Sub–turn-on exciton quenching due to molecular orientation and polarization in organic light-emitting devices

John S. Bangsund, Jack R. Van Sambeek, Nolan M. Concannon, Russell J. Holmes*

The efficiency of organic light-emitting devices (OLEDs) is often limited by roll-off, where efficiency decreases with increasing bias. In most OLEDs, roll-off primarily occurs due to exciton quenching, which is commonly assumed to be active only above device turn-on. Below turn-on, exciton and charge carrier densities are often presumed to be too small to cause quenching. Using lock-in detection of photoluminescence, we find that this assumption is not generally valid; luminescence can be quenched by >20% at biases below turn-on. We show that this low-bias quenching is due to hole accumulation induced by intrinsic polarization of the electron transport layer (ETL). Further, we demonstrate that selection of nonpolar ETLs or heating during deposition minimizes these losses, leading to efficiency enhancements of >15%. These results reveal design rules to optimize efficiency, clarify how ultrastable glasses improve OLED performance, and demonstrate the importance of quantifying exciton quenching at low bias.

INTRODUCTION

While organic light-emitting devices (OLEDs) have been successfully commercialized in mobile displays, their performance at high brightness is still limited by efficiency roll-off and degradation (1, 2), hindering their viability for lighting, automotive, and outdoor applications (3). Frequently, these detrimental processes are driven by bimolecular reactions such as exciton-polaron quenching (EPQ) and exciton-exciton annihilation (EEA). Of these, quenching by charge carriers (i.e., EPQ) has often been found to be the dominant mechanism (4–6). The density of charges within an OLED therefore plays a critical role in device performance, and higher densities have been correlated with reduced lifetime and increased roll-off (7–10).

It is typically assumed that EPQ and EEA processes are negligible at biases below the threshold for device turn-on (1, 6, 11–13), as the exciton density in this regime is vanishingly small and the polaron density in organic semiconductors is negligible in the absence of charge injection. However, large charge densities can be injected into the device even at biases below the built-in voltage due to spontaneous orientation polarization (SOP) (14, 15). A common phenomenon in organic thin films, SOP is the spontaneous ordering of permanent, molecular dipole moments (PDMs), leading to a net polarization. In a device, the polarization charge from SOP leads to the accumulation of charge carriers, typically holes, adjacent to the polar layer (16), as shown schematically in Fig. 1A. While it has been speculated that this SOP–induced hole density can quench excitons and accelerate degradation (14, 17), direct quantification of these effects has been limited. Only recently has it been appreciated that SOP can cause exciton quenching in fluorescent emitters (18).

Here, we directly quantify exciton quenching due to SOP–induced hole accumulation in archetypical phosphorescent OLEDs. We find that SOP can lead to quenching of photoluminescence (PL) by 20 to >35% at biases below device turn-on, reducing peak device efficiency by >15%. We show that failing to account for this effect can lead to incorrect conclusions about exciton kinetics and the factors that govern device efficiency. Further, we demonstrate that this effect can be nearly eliminated by heating during deposition or by selecting materials with negligible SOP. These findings underscore the importance of considering SOP during materials selection and device fabrication to minimize these losses.

RESULTS

Comparing polar and nonpolar electron transport materials

To determine whether SOP–induced hole accumulation influences exciton quenching, comparison devices were fabricated incorporating polar (i.e., exhibiting SOP) and nonpolar electron transport layers (ETLs). We selected two widely studied materials: tris-(1-phenyl-1H-benzimidazole) (TPBi) for the polar ETL and 4,6-bis(3,5-di(pyridin-3-yl)phenyl)-2-methylpyrimidine (B3PyMPM) for the nonpolar ETL (molecular structures shown in Fig. 1B) (19). TPBi has a PDM of 2.01 D and a giant surface potential (GSP) slope of 40 to 70 mV/nm (16), which is a figure of merit for the magnitude of SOP. B3PyMPM has a larger PDM of 4.29 D but its GSP slope is almost negligible, only ~3 mV/nm (19). The small magnitude of SOP in B3PyMPM films has been attributed to a strong intermolecular interaction that leads to the antiparallel alignment of PDMs, canceling out the overall polarization (19).

Devices contained a 10-nm-thick emissive layer (EML) of the archetypical carbazole host, 4,4′-bis(N-carbazolyl)-1,1′-biphenyl (CBP) and the green phosphorescent emitter, fac-tris(2-phenylpyridine) iridium(III) (Ir(ppy)$_3$) (see Fig. 1B), both of which are nonpolar (16, 19). The thin EML was chosen to minimize error due to spatial mismatch between optical and electrical excitation of the EML (20). Aside from the ETL, all layers in these devices were deposited in the same run.

To characterize exciton quenching as a function of applied bias, PL is measured using a lock-in amplifier upon excitation of the EML with a chopped $\lambda = 405$-nm laser. This wavelength selectively pumps Ir(ppy)$_3$, so that only the relative PL efficiency of the emitter is probed (see absorption spectra for materials used here in fig. S1A). Lock-in detection excludes any background photoluminescence (EL) from the PL measurement, allowing relative PL changes due to
Fig. 1. Comparison of polar and nonpolar ETL device performance. (A) Schematic of SOP-induced hole accumulation. Preferred orientation of PDMs (denoted as arrows) in the electron transport layer (ETL) leads to net polarization sheet charges on each side of the ETL ($\delta^+$ and $\delta^-$). These polarization charges are compensated by hole accumulation within the EML (red circles with positive signs). (B) Device schematic and molecular structures of tris-(1-phenyl-1H-benzimidazole) (TPBi; polar ETL) and 4,6-bis(3,5-di(pyridin-3-yl)phenyl)-2-methylpyrimidine (B3PyMPM; nonpolar ETL). (C) Normalized photoluminescence (PL; symbols) and luminance (solid lines) as a function of voltage for devices with TPBi (red circles) and B3PyMPM (blue squares) ETLs with thicknesses of 50 and 47 nm, respectively. (D) Internal quantum efficiency (IQE; solid lines) and normalized lock-in PL intensity (symbols) as a function of absolute current density for devices with a B3PyMPM or TPBi ETL. Normalized PL data are multiplied by $C_{4,6}$, to allow comparison with the intrinsic PL efficiency of Ir(ppy)$_3$ at this doping concentration ($\eta_{PL} = 92\%$). The IQE reaches near unity (~92%) in the B3PyMPM devices, almost identical to the intrinsic PL efficiency ($\eta_{PL} = 92\%$) of Ir(ppy)$_3$ at this doping concentration (26). To understand the impact of sub–turn-on exciton quenching on device performance, we compare the dependence of both the normalized PL and the device internal quantum efficiency (IQE) on current density ($J$). The IQE, which is the electron-to-photon conversion efficiency, is calculated by dividing the measured external quantum efficiency (EQE; see fig. S2) by the simulated optical out-coupling efficiency, $\eta_{OC}$, for each architecture ($\eta_{OC} = 18.8\%$ for B3PyMPM and 24.1% for TPBi; see Materials and Methods). The IQE can be expressed as (13)

$$\text{IQE} = \text{EQE}/\eta_{OC} = \chi \eta_{PL}$$

where $\chi$ is the spin fraction or the fraction of excitons that have a quantum-mechanically allowed radiative transition; $\gamma$ is the charge balance or the exciton formation efficiency, which equals excitons formed per injected electron; and $\eta_{PL}$ is the PL efficiency, representing the fraction of excitons that emit a photon upon relaxation. For the phosphorescent emitter used here, $\chi = 1$ and does not limit IQE.

