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From a design, optimization and fabrication perspective, an organic light-emitting diode (OLED) consisting of only one single layer of a neat semiconductor would be highly attractive. Here, we demonstrate an efficient and stable OLED based on a single layer of a neat thermally-activated delayed fluorescence (TADF) emitter. By employing Ohmic electron and hole contacts, charge injection is efficient and the absence of heterojunctions results in an exceptionally low operating voltage of 2.9 V at a luminance of 10,000 cd/m^2. Balanced electron and hole transport results in a maximum external quantum efficiency of 19% at 500 cd/m^2 and a broadened emission zone, which greatly improves the operational stability, allowing a LT_{50} lifetime of 1880 hours for an initial luminance of 1000 cd/m^2. As a result, this single-layer concept combines a high power efficiency with a long lifetime in a simplified architecture, rivalling and even exceeding the performance of complex multilayer devices.

Introduction

After the discovery of electroluminescence in thin films of evaporated organic small molecules [1] and conjugated polymers [2], tremendous efforts have been made to utilize these materials in electronic devices like organic light-emitting diodes (OLEDs). Devices based on conjugated polymers were considered attractive due to their simple device structure, one organic layer sandwiched between two electrodes, opening up applications such as printable large-area flexible displays. In order to ensure efficient hole injection from conventional electrodes like indium-tin oxide or poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), the ionization energies of the organic semiconductors were designed not to be higher than ~5.3 eV. As a result, depending on the emission colour, the electron affinities then typically ranged from 2 to 3 eV. This choice in the design of organic semiconductors turned out to have a number of unfavourable consequences. First, the high electron affinity requires the use of highly reactive cathodes, such as calcium or barium for efficient electron injection, putting high demands on the quality of the OLED encapsulation. Furthermore, the electron and hole transport were found to be highly unbalanced with differences up to several orders of magnitude [3]. This was found to be the result of a universal trap level situated at a depth of 3.6 eV below vacuum, leading to heavily trap-limited electron transport in organic semiconductors with low electron affinities [4]. Electron trapping confines the emission zone close to the cathode, leading to efficiency losses due to exciton quenching, as well as non-radiative trap-assisted recombination [5].

The way to overcome some of these limitations was to increase the amount of organic layers, which could easily be done using thermally evaporated molecules. Already in 1987, Tang and VanSlyke employed a double-layer structure, consisting of a hole-transport layer and an emissive layer, to separate the recombination zone from the electrodes [1]. In subsequent years, the efficiency of OLEDs was further improved by using more extensive multilayer structures for a better tuning of the injection, charge transport, and positioning of the recombination zone [6].

Another important step forward was achieved in the emissive layer by employing phosphorescent heavy-metal complexes to harvest triplet excitons [7,8], which decay nonradiatively in

fluorescent emitters. These phosphorescent molecules were applied as dopants (typically 8-10 wt.%) in a large-gap host to avoid concentration quenching. As a next step, it was found that the hole- and electron-transport layers can additionally be doped electrically with p- or n-type dopants, resulting in increased conductivity and, as a result, a reduced operating voltage [9-11]. The resulting p-i-n devices furthermore required the use of additional undoped exciton- and charge-blocking layers to prevent exciton quenching by the dopants, resulting typically in a 5-layer device. Since these undoped blocking layers do not necessarily consist of the same material as the host or the doped transport layers, a multilayer OLED can easily contain up to 8 different organic compounds [11].

Recently, it was demonstrated by Uoyama et al. that high electroluminescence quantum yields could also be obtained with metal-free organic emitters, by using the concept of thermally-activated delayed fluorescence (TADF) [12]. Here, the small gap between the energy of the singlet and triplet excited state allows thermally-activated back transfer of the nonradiative triplet excitons to the fluorescent singlet state. Most research has been devoted to the design and fabrication of TADF OLEDs with high external quantum efficiency [13]. However, an unresolved problem in TADF multilayer OLEDs is their limited operational stability. A notable increase in operational lifetime was achieved by using n-type hosts, resulting in a broadened recombination zone [14].

