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ABSTRACT

Quantum dot light emitting diodes (QLEDs) emitting at 410 nm were studied by time-resolved electroluminescence measurements. A transient overshoot after voltage turn-off was seen, which is attributed to the accumulation and storage of charge carriers at the ligand-quantum dot interface. Shorter ligands showed a faster rise time and prevented the formation of an overshoot, whereas longer ligands caused the storage of charges, responded slower, and showed an overshoot. When the external voltage was switched off, the electric field between the injected and stored electrons and holes led to the occurrence of the overshoot. Applying a dual voltage pulse avoided this overshoot and instead a delayed luminescence was observed. As the accumulated charges were immobile and trapped in shallow states, a reverse pulse was applied to fully deplete the emissive layer. Because the transient overshoot disappeared after the device had been turned on, this can be used as a measure of the degradation of QLEDs. The ligands constitute a major obstacle for an efficient and long lasting blue/purple quantum dot emitter.

I. INTRODUCTION

Over the last few decades, tremendous improvements in lifetime and brightness have enabled the integration of red and green organic light emitting diodes (OLEDs) into smartphone displays and TV screens.[1–4] Despite extensive research, the lifetime of blue/purple organic emitters is still significantly reduced compared to their red and green counterparts, with the mechanism of their degradation pathways also remaining unclear. Furthermore, their emission is spectrally broad, typically reaching into the green and red.[2]

In a light emitting diode (LED), charge carriers need to be injected into the device and transported to the emissive layer before they can recombine radiatively or nonradiatively. On their way to recombination, charges can accumulate[5] and thereby reduce the efficiency of the diode. In OLEDs, high charge carrier densities in the emissive layer lead to field induced exciton quenching where the electric field dissociates electron-hole pairs[6–8] and to triplet-polaron annihilation.[9] Time-resolved electroluminescence measurements have proved to be an efficient diagnostic tool for describing both charge transport[10–12] and annihilation phenomena in organic LEDs.[13,14] A slower response time to a rectangular bias after current stress has been attributed to an increase in interface trap states, and this effect can be used as an indicator of degradation in OLEDs.[15] Under high current densities, the decrease in external quantum efficiency follows a singlet-singlet annihilation model, suggesting that possible heating effects in high current OLEDs are negligible.[16]

Weichsel *et al.*[7] have shown that the accumulation of charge carriers in the active layer of an OLED can be studied with time-resolved electroluminescence (EL) measurements following a rectangular bias. Transient overshoots after a bias turn-off have been widely reported in various OLEDs. Delayed fluorescence caused by triplet-triplet annihilation,[17–19] the release and recombination of trapped charge carriers,[20] and field induced exciton quenching,[21] as well as changes in the drift and diffusion currents,[22] can lead to a characteristic overshoot in the transient EL spectrum. Poor hole injection and the accumulation of electrons have been found to cause delayed luminescence.[23] Weichsel *et al.*[7] have localized the storage of charge carriers on the emitter molecules in OLEDs. Finally, Zhang *et al.*[24] reported the storage of charges in a thin PMMA passivation layer under the emitter layer and linked the storage to the electroluminescence, and suggested that an AC driven OLED could be used to improve stability issues.[8] In this report, we apply transient EL measurements for the first time to a quantum dot LED (QLED) to study the ligand-dependent accumulation of charge carriers. In a QLED, quantum dots (QDs) are typically

surrounded by organic, electrically insulating ligands that are likely to trap charges prior to recombination. By looking at a set of five different ligands of various lengths and electrical conductivity, we relate the transient overshoot after a rectangular voltage pulse to the accumulation of charges on the ligands. Driving a QLED with a double rectangular pulse removes the overshoot and instead leads to a delayed luminescence from the stored charge carriers. These stored and immobile charges are finally released from their trap states with a reversed pulse and lead to a delayed luminescence response. We further investigate the luminescence rise time as well, as the formation of a transient overshoot before and after turn on, to elucidate the degradation pathway in QLEDs. With the disappearance of the overshoot after the device operation, we present for the first time an indicator for the degradation of QLEDs. Our findings suggest that the ligands surrounding the nanoparticle are a major obstacle for the realization of a stable and efficient blue/purple quantum dot light emitting diode.