The IQE reaches near unity (~92%) in the B3PyMPM devices, almost identical to the intrinsic PL efficiency ($\eta_{PL} = 92\%$) of Ir(ppy)$_3$ at this doping concentration (26). In the TPBi devices, IQE reaches only 70%. This difference in peak IQE is almost entirely explained by the PL quenching at low biases (Fig. 1D). When the TPBi device initially turns on, the IQE at $J = 10^{-3}$ mA/cm$^2$ is 56% and nearly equivalent to the normalized PL at the same bias (61%). The PL and IQE then rise with a similar slope between $J = 10^{-3}$ and $10^{-1}$ mA/cm$^2$. These similarities indicate that IQE is predominantly limited by exciton quenching at low-to-moderate biases ($<10^{-1}$ mA/cm$^2$) and that charge balance is near unity. This finding stands in contrast to, and calls
into question, the common practice of ascribing lower-than-expected peak EQE values to charge balance or electrical losses (13, 27).

Above $J = 10^{-1}$ mA/cm$^2$, the PL and IQE curves begin to diverge slightly, with the IQE showing a steeper roll-off than PL in all devices. This may indicate that charge balance losses contribute to roll-off at higher current densities (12, 24), but error due to spatial mismatch between the recombination zone and the electric field of the pump laser could also contribute (20). In any case, the majority of roll-off in both devices arises from exciton quenching.

We sought to further confirm that the observed sub–turn-on exciton quenching is due to hole accumulation from the orientation polarization of the ETL. A key feature of thin films exhibiting exciton quenching is that their surface potential scales with film thickness (14, 15). In a device, this leads to a linear dependence of the hole injection voltage on the thickness of the polar layer (note that the interface charge is independent of film thickness). This dependence was investigated by fabricating TPBi and B3PyMPM devices with a range of ETL thicknesses ($d_{\text{ETL}}$). Actual ETL thicknesses for TPBi devices were (33 ± 1), (50 ± 1), and (68 ± 1) nm; those for B3PyMPM devices were (32 ± 1), (47 ± 1), and (64 ± 1) nm.

Displacement current measurements (DCMs), shown in Fig. 2 (A and B), were used to measure the hole-injection voltage ($V_{\text{inj}}$) (see Materials and Methods). DCM is a widely applied capacitance-voltage–type measurement useful for evaluating charge injection and accumulation in OLEDs (16, 28). This approach involves applying a triangular voltage waveform to the device and measuring the response current, which is a combination of the displacement and conduction currents. Since the displacement current is proportional to the device capacitance, these measurements are sensitive to changes in the charge density within the device (14, 16). $V_{\text{inj}}$ is assigned on the basis of the onset of slope change in the DCM sweep (see vertical dashed lines in Fig. 2, A and B), which is when the capacitance of the device (and the accumulated charge density) begins to increase.

Increasing the thickness of the TPBi ETL shifts the hole-injection voltage from (−0.08 ± 0.25) V for $d_{\text{ETL}} = 33$ nm to (−3.00 ± 0.32) V for $d_{\text{ETL}} = 68$ nm (Fig. 2C), as expected for an ETL showing SOP (14). No shift of $V_{\text{inj}}$ is discernible when increasing the thickness of the B3PyMPM ETL (Fig. 2B), confirming that B3PyMPM films are nonpolar. Comparing the DCM data to PL measurements, we see that the onset of the PL roll-off coincides exactly with the hole-injection voltage. This result provides strong support for the conclusion that hole accumulation induced by SOP of the ETL is responsible for exciton quenching before turn-on.

For comparison purposes, the GSP slope can also be extracted from these measurements based on the slope of $V_{\text{inj}}$ versus ETL thickness (Fig. 2C). We measure a GSP slope of 88 ± 4 mV/nm, which is double the 43 mV/nm value reported by Noguchi et al. (16) but agrees reasonably with an earlier report of −70 mV/nm (29). This variability in reported values could arise from differences in the initial surface [α-NPD [N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine] in (16) and 1′-TNATA [4,4′,4″-tris(N-1-naphthyl-N-phenylamino)-triphenylamine] in (29), compared to CBP:Ir(ppy)₃ here] or other deposition conditions, such as the deposition rate or the substrate temperature. Notably, the substrate temperature is usually not monitored and could depend on deposition chamber; the role of this parameter is discussed in the next section.

DCM sweeps can also be integrated to estimate the injected hole density before turn-on ($\sigma_h$; see Materials and Methods and raw data in fig. S3). We measure $\sigma_h = (1.6 ± 0.2) \times 10^{12}$ cm$^{-2}$ (or 2.6 mC/m$^2$), which is independent of $d_{\text{ETL}}$ (Fig. 2C). As with the GSP slope, which is proportional to $\sigma_h$, (16), this value is about twice as large as previous reports for TPBi (−1.1 mC/m$^2$) (16), but it is still well below the theoretical maximum charge density based on the PDM of TPBi ($\sigma_{\text{max}} = 5.2 \times 10^{12}$ cm$^{-2}$ = 8.3 mC/m$^2$).

Figure 2D shows the full voltage dependence of PL for both TPBi and B3PyMPM devices. Normalized PL at device turn-on (2.5 V) is

---

**Fig. 2. Displacement current and lock-in PL measurements for various ETL thicknesses.** (A) DCM sweeps (top) and lock-in PL measurements (bottom) as a function of applied voltage for different thicknesses ($d_{\text{ETL}}$) of the TPBi ETL. For visualization clarity, current is normalized to the value at 2 V (raw data shown in fig. S3). The onset of the roll-off in PL intensity coincides with the hole-injection voltage ($V_{\text{inj}}$, denoted with dashed arrows). (B) The same measurements for a B3PyMPM ETL, which show no discernible shift in hole-injection voltage or quenching of PL before device turn-on. (C) $V_{\text{inj}}$ and hole sheet density ($\sigma_h$) for TPBi devices extracted from the DCM sweeps in (A). Error bars represent SDs over at least three pixels. (D) Full voltage dependence of lock-in PL data for devices with an ETL composed of TPBi or B3PyMPM. Colors correspond to the legends in (A) and (B). Shaded regions are 95% confidence intervals of the mean weighted by Student’s $t$ factor based on measurements of three to six separate pixels.

---

Bangsund et al., Sci. Adv. 2020; 6 : eabb2659 7 August 2020
similar for the different ETL thicknesses, which is expected as the interface charge density is independent of film thickness. The slight monotonic decrease in PL at this point for higher ETL thicknesses (from ~67% for $d_{\text{ETL}} = 33$ nm to ~63% for a $d_{\text{ETL}} = 68$ nm) is consistent with a SOP-induced charge density that is expected to be peaked at the EML/ETL interface (14). That is, the peak in the optical field of the pump laser moves toward the EML/ETL interface as ETL thickness is increased (fig. S4A), leading to more overlap between the optically generated exciton population and the charge density.