As is the case for phosphorescent OLEDs, TADF devices make use of similar complex multilayer device architectures. This complicates their design, as the properties of the charge-transport, host, and blocking layers all need to be tuned to the emitter with regard to energy levels, triplet energies, and charge-transport properties. The complexity further hinders the interpretation of efficiency and stability of these devices. Ideally, an OLED would consist of only one active organic semiconducting layer, in which charges are efficiently injected. Subsequently, both types of carriers are transported efficiently toward each other, after which the electrons and holes recombine through excitons with a high radiative yield via the TADF mechanism. An advantage of TADF emitters is that they are able to harvest triplet excitons even in undoped films, so a host-guest emissive layer is not always required [15]. Balanced transport can be achieved by using an organic semiconductor with an electron affinity of around 3.6 eV (or higher) to

strongly reduce or even eliminate electron trapping [4]. This would not only reduce the nonradiative recombination losses due to exciton quenching and trap-assisted recombination [5], but would also allow the usage of non-reactive electron-injection layers, thereby enhancing the air stability of the device and the starting materials. A major challenge to overcome is then that a deeper lowest unoccupied molecular orbital (LUMO) of around -3.6 eV also leads to a lowering of the highest occupied molecular orbital (HOMO) even beyond -6 eV, in order to maintain the energy gap for visible light emission. Such a deep HOMO poses a significant challenge for hole injection, that currently cannot be solved by p-type doped transport layers. Recently, we have developed a strategy to overcome this problem [16]. By using high work function transition metal oxides, such as MoO_3, in combination with an organic interlayer with a high ionization energy, Ohmic hole contacts were formed on organic semiconductors with a HOMO at -6 eV and deeper. A similar strategy to create truly Ohmic electron contacts would be highly desirable to enable efficient bipolar injection in an OLED device.

Here, we demonstrate that a high efficiency, low operating voltage and high stability can be realized in a simplified TADF OLED comprising only a single layer of a neat emitter sandwiched between Ohmic electron and hole contacts. The efficient charge injection and the absence of heterojunctions lead to barrier-free flow of electrons and holes toward each other, yielding exceptionally low operating voltages. Balanced transport is achieved by choice of the energy levels of the emitter. The resulting broadened recombination zone gives rise to a greatly enhanced operational stability. Notably, the Ohmic electron contact is formed without the requirement of air-sensitive dopants or injection layers, resulting in an OLED with improved air stability.

Device concept

As a candidate for the active material to be used in a single-layer OLED, we selected the TADF emitter CzDBA [9,10-bis(4-(9*H*-carbazol-9-yl)-2,6-dimethylphenyl)-9,10-diboraanthracene; Fig. 1(b)]. This emitter has its HOMO at -5.93 and its LUMO at -3.45 eV [17], which should be sufficiently low to alleviate the impact of electron traps on the electron transport. The donor moieties of CzDBA consist of

carbazole, which is a known hole-transport unit. However, the electron- and hole transport in CzDBA have not been investigated so far. Furthermore, CzDBA showed excellent external quantum efficiencies in conventional doped multilayer stack OLEDs, as well as exhibiting high photoluminescence quantum yields in both doped (~100% in 4,4′-bis(*N*-carbazolyl)-1,1′-biphenyl; CBP) and neat films (90.6%) [17].

In Fig.1(a), the device layout of our single-layer OLED is shown. For hole injection, we use an interlayer of C_{60} to form an Ohmic hole contact in combination with MoO_3, as we have demonstrated in earlier work [16]. For electron injection, we do not use a conventional reactive injection layer, such as LiF, calcium, or barium. Instead, we use a thin (4 nm) interlayer of the electron-transport material TPBi [1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene], which has a higher LUMO (-2.7 eV) than CzDBA, following a concept similar to the interlayer strategy for hole injection. TPBi is capped with a 100 nm aluminium layer, which has an effective work function of 3.4 eV at organic/evaporated metal interfaces [18].

