of SOP formation on a semi-quantitative level⁶⁵ and reproduces SOP data trends,⁷² no comprehensive quantitative model able to accurately predict the polarization sign and magnitude has emerged. Such a model could be used as a screening tool to obtain the SOP of an unknown material without the need to perform resource-consuming experiments. Second, better understanding of the spatial location of accumulated charge within the OLED is required to develop effective methods to “move” this charge away from the emissive layer. Several techniques have already been introduced to address this challenge,^{79,144} although spatial resolutions on the order of 1 nm still need to be reached. Additionally, development of synthetic methods to tune the sign and magnitude of SOP via functional groups^{15,71,87} and also design entirely new polar materials would be beneficial for several reasons. Such methods might enable engineering of polar hole transporting materials to aid in hole injection, or potentially an electron blocking layer (EBL) that is able to cancel the polarization charge of an ETL to prevent the charge accumulation.

More broadly, novel synthetic methods can lead to new molecules that maximize the SOP-induced electric field, which is advantageous for other types of organic semiconductor-based devices. For example, the built-in electric field due to SOP can be used for charge dissociation in organic solar cells. While this concept has been demonstrated experimentally,^{145,146} a high efficiency device utilizing this method is yet to be fabricated. Additionally, SOP films have been successfully applied as an electret material for vibrational power generators. An electret-based generator is a device consisting of a base electrode with a permanently polarized electret material on it, along with a vibrating counter electrode separated from the base electrode by an air gap.^{147–149} Relative motion of the top electrode induces a current, which is then converted into energy. Device performance relies on the ability of the electret to store permanent polarization charge, and several charging methods have been developed, among which corona charging is the most common.¹⁵⁰ However, the charging is energetically intensive as it frequently requires thermal annealing.^{151,152} Employing an inherently polarized SOP material completely eliminates the charging step, and further advances in engineering an even higher degree of polarization would improve device performance.^{148,149}

In summary, this work provides a comprehensive overview of the phenomenon of spontaneous orientation polarization and its role in organic electronics. The engineering of molecular anisotropy in organic thin films has been used for over a decade to improve device performance, and permanent dipole alignment shows a potential to benefit several types of organic electronic devices for light-emission and energy conversion. Its successful implementation relies heavily on the ability to understand and manipulate the dipole alignment, and this work discusses recent progress in these areas. While ongoing advances are promising, providing a semi-quantitative model of SOP formation and offering overwhelming experimental evidence for the significance of this phenomenon in OLEDs, several challenges outlined in this review should be resolved to realize the full potential of SOP in organic electronics.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Evgeny Pakhomenko: Conceptualization (equal); Writing – original draft (lead); Writing – review & editing (equal). **Siliang He:** Writing – review & editing (supporting). **Russell J. Holmes:** Conceptualization (equal); Funding acquisition (lead); Writing – original draft (supporting); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

- 1C. W. Tang and S. A. Vanslyke, *Appl. Phys. Lett.* **51**, 913 (1987).
- 2G. Hong, X. Gan, C. Leonhardt, Z. Zhang, J. Seibert, J. M. Busch, S. Bräse, G. Hong, X. Gan, C. Leonhardt, Z. Zhang, J. Seibert, J. M. Busch, and S. Bräse, *Adv. Mater.* **33**, 2005630 (2021).
- 3M. Kleper, *Advanced Display Technologies: An Investigation of the Emerging and Developing Technologies Related to the Generation beyond Print-on-Paper* (Printing Industry Center at RIT, Rochester, NY, 2003).
- 4DSCC, *Statista* (DSCC, 2021).
- 5M. Koden, *OLED Displays and Lighting*, 1st ed. (John Wiley & Sons, Chichester, United Kingdom, 2016).
- 6R. Pode, *Renewable Sustainable Energy Rev.* **133**, 110043 (2020).
- 7W.-J. Joo and M. L. Brongersma, *Science* **377**, 1376 (2022).