### Eliminating polarization by heating during deposition

Fabricating OLEDs at elevated temperatures has recently been shown to improve efficiency and lifetime; these enhancements were attributed to the formation of ultrastable glasses, and it was hypothesized that increased rigidity in these dense glasses suppressed nonradiative decay (30). TPBi served as the host and ETL in these devices, and the devices fabricated above room temperature showed increased exciton lifetime, consistent with reduced exciton quenching. Considering that molecular orientation has been shown to be tunable with deposition temperature (31), it is plausible that these results instead reflect reduced SOP and hole accumulation within the device. Notably, the reported increases in peak efficiency (14 to 28%) and exciton lifetime (15 to 17%) achieved by this method are similar to those obtained using a nonpolar ETL (10% increase in peak EQE and 20% increase in PL at 0 V; Fig. 1B and fig. S2).

To assess this possibility, we made devices with a similar structure to that used by Ráfols-Ribé et al. (30) (see Fig. 3A and Materials and Methods) and varied the substrate temperature during deposition of the EML and ETL from 25° to ~107°C. Peak EQE increases sharply at elevated deposition temperature and eventually saturates at ~23.5% above 70°C, showing a (18.1 ± 0.5)% enhancement at ~61°C compared to 25°C [see Fig. 3B and fig. S5; the median peak EQE increased from (19.7 ± 0.4)% at 25°C to (23.3 ± 0.5)% at ~61°C]. Over this range, the current-voltage characteristics are within error (Fig. 3C and fig. S5), suggesting that heating does not significantly influence charge transport properties.

This enhancement in EQE is similar in magnitude to the previous report, but the trend differs: instead of reaching an optimum near 66°C (30), the EQE here is monotonic over the entire temperature range. This distinction is important because the density of vapor-deposited glasses is generally maximized when the substrate temperature is near 85% of the glass transition temperature ($T_g$) in kelvin (31), which is ~65°C here given $T_g = 124°C$ for the TPBi host (32). If glass density influenced efficiency, then EQE should peak at ~65°C and decline at higher temperatures. Another mechanism must be responsible for the observed increase in efficiency.

It is worth noting that the difference in these EQE trends is not necessarily contradictory. The device used by Ráfols-Ribé et al. (30) contained a horizontally oriented emitter, Ir(ppy)$_2$(acac), which showed reduced outcoupling efficiency at high temperatures due to a shift to more isotropic or vertically oriented transition dipole moments (TDMs). This reduction in $\eta_{\text{OC}}$ is likely responsible for the observed optimum (both EQE and calculated $\eta_{\text{OC}}$ fell by ~8% from their peak by 90°C) (30), whereas the Ir(ppy)$_3$-based devices used here show no reduction in $\eta_{\text{OC}}$ due to Ir(ppy)$_3$’s symmetric TDMs (33).

The rise in EQE is accompanied by an increase in the hole-injection voltage and a commensurate shift in the onset of PL roll-off to higher voltages (Fig. 3, C and D). Further, the amount of quenching at
device turn-on (~2.5 V) decreases monotonically at higher temperatures (Fig. 3D). At biases near peak EQE ($J = 3 \times 10^{-2} \text{mA/cm}^2$), the normalized PL is (20.5 ± 1.1)% higher in devices fabricated at ~61°C than at 25°C, remarkably similar to the enhancement in peak EQE (Fig. 4A). The agreement between EQE and PL holds across all temperatures for a range of biases (fig. S6), only breaking down above ~6 V (~1 mA/cm$^2$), when, as mentioned above, charge balance roll-off or spatial mismatch effects could become more substantial (20). These reductions in PL quenching are mirrored by reductions in the SOP-induced hole sheet density from ~1.6 × 10$^{12}$ cm$^{-2}$ at 25°C to ~0.2 × 10$^{12}$ cm$^{-2}$ at 107°C (Fig. 4B).

Together, these concurrent changes in PL quenching and hole injection confirm that heating during deposition reduces or even eliminates SOP in TPBI, thereby reducing the concentration of holes in the EML. Exciton quenching is thus reduced, increasing the exciton lifetime and device efficiency. Further, the close agreement between EQE and PL demonstrates that the efficiency enhancement results almost entirely from reduced EPQ.

Nonetheless, these relative measurements of PL cannot rule out increases in the intrinsic PL efficiency ($\eta_{\text{PL}}$), which would uniformly boost PL intensity and EQE independent of bias. To remove this ambiguity, we evaluated whether heating during deposition affects exciton kinetics in TPBI:Ir(ppy)$_3$ [8 volume percent (volume %)] films on glass, outside of a device such that holes cannot be injected from electrodes. The exciton lifetime ($\tau$), extracted from transient PL measurements (see Materials and Methods), shows a slight linear increase with deposition temperature (fig. S7; note that $\eta_{\text{PL}}$ is proportional to $\tau$, i.e., $\eta_{\text{PL}} = k_t\tau$ where $k_t$ is the radiative rate). Relative to 25°C films, $\tau$ increases by only ~2.6% at ~67°C and ~3.8% at ~90°C, further demonstrating that suppressed nonradiative decay due to the higher density of the glass cannot explain the observed efficiency increases of >15%. In addition, because $\tau$ does not peak at the temperature of maximum glass density (~0.85 $T_g$ ~65°C), this trend is more likely due to reduced impurity incorporation at elevated temperature (34).

Heating during deposition could also influence device stability. For instance, reduced SOP-induced hole accumulation at high temperatures could lower the rate of exciton-polaron–mediated degradation (2, 5), while ultrastable glass formation can improve intrinsic photostability (35). Ráfols-Ribé et al. (30) argued that this latter effect was responsible for an observed 86 to 500% enhancement in electrical lifetime, which was peaked at substrate temperatures near 0.8 to 0.85 $T_g$. We sought to reproduce this finding and better understand how heating influences stability by comparing degradation under optical and electrical pumping. We photodegraded TPBI:Ir(ppy)$_3$ films deposited on glass substrates, outside of a device to avoid the potential influence of SOP-induced hole density within the EML ($\lambda = 405$-nm laser, ~1 W/cm$^2$). Films heated at 45° to 60°C showed a (43 ± 16)% enhancement in lifetime relative to room temperature films, increasing from $t_{\text{PL}} = (7.7 \pm 2.0)$ hours at 25°C to $t_{\text{PL}} = (11 \pm 3)$ hours at 45°C (fig. S8A), where $t_{\text{PL}}$ is the time it takes for PL to degrade to 70% of its initial intensity. We observed a similar increase in photostability when photodegrading films within a device ($\lambda = 405$-nm laser, ~20 W/cm$^2$; see fig. S8B). These devices were degraded at open circuit (~ 2 V at this illumination intensity), meaning that SOP-induced holes were accumulated during the test. Since the enhancement is similar, we infer that the SOP-induced hole density does not substantially accelerate photodegradation in these devices and that ultrastable glass effects may be responsible for this improvement (35).