The concept of Ohmic contact formation with the help of a thin organic interlayer is based on Fermi level alignment of the electrode with the HOMO or LUMO of the active organic semiconductor. The interlayer acts as a spacer, eliminating the electrostatic interactions between electrode and organic semiconductor that result in barrier formation. The interlayer is virtually transparent for charges and thus does not result in any additional electrical resistance [16]. The interlayer can thus be regarded as part of the electrode, rather than as a charge-transport layer. As demonstrated previously for the formation of Ohmic hole contacts, we now show that a similar strategy can also be applied for electron injection.

Results and discussion

In order to find out if CzDBA exhibits good charge transport, as well as to investigate the electron injection from the TPBi/Al top electrode, we fabricated single-carrier devices. Electron-only devices consisted of an Al/CzDBA/TPBi(4 nm)/Al layout and hole-only devices were fabricated with a layer of CzDBA sandwiched between two Ohmic C_{60}(3 nm)/MoO_3 hole contacts. The current density-voltage characteristics are displayed in Fig. 2(a). The electron and hole currents are very similar, indicating

balanced bipolar charge transport in CzDBA. For both electron- and hole-only devices, it is observed that the current density has a close to quadratic dependence on voltage at voltages higher than approximately 1 V, characteristic of a trap-free space-charge-limited current. However, at lower voltages, the current depends slightly stronger on voltage. Such behaviour corresponds to trap filling [19]. After reaching the trap-filled limit, of which the voltage depends on the trap density [19], a transition to trap-free transport is observed.

To obtain quantitative charge-transport parameters, the electron and hole currents were fitted with numerical drift-diffusion simulations [20]. First, the mobility was determined at higher voltages in the trap-filled limit. The electron mobility amounted to 5×10^{-5} cm^2 V^{-1} s^{-1}, whereas the hole mobility had a slightly lower value of 3×10^{-5} cm^2 V^{-1} s^{-1}. Subsequently, the full *J-V* characteristics of the electron- and hole-only devices were fitted by including an electron-trap density of 1.4×10^{16} cm^{-3} and a hole-trap density of 1.7×10^{16} cm^{-3}, respectively. These are remarkably low numbers of trap states, which are frequently an order of magnitude higher in organic semiconductors [4]. The obtained mobility and trapping parameters were verified for different layer thicknesses, yielding excellent agreement between simulation and experiment (see Supplementary Information; SI). In the simulations, injection barriers were assumed to be absent. The fact that the same charge-transport parameters are obtained for different layer thicknesses shows that the newly-designed TPBi/Al electrode is indeed an Ohmic electron contact, notably without the use of reactive metals or n-type dopants. The obtained mobilities, although good, are not unusually high for organic semiconductors [21]. It is mainly the low trap densities for both electron and holes in combination with Ohmic contacts that result in high and balanced electron and hole currents.

The balanced electron and hole mobility should also result in a broad recombination zone. This is indeed observed in the recombination profile simulated for the CzDBA OLED, as shown in Fig. 2(b). The bimolecular recombination was assumed to follow the Langevin mechanism, as is typical for single-layer OLEDs [22]. Since the electron mobility is slightly higher than the hole mobility, the recombination maximum is situated closer to the anode. The recombination zone broadens with voltage, due to an increased overlap between the electron and hole density, with the maximum shifting in the anode

direction. A broad recombination zone is expected to be beneficial for the operational stability of OLEDs, reducing exciton-polaron interactions associated with degradation [23-26].

