An Amorphous Spirobifluorene-Phosphine-Oxide Compound as the Balanced n-Type Host in Bright and Efficient Light-Emitting Electrochemical Cells with Improved Stability

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A rational host–guest concept design for the attainment of high efficiency at strong luminance from light-emitting electrochemical cells (LECs) by suppression of exciton-polaron quenching [Tang et al., Nature Communications 2017, 8, 1190] has been reported. However, a practical drawback with the presented host–guest LEC devices was that the operational stability is insufficient for many applications. Here, a systematic study is performed, revealing that a major culprit for the limited operational stability is that the employed n-type host, 1,3-bis[2-(4-tert-butylphenyl)-1,3,4-oxadiazo-5-yl]benzene (OXD-7), has a strong propensity for crystallization and that this crystallization results in a detrimental phase separation of the constituents in the active material during device operation. The authors, therefore, identify an alternative class of concept-functional n-type hosts in the form of spirobifluorene-phosphine-oxide compounds, and report that the replacement of OXD-7 with amorphous 2,7-bis(diphenylphosphoryl)-9,9′-spirobifluorene results in a much improved operational lifetime of 700 h at >100 cd m⁻² during constant-bias driving at an essentially retained high current efficacy of 37.9 cd A⁻¹ and a strong luminance of 2940 cd m⁻².

1. Introduction

The light-emitting electrochemical cell (LEC) is touted as a low-cost alternative[1] to the organic light-emitting diode (OLED), because its characteristic air-stable and robust device structure enables cost-efficient printing and coating fabrication under ambient air.[2] The LEC is defined by that mobile ions are blended with the organic semiconductor (OSC) in the active material,[3] and that the redistribution of these mobile ions during the initial LEC operation paves the way for electrochemical doping of the OSC.[4] This in situ electrochemical doping results in the formation of a p–n junction doping structure within the active material, so that subsequently injected electrons and holes can recombine into excitons at the p–n junction.[5]

In addition to rendering for efficient injection, transport, and recombination of electrons and holes (commonly termed polarons in OSCs), this electrochemical doping process also results in that LEC devices exhibit very high concentrations of mobile polarons (as enabled by the electrostatic screening of the mobile ions) and a high concentration of excitons (within the thin p–n junction) during high-luminance operation. An unfortunate consequence of a spatial overlap of high concentrations of mobile polarons and excitons in an OSC is that exciton-polaron quenching interactions become prominent, and for this reason, it has been questioned whether it is even possible for an LEC device to attain high efficiency at high luminance.[6]

However, in a recent study,[7] it was demonstrated that this detrimental exciton–polaron quenching can be efficiently suppressed in appropriately designed host–guest LEC devices by a spatial separation of the polaron and exciton distributions, and that such designed LECs indeed can emit with strong luminance at high efficiency.[7–8] More specifically, the presented design criteria resulted in a steady-state p–n junction doping structure, where the polaron (or doping) concentrations drop sharply to a low value at the edge boundary of the p–n junction while the exciton concentration is highly centered within the p–n junction region. This implies that the doping structure in these host-guest LECs more resembles that of a p–i–n junction than a p–n junction, but for simplicity, we have opted to stay with the more common term p–n junction throughout this publication. The drawback with the host–guest LEC devices presented in these initial studies was that their operational lifetime was modest.[7–8]

Herein, we address this issue by showing that the limited operational lifetime can be attributed to that one of the two original host compounds, the electron-transporting 1,3-bis[2-(4-tert-butylphenyl)-1,3,4-oxadiazo-5-yl]benzene (OXD-7), has a strong propensity for crystallization, and that the operational-induced crystallization of OXD-7 results in a phase separation of the constituents in the active material and an associated suppressed host-to-guest energy transfer. We further identify a set
of alternative n-type host compounds, in the form of spirobifluorene-phosphine-oxide derivatives, which in combination with the p-type host poly(9-vinylcarbazole) (PVK), the guest emitter tris[2-(5-substituent-phenyl)-pyridinato] iridium(III) (Ir(R-ppy)₃), and the electrolyte tetrahexylammonium tetrafluoroborate (THABF₄), effectively fulfill the identified high-efficiency/high-luminance design criteria. We note that similar spirobifluorene-phosphine-oxide derivatives have been employed in OLEDs,[9] and that Pertegas and co-workers introduced such a compound in an LEC that delivered a respectable luminance of 420 cd m⁻² at a high current efficacy of 5 cd A⁻¹ during pulsed-bias operation, but with a short operational lifetime of 1 h above 100 cd m⁻².[10] Here, we show that an appropriately designed host-guest LEC device based on the amorphous n-type host 2,7-bis(diphenylphosphoryl)-9,9′-spirobifluorene (SPPO13) delivers a strong luminance of 2940 cd m⁻² at a high current efficacy of 37.9 cd A⁻¹ and a much improved operational lifetime of 700 h at >100 cd m⁻² during constant-bias operation.