In contrast, the device lifetime under electrical pumping shows no enhancement and instead declines slightly as the deposition temperature is increased (initial luminance of $L_0 = 1000$ cd/m$^2$; fig. S8, C and D). This discrepancy suggests that electrical and optical stability are limited by different factors in our devices. Since exciton and charge densities are likely lower in heated devices, due to their higher efficiency and reduced SOP, degradation reactions dictated by exciton and charge kinetics are unlikely to explain this deviation (5). One possibility is that processing-dependent impurities limit the electrical stability and depend on deposition temperature. For instance, impurities from the vacuum chamber can be incorporated in the device during deposition and lower lifetime (36), an effect that becomes more detrimental for longer deposition times. The fabrication procedure or even the specifics of the deposition tool may therefore critically affect lifetime and could explain the disagreement with (30). However, the source material purity is likely comparable given the agreement observed for the lifetime of the control device fabricated at room temperature [for $L_0 = 1000$ cd/m$^2$, EL $t_{70} = 55$ to 65 hours, compared with 60 hours in (30)]. These results indicate that while ultrastable glass layers show improved photostability (35), the benefit to electrical lifetime may not be universal and can be complicated by other factors.

**Modeling SOP-induced exciton quenching**

Exciton kinetic modeling was carried out to (i) better understand how SOP-induced charge density quantitatively relates to exciton
quenching and (ii) to estimate how exciton quenching and charge density vary spatially. We model the steady-state triplet exciton density, \( n_T \), near device turn-on (~2.5 V), allowing for diffusion and triplet-polaron quenching with holes accumulated because of SOP. At this bias, the hole density should mostly reflect the SOP-induced population, and the electrically generated exciton density is small enough to neglect EEA processes. The rate equation for \( n_T \) under these conditions is

\[
\frac{dn_T}{dt} = D \frac{\partial^2 n_T}{\partial x^2} - n_T \left( \frac{1}{\tau} + k_{TP} n_h \right) + G
\]

where \( x \) is the out-of-plane spatial coordinate, \( D \) is the triplet exciton diffusivity, \( \tau \) is the cavity-modified exciton lifetime \((37)\), \( k_{TP} \) is the triplet EPQ rate constant, \( n_h \) is the SOP-induced hole density, and \( G \) is the exciton generation rate. It is commonly assumed that SOP-induced holes are concentrated within a few nanometers of the polar layer \((17,28)\). For simplicity, we assume that \( n_h \) decays exponentially with width \( w \) from the EML/ETL interface in CBP:Ir(ppy)_3 devices (Fig. 1A). The magnitude of \( n_h \) is set by the hole density measured using DCM, assuming that holes only accumulate within the EML (see Eq. 4 in Materials and Methods). When simulating PL, \( G \) is calculated using the transfer matrix formalism \((38)\). Under electrical excitation, \( G \) is taken to have the same spatial dependence as \( n_h \), as the probability of exciton formation will be highest where the hole density is large.

For the CBP:Ir(ppy)_3 device in Fig. 1A, the normalized PL is ~66% and EQE = 13.4% \((IQE \approx 57\%) \) near turn-on at ~2.5 V (Fig. 1C). Minimizing the difference between these measured values and the output of Eqs. 5 and 6 \((\text{see Materials and Methods})\) allows us to identify the feasible region for the unknown parameters \((D, k_{TP}, \text{and } w)\). Figure 5 (A to C) shows contour plots of parameter combinations that give solutions within 2 to 6% of the measured PL and EQE values. Notably, the best-fit \( k_{TP} \) value of \((5 \pm 1) \times 10^{-13} \text{ cm}^3/\text{s} \) is independent of the other two parameters and agrees well with previous reports \((11,13)\). The diffusivity and hole distribution width are dependent on one another. When the exciton diffusion length \(L_D = (Dt)^{1/2} \) is small, the model can only simultaneously match PL and EQE when the charges are distributed across at least half the EML \((w > 4.5 \text{ nm})\). At higher diffusivities, a wider range of charge distributions can describe the data, and when \( L_D > 8 \text{ nm} \), holes are confined to the first ~1 nm of the EML/ETL interface in the best solutions. Given the uncertainty in our measurements, hole distributions ranging from 1 to 10 nm wide would be reasonably consistent with our data in this high-diffusivity limit (Fig. 5C). In other words, the close agreement we observe between measured EQE and quenching in PL can only be described by our model when either excitons, holes, or both species are distributed across at least 40% of the EML. This result is

![Fig. 5. Modeling exciton quenching under electrical and optical pumping. (A to C) Contour plots of the percent difference between modeled and measured EQE (red) and PL (blue) at 2.5 V as a function of input parameters for the CBP:Ir(ppy)_3 device in Fig. 1A. The hole distribution width \((w)\) characterizes exponential decay \(e^{-w/x}\) from the EML/ETL interface. Exciton diffusivities are (A) \( D = 1.4 \times 10^8 \text{ nm}^2/\text{s} (L_D \sim 1 \text{ nm}) \), (B) \( D = 2.2 \times 10^7 \text{ nm}^2/\text{s} (L_D \sim 4 \text{ nm}) \), and (C) \( D = 1 \times 10^6 \text{ nm}^2/\text{s} (L_D \sim 9 \text{ nm}) \). (D) Hole \((n_h, \text{top})\) and exciton \((n_e, \text{bottom})\) density of one plausible solution for the CBP:Ir(ppy)_3 device in Fig. 1A. \( n_e \) with and without hole quenching is shown in solid and dashed lines, respectively. Solution parameters are \( D = 2 \times 10^7 \text{ nm}^2/\text{s} (L_D \sim 3.9 \text{ nm}) \), \( k_{TP} = 5 \times 10^{-13} \text{ cm}^3/\text{s} \), and \( w = 3 \text{ nm} \). (E) Modeled and measured PL at turn-on (2.5 V) as a function of deposition temperature for the TPBi:Ir(ppy)_3 device in Fig. 3A. The measured charge densities in Fig. 48 are the only model inputs, which vary with temperature. Temperature-independent parameters are \( D = 2 \times 10^7 \text{ nm}^2/\text{s} (L_D \sim 3.9 \text{ nm}) \), \( k_{TP} = 3 \times 10^{-13} \text{ cm}^3/\text{s} \), and \( w = 4 \text{ nm} \) (exponential decay from HTL/EML interface).
expected because the PL measurement probes the EML nearly uniformly (fig. S4).

Without direct characterization of $L_D$ or $w$, we favor a scenario between these two extremes, such as the solution shown in Fig. 5D, where charges are moderately distributed within 2 to 3 nm of the EML/ETL interface ($w = 3$ nm) and excitons are modestly diffusive with $L_D = 3.8$ nm ($D = 2 \times 10^7$ nm$^2$/s). This magnitude of $L_D$ is supported by previous measurements of Ir(ppy)$_3$ in a BCP (bathocuproine) host, which yield an estimated $L_D$ of 4 to 9 nm depending on intermolecular spacing (39).