Having verified nearly balanced electron- and hole-transport, we have fabricated an OLED with the structure displayed in Fig. 1(a). The measured current density and luminance as a function of voltage are shown in Fig. 3(a), with the external quantum efficiency (EQE) displayed in Fig. 3(b). The EQE reaches 19%, which is a high value for a single-layer OLED, but not unusual for multilayer TADF OLEDs. We note that a similar EQE has been reached previously for a multilayer stack employing a neat emissive layer instead of a host-guest system [15]. However, the corresponding single-layer device in that study yielded an EQE of only ~0.1%. We anticipate that the much higher value in our case is a combination of more balanced transport in combination with improved charge injection. In the case of Ohmic injecting contacts, a large density of electrons and holes is situated at the cathode and anode, respectively, as shown in the SI, which prevents the charge carriers from reaching the opposite electrode. This effectively results in a built-in charge-blocking effect. Insertion of an additional electron- and exciton blocking layer (CBP) between the C_{60} interlayer and CzDBA indeed did not improve the EQE (see SI), confirming that blocking layers are not required when using Ohmic contacts. Furthermore, without special measures to enhance optical outcoupling, the outcoupling losses of OLEDs are estimated to be around 70-80% [27], meaning that our device has a high internal quantum efficiency. The light distribution pattern was measured to follow that of an ideal Lambertian source (see SI).

Remarkably, the single-layer CzDBA OLED reaches a luminance of 1000 cd/m^2 already at 2.41 V, and 10,000 cd/m^2 at 2.89 V. In addition, the turn-on voltage of 2.10 V, measured at 1 cd/m^2, is considerably lower than the optical gap of 2.48 eV reported for CzDBA [17] and lower than the photon energy of 2.21 eV at the emission maximum, which is possible due to recombination of diffused carriers injected below the built-in voltage [28,29]. These low operating voltages are even slightly superior to state-of-the-art phosphorescent OLED stacks [9,10,30,31]. In our case, the low driving voltages are obtained without dedicated hole- and electron transport layers and without electrical doping. Owing to the relatively high hole and electron mobility of CzDBA and in particular the low trap densities, charge

transport on the emitter itself is efficient. In combination with the used Ohmic contacts and the absence of further barriers induced by heterojunctions, this results in exceptionally low driving voltages. In particular at high luminance, the obtained operating voltages are markedly lower than previously reported for TADF multilayer OLEDs [32,33].

The low operating voltage also results in a high power efficiency of 82 lm/W at 1000 cd/m^2, with a maximum of 87 lm/W [Fig. 3(b)]. Power efficiencies in excess of 100 lm/W at 1000 cd/m^2 have been reported for multilayer TADF OLEDs, owing to a higher external quantum efficiency [17,32]. However, it is important to note that the operational stability of these highly-efficient TADF devices has not been reported, while extended lifetimes are usually obtained at the expense of device efficiency. As we will demonstrate below, our single-layer OLED combines a high power efficiency with a long lifetime.

As shown in Fig. 2(b), a fairly broad emission zone is expected, due to balanced bipolar transport and the absence of blocking layers. Previous research has shown that broadening of the emission zone results in increased operational stability [24,25], due to a decrease in exciton-polaron interactions [23-26]. We have performed lifetime measurements on our single-layer CzDBA OLEDs in nitrogen atmosphere at constant current density, with initial luminance of 1000 cd/m^2 and 5000 cd/m^2. As demonstrated in Fig. 4, lifetimes to 50% of the initial luminance (LT_{50}) of 1880 and 414 hours are obtained, respectively. Interestingly, these lifetimes are markedly longer than the lifetime reported for the same CzDBA emitter in a more complex multilayer configuration. For the multilayer structure used in the degradation test in Ref. 17, which has a similar power efficiency to our device at 1000 cd/m^2, the LT_{50} at 1000 cd/m^2 reached only 97 hours [17]. This demonstrates that a single-layer OLED configuration cannot only match the stability of a multilayer stack, but can even greatly extend the lifetime, retaining similar power efficiencies. The operational lifetimes at 5000 cd/m^2 are comparable to the values obtained for the stable green TADF emitter 4CzIPN (1,2,3,4-tetrakis(carbazol-9-yl)-5,6-dicyanobenzene) in multilayer structures with n-type hosts, with similar EQE, but with lower operating voltage in our case, resulting in an approximately doubled power efficiency at 1000 cd/m^2 [14]. It should be noted that there is a slight difference in the emitted wavelength. In addition, the driving voltages were observed to be very stable,