The smallest SPPO1 molecule is in a mixed glassy/crystalline, thermally very rigid, and is as such expected to feature a good thermal stability. This is manifested in that, for example, 9,9′-spirobifluorene trimers exhibit a high glass transition temperature (Tg) that is exceeding 200 °C,[14] which is attractive in electrically driven light-emitting devices that can reach high temperatures during high-luminance operation.[15] The phosphine oxide group is polar, by the virtue of the electron-donating phosphorus atom that is chemically connected by a double bond to an electron-accepting oxygen atom, and exhibits a tetrahedral geometry with a broken conjugation, which is anticipated to lead to a high triplet energy.[16] A high triplet energy for the host compound is desirable in that it can pave the way for an efficient host-to-guest energy transfer by the Dexter mechanism in light-emitting devices.

The bulk thermal properties of the active-material compounds were measured with differential scanning calorimetry (DSC). Figure 2a presents the second DSC heating scan, which was recorded following an initial “equilibration cycle” to eliminate the thermal history, comprising directly subsequent heating and cooling scans between room temperature and 300 °C performed at a scan rate of 5 °C min⁻¹. The Ir(R-ppy)₃ guest emitter features no distinct thermal transition between 25 and 300 °C, but it is plausible that a smeared out glass transition could exist within this temperature interval. The PVK polymer (the p-type host) is amorphous and exhibits a characteristic glass transition from the glassy to the rubbery state at Tg = 220 °C; and we note that a similar value for Tg of PVK has been reported in the literature.[17] The OXD-7 small molecule (the “old” n-type host) is in contrast highly crystalline at room temperature, and the melting temperature of crystalline OXD-7 is determined to be located at Tm = 241 °C.[18] However, in this context, we wish to emphasize that the blending, or fast cooling, of a crystalline material, such as OXD-7,[19] can result in that the crystallization becomes spatially or kinetically inhibited so that the crystalline compound instead is locked up in an amorphous state.[20]

The three “new” n-type hosts exhibit different thermal behavior. The smallest SPPO1 molecule is in a mixed glassy/crystalline,
that is, semicrystalline, state at room temperature (following the equilibration cycle), with the minority amorphous phase featuring a $T_g$ of 115 °C while the majority ordered crystalline phase exhibits a $T_m$ of 235 °C. The larger molecules SPPO13 and SPPO21 are both solely amorphous, with a $T_g$ of 123 and 139 °C, respectively. We attribute the lack of crystallinity for the latter two compounds to their more complex and larger molecular structure, which will render ordering and crystallization more difficult also in the neat form.

The DSC data were recorded on bulk neat materials, but we have also investigated the four n-type hosts in thin blend films that were used as the active material in the LEC devices. More specifically, Figures 2b–e present the surface morphology, as probed by atomic force microscopy (AFM), of 120-nm thick active-material films fabricated by spin-coating onto quartz substrates, using the device-fabrication protocol detailed in the Experimental Section. The four active-material films are solely distinguished by the selection of the n-type host, as identified in the upper left corner of the micrographs. It should be noted that the spin-coated active-material films were dried at 70 °C for 2 h, which is well below any of the thermal transitions depicted in Figure 2a.

We first call attention to that all four active-material films feature a uniform and pinhole-free surface morphology, which is an obvious requirement in order to avoid catastrophic short circuits between the two electrodes in planar light-emitting devices, such as LECs and OLEDs. A closer inspection reveals that the most flat and uniform surface belongs to the films based on the n-type hosts SPPO13 (root-mean-square, RMS = 0.63 nm) and SPPO21 (RMS = 0.50 nm), which is in line with that all of the constituents in these films were measured to be amorphous in the DSC (see Figure 2a). In contrast, the SPPO1 based active material features the roughest film surface (RMS = 1.07 µm), which we attribute to that SPPO1 has a high capacity for crystallization, as established by DSC. The OXD-7 based active-material film exhibits an intermediate roughness (RMS = 0.83 nm), despite that OXD-7 was found to be highly crystalline in neat form in the DSC. This observation indicates that the propensity of the n-type host OXD-7 for crystallization is suppressed by its good chemical compatibility with the other constituents in the active material, primarily the p-type host PVK. Nevertheless, the rougher surface structure of the OXD-7 based film in comparison to the SPPO13 and SPPO21 films suggests that small OXD-7 crystals have formed in the OXD-7 based active-material film following spin-coating and drying at 70 °C.