It is also possible that the distributed charge density predicted by our model is an artifact of its simplified description of EQE. EQQ may occur either by nearest-neighbor interactions or by long-range Förster transfer (6, 40), which requires overlap between the emission spectrum of the emitter and the absorption spectrum of the cation. Here, the holes responsible for quenching most likely reside on Ir(ppy)$_3$ molecules, as the Ir(ppy)$_3$$^+$ cation absorbs near 600 nm (41) and Ir(ppy)$_3$ has a shallower highest occupied molecular orbital energy than CBP, TPBi, and 4,4′,4″-tris(N-carbazolyl)triphenylamine (TCTA), leading to hole trapping. This view is also supported by kinetic Monte Carlo simulations, which found that holes in a CBP:Ir(ppy)$_3$ device spend >95% of the time on Ir(ppy)$_3$ molecules (42). The typical Förster radius for energy transfer from a phosphorescent emitter to its cation has been estimated at 2 to 3 nm (40), similar to the hole distribution width extracted here. If Förster-type EQQ is active here, then a narrower charge distribution could be consistent with our results. Nonetheless, a confined charge density would also result in heighten quenching under electrical excitation, which should lead to a larger discrepancy between PL and EQE than is observed.

Quenching was also modeled in TPBi:Ir(ppy)$_3$ devices as a function of substrate temperature (Fig. 3A). Since the host is polar in this device, unlike CBP (14), we assumed that holes are concentrated near the hole transport layer (HTL)/EML interface. A fraction of these holes may be accumulated within the HTL, but these are unlikely to quench excitons because (i) they are spatially separated from the EML and (ii) TCTA cations show very weak absorption in the emission range of Ir(ppy)$_3$ (43), suggesting that energy transfer from Ir(ppy)$_3$ to TCTA$^-$ should be inefficient. For these reasons, we continue to assume that all holes are accumulated in the EML ($\sigma_H$, input from Fig. 4B) and that they decay exponentially from the HTL/EML interface. As shown in Fig. 5E, the modeled and measured PL ratios (see Eq. 5) agree within error across the full range of temperatures, indicating that the independent measure of charge density (from DCM) can fully explain the observed changes in quenching.

The best-fit $k_{TP}$ value of $(3 \pm 1) \times 10^{-13}$ cm$^3$/s is ~40% lower than in CBP:Ir(ppy)$_3$ devices, which reflects the higher IQE and less severe PL quenching in the TPBi:Ir(ppy)$_3$ devices (~27% reduction in PL near turn-on compared to a ~35% reduction in CBP:Ir(ppy)$_3$). This lower degree of EQQ has several possible explanations: (i) a portion of the hole density is accumulated within the HTL, where holes cannot efficiently quench excitons; (ii) if holes residing on TCTA can quench excitons, then they would have a different characteristic $k_{TP}$ due to their different absorption characteristics and spatial separation from the EML; or (iii) the host (TPBi versus CBP) could modify the interaction between excitons and charges, changing $k_{TP}$. We favor the first scenario, which is supported qualitatively by the slight lag between the start of hole-injection voltage (Fig. 3C) and the onset of PL roll-off (Fig. 3D). In other words, holes accumulate within the device (presumably in the HTL) before EQQ is observed. This contrasts with the CBP:Ir(ppy)$_3$ devices in which these two processes occur in lockstep (Fig. 2A).

**DISCUSSION**

The findings of this work underscore the importance of carefully considering hole accumulation at biases below device turn-on when quantifying exciton quenching. While several groups have shown that quenching can occur at unexpectedly low current densities (4, 24, 25), the assumption that no quenching occurs before device turn-on has been widely applied, usually because of a lack of a convenient method to characterize quenching in this regime. Many previous studies of exciton quenching did not look at reverse biases (4, 12, 24), which, depending on ETL thickness and polarization (and the resulting hole-injection voltage), can be necessary to fully quantify quenching. In other words, using the PL intensity or lifetime of an unbiased OLED is not necessarily a valid reference point, when holes can be accumulated in the device even at 0 V (or the open-circuit voltage).

As a result, deviations in efficiency from optical simulations in many studies may have been incorrectly ascribed to other mechanisms, such as the charge balance factor (electrical losses) (27). Because many conventional electron transport materials exhibit SOP (such as Alq$_3$ [tris-(8-hydroxyquinolate) aluminum], BCP, and BPhen (4,7-diphenyl-1,10-phenanthroline)) (14), these sub–turn-on quenching effects are likely widespread in the literature. In work from our own group, a charge balance factor of ~80% was extracted—for devices similar to those in Fig. 1 except with a BPhen ETL—based on kinetic modeling of steady-state and transient EL measurements (13). In the current work, the PL intensity near peak EQE is quenched to ~75% by holes accumulated because of SOP. It therefore seems likely that charge balance in similar state-of-the-art OLEDs is closer to unity than previously thought.

This work also provides more clarity for the mechanism of enhanced efficiency in OLEDs containing ultrastable glasses. The primary conclusion drawn by Ráfols-Ribé et al. (30) is that ultrastable glasses reduce nonradiative decay and thereby increase the effective PL efficiency; they speculate that the concentration of exciton traps is reduced or that the increased density of ultrastable glass suppresses thermal relaxation (30). While our results confirm that nonradiative decay is suppressed when devices are heated during deposition, they point to a different underlying mechanism: heating reduces polarization of the ETL, in turn lowering the concentration of holes in the device, resulting in less EQP. Consequently, the generality of improving device performance with heated deposition may be less broad than previously thought: Devices containing nonpolar hosts and ETLS will not show the same benefits from this method. Our results do not, however, exclude the possibility that nonpolar ETLS could experience a lifetime enhancement from heated deposition, due to either reduced impurity incorporation or the intrinsic stability of ultrastable glasses (34, 35). This possibility should be examined more closely in further studies.

The mechanism for reduced SOP with increasing deposition temperatures is likely related to the fact that higher deposition temperatures tend to randomize molecular orientation, evidenced by reduced optical anisotropy (31). SOP originates from preferred orientation of molecules with a PDM (14), leading to a net polarization of the film. It is sensible, then, that the more randomized molecular orientation at higher temperatures would reduce SOP. Supporting this view, the threshold substrate temperature for eliminating SOP of
used as received: TCTA, CBP, Ir(ppy)$_3$, TPBi, and B3PyMPM. The Sigma-Aldrich) was spin-cast on the ITO anode in a N$_2$ glovebox tin-oxide (ITO; Xinyan). Substrates were cleaned with solvents followed substrates prepatterned with a 120-nm-thick anode layer of indium-

These findings could also be important for other LED technolo-
gies, such as quantum dot and metal-halide perovskite LEDs (PeLEDs) (21, 22). Many record efficiency PeLEDs have used TPBi (46), and it seems likely that the polarization of TPBi influences device per-
formance, given that PeLED efficiency and ion migration within perovskites are sensitive to both hole density and electric field (47). A recent study showed that performance can be optimized by using a mixed ETL consisting of B3PyMPM and TPBi (48), which could reflect the drastic difference in SOP in these materials. These findings may also have implications for the stability of PeLEDs, as the pres-
ence of holes can destabilize metal halide perovskites (47). Hence, the increased hole density in a device containing a polar ETL could reduce device lifetime.