increasing only marginally to 2.56 V after 1350 hours of aging at 1000 cd/m^2 and to 2.80 V after reaching LT_{50} at 5000 cd/m^2 (Fig. 4), In addition, the electroluminescence spectrum was unaltered after stressing (SI). Besides the high operational stability, these single-layer architectures would greatly simplify a quantitative study to the cause of degradation in small-molecule OLEDs, which is a subject of further study.

These measurements show that single-layer OLEDs can be a viable or even superior alternative to multilayer stacks in terms of efficiency and operational stability. Another noteworthy feature of our OLED is the absence of reactive electron-injection layers or n-type doping. These layers are the most prominent cause of the rapid degradation of OLEDs in ambient atmosphere [34,35]. Therefore, we expect our OLED to be more stable in air. In Fig. 5, photographs are depicted of an unencapsulated device operating in ambient conditions after being stored in air for set periods of time. The photographs are captured with the OLED being biased at 2.15 V, corresponding to an initial luminance of around 4 cd/m^2. A low luminance was used to minimize flare in the photographs, aiding the visibility of black spots appearing. After storage in air for 4 hours, the emission remains practically uniform. After 24 hours of storage in air, black spots have appeared. These black spots are usually associated with oxidation or delamination of the cathode [34-36]. The black spots are still comparatively small, considering that complete device failure after a day of storage in air has been reported for some OLEDs [36,37]. After 5 days of storage in air, the black spots have grown in size, although 95% of the area still emits light. The ambient stability in air for various hours without encapsulation benefits the flexibility in the OLED production process. An alternative example of a single-layer device with air-stable electrodes is the light-emitting electrochemical cell, which, however, typically suffers from low operational stability and high operating voltages [38].

As a design rule for efficient OLEDs with low operating voltages, our study shows that it is more important to create Ohmic contacts and use materials with a low trap density, rather than focusing on the charge-carrier mobility. While a high mobility remains important to obtain high currents at low voltages, the current is far more sensitive to injection and trapping, the latter phenomenon receiving surprisingly

little attention in the design of charge-transport materials and OLED stacks. Here, we have demonstrated that it is even possible to combine excellent bipolar charge-transport properties and emitter characteristics in a single organic semiconductor, providing a concept for stable and efficient single-layer OLEDs. These emitter requirements, shown here for a yellow emitter, are identical for blue- or red-emitting devices, with high photoluminescence quantum yields having been reported for many TADF emitters in neat films [39]. Furthermore, the crucial formation of Ohmic contacts has been demonstrated for a wide energy range, even enabling near-ultraviolet emission with direct charge injection [16]. For the widely used green TADF emitter 4CzIPN, the presence of Ohmic contacts still ensures decent device performance in a single-layer architecture, in spite of strongly unbalanced electron- and hole transport (SI). The combination of transport and light emission in a single material and the use of Ohmic contacts obviates the need for developing host, transport, and blocking layers with matching energy levels and triplet energies, which is a large challenge especially in the design of stable blue OLEDs with low operating voltages.

Conclusion

In conclusion, we have demonstrated that efficient and stable OLEDs can be achieved in a structure with a single layer of a TADF emitter sandwiched between two Ohmic contacts. The TADF emitter showed excellent bipolar charge transport with low trap densities, which, in combination with truly Ohmic electron and hole contacts resulted in remarkably low operating voltages. The obtained driving voltages both at low and high luminance were lower than reported for phosphorescent and TADF OLEDs featuring dedicated electron and hole transport layers, or p-i-n doped structures, yielding high power efficiencies. As a result of a broadened recombination zone, the operational stability could be greatly improved in comparison with a conventional multilayer OLED structure. Furthermore, the newly-designed Ohmic electron contact does not feature air-sensitive interlayers or n-type doping, resulting in enhanced air stability of the TADF OLED.