- 8A. J. C. Kuehne and M. C. Gather, *Chem. Rev.* **116**, 12823 (2016).
- 9J. Bauri, R. B. Choudhary, and G. Mandal, *J. Mater. Sci.* **56**, 18837 (2021).
- 10H.-W. Lin, C.-L. Lin, H.-H. Chang, Y.-T. Lin, C.-C. Wu, Y.-M. Chen, R.-T. Chen, Y.-Y. Chien, and K.-T. Wong, *J. Appl. Phys.* **95**, 881 (2004).
- 11S. Berleb, W. Brütting, and G. Paasch, *Org. Electron.* **1**, 41 (2000).
- 12E. Ito, Y. Washizu, N. Hayashi, H. Ishii, N. Matsuie, K. Tsuboi, Y. Ouchi, Y. Harima, K. Yamashita, and K. Seki, *J. Appl. Phys.* **92**, 7306 (2002).
- 13Y. Noguchi, W. Brütting, and H. Ishii, *Jpn. J. Appl. Phys., Part 1* **58**, SF0801 (2019).
- 14A. Hofmann, M. Schmid, and W. Brütting, *Adv. Opt. Mater.* **9**, 2101004 (2021).
- 15Y. Noguchi, Y. Tanaka, H. Ishii, and W. Brütting, *Synth. Met.* **288**, 117101 (2022).
- 16D. Yokoyama, *J. Mater. Chem.* **21**, 19187 (2011).
- 17D. Yokoyama, A. Sakaguchi, M. Suzuki, and C. Adachi, *Org. Electron.* **10**, 127 (2009).
- 18D. Yokoyama and C. Adachi, *J. Appl. Phys.* **107**, 123512 (2010).
- 19C. Bishop, Z. Chen, M. F. Toney, H. Bock, L. Yu, and M. D. Ediger, *J. Phys. Chem. B* **125**, 2761 (2021).
- 20J. Gómez, J. Jiang, A. Gujral, C. Huang, L. Yu, and M. D. Ediger, *Soft Matter* **12**, 2942 (2016).
- 21J. Frischeisen, D. Yokoyama, C. Adachi, and W. Brütting, *Appl. Phys. Lett.* **96**, 073302 (2010).
- 22T. D. Schmidt, D. S. Setz, M. Flämmich, J. Frischeisen, D. Michaelis, B. C. Krummacher, N. Danz, and W. Brütting, *Appl. Phys. Lett.* **99**, 163302 (2011).
- 23C. Mayr and W. Brütting, *Chem. Mater.* **27**, 2759 (2015).
- 24T. Komino, Y. Sagara, H. Tanaka, Y. Oki, N. Nakamura, H. Fujimoto, and C. Adachi, *Appl. Phys. Lett.* **108**, 241106 (2016).

- ²⁵K. Osada, K. Goushi, H. Kaji, C. Adachi, H. Ishii, and Y. Noguchi, *Org. Electron.* **58**, 313 (2018).
- ²⁶Y. Noguchi, Y. Miyazaki, Y. Tanaka, N. Sato, Y. Nakayama, T. D. Schmidt, W. Brütting, and H. Ishii, *J. Appl. Phys.* **111**, 114508 (2012).
- ²⁷Y. Noguchi, K. Osada, K. Ninomiya, H. Gunawardana, R. K. Koswattage, and H. Ishii, *J. Soc. Inf. Disp.* **29**, 29 (2020).
- ²⁸Y. Noguchi, H. Lim, T. Isoshima, E. Ito, M. Hara, W. Won Chin, J. W. Han, H. Kinjo, Y. Ozawa, Y. Nakayama, and H. Ishii, *Appl. Phys. Lett.* **102**, 203306 (2013).
- ²⁹H. Gunawardana, K. Osada, R. K. Koswattage, and Y. Noguchi, *Surf. Interface Anal.* **53**, 460 (2021).