In summary, this work demonstrates that SOP of organic thin films strongly influences OLED performance. When a device in-
cludes a polar layer, mobile charge carriers accumulate in an adjacent layer to compensate for the bound polarization charge. These charge carriers, which are usually holes, quench excitons at biases below device turn-on and can ultimately reduce peak efficiency by >15%. We show that quenching losses of this sort can be mitigated by select-
ing nonpolar materials or by heating samples during deposition to eliminate SOP. Further, the reduction in exciton quenching in heated samples is nearly identical to the efficiency enhancement, clarifying the mechanism for efficiency improvement in OLEDs containing ultrastable glasses. Exciton quenching modeling further sup-
ports this mechanism, showing that the observed changes in PL and EQE can be entirely described by independent measurements of SOP-induced charge density. Our findings illustrate that properly measuring and accounting for SOP-induced exciton quenching are critical to fully quantifying and understanding both peak efficiency and efficiency roll-off in OLEDs. SOP should be considered during the design and selection of materials and the optimization of device fabrication processes.

**MATERIALS AND METHODS**

**Device fabrication**

Devices with an active area of 25 mm$^2$ were fabricated on glass substrates prepatterned with a 120-nm-thick anode layer of indium-

for heated depositions, substrates were mounted on a solid cop-
able (Hamamatsu S3584-08) were used to measure device current and luminance as a function of bias, and Lambertian emission was assumed for luminance calculations. A Princeton Instruments FERGIE integrated spectrograph was used to collect EL spectra.

The bias-dependent PL measurements applied here are similar to previously reported methods (21, 22). A Keithley 2636B was used to source a constant device voltage and measure current. Sweeps were taken from −4 to 8 V with a step size of 0.2 V, a settle time of 0.25 s, and an integration time of ~1 s per step. Sweep rate was not found to have a significant effect on the measured magnitude of PL quenching, although noise was higher for faster sweeps. Control software for these measurements is provided at https://github.com/jsbangsund/ measurement-automation-tools. Devices were optically pumped with a 100 mW $\lambda = 405$-nm laser (Coherent OBIS 405LX), which was attenuated with a neutral density filter, chopped at 2 kHz, and expanded with a Thorlabs GBE05-A 5x achromatic Galilean beam expander to a 1/e$^2$ diameter of ~4 mm. Beam expansion serves to improve signal without increasing the exciton density. Devices were masked and the beam was passed through an adjustable iris to prevent excitation outside the device area. The PL signal was passed through a 450-nm-long pass filter to prevent detection of stray laser light, collected with a Thorlabs PDA36A Si adjustable gain photodetector, and measured with a Stanford Research Systems SR810 lock-in amplifier. The lock-in amplifier serves to reject the baseline EL signal, ensuring that only PL is measured. The PL signal was kept

$\sim$0.9 $T_b$ agrees well with the temperature at which common molecu-
lar glasses become optically isotropic (31). We note that while optical anisotropy is not correlated with SOP (19) (preferred orientation of TDMs does not necessarily correspond to orientation of PDMs), randomization of molecular orientation eliminates both types of anisotropy (31, 44, 45).

The holder was backside heated by a lamp, and temperature was monitored by a freestanding reference thermocouple placed above the backside of the holder. The reference thermocouple was calibrated before deposition with a thermocouple mounted on a glass slide on the front surface of the sample holder. The substrate surface temperature during deposition was also confirmed with one-time use temperature indicators (McMaster-Carr) placed on a glass slide next to the substrate. The lamp was turned off immediately before deposition, resulting in a 1° to 3°C decline in temperature over the course of the deposition; this decline is reflected in the quoted temperature error bars. The deposition tooling factor decreased at higher temperatures and was calibrated before fabrication of devices. To confirm tooling factor accuracy, the combined thickness of the EML and ETL of each device was measured with a Si substrate placed next to the device active area; all heated deposition devices reported here had a combined EML/ETL thickness of (70 ± 5) nm, except for the device grown at 107°C, which had a combined thickness of 82 nm (see table S1).

Heated depositions were made sequentially with vacuum breaks between each deposition, starting at room temperature and increasing substrate temperature with each batch to reduce cooling time be-
tween depositions. Devices were fabricated on 2 days to reproduce trends: Average deposition temperatures were 25°, 47°, 61°, 72°, and 87°C on the first day and 25°, 74°, and 107°C on the second day.

**Electrical and optical characterization**

An Agilent 4155C parameter analyzer and a large area photodiode (Hamamatsu S3584-08) were used to measure device current and luminance as a function of bias, and Lambertian emission was assumed for luminance calculations. A Princeton Instruments FERGIE integrated spectrograph was used to collect EL spectra.

The bias-dependent PL measurements applied here are similar to previously reported methods (21, 22). A Keithley 2636B was used to source a constant device voltage and measure current. Sweeps were taken from −4 to 8 V with a step size of 0.2 V, a settle time of 0.25 s, and an integration time of ~1 s per step. Sweep rate was not found to have a significant effect on the measured magnitude of PL quenching, although noise was higher for faster sweeps. Control software for these measurements is provided at https://github.com/jsbangsund/ measurement-automation-tools. Devices were optically pumped with a 100 mW $\lambda = 405$-nm laser (Coherent OBIS 405LX), which was attenuated with a neutral density filter, chopped at 2 kHz, and expanded with a Thorlabs GBE05-A 5x achromatic Galilean beam expander to a 1/e$^2$ diameter of ~4 mm. Beam expansion serves to improve signal without increasing the exciton density. Devices were masked and the beam was passed through an adjustable iris to prevent excitation outside the device area. The PL signal was passed through a 450-nm-long pass filter to prevent detection of stray laser light, collected with a Thorlabs PDA36A Si adjustable gain photodetector, and measured with a Stanford Research Systems SR810 lock-in amplifier. The lock-in amplifier serves to reject the baseline EL signal, ensuring that only PL is measured. The PL signal was kept
below an equivalent brightness of 50 cd/m² (pump power density of ~5 mW/cm²), ensuring that the probe has minimal impact on quenching. A schematic of the measurement setup is shown in fig. S1B.

Transient PL was collected with a Thorlabs APD430A avalanche photodiode and recorded with a Tektronix TDS5104B digital phosphor oscilloscope. Films were excited with an Optical Building Blocks pulsed nitrogen laser (λ = 337 nm) with a pulse width of ~1 ns and a repetition rate of 6 Hz. Emission was focused on the photodiode with a series of lenses. Exciton lifetimes were extracted by fitting an exponential decay to the data from 2 to 5 µs after the laser pulse, to avoid any nonlinearity due to triplet–triplet annihilation at short times. Device lifetime measurements with simultaneous EL and PL characterization were carried out using previously described methods (20).

DCM sweeps were collected using a Pine Research WaveDriver 10 potentiostat. Displacement current was measured during triangle wave sweeps with a sweep rate of 1 V/s, a step size of 5 mV, a lower potential varying from −5 to −3 V, and an upper potential of +3 V. Sweep cycles were repeated three times for each measurement. Raw data are smoothed using a moving average with a window of 0.1 V.