The host-guest approach was originally introduced in OLED (and LEC) devices in order to suppress exciton–exciton quenching interactions by immobilization (i.e., trapping) of the excitons on low-energy-gap guest molecules that are well dispersed within a majority larger-energy-gap host matrix. This approach is especially useful during the high-luminance operation of triplet-emitting devices since the corresponding high concentration of long-lived triplet excitons renders exciton–exciton quenching particularly severe.

We developed the host-guest concept to also mitigate issues with exciton-polaron quenching interactions that are particularly problematic in LEC devices, because of their characteristic high polaron concentrations (as enabled by the electrostatic concentration of the polarons by the counter-ions) and high exciton concentration (the result of that the exciton formation is confined to the thin p–n junction region). The latter issue is obviously strongly amplified during the high-luminance operation of triplet-emitting devices. This is thus the explanation to why it has proven very difficult to realize high-efficiency LEC operation at strong luminance, whereas high-efficiency LEC operation at low luminance is common.

However, a recent study demonstrated, by experiment and simulation, that if three baseline criteria are fulfilled, then the polaron and exciton populations can be significantly separated in space so that the non-desired exciton-polaron quenching is suppressed and high-efficiency operation at strong luminance is attained. The three key enabling design criteria were: i) that the host and guest compounds can be electrochemically doped, both p- and n-type; ii) the attainment of similar-sized electron and hole trap depths, which in this context are defined as the...
The energy difference between the host and guest compounds’ LUMO and HOMO levels, respectively; and iii) the attainment of a balance between the electron and hole mobility on the host compound(s). In addition, in line with the general guidelines for the efficient operation of host-guest systems, it is further important that the exciton is efficiently transferred to, and/or efficiently formed directly on the guest compound.[23]

In order to investigate whether the three new n-type host compounds can fulfill these baseline criteria, we have first performed a CV study. Figure 3 presents the cyclic voltammetry (CV) traces recorded on thin films of the old n-type host OXD-7 (as reference) and the three new n-type hosts. We find that all four n-type hosts demonstrate capacity for electrochemical n-type doping as well as p-type doping, with the latter reaction being more reversible than the former. We have previously demonstrated that the employed guest emitter Ir(R-ppy)$_3$ also can be electrochemically p- and n-type doped, which shows that criterion (i) is fulfilled in host-guest systems based on all four n-type hosts.[7]

The fulfillment of criterion (ii) was investigated by translating the measured onsets for the redox reactions (versus the Fe/Fe$^+$ reference electrode) to electrode levels on the vacuum-level scale with the following equation: $E_{\text{vacuum level}} = -e(4.8 \text{ V } V_{\text{Fe}/\text{Fe}^+})$. We find that the three new n-type hosts feature a similar LUMO value ranging between −2.5 and −2.6 eV, which is slightly higher than that of OXD-7 at −2.7 eV. As the LUMO of the Ir(R-ppy)$_3$ guest emitter is positioned at −3.0 eV,[7] this results in that the electron trap depth ($E_{\text{trap}}^-$) in the host-guest system ranges between 0.3 and 0.5 eV, as specified in the right-hand panels in Figures 3a–d.

We further find that the HOMO of the four n-type hosts is located between −5.9 and −6.3 eV, while the HOMO of the Ir(R-ppy)$_3$ guest is −5.2 eV.[7] This results in that the hole trap depth ($E_{\text{trap}}^+$) ranges between −0.7 and 1.1 eV, which is much higher than the above-derived value for $E_{\text{trap}}^-$. Therefore, in order to render the trap depths more balanced and fulfill the qualifying criterion (iii), we elected to include PVK as the p-type host in the host-guest system. This allows for a lowering of the hole trap depth to $E_{\text{trap}}^+=0.4$ eV, so that the $E_{\text{trap}}^-/E_{\text{trap}}^+$ ratio for the complete PVK:n-type-host:Ir(R-ppy)$_3$:THABF$_4$ host-guest system is 1.25 (n-type host = SPO1, SPO21), 1.0 (n-type host = SPO13), or 0.75 (n-type host = OXD-7). In this context, we mention that PVK cannot be electrochemically n-type doped, and that the THABF$_4$ electrolyte, as desired, is electrochemically silent (or inert) within the potential range spanned by the electrochemical n-type doping level of the n-type host and the p-type doping level of PVK.[7]

The third design criterion constituted the attainment of a balance between the mobility of the electrons and holes on the host compound(s). As we have selected to use two different host compounds for the n-type electron transport and the p-type hole transport, this study encompasses the study of the four blend-host systems, that is, each one of the four n-type hosts blended with the p-type host PVK in a 1:1 mass ratio.