Methods

Materials: CzDBA was purchased from Luminescence Technology Corp. in sublimed grade, C_{60} and TPBi were purchased from Sigma-Aldrich. All materials were used as received.

Device Fabrication: Hole-only devices were fabricated on glass substrates prepatterned with indium-tin oxide (ITO). Substrates were thoroughly cleaned by washing with detergent solution and ultrasonication in acetone and isopropyl alcohol, followed by UV-ozone treatment. A 40 nm layer of PEDOT:PSS [poly(3,4-ethylenedioxythiophene):polystyrene sulfonate; CLEVIOS™ P VP AI 4083] layer was applied by spin coating and annealed at 140 °C for 10 minutes in air. The substrates were then transferred into a nitrogen-filled glove box, and were not exposed to air in the subsequent steps. Next, a 6 nm layer of MoO_3, a 3 nm C_{60} interlayer, a CzDBA layer and again a 3 nm C_{60} interlayer were all thermally evaporated at a base pressure of 4-6 × 10^{-7} mbar. Subsequently, a MoO_3(10 nm)/Al(100 nm) top electrode was thermally evaporated to complete the device.

For electron-only devices, 35 nm of Al was thermally evaporated on cleaned glass substrates, followed by thermal evaporation of a layer of CzDBA and a 4 nm TPBi interlayer. The device was completed by evaporation of an Al(100 nm) top electrode.

For OLEDs, the device configuration is glass/ITO/PEDOT:PSS/MoO_3/C_{60}/CzDBA/TPBi/Al, where the individual layers were fabricated using the methods described above.

Measurements: Electrical characterization was carried out under N_2 atmosphere with a Keithley 2400 source meter and light output was recorded with a Si photodiode with NIST-traceable calibration, placed close to the OLED, following the procedure described by Forrest et al. [41]. The EQE and power efficiency were calculated accordingly. Electroluminescence spectra were obtained with a USB4000-UV-VIS-ES spectrometer. The angular dependence of electroluminescence was obtained with a home-built setup based on a goniometer and a Si photodiode.

Data availability

The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request

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Author contributions

G.A.H.W. proposed the project. G.A.H.W. and N.B.K. designed experiments. N.B.K. carried out device fabrication and measurements. G.A.H.W. performed simulations. G.A.H.W. and P.W.M.B. supervised the project and wrote the manuscript.

Competing interests statement

The authors declare no competing financial interests.