DCM data were analyzed with the methods outlined in (16): The hole-injection voltage, \( V_{\text{inj}} \), was extracted from DCM sweeps by finding the intersection between lines fit to the lower reverse bias plateau and the accumulation region, where current begins to increase. The total hole density, \( \sigma_h \), which is injected before the turn-on voltage, \( V_{\text{th}} \), is calculated by integrating the DCM swept from \( V_{\text{inj}} \) to \( V_{\text{th}} \)

\[
\sigma_h = \int_{V_{\text{inj}}}^{V_{\text{th}}} C_{\text{app}} dV = \int_{V_{\text{inj}}}^{V_{\text{th}}} J_{\text{DCM}} \frac{dV}{dt} dV
\]

where \( C_{\text{app}} \) is the apparent capacitance of the device, \( J_{\text{DCM}} \) is the measured current density, and \( dV/dt \) is the voltage sweep rate. Measurements were taken in the quasistatic regime, which was verified by increasing sweep rate and observing no change in the sweep rate-normalized current. Hence, the conduction current below device turn-on is negligible and \( J_{\text{DCM}} = C_{\text{app}} \times dV/dt \) (28).

**Optical outcoupling calculations**

Light outcoupling efficiency was calculated using a classical dipole emission model (37). Calculations were evenly weighted by five dipole emission planes spread across the EML (i.e., a flat emission zone was assumed). Dipole orientation was assumed to be isotropic, and input optical constants were measured using spectroscopic ellipsometry. Note that a lower outcoupling efficiency was calculated for B3PyMPM devices than TPBi devices due to the higher index of refraction of B3PyMPM (n = 1.99 for B3PyMPM and n = 1.77 for TPBi at 510 nm, the peak emission wavelength of Ir(ppy)₃) (49). When modeling exciton quenching, outcoupling was calculated with a finer grid, and the emission zone was input based on the stated model assumptions. Changes to the radiative rate, exciton lifetime, and effective PL efficiency due to the Purcell effect were calculated using the following intrinsic emissive properties of dilute Ir(ppy)₃: the exciton lifetime, \( \tau \), was measured as 1.3 µs (fig. S7), and the PL efficiency, \( \eta_{\text{PL}} \), was assumed to be 92%, both of which are consistent with reported values (11, 26). Code for these calculations is provided at https://github.com/jsbangsund/oledpy/. Results of the outcoupling code were validated with Setfos 5.0 (Fluxim AG) and found to differ by less than 5% (relative).

**Exciton quenching model**

\( n_h \) is calculated with coordinates in the appropriate reference frame (based on exponential decay from either the HTL/EML interface or the EML/ETL interface) as

\[
\sigma_h \int_{0}^{d_{\text{EML}}} e^{-x/x_w} dx
\]

where \( \sigma_h \) is the measured hole sheet density (Figs. 2C and 4B) and \( d_{\text{EML}} \) is the EML thickness (10 nm). Equation 2 is then solved numerically, applying reflecting boundary conditions (\( d\mu_T/dt = 0 \)) at each interface of the EML. The normalized PL can then be calculated by dividing the outcoupled photon flux when holes are present (at the turn-on voltage, \( V = 2.5 \)) by the outcoupled photon flux when no holes are accumulated in the device (at \( V = -3 \))

\[
\text{PL}_{\text{norm}} = \frac{\text{PL}(V = 2.5)}{\text{PL}(V = -3)} = \frac{\int \eta_{\text{OC}k_n n_T(n_h) dx}}{\int \eta_{\text{OC}k_n n_T(n_h = 0) dx}}
\]

where \( k_n \) is the cavity-modified radiative decay rate and \( \eta_{\text{OC}} \) is the outcoupling efficiency, both integrated over the PL spectrum of Ir(ppy)₃ and calculated using a classical dipole emission model assuming isotropic dipole orientation (37). In calculating EQE, we assume that both charge balance and the spin fraction are unity, which is supported by the results in Fig. 1C. In other words, every injected charge forms an exciton that can decay radiatively. The EQE is then equal to the outcoupled photon flux divided by the exciton generation rate. This is equivalent to the outcoupled radiative decay rate divided by the total decay rate (13, 37)

\[
\text{EQE} = \frac{\int \eta_{\text{OC}k_n n_T dx}}{\int (k_n + k_m + k_{\mu_T} n_h) n_T dx}
\]

Code for these calculations is provided at https://github.com/jsbangsund/low-bias-quenching/.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/6/32/eabb2659/DC1.

**REFERENCES AND NOTES**

1. C. Murawski, K. Lee, M. C. Gather, Efficiency roll-off in organic light-emitting diodes. Adv. Mater. 25, 6801–6827 (2013).
2. S. Scholz, D. Kondakov, B. Lüssem, K. Leo, Degradation mechanisms and reactions in organic light-emitting devices. Chem. Rev. 115, 8449–8503 (2015).
3. S. Reineke, M. Thomschke, B. Lüssem, K. Leo, White organic light-emitting diodes: Status and perspective. Rev. Mod. Phys. 85, 1245–1293 (2013).
4. S. Wehrmeister, L. Jäger, T. Wehlu, A. F. Rausch, T. C. G. Reusch, T. D. Schmidt, W. Brütting, Combined electrical and optical analysis of the efficiency roll-off in phosphorescent organic light-emitting diodes. Phys. Rev. Applied 3, 024008 (2015).
5. N. C. Giebink, B. W. D’Andrade, M. S. Weaver, J. J. Brown, S. R. Forrest, Direct evidence for degradation of polaron excited states in organic light emitting diodes. J. Appl. Phys. 105, 124514 (2009).
6. H. van Eersel, P. A. Bobbert, R. A. J. Janssen, R. Coehoorn, Monte Carlo study of efficiency roll-off of phosphorescent organic light-emitting diodes: Evidence for dominant role of triplet-polaron quenching. Appl. Phys. Lett. 105, 143303 (2014).
7. D. Zhao, H.-P. Loeb, The accumulation of diffusive charges in organic light-emitting diodes. Org. Electron. 24, 147–152 (2015).
8. D. Song, S. Zhao, Y. Luo, H. Aiz, Causes of efficiency roll-off in phosphorescent organic light-emitting devices: Triplet-triplet annihilation versus triplet-polaron quenching. Appl. Phys. Lett. 97, 243304 (2010).
9. J.-M. Kim, J.-J. Kim, Charge transport layers manage mobility and carrier density balance in light-emitting layers influencing the operational stability of organic light-emitting diodes. *Org. Electron.* 67, 43–49 (2019).

10. J.-M. Kim, C.-H. Lee, J.-J. Kim, Mobility balance in the light-emitting layer governs the polaron accumulation and operational stability of organic light-emitting diodes. *Appl. Phys. Lett.* 111, 203301 (2017).

11. S. Reineke, K. Walzer, K. Leo, Triple-exciton quenching in organic phosphorescent light-emitting diodes with Ir-based emitters. *Phys. Rev. B.* 75, 125328 (2007).

12. N. C. Geibink, S. R. Forrest, Quantum efficiency roll-off at high brightness in fluorescent and phosphorescent organic light-emitting diodes. *Phys. Rev. B.* 77, 235215 (2008).