- ³⁰A. Gujral, K. A. O'hara, M. F. Toney, M. L. Chabiny, and M. D. Ediger, *Chem. Mater.* **27**, 3341 (2015).
- ³¹J. A. Woollam, B. D. Johs, C. M. Herzinger, J. N. Hilfiker, R. A. Synowicki, and C. L. Bungay, *Proc. SPIE* **10294**, 1029402 (1999).
- ³²B. Johs, J. A. Woollam, C. M. Herzinger, J. N. Hilfiker, R. A. Synowicki, and C. L. Bungay, *Proc. SPIE* **10294**, 1029404 (1999).
- ³³D. M. Walters, L. Antony, J. J. De Pablo, and M. D. Ediger, *J. Phys. Chem. Lett.* **8**, 3380 (2017).
- ³⁴D. Yokoyama, A. Sakaguchi, M. Suzuki, and C. Adachi, *Appl. Phys. Lett.* **93**, 173302 (2008).
- ³⁵D. Yokoyama, Y. Setoguchi, A. Sakaguchi, M. Suzuki, and C. Adachi, *Adv. Funct. Mater.* **20**, 386 (2010).
- ³⁶Y. Z. Chua, M. Ahrenberg, M. Tylinski, M. D. Ediger, and C. Schick, *J. Chem. Phys.* **142**, 54506 (2015).
- ³⁷S. S. Dalal, D. M. Walters, I. Lyubimov, J. J. De Pablo, and M. D. Ediger, *Proc. Natl. Acad. Sci. U. S. A.* **112**, 4227 (2015).
- ³⁸C. Bishop, A. Gujral, M. F. Toney, L. Yu, and M. D. Ediger, *J. Phys. Chem. Lett.* **10**, 3536 (2019).
- ³⁹M. E. Fiori, K. Bagchi, M. F. Toney, and M. D. Ediger, *Proc. Natl. Acad. Sci. U. S. A.* **118**, e2111988118 (2021).
- ⁴⁰R. R. Chance, A. Prock, and R. Silbey, *J. Chem. Phys.* **60**, 2744 (1974).
- ⁴¹W. L. Barnes, *J. Mod. Opt.* **45**, 661 (1998).
- ⁴²S. Nowy, B. C. Krummacher, J. Frischeisen, N. A. Reinke, and W. Brütting, *J. Appl. Phys.* **104**, 123109 (2008).
- ⁴³M. Furno, R. Meerheim, S. Hofmann, B. Lüssem, and K. Leo, *Phys. Rev. B* **85**, 115205 (2012).
- ⁴⁴M. Flämmich, J. Frischeisen, D. S. Setz, D. Michaelis, B. C. Krummacher, T. D. Schmidt, W. Brütting, and N. Danz, *Org. Electron.* **12**, 1663 (2011).
- ⁴⁵J. Frischeisen, D. Yokoyama, A. Endo, C. Adachi, and W. Brütting, *Org. Electron.* **12**, 809 (2011).
- ⁴⁶T. D. Schmidt, T. Lampe, D. Sylvinson, P. I. Djurovich, M. E. Thompson, and W. Brütting, *Phys. Rev. Appl.* **8**, 037001 (2017).
- ⁴⁷H. Shin, J.-H. Lee, C.-K. Moon, J.-S. Huh, B. Sim, J.-J. Kim, H. Shin, J.-H. Lee, C.-K. Moon, J.-S. Huh, B. Sim, and J.-J. Kim, *Adv. Mater.* **28**, 4920 (2016).
- ⁴⁸M. Flämmich, M. C. Gather, N. Danz, D. Michaelis, A. H. Bräuer, K. Meerholz, and A. Tünnermann, *Org. Electron.* **11**, 1039 (2010).
- ⁴⁹M. J. Jurow, C. Mayr, T. D. Schmidt, T. Lampe, P. I. Djurovich, W. Brütting, and M. E. Thompson, *Nat. Mater.* **15**, 85 (2016).