Figure 4a presents the measured current density as a function of the applied voltage for ITO/Al+/blend-host/Ca(--)/Al electron-only devices (solid symbols) and ITO/PEDOT:PSS(+)/blend-host/Au(--) hole-only devices (open symbols), with the selection for the n-type host presented in the inset. In the low-voltage regime, the current density is affected by the (small) energy barriers at the two electrode interfaces, whereas in the high-voltage regime (here, V > 10 V for the electron-only devices and V > 20 V for the hole-only devices) the current is primarily limited by the transport within the bulk of the blend-host film. We were not able to fit the high-voltage data with the space-charge-limited-current equation and a constant value for the mobility, but had better success with the equation for the space-charge-limited current modified by the Poole–Frenkel effect:

$$j = \frac{9}{8} e \varepsilon_0 \mu_0 \frac{E^2}{L} \exp(\beta \sqrt{E})$$

(1)

where $\varepsilon$ is the relative dielectric constant, $\varepsilon_0$ the permittivity of free space, $E$ the electric field, $L$ the active-material thickness, $\mu_0$ the zero-field mobility, and $\beta$ the Poole–Frenkel factor. The dependence of the mobility on the electric field can then be derived with the following equation:

$$\mu = \mu_0 \exp(\beta \sqrt{E})$$

(2)
Figure 4. a) The current density as a function of the applied voltage for electron-only ITO/Al(+)blend-host/Ca/Al(−) devices (solid symbols) and ITO/PEDOT:PSS(+)blend-host/Au(−) hole-only devices (open symbols). The n-type host in the blend-host film is identified in the inset, while the p-type host is PVK. The PVK:n-type-host mass ratio is 1:1. b) The corresponding electron mobility (solid symbols) and hole mobility (open symbols) of the blend-host film as a function of the electric field, as derived by fitting the equation for the space-charge limited current modified by the Poole–Frenkel effect.

Figure 4b shows that both the electron mobility and the hole mobility for all four blend-host films are strongly dependent on the electric field, and that the mobility increases strongly with increasing electric field. In order to obtain the values for the mobility within the p–n junction, we estimate the electric field in the p–n junction by subtracting the energy-gap potential from the steady-state voltage and dividing by the width of the p–n junction. A typical value for the steady-state voltage is 9 V (cf. Figure 6b), the energy-gap potential of the blend-host is $\approx 3$ V (see Figure 3), whereas the simulation in ref. [7] delivered a value for the width of the p–n junction of $\approx 40$ nm, which results in that the electric field in the p–n junction is $\approx 0.15$ V nm$^{-1}$.

Table 1 presents a summary of the derived values for the electron and hole mobility in the p–n junction for the four blend-host films, and the consistent finding is that the electron mobility is larger than the hole mobility. Specifically, the PVK:OXD-7 blend-host presents the most balanced mobility at $\mu_e/\mu_h = 28$, followed by PVK:SPPO21 at 145, whereas the PVK:SPPO21 blend-host exhibits the most imbalanced mobility at $\mu_e/\mu_h = 1310$. We note that the slightly deeper electron trap in the SPPO-based active materials thus could be compensated by the significantly higher electron mobility in the blend-host only material. In this context, we also remember that the simulation in the original publication[7] revealed that the detrimental polaron–exciton quenching is more sensitive to an imbalance in the trap depths than in the mobility.

Figure 5a–d presents the photoluminescence (PL) spectra of thin films of the blend-host and its two constituents, as identified in the insets. A comparison of the PL spectra of the neat spirobifluorene-phosphine oxide films (open solid squares in Figures 5b–d) reveals that the PL spectrum, as expected, is red-shifting with increasing molecular size from SPPO1 (PL peak $= 351$ nm), over SPPO13 (PL peak $= 374$ nm), to SPPO21 (PL peak $= 410$ nm). Figure 5a further shows that the PL spectrum of the PVK:OXD-7 blend-host (PL peak $= 340$ nm) is red-shifted with respect to both its constituents in the form of the neat PVK (PL peak $= 410$ nm) and the neat OXD-7 (PL peak $= 350$ nm). We assign this redshift to significant exciplex emission within a well-mixed PVK:OXD-7 blend on the molecular level, with the hole located on the PVK polymer and the electron on the OXD-7 molecule.

The combined results from the preceding DSC, AFM, mobility, and PL measurements thus suggest that the spin-coated film of PVK and OXD-7 comprises molecules that are well mixed, but also that some small OXD-7 crystals have formed already in the spin-coated PVK:OXD-7 film. Note that all of the investigated films were spin-coated from freshly prepared inks using a “good” solvent of chlorobenzene, and subsequently dried at 70 °C for 2 h. Thus, the drying was invariably performed at a temperature well below the thermal transitions identified in the DSC investigation in Figure 2a.