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Figures and captions

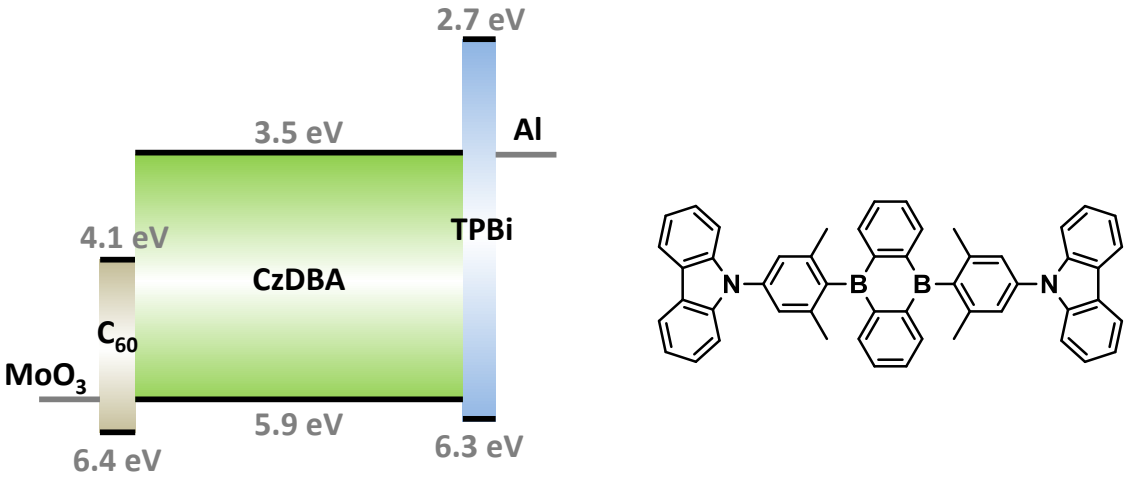

Fig. 1 | Device layout and molecular structure of the TADF emitter CzDBA. (left) Schematic energy band diagram of the single-layer OLED. A CzDBA layer is sandwiched between a MoO_3 bottom anode and an Al top cathode, using a thin C_{60} and TPBi interlayer for the formation of an Ohmic hole and electron contact, respectively. (right) Chemical structure of CzDBA.

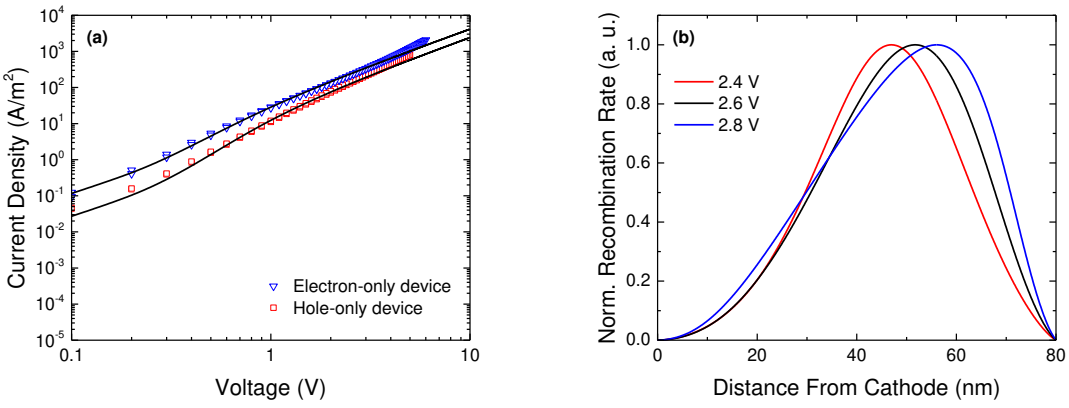

Fig. 2 | Charge transport in CzDBA and simulated recombination profile. (a) Current density-voltage characteristics of CzDBA electron- and hole-only devices (symbols) with a CzDBA layer thickness of 155 nm. Solid lines are fits with a numerical drift-diffusion model. (b) Normalized recombination profile simulated for an 80 nm CzDBA OLED at different driving voltages.