II. EXPERIMENTAL PROCEDURES

A. QD synthesis and device fabrication

The QDs were synthesized following a protocol developed by Bae *et al.*[25] whereby 0.5 mmol of cadmium oxide (CdO) (99.95%), 5 mmol of zinc acetate dihydrate [Zn(*acet*)$_2$] (>98%, reagent grade), 7 ml of 1-octadecene (ODE) (tech grade, 90%), and 3.5 ml of oleic acid (OA) (tech grade, 90%) were firstly placed in a 50 ml round bottom flask. The mixture was heated to 100 °C and degassed under vacuum for 1 h before it was heated to 310 °C under N_2 to form a transparent solution of the metal oleates, $Cd(OA)_2$ and $Zn(OA)_2$. At this temperature, 3 mmol of sulfur powder (99.98%) dissolved in 3 ml of 1-ODE, which was heated to 150 °C, was swiftly injected into the reaction flask to trigger the growth of $Cd_{1-x}Zn_xS$ cores. After 6 min, 4 mmol of sulfur powder dissolved in tributylphosphine (TBP) (97%) was introduced into the reactor to overcoat the existing $Cd_{1-x}Zn_xS$ cores with a ZnS shell. The reaction was stopped after 70 min and the flask cooled down to room temperature. The QDs were purified through 3 centrifuge steps: The crude solution was washed by adding acetone until the solution became turbid, usually by doubling the volume. The addition of small amounts of ethanol helped to quantitatively precipitate the particles. The precipitate was collected after centrifugation at 4000 rpm and redispersed in a minimal volume of toluene. The batch was then split into 5 parts and a ligand exchange was performed: For the insulating ligands [butylamine (99%), octylamine (99%), and oleylamine (70%, technical grade)], an excess of the appropriate amine was added to the QD solution, while for the electrically conducting ligands [aniline (>99.5%) and triphenylamine (98%)], a 1 wt. % to 10 wt. % was added based on the ligand to QD mass ratio as determined by UV-VIS absorption spectroscopy. All QDs were precipitated another 3 times to ensure that nonbinding ligands were washed away. UV-VIS absorption and fluorescence spectra of the ligand exchanged quantum dots are shown in Fig. S1 of the supplementary material.

The QLEDs in this study were prepared in a clean room environment and using a sandwich architecture based on a patterned 150 nm thick indium tin oxide (ITO) covered glass substrate. The substrates were cleaned in an ultrasonicator with ethanol and water. A 70 nm thick PEDOT:PSS (Al 4083) layer was deposited by spin coating. After annealing at 200 °C for 10 min, a 50 nm thick poly(9-vinylcarbazole) (PVK) film was cast from a 10 mg/ml chlorobenzene solution and annealed for 30 min at 180 °C. The samples were then transferred into a nitrogen filled glovebox. A 25 nm QD film was deposited from toluene by spin coating and dried at 120 °C for 20 min. A 25 nm thick layer of 3, 3′, 5, 5′-tetra[(m-pyridyl)-phen-3-yl]biphenyl (BP4mPy) was thermally deposited as the electron transport layer followed by a LiF/Al (1 nm/100 nm) electrode.

All chemicals were purchased from Sigma Aldrich and were used without further purification. Acetone and ethanol were purchased as analytical grade from Univar. Toluene and chlorobenzene were purchased from ChemSupply. TBP was purchased from Capot Chemical Co. Ltd. PEDOT:PSS was purchased from Heraus Clevios. PVK [>99% measured by high-performance liquid chromatography (HPLC)] and BP4mPy [>99% (HPLC)] were purchased from Luminescence Technology Corp.

UV-visible absorbance measurements were performed on an HP Agilent 8453 spectrophotometer. Fluorescence emission and excitation spectra were recorded on a Horiba Jobin Yvon Fluorolog-3 spectrometer.

B. Device testing

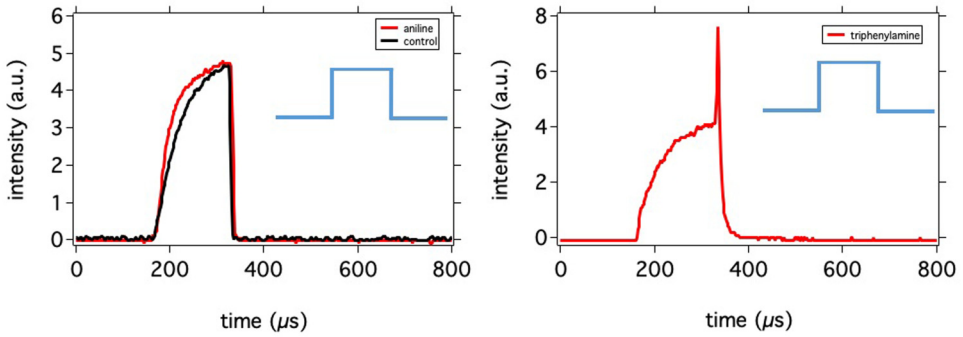
Luminescence and I–V characteristics were obtained with a luminescence color meter (Topcon MB-7A) and a Keithley 2400 source-measure unit. The pulse shapes were generated by a RIGOL DG4162 Function/Arbitrary Waveform Generator. The characteristics of transient EL were collected with a Hamamatsu Photonics H10721-110 photomultiplier tube and recorded with a RIGOL DG1202 CA digital oscilloscope. All measurements were carried out at room temperature under an ambient atmosphere.