- ⁵⁰K.-H. Kim, J.-Y. Ma, C.-K. Moon, J.-H. Lee, J. Y. Baek, Y.-H. Kim, J.-J. Kim, Y. Ma, J. Jae, C.-K. Moon, J.-H. Lee, J. Y. Baek, Y.-H. Kim, and J.-J. Kim, *Adv. Opt. Mater.* **3**, 1191 (2015).
- ⁵¹A. Graf, P. Liehm, C. Murawski, S. Hofmann, K. Leo, and M. C. Gather, *J. Mater. Chem. C* **2**, 10298 (2014).
- ⁵²C.-K. Moon, S.-Y. Kim, J.-H. Lee, and J.-J. Kim, *Opt. Express* **23**, A279 (2015).
- ⁵³T. Lampe, T. D. Schmidt, M. J. Jurow, P. I. Djurovich, M. E. Thompson, and W. Brütting, *Chem. Mater.* **28**, 712 (2016).
- ⁵⁴K.-H. Kim, E. S. Ahn, J.-S. Huh, Y.-H. Kim, and J.-J. Kim, *Chem. Mater.* **28**, 7505 (2016).
- ⁵⁵D. Yokoyama, Y. Park, B. Kim, S. Kim, Y.-J. Pu, J. Kido, and J. Park, *Appl. Phys. Lett.* **99**, 123303 (2011).
- ⁵⁶T. Komino, H. Tanaka, and C. Adachi, *Chem. Mater.* **26**, 3665 (2014).
- ⁵⁷M. Tanaka, H. Noda, H. Nakanotani, and C. Adachi, *Appl. Phys. Lett.* **116**, 023302 (2020).
- ⁵⁸F. Tenopala-Carmona, O. S. Lee, E. Crovini, A. M. Neferu, C. Murawski, Y. Olivier, E. Zysman-Colman, and M. C. Gather, *Adv. Mater.* **33**, 2100677 (2021).
- ⁵⁹T.-A. Lin, T. Chatterjee, W.-L. Tsai, W.-K. Lee, M.-J. Wu, M. Jiao, K.-C. Pan, C.-L. Yi, C.-L. Chung, K.-T. Wong, and C.-C. Wu, *Adv. Mater.* **28**, 6976 (2016).
- ⁶⁰R. Braveenth, H. Lee, J. D. Park, K. J. Yang, S. J. Hwang, K. R. Naveen, R. Lampande, and J. H. Kwon, *Adv. Funct. Mater.* **31**, 2105805 (2021).
- ⁶¹Y.-K. Chen, J. Jayakumar, C.-M. Hsieh, T.-L. Wu, C.-C. Liao, J. Pandidurai, C.-L. Ko, W.-Y. Hung, C.-H. Cheng, Y.-K. Chen, J. Jayakumar, C.-M. Hsieh, T.-L. Wu, C.-C. Liao, J. Pandidurai, C.-H. Cheng, C.-L. W. Ko, and Y. Hung, *Adv. Mater.* **33**, 2008032 (2021).
- ⁶²S. Singh and J. J. De Pablo, *J. Chem. Phys.* **134**, 194903 (2011).
- ⁶³K. Dawson, L. A. Kopff, L. Zhu, R. J. McMahon, L. Yu, R. Richert, and M. D. Ediger, *J. Chem. Phys.* **136**, 094505 (2012).
- ⁶⁴K. J. Dawson, K. L. Kearns, L. Yu, W. Steffen, and M. D. Ediger, *Proc. Natl. Acad. Sci. U. S. A.* **106**, 15165 (2009).
- ⁶⁵K. Bagchi, N. E. Jackson, A. Gujral, C. Huang, M. F. Toney, L. Yu, J. J. De Pablo, and M. D. Ediger, *J. Phys. Chem. Lett.* **10**, 164 (2019).
- ⁶⁶C. Bishop, K. Bagchi, M. F. Toney, and M. D. Ediger, *J. Chem. Phys.* **156**, 14504 (2022).