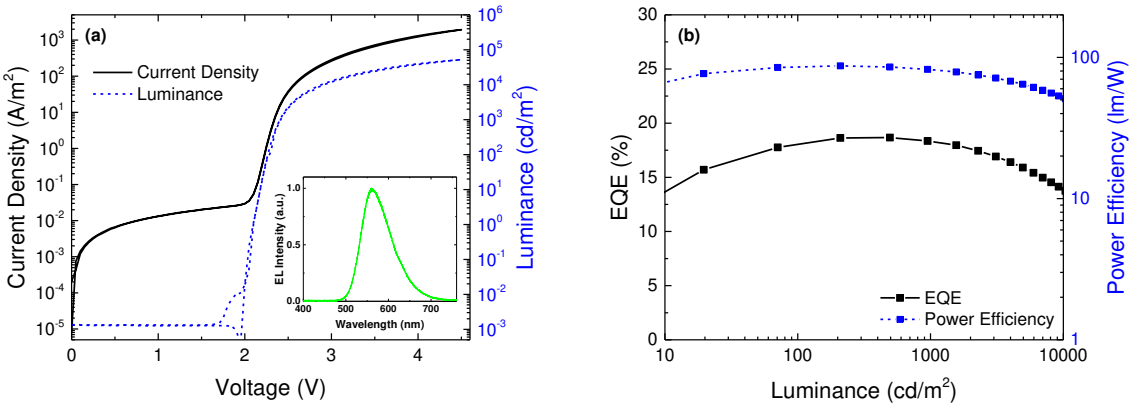

Fig. 3 | Device performance of single-layer CxDBA OLEDs. (a) Current density-voltage and luminance-voltage characteristics of a CzDBA single-layer OLED with a CzDBA thickness of 75 nm. The inset shows the electroluminescence (EL) spectrum, having its maximum at a wavelength of 560 nm. (b) Corresponding EQE and power efficiency as a function of luminance.

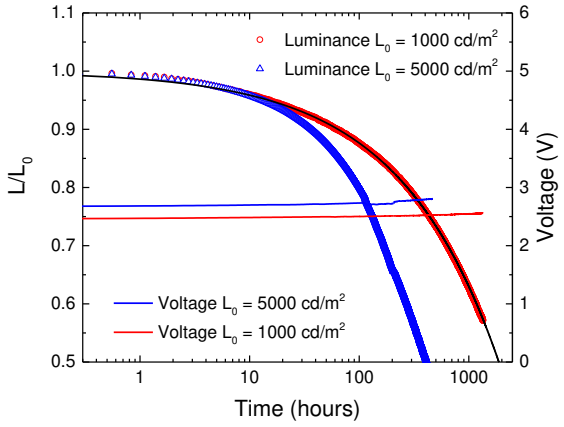

Fig. 4 | Operational lifetime of CzDBA OLEDs. Normalized luminance (symbols; left axis) and driving voltage (lines; right axis) as a function of operation time in nitrogen atmosphere, with an initial luminance of L_0 = 1000 cd/m^2 and L_0 = 5000 cd/m^2 at constant driving current. The luminance decay was fitted (black line) with a function $L/L_0 = 1\text{-}At^{(1/\alpha)}$ with $\alpha = 2.1$ [40] to extrapolate to LT_{50} for. L_0 = 1000 cd/m^2.

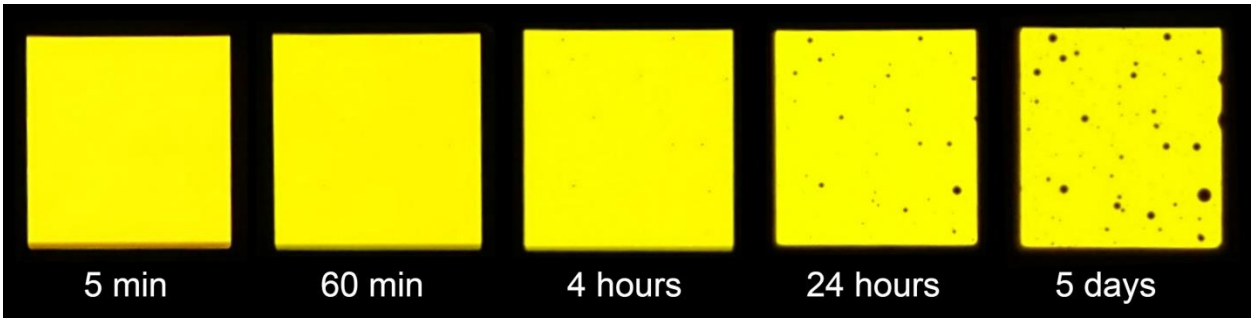

Fig. 5 | Ambient stability of a CzDBA OLED. (a) Photographs of an unencapsulated CzDBA OLED operating in ambient as a function of time stored in air. The OLED has an active area of 1 × 1 cm.