Figures 5c–d show that the PL spectra of the blend-host films of PVK:SPPO13 (PL peak $= 440$ nm) and PVK:SPPO21 (PL peak $= 435$ nm) also are red-shifted with respect to the neat spectra of their constituent materials, which implies exciplex emission and that the two host constituents are well blended on the molecular scale. In contrast, Figure 5b reveals that the PL spectrum of the PVK:SPPO1 blend-host film (PL peak $= 386$ nm) is largely a superposition of the PL spectra of the PVK (PL peak $= 410$ nm) and SPPO1 (PL peak $= 351$ nm) constituents. This

| Table 1. Summary of electronic and optical data for the different n-type host materials in the active material of the LEC devices. |
|---|---|---|---|---|---|---|---|---|
| n-type host | $E_{trp}$ [eV]$^a$ | $E_{trap}$ [eV]$^a$ | $E_{trap}/E_{trap}$ | $\mu_e$ in blend-host [cm$^2$ V$^{-1}$ s$^{-1}$]$^b$ | $\mu_h$ in blend-host [cm$^2$ V$^{-1}$ s$^{-1}$]$^b$ | $\mu_e/\mu_h$ | PLQY of blend-host [%]$^c$ | PLQY of active material [%]$^d$ | Triplet energy [eV] |
| SPPO1 | 0.5 | 0.4 | 1.25 | $8.7 \times 10^{-3}$ | $6.0 \times 10^{-9}$ | 145 | 19.6 | 8.4 | 49.5 | 2.7 |
| SPPO13 | 0.4 | 0.4 | 1.0 | $1.9 \times 10^{-1}$ | $2.5 \times 10^{-9}$ | 76 | 16.6 | 6.2 (Exciplex) | 53.4 | 2.7 |
| SPPO21 | 0.5 | 0.4 | 1.25 | $1.7 \times 10^{-4}$ | $1.3 \times 10^{-9}$ | 1310 | 12.7 | 4.4 (Exciplex) | 16.2 | 2.3 |
| OXD-7 | 0.3 | 0.4 | 0.75 | $1.0 \times 10^{-3}$ | $3.6 \times 10^{-9}$ | 28 | 33.0 | 8.3 (Exciplex) | 56.2 | 2.7 |

$^a$Defined as the energy offset between the LUMO/HOMO levels of the n-type/p-type host and the guest; $^b$at an electric field of 0.15 V nm$^{-1}$; $^c$in a thin film.
observation suggests that the two components are significantly phase-separated, most probably as a result of the significant crystallization of SPPO1, as clearly detected with DSC and AFM.

As an exciplex commonly features a significantly lowered emission efficiency in comparison to its constituent neat materials,[24] a comparison of the PLQY of the blend-host film with the average PLQY of the two constituent host films provides a further test of the above assignments. The PLQY of the PVK:SPPO1 film is 8.4%, which corresponds to a comparatively modest PLQY drop of 43% in comparison to the average PLQY of 14.8% of the neat PVK film (10.0%) and the neat SPPO1 film (19.6%). The corresponding PLQY drop for the three other blend-host systems is higher at 61% for PVK:OXD-7, 53% for PVK:SPPO13, and 61% for PVK:SPPO21. Thus, the PLQY data provide further support that the PVK:SPPO1 film is strongly phase-separated, whereas the other three blend-hosts are better mixed and as a consequence feature exciplex emission.

The active material in the LEC devices comprises one of the four blend-hosts at 64.6 mass % mixed with the Ir(R-ppy)3 guest emitter at 29.0 mass % and the THABF4 electrolyte at 6.4 mass %. Figure 5e shows that the PL spectrum of all four blend-host films features a significant spectral overlap with the absorption spectrum of the Ir(R-ppy)3 guest, with the desired consequence being that a critical prerequisite for efficient

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**Figure 5.** a–d) The PL spectra of thin films of the neat PVK p-type host (solid black line), the neat n-type host (open solid squares), and the blend-host (solid black squares). e) The absorption spectrum (dashed red line) and the PL spectrum (solid red line) of a neat film of the Ir(R-ppy)3 guest emitter, and the PL spectra of the four blend-host films. f) The PL spectra of the active materials, with the n-type host and the corresponding PLQY identified in the inset.
Förster energy transfer from the blend-host to the guest emitter is fulfilled.