- ⁶⁷Y. Noguchi, H. Kim, R. Ishino, K. Goushi, C. Adachi, Y. Nakayama, and H. Ishii, *Org. Electron.* **17**, 184 (2015).
- ⁶⁸S. Sato, M. Takada, D. Kawate, M. Takata, T. Kobayashi, and H. Naito, *Jpn. J. Appl. Phys., Part 1* **58**, SFFA02 (2019).
- ⁶⁹Y. Noguchi, A. Hofmann, and W. Brütting, *Adv. Opt. Mater.* **10**, 2201278 (2022).
- ⁷⁰T. Yamanaka, H. Nakanotani, and C. Adachi, *Sci. Adv.* **8**, eabj9188 (2022).
- ⁷¹T. Isoshima, Y. Okabayashi, E. Ito, M. Hara, W. W. Chin, and J. W. Han, *Org. Electron.* **14**, 1988 (2013).
- ⁷²P. Friederich, V. Rodin, F. Von Wrochem, and W. Wenzel, *Appl. Mater. Interfaces* **10**, 1881 (2018).
- ⁷³E. Pakhomenko, S. He, and R. J. Holmes, *Adv. Opt. Mater.* **10**, 2201348 (2022).
- ⁷⁴W. Brütting, S. Berleb, and A. G. Mückel, *Org. Electron.* **2**, 1 (2001).
- ⁷⁵D. Y. Kondakov, J. R. Sandifer, C. W. Tang, and R. H. Young, *J. Appl. Phys.* **93**, 1108 (2003).
- ⁷⁶Y. Noguchi, N. Sato, Y. Tanaka, Y. Nakayama, and H. Ishii, *Appl. Phys. Lett.* **92**, 203306 (2008).
- ⁷⁷D. Y. Kondakov, *J. Appl. Phys.* **99**, 024901 (2006).
- ⁷⁸T. D. Schmidt, L. Jäger, Y. Noguchi, H. Ishii, and W. Brütting, *J. Appl. Phys.* **117**, 215502 (2015).
- ⁷⁹E. Pakhomenko and R. Holmes, *Proc. SPIE* **12208**, 122080A (2022).
- ⁸⁰Y. Noguchi, K. Ninomiya, and K. Sato, *J. Phys. Chem. C* **126**, 18520 (2022).
- ⁸¹Y. Noguchi, Y. Tanaka, Y. Miyazaki, N. Sato, Y. Nakayama, and H. Ishii, in *Physics of Organic Semiconductors*, 2nd ed., edited by W. Brütting and C. Adachi (Wiley-VCH, Weinheim, Germany, 2012), pp. 119–154.
- ⁸²J. S. Bangsund, J. Sambeek, N. M. Concannon, and R. J. Holmes, *Sci. Adv.* **6**, eabb2659 (2020).
- ⁸³Y. Esaki, M. Tanaka, T. Matsushima, and C. Adachi, *Adv. Electron. Mater.* **7**, 2100486 (2021).
- ⁸⁴E. O. Afolayan, I. Dursun, C. Lang, E. Pakhomenko, M. Kondakova, M. Boroson, M. Hickner, R. J. Holmes, and N. C. Giebink, *Phys. Rev. Appl.* **17**, L051002 (2022).
- ⁸⁵S. He, E. Pakhomenko, and R. J. Holmes, *ACS Appl. Mater. Interfaces* **15**, 1652 (2023).
- ⁸⁶W.-C. Wang, K. Nakano, D. Hashizume, C.-S. Hsu, and K. Tajima, *ACS Appl. Mater. Interfaces* **14**, 18773 (2022).
- ⁸⁷M. Tanaka, M. Auffray, H. Nakanotani, and C. Adachi, *Nat. Mater.* **21**, 819 (2022).