13. K. W. Hershey, R. J. Holmes, Unified analysis of transient and steady-state electrophosphorescence using exciton and polaron dynamics modeling. *J. Appl. Phys.* 120, 195501 (2016).

14. Y. Noguchi, W. Brütting, H. Iishi, Spontaneous orientation polarization in organic light-emitting diodes. *Jpn. J. Appl. Phys.* 58, S8081 (2019).

15. E. Ito, Y. Washizu, N. Hayashi, H. Iishi, N. Matsue, K. Tsuboi, Y. Ouchi, Y. Harima, K. Yamashita, K. Seki, Spontaneous buildup of giant surface potential by vacuum deposition of Alq3, and its removal by visible light irradiation. *J. Appl. Phys.* 92, 7306–7310 (2002).

16. Y. Noguchi, Y. Miyazaki, Y. Tanaka, N. Sato, Y. Nakayama, T. D. Schmidt, W. Brütting, H. Iishi, Charge accumulation at organic semiconductor interfaces due to a permanent dipole moment and its orientational order in bilayer devices. *J. Appl. Phys.* 111, 114508 (2012).

17. T. Yamanaka, H. Nakanotani, C. Adachi, Slow recombination of spontaneously dissociated organic fluorophore excitons. *Nat. Commun.* 10, 5748 (2019).

18. K. Osada, K. Goushi, H. Kaji, C. Adachi, H. Iishi, Y. Noguchi, Observation of spontaneous orientation polarization in evaporated films of organic light-emitting diode materials. *Org. Electron.* 58, 313–317 (2018).

19. J. S. Bangsund, K. W. Hershey, R. J. Holmes, Isolating degradation mechanisms in mixed emissive layer organic light-emitting devices. *ACS Appl. Mater. Interfaces* 10, 5693–5699 (2018).

20. Y. Shirasaki, G. J. Supran, W. A. Tsidale, V. Bulović, Origin of efficiency roll-off in colloidal quantum-dot light-emitting diodes. *Phys. Rev. Lett.* 110, 217403 (2013).

21. W. Zou, R. Li, S. Zhang, Y. Liu, N. Wang, Y. Cao, Y. Miao, M. Xu, Q. Guo, D. Di, L. Zhang, C. Yi, F. Gao, R. H. Friend, J. Wang, W. Huang, Minimising efficiency roll-off in high-brightness perovskite light-emitting diodes. *Nat. Commun.* 9, 608 (2018).

22. J. S. Bangsund, R. J. Holmes, Organic and Hybrid Light Emitting Materials and Devices XXIII (International Society for Optics and Photonics, 2019), vol. 11093, p. 110930L.

23. R. Meerheim, M. Furno, S. Hofmann, B. Lüssem, K. Leo, Efficiency and rate of spontaneous emission in organic electroluminescent devices. *Phys. Rev. B.* 85, 115205 (2012).

24. S. J. Byrnes, Multilayer Optical Calculations (2016); arXiv:1603.02720.

25. Y. Divayana, X. W. Sun, Existence of optimum intermolecular spacing for maximum exciton diffusion length in tris(2-phenylpyridine)iridium(III). *Org. Electron.* 11, 67–73 (2010).

26. R. Coehoorn, P. A. Bobbert, H. van Eersel, Förster-type triplet-polaron quenching in disordered organic semiconductors. *Phys. Rev. B.* 96, 184203 (2017).

27. T. Matsuhashi, G.-H. Jin, Y. Kanai, T. Yokota, S. Kitada, T. Kishi, H. Murata, Interfacial charge transfer and charge generation in organic electronic devices. *Org. Electron.* 12, 520–528 (2011).

28. S. Sanderson, B. Philippa, G. Vamvounis, P. L. Burn, R. D. White, Understanding charge transport in Ir(ppy)3:CBP OLED films. *J. Chem. Phys.* 150, 094110 (2019).

29. B. Nell, K. Orthein, O. V. Boltalina, K. Vandalov, Influence of dopant-host energy level offset on thermoelectric properties of doped organic semiconductors. *J. Phys. Chem. C* 112, 11730–11735 (2018).

30. N. Kajimoto, T. Manaka, M. Iwamoto, Decay process of a large surface potential of Alq3 films by heating. *J. Appl. Phys.* 100, 053707 (2006).

31. M. Oh-E, H. Ogata, F. Arakawa, Randomization and constraint of molecular alignment and orientation: Temperature-dependent anisotropy and phase transition in vapor-deposited thin films of an organic cross-shaped molecule. *ACS Omega* 4, 39–47 (2019).

32. X. Zhao, J. D. A. Ng, R. H. Friend, Z.-K. Tan, Opportunities and challenges in perovskite light-emitting devices. *ACS Photonics* 5, 3866–3875 (2018).

33. H. Kim, L. Zhao, J. S. Price, A. J. Grede, K. Roh, A. N. Brigeman, M. Lopez, B. P. Rand, N. C. Geibink, Hybrid perovskite light-emitting diodes under intense electrical excitation. *Nat. Commun.* 9, 4693 (2018).

34. F. Yan, J. Xing, G. Xing, L. Quan, S. T. Tan, J. Zhao, R. Su, L. Zhang, S. Chen, Y. Zhao, A. Huan, E. H. Sargent, Q. Xiong, H. V. Demir, Highly efficient visible colloidal lead-halide perovskite nanocrystal light-emitting diodes. *Nano Lett.* 18, 3157–3164 (2018).

35. A. Salehi, S. Ho, Y. Chen, C. Peng, H. Yersin, F. So, Highly efficient organic light-emitting diode using a low refractive index electron transport layer. *Adv. Opt. Mater.* 5, 1700197 (2017).

Acknowledgments: We acknowledge P. Trefonas, D. C. K. Rathwell, J.-H. Jeon, and H.-Y. Na for useful discussions and the lab of C. D. Fristoe for the use of the potentiostat. Funding: This work was supported by DuPont Electronics and Imaging. J.S.B. and N.M.C. acknowledge support from the NSF Graduate Research Fellowship under grant no. 00074041. R.J.H. acknowledges support from Ronald L. and Janet A. Christensen. Parts of this work were carried out in the Characterization Facility, University of Minnesota, which receives partial support from the NSF through the MRSEC program. Author contributions: J.S.B. conceived of the project, designed the experiments, built the experimental apparatuses, and carried out characterization. J.R.V.S. fabricated samples, performed the heated deposition experiments, and assisted with characterization and analysis. J.S.B. and N.M.C. carried out excited quenching and optical modeling. J.S.B. and R.J.H. interpreted the results and wrote the manuscript. All authors discussed and reviewed the manuscript. R.J.H. supervised the work. Competing interests: R.J.H. has served as a consultant for DuPont Electronics and Imaging, the sponsor of this work. All other authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 13 February 2020
Accepted 25 June 2020
Published 7 August 2020
10.1126/sciadv.abb2659

Citation: J. S. Bangsund, J. R. Van Sambeek, N. M. Concannon, R. J. Holmes, Sub–turn-on exciton quenching due to molecular orientation and polarization in organic light-emitting devices. *Sci. Adv.* 6, eabb2659 (2020).