Table 1 presents the triplet energies of the neat host materials and the guest emitter for an analysis of the host-to-guest energy transfer by the Dexter mechanism. For the PVK:SPPO1 based active material, the higher triplet energy of both the PVK host (3.0 eV)\(^\text{[25]}\) and the SPPO1 host (2.7 eV)\(^\text{[11]}\) than the Ir(R-ppy)$_3$ guest emitter (2.4 eV) implies that the Dexter transfer to the guest will be efficient in this active material. For the three other active materials, this analysis is more complex since the blend-host exciplex contributes with an additional triplet state that needs to be considered. Specifically, an exciplex is characterized by singlet and triplet states that are positioned at approximately the same energy, and between which the exciton can cycle back and forth at a relatively high rate.\(^\text{[26]}\) Thus, the energy of the exciplex triplet is well estimated by the exciplex singlet, which is located at 2.9 eV for the PVK:OXD-7 active material, 2.8 eV for the PVK:SPPO13 active material, and 2.9 eV for the PVK:SPPO21 active material (as derived from the PL spectra in Figures 5a,b,d). Accordingly, the energy transfer from the exciplex triplet to the guest triplet should be facile.

However, as it is reasonable to anticipate that some of the host molecules are not locked up in exciplex states, we need to also consider the triplet energy of such “free” host molecules. Table 1 reveals that for the PVK:OXD-7 and PVK:SPPO13 systems, the triplet energies of both of the “free” host compounds are higher than that of the Ir guest emitter, but that for the PVK:SPPO21 system the triplet energy of the SPPO21 host is lower at 2.3 eV\(^\text{[13]}\) than that of the Ir guest emitter at 2.4 eV. This has the undesired consequence that triplets formed during optical excitation (by intersystem crossing from the exciplex singlet to the exciplex triplet) and electric excitation will be trapped on the “free” SPPO21 molecules and not on the Ir guest.\(^\text{[27]}\)

This triplet trapping on the poorly emissive SPPO21 host compound is manifested in the significantly lower PLQY of 16.2% of the SPPO21 based active material in comparison to the much higher PLQY of ≈50% for the three other active materials, for which all of the triplet levels are located at a higher energy than the guest triplet. Specifically, the highest PLQY is 56.2% for the OXD-7 based active material, followed closely by the 53.4% for the SPPO13 and 49.5% for the SPPO1 active materials. Nevertheless, Figure 5f demonstrates that all four active materials, as desired, feature PL emission from solely the Ir guest, with the PL peak located at 525 nm (for the characteristic Ir-guest emission see Figure 5e). Note that the dark triplets trapped on the “free” SPPO21 host molecules are lost to heat and thus do not contribute to the emission.

We now turn our attention to the implementation and evaluation of the new n-type hosts in LEC devices. The LECs were fabricated in an ITO/PEDOT:PSS/PVK:n-type-host:Ir(R-ppy)$_3$:THABF$_4$/Al architecture, with the active-material thickness being 120 nm. The mass concentration of the Ir(R-ppy)$_3$ guest emitter and the THABF$_4$ electrolyte were 29.4% and 6.4%, respectively, while the mass ratio between the PVK p-type host and the n-type host was optimized for peak emission performance to the following values: 1:1 for PVK:OXD-7, 1:1.2 for PVK:SPPO1, 1:1.2 for PVK:SPPO13, and 1:0.8 for PVK:SPPO21. Key device metrics recorded during this optimization procedure are presented in Table S1, Supporting Information.

Figure 6a–b presents the temporal evolution of the luminance and voltage during driving by a constant current density of \(j = 7.7 \text{ mA cm}^{-2}\). c) The EL spectrum of the LEC devices recorded at peak luminance, with the selection of the n-type host presented in the inset. d) The long-term operation of the LEC device with OXD-7 and SPPO13 as the n-type host when driven by \(j = 2.5 \text{ mA cm}^{-2}\).
of 77 mA cm$^{-2}$, whereas Figure 6c presents the EL spectrum recorded at peak luminance. Table 2 presents a summary of the key device metrics. We find that all four devices feature an increasing luminance and a decreasing voltage during the initial operation, which implies that the LEC-characteristic electrochemical doping and p–n junction doping formation takes place, which is in line with our analysis of the CV data in Figure 3. All four pristine devices exhibit a fast turn-on time of less than 2 s to a significant luminance (>1000 cd m$^{-2}$), and essentially identical EL spectra with the main EL peak positioned at 523 nm. The former observation shows that the motion of the bulky electrolyte ions within the active material is facile, whereas the latter observation demonstrates that the emission is originating from the Ir(R-ppy)$_3$ guest emitter. We further note that the EL spectrum is weakly blue shifted (peak shift by 2 nm) in comparison to the PL spectrum of the same active material (Figure 5f), and we propose that this very slight change could be caused by the motion of the bulky ions during the LEC operation$^{[28]}$ or to interference effects within the LEC microcavity.$^{[30]}$

An impressive emission/efficiency performance is measured for the OXD-7 based LEC, which delivers a peak luminance of 3100 cd m$^{-2}$ at a current efficacy of 39.9 cd A$^{-1}$. We mention that a slightly higher value by 4–5% was reported in the original study, and we tentatively attribute this drop in performance to a batch-to-batch variation of the guest emitter. In this context, we mention that all of the devices presented in this study were fabricated from the same batch of materials.