- ⁸⁸T. Nishino, M. Meguro, K. Nakamae, M. Matsushita, and Y. Ueda, *Langmuir* **15**, 4321 (1999).
- ⁸⁹M. Schmid, K. Harms, C. Degitz, T. Morgenstern, A. Hofmann, P. Friederich, H.-H. Johannes, W. Wenzel, W. Kowalsky, and W. Brütting, *ACS Appl. Mater. Interfaces* **12**, 51709 (2020).
- ⁹⁰L. Jäger, T. D. Schmidt, and W. Brütting, *AIP Adv.* **6**, 095220 (2016).
- ⁹¹A. J. L. Hofmann, S. Züfle, K. Shimizu, M. Schmid, V. Wessels, L. Jäger, S. Altazin, K. Ikegami, M. R. Khan, D. Neher, H. Ishii, B. Ruhstaller, and W. Brütting, *Phys. Rev. Appl.* **12**, 064052 (2019).

- ⁹²K. Bagchi, C. Deng, C. Bishop, Y. Li, N. E. Jackson, N. E. Jackson, L. Yu, L. Yu, M. F. Toney, J. J. De Pablo, J. J. De Pablo, and M. D. Ediger, *ACS Appl. Mater. Interfaces* **12**, 26717 (2020).
- ⁹³Y. Okabayashi, E. Ito, T. Isoshima, and M. Hara, *Appl. Phys. Express* **5**, 55601 (2012).
- ⁹⁴Y. Okabayashi, E. Ito, T. Isoshima, H. Ito, and M. Hara, *Thin Solid Films* **518**, 839 (2009).
- ⁹⁵H. A. Al Attar and A. P. Monkman, *Adv. Mater.* **28**, 8014 (2016).
- ⁹⁶N. Kajimoto, T. Manaka, and M. Iwamoto, *J. Appl. Phys.* **100**, 053707 (2006).
- ⁹⁷S. F. Swallen, K. L. Kearns, M. K. Mapes, Y. Seol Kim, R. J. McMahon, M. D. Ediger, T. Wu, L. Yu, and S. Satija, *Science* **315**, 353 (2007).
- ⁹⁸I. Lyubimov, L. Antony, D. M. Walters, D. Rodney, M. D. Ediger, and J. J. de Pablo, *J. Chem. Phys.* **143**, 094502 (2015).
- ⁹⁹K. Yoshizaki, T. Manaka, and M. Iwamoto, *J. Appl. Phys.* **97**, 23703 (2005).
- ¹⁰⁰L. Yan, N. J. Watkins, S. Zobra, Y. Gao, and C. W. Tang, *Appl. Phys. Express* **81**, 2752 (2002).
- ¹⁰¹H. Ishii, N. Hayashi, E. Ito, Y. Washizu, K. Sugi, Y. Kimura, M. Niwano, Y. Ouchi, and K. Seki, *Phys. Status Solidi* **201**, 1075 (2004).
- ¹⁰²Y. Nakayama, Y. H. Huang, C. H. Wei, T. Kubo, S. I. MacHida, T. W. Pi, S. J. Tang, Y. Noguchi, and H. Ishii, *J. Appl. Phys.* **108**, 053702 (2010).
- ¹⁰³Y. Nakayama, M.-K. Lin, C.-Y. Wang, T.-W. Pi, H. Ishii, and S.-J. Tang, *e-J. Surf. Sci. Nanotechnol.* **10**, 149 (2012).
- ¹⁰⁴Y. Nakayama, S. Machida, Y. Miyazaki, T. Nishi, Y. Noguchi, and H. Ishii, *Org. Electron.* **13**, 2850 (2012).
- ¹⁰⁵Y. Gao, *Mater. Sci. Eng. R* **68**, 39 (2010).
- ¹⁰⁶H. Kinjo, H. Lim, T. Sato, Y. Noguchi, Y. Nakayama, and H. Ishii, *Appl. Phys. Express* **9**, 021601 (2016).