Interestingly, we find that the SPPO13 based LEC features a similar high peak emission/efficiency performance of 2940 cd m$^{-2}$ at 379 cd A$^{-1}$ as the original OXD-7 device, whereas the two LEC devices based on the SPPO1 and SPPO21 n-type hosts deliver a markedly lower performance of 2300 cd m$^{-2}$ at 29.7 cd A$^{-1}$ and 1230 cd m$^{-2}$ at 15.5 cd A$^{-1}$, respectively (see Table 2 for details). We attribute the lower peak performance of the SPPO1 based LEC to phase separation within the active material, as induced by the propensity for SPPO1 to crystallize (see Figure 2) and as manifested in a rough surface morphology (Figure 3b) and the emergence of superposition emission in PL (Figure 5b). The poor performance of the SPPO21 LEC is assigned to the low triplet energy of the SPPO21 host (see Table 1), which inhibits the Dexter energy transfer of triplet excitons to the guest compound and also is manifested in the relatively low PLQY value of this active material (see inset in Figure 5f).

Importantly, we find that the operational stability of the new high-luminance/high-efficiency SPPO13 based LEC is significantly improved in comparison to the incumbent OXD-7 LEC. More specifically, at a constant drive, current density of 77 mA cm$^{-2}$ the operational lifetime above 1000 cd m$^{-2}$ is improved from 2.6 to 14.4 h, while the corresponding improvement is from 31 h to 300 h at the lower luminance threshold of 100 cd m$^{-2}$. Figure 6f and Table 2 further show that the same trend also holds at a lower drive current density of 2.5 mA cm$^{-2}$, for which the stability improvement is from 145 h to a quite respectable 700 h.

In order to shed light on the origin for the improved operational stability of the SPPO13 based LEC over the original OXD-7 based device, we have investigated the evolution of a number of device properties during LEC operation and following a thermal treatment. Figures 7a,b provide a comparison of the PL spectrum and the PLQY of the “pristine” active-material films (spin-coated and dried at 70 °C for 2 h) that were employed in the LEC devices with the same films that had been additionally “thermally treated” at 110 °C for 36 h.

We find that the PL spectrum of the active-material films based on SPPO13 (as well as SPPO1 and SPPO21) remained invariant during this thermal treatment, whereas a new peak at $\sim$380 nm emerged for the OXD-7 based active material. A comparison with the PL spectrum for the systems depicted in Figure 5a suggests that this new emission peak should be due to “superposition” host emission from phase-separated PVK (PL$_{\text{peak}}$ = 410 nm) and OXD-7 (PL$_{\text{peak}}$ = 350 nm). We also find that the drop in PLQY following the thermal treatment is much stronger for the OXD-7 based active material at 13.4% than for the SPPO13 active material at 6.8% (and the SPPO1 and SPPO21 active materials at 5.0 and 6.9%, respectively). We further find that the same thermal treatment of a PVK-ODX-7 film results in a much rougher surface morphology in AFM (see Figure S1, Supporting Information).

All of these observations can be rationalized by that the OXD-7 compound has formed significant crystals within the active material during the thermal treatment, and that this crystallization causes significant phase separation; whereas the other three active materials feature a morphology that remains intact during the thermal treatment. In this context, we remember that our earlier investigations revealed that OXD-7 features a strong propensity for crystallization (see DSC data in Figure 2a), but that this crystallization is inhibited in the pristine active-material film (see AFM data in Figure 2b and PL data in Figure 5a). The consequences of the OXD-7 crystallization and the concomitant phase separation within the active material are that the host-to-guest transfer is suppressed, as evidenced by the emergence of host emission and the lowered PLQY, and that the blend-host exciplex emission at 410 nm (Figure 5a) has transformed into a host superposition emission at 380 nm (Figure 7b).