- ¹⁰⁷S. Altazin, S. Züfle, E. Knapp, C. Kirsch, T. D. Schmidt, Y. Noguchi, W. Brütting, B. Ruhstaller, L. Jäger, Y. Noguchi, W. Brütting, and B. Ruhstaller, *Org. Electron.* **39**, 244 (2016).
- ¹⁰⁸R. Coehoorn, X. Lin, C. H. L. Weijtens, S. Gottardi, and H. Van Eersel, *Phys. Rev. Appl.* **16**, 034048 (2021).
- ¹⁰⁹A. Dieckmann, H. Bässler, and P. M. Borsenberger, *J. Chem. Phys.* **99**, 8136 (1993).
- ¹¹⁰R. H. Young, *Philos. Mag. B* **72**, 435 (1995).
- ¹¹¹G. G. Malliaras, Y. Shen, D. H. Dunlap, H. Murata, and Z. H. Kafafi, *Appl. Phys. Lett.* **79**, 2582 (2001).
- ¹¹²R. H. Young, C. W. Tang, and A. P. Marchetti, *Appl. Phys. Lett.* **80**, 874 (2002).
- ¹¹³T. Haskins, A. Chowdhury, R. H. Young, J. R. Lenhard, A. P. Marchetti, and L. J. Rothberg, *Chem. Mater.* **16**, 4675 (2004).
- ¹¹⁴H. Z. Siboni and H. Aziz, *Appl. Phys. Lett.* **101**, 63502 (2012).
- ¹¹⁵R. Coehoorn, P. A. Bobbert, and H. Van Eersel, *Phys. Rev. B* **96**, 184203 (2017).
- ¹¹⁶N. C. Erickson and R. J. Holmes, *Adv. Funct. Mater.* **24**, 6074 (2014).
- ¹¹⁷N. C. Erickson and R. J. Holmes, *Adv. Funct. Mater.* **23**, 5190 (2013).
- ¹¹⁸F. X. Zang, T. C. Sum, A. C. H. Huan, T. L. Li, and F. Zhu, *Appl. Phys. Lett.* **93**, 23309 (2008).
- ¹¹⁹H. Van Eersel, P. A. Bobbert, R. Janssen, and R. Coehoorn, *Appl. Phys. Lett.* **105**, 143303 (2014).
- ¹²⁰M. Hasan, S. Saggat, A. Shukla, F. Bencheikh, J. Sobus, S. K. M. McGregor, C. Adachi, S.-C. C. Lo, and E. B. Nardas, *Nat. Commun.* **13**, 254 (2022).
- ¹²¹N. C. Giebink, B. W. D'Andrade, M. S. Weaver, J. J. Brown, and S. R. Forrest, *J. Appl. Phys.* **105**, 124514 (2009).
- ¹²²C. Murawski, K. Leo, and M. C. Gather, *Adv. Mater.* **25**, 6801 (2013).
- ¹²³B. Sim, C.-K. Moon, K.-H. Kim, and J.-J. Kim, *Appl. Mater. Interfaces* **8**, 33010 (2016).
- ¹²⁴J. Ràfols-Ribé, P. A. Will, C. Hännisch, M. Gonzalez-Silveira, S. Lenk, J. Rodríguez-Viejo, and S. Reineke, *Sci. Adv.* **4**, eaar8332 (2018).
- ¹²⁵N. Chopra, J. Lee, Y. Zheng, S.-H. Eom, J. Xue, and F. So, *ACS Appl. Mater. Interfaces* **1**, 1169 (2009).
- ¹²⁶C. Adachi, M. A. Baldo, M. E. Thompson, and S. R. Forrest, *J. Appl. Phys.* **90**, 5048 (2001).
- ¹²⁷Y. Esaki, T. Matsushima, and C. Adachi, *Org. Electron.* **67**, 237 (2019).
- ¹²⁸J. S. Bangsund and R. J. Holmes, *Proc. SPIE* **11093**, 110930L (2019).