It is well established that electrically driven light-emission devices, such as LECs, turn warm during operation$^{[35]}$ and it
is plausible that this self-heating drives the crystallization of the OXD-7. Moreover, it is plausible that the redistribution of bulky ions that takes place within the active material during the initial LEC operations can further contribute to effectuate kinetically hindered phase transitions, such as the crystallization of the OXD-7 constituent. Figures 7c–f contribute with additional evidence that the OXD-7 molecules indeed are crystallizing in the active material during LEC operation, and that this event is a
primary cause for the limited operational lifetime of OXD-7 LECs. The initially uniform emission from the large-area OXD-7 LEC device in both PL and EL has already after 3 h of high-luminance operation transformed into spotty regions with stronger and weaker emission intensity, whereas the emission from the corresponding SPPO13 LEC remains uniform during the entire measurement period up to 30 h.

In this context, we remember previous studies that have attributed the emergence of similar spot-like patterns to the delamination of the top electrode,[16] but note that such a delamination effect should only be visible in spatial EL probing and not in spatial PL probing (since it effectively blocks the injection of charge carriers from the delaminated top electrode). Figure S2, Supporting Information, presents a spatial PL probing performed at approximately the same time as the spatial EL probing in Figure 7f, and the similarity in the spot patterns suggest that the major cause of the OXD-7 crystallization indeed is suppression of host-guest energy transfer and not delamination of the top electrode.

3. Conclusions

We report on the development of LEC devices with a simple device architecture, including air-stable electrodes, which simultaneously feature fast turn-on, strong luminance at high efficiency, and reasonable stress stability. This achievement is effectuated by employing a rationally designed host-guest active material, in which all constituents remain amorphous during long-term operation. More specifically, we present evidence that the limited stress stability of previously reported high-efficiency and strong-luminance LECs can be attributed to one of its active-material constituents, the n-type host OXD-7, crystallizes during long-term operation, and that this crystallization results in phase separation and suppressed energy transfer within the active material. By replacing the crystalline-prone OXD-7 with amorphous SPPO13, with similar attractive electronic and optical properties for the n-type host, we realize an LEC device that turns on and emits >1000 cd m\(^{-2}\) within 2 s, which delivers a strong luminance of 2940 cd m\(^{-2}\) at a high current efficacy of 379 cd A\(^{-1}\), and which features a stress lifetime of 700 h above 100 cd m\(^{-2}\).

4. Experimental Section

The chemical structure of the host materials poly(9-vinylcarbazole) (PVK, M\(_n\) = 1.1 × 10\(^6\) g mol\(^{-1}\), Sigma-Aldrich), 1,3-bis[2-(4-tert-butylphenyl)-1,3,4-oxadiazo-5-yl]benzene (OXD-7, Lumtec), 2-diphenylphosphine oxide-9,9′-di-octylfluorene (SPPO1, Lumtec), 2,7-bis(diphenylphosphoryl)-9,9′-spirofluorene (SPPO13, Lumtec), 2,7-bis(diphenylphosphoryl)-9,9′-spiro(benzofluorene-7,11-diylfluorene) (SPPO21, Lumtec), the guest compound tris[2-(5-substituent-phenyl)-2-pyridinato] iridium(III) (Ir(R-ppy)\(_3\), Merck), and the electrolyte tetrathylelammonium tetrafluoroborate (THABF\(_4\), Sigma-Aldrich) are presented in the Figure 1. All of the materials were used as received. The master solutions were prepared by separately dissolving the active material compounds in chlorobenzene in a concentration of 20 g L\(^{-1}\) under stirring at 70 °C on a magnetic hot plate. The carefully cleaned indium-tin-oxide (ITO) coated glass substrates (20 Ω sq\(^{-1}\), Thin Film Devices) were spin-coated by a poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) ink (Clevios P VP Al 4083, Heraeus) at 4000 rpm for 60 s, and thereafter dried at 120 °C for 30 min. The dry PEDOT:PSS layer was spin-coated with the active-material ink at 2000 rpm for 60 s, and thereafter dried at 70 °C for 2 h. The dry thickness of the PEDOT:PSS and the active-material layers was 40 and 120 nm, respectively, as measured with a profilometer (DekTak XT, Bruker). Finally, a set of 100 nm thick Al cathodes were deposited on top of the active material by thermal vacuum evaporation at p < 5 × 10\(^{-6}\) mbar. The 2 × 2 mm\(^2\) emission area was defined by the overlap between the ITO anode and the Al cathode. The LEC devices were driven and measured with a computer-controlled current-voltage-luminance system (OLED Lifetime Tester M6000, McScience). The electroluminescence spectrum was measured with a calibrated spectrometer (USB2000+, Ocean Optics). All of the above procedures, with the exception of the deposition of PEDOT:PSS, were carried out in two interconnected N\(_2\)-filled glove box to exclude any possible contamination.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data available on request from the authors.
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