- ¹²⁹Y. Divayana and X. W. Sun, *Org. Electron.* **11**, 67 (2010).
- ¹³⁰S. Reineke, K. Walzer, and K. Leo, *Phys. Rev. B* **75**, 125328 (2007).
- ¹³¹K. W. Hershey and R. J. Holmes, *J. Appl. Phys.* **120**, 195501 (2016).
- ¹³²Y. Noguchi, H. J. Kim, T. Tamura, H. J. Kim, and H. Ishii, *J. Photonics Energy* **2**, 021214 (2012).
- ¹³³E. J. Meijer, A. V. G. Mangnus, C. M. Hart, D. M. De Leeuw, and T. M. Klapwijk, *Appl. Phys. Lett.* **78**, 3902 (2001).
- ¹³⁴I. Torres and D. M. Taylor, *J. Appl. Phys.* **98**, 073710 (2005).
- ¹³⁵D. Rossi, D. Palazzo, A. Di Carlo, and M. Auf der Maur, *Adv. Electron. Mater.* **6**, 2000245 (2020).
- ¹³⁶T. Van Woudenberg, P. W. M. Blom, M. Vissenberg, and J. N. Huiberts, *Appl. Phys. Lett.* **79**, 1697 (2001).
- ¹³⁷J. Cottaar, L. J. A. Koster, R. Coehoorn, and P. A. Bobbert, *Phys. Rev. Lett.* **107**, 136601 (2011).
- ¹³⁸Q. Wang and H. Aziz, *Adv. Opt. Mater.* **3**, 967 (2015).
- ¹³⁹N. C. Giebink, B. W. D'Andrade, M. S. Weaver, P. B. Mackenzie, J. J. Brown, M. E. Thompson, and S. R. Forrest, *J. Appl. Phys.* **103**, 044509 (2008).
- ¹⁴⁰Q. Wang and H. Aziz, *Appl. Mater. Interfaces* **5**, 8733 (2013).
- ¹⁴¹H. Aziz, Z. D. Popovic, N.-X. Hu, A.-M. Hor, and G. Xu, *Science* **283**, 1900 (1999).
- ¹⁴²T. Miyamae, N. Takada, T. Yoshioka, S. Miyaguchi, H. Ohata, and T. Tsutsui, *Chem. Phys. Lett.* **616–617**, 86 (2014).
- ¹⁴³D. Y. Kondakov, W. C. Lenhart, and W. F. Nichols, *J. Appl. Phys.* **101**, 24512 (2007).
- ¹⁴⁴T. Ferschke, A. Hofmann, W. Brütting, and J. Pflaum, *ACS Appl. Electron. Mater.* **2**, 186 (2020).
- ¹⁴⁵T. Yamanaka, H. Nakanotani, and C. Adachi, *Nat. Commun.* **10**, 5748 (2019).
- ¹⁴⁶Y. Ueda, H. Nakanotani, T. Hosokai, Y. Tanaka, H. Hamada, H. Ishii, S. Santo, C. Adachi, H. Nakanotani, and C. Adachi, *Adv. Opt. Mater.* **8**, 2000896 (2020).
- ¹⁴⁷Y. Suzuki, *IEEE Trans. Electr. Electron. Eng.* **6**, 101 (2011).
- ¹⁴⁸Y. Tanaka, N. Matsuura, and H. Ishii, *Sci. Rep.* **10**, 6648 (2020).
- ¹⁴⁹Y. Tanaka, N. Matsuura, and H. Ishii, *Sens. Mater.* **34**, 1859 (2022).
- ¹⁵⁰G. M. Sessler, *Electrets*, 3rd ed. (California, 1998).
- ¹⁵¹S. S. Bamji, K. J. Jao, and M. M. Perlman, *J. Electrostat.* **6**, 373 (1979).
- ¹⁵²G. M. Sessler, *IEEE Trans. Dielectr. Electr. Insul.* **4**, 614 (1997).