III. RESULTS AND DISCUSSION

Time-resolved EL measurements reveal a ligand-dependent transient overshoot after the applied rectangular voltage pulse is turned off (Fig. 1). Figure 1(a) shows the transient EL measurements for aniline-capped QDs and for a control device. The control device has the same architecture as the other devices with the QDs being omitted. We expect electroluminescence from the control device due to recombination between the hole and electron transport layer (Fig. S5 in the supplementary material).

The transient EL rises once the voltage pulse is applied and stops when it is turned off. In Fig. 1(b), however, where the ligand has been changed to triphenylamine, the transient exhibits an overshoot; i.e., there is an electroluminescence spike immediately after the bias is turned off. Given the difference in the response behavior and the fact that the electroluminescence spectrum, Fig. S1 in the supplementary material, does not change during the pulsed operation, we can confirm that the QDs with their ligands surrounding them are the active component leading to the transient overshoot. We have, therefore, performed experiments to explain the mechanism leading to this overshoot and relate it to the degradation of QLEDs.

Table I summarizes the transient overshoot behavior with respect to the ligand-capping quantum dots. In total, 12 pixels for each of the 5 ligands were manufactured and tested. Interestingly, we can see the transient overshoot even below the actual turn-on



(a) Transient EL response of an aniline capped QLED and a control device.

(b) Transient EL response of a triphenylamine capped QLED.

FIG. 1. The effect of a QD capping ligand on the occurrence of a transient overshoot with (a) not showing an overshoot, whereas (b) does.

voltage of the device that is required for the emission of 1 cd/m^2 (Fig. S4 in the supplementary material). By measuring the smallest recombination, we conclude that charges accumulate and the trap states are filled before the device lights up completely.

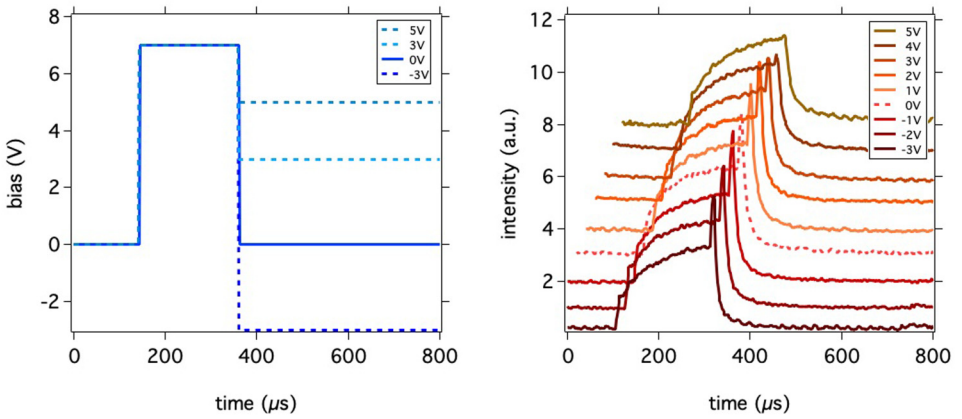
A. Influence of the off-bias

We have investigated the origin of the transient overshoot in the EL to prove that it is an electrical phenomenon, and due to an accumulation of charge carriers. The device is, therefore, subjected to a rectangular pulse that consists of three steps: first, a bias of 0 V is applied, followed by a pulse above the turn-on voltage V_{on}, typically 1 V above V_{on}, and a variable off-bias ranging from −3 V to +5 V [Fig. 2(a)]. Figure 2(b) summarizes the transient EL pulses based on a change in the off-bias. It becomes clear that the height of the overshoot decreases and the overshoot becomes wider when the off-bias is increased to a positive bias. A larger difference between driving and off-bias leads to a stronger electric field difference and a sharper, narrower transient response after the driving bias is turned off. When the off-bias is close to the main bias, typically 1 V below, the overshoot disappears completely. When the off-bias is decreased, the overshoot occurs earlier and exhibits a sharper profile. Following Weichsel *et al.*,[7] the transient overshoot in QLEDs is clearly an electrical, charge accumulating effect. Because the off-bias changes both the duration and the height of the overshoot, comparisons to a field induced quenching while the device is turned on are not meaningful.[7,21] After the bias is turned off, the accumulated charges can diffuse and drift to the QD core and recombine, resulting in the overshoot. Because the overshoot appears faster with decreasing off-bias and slower with increasing off-bias, we assume that there is an accumulation of charges at the QD-ligand interface.

TABLE I. Summary of the different ligand-capped QDs with regard to their transient overshoot behavior.

		Transient overshoot		
			Device after stress	
Amine	Voltage (V)	Fresh device	Stress below V_{on}	Stress above V_{on}
Butylamine (V_{on} = 3 V)	3–10	×	×	×
Octylamine (V_{on} = 3.5 V)	3.2–6.8	√	√	×
	7.0–10	×	×	×
Oleylamine (V_{on} = 5 V)	4.6–8.2	√	√	×
	8.4–10	×	×	×
Aniline (V_{on} = 4 V)	4–10	×	×	×
Triphenylamine (V_{on} = 5 V)	4.6–8.6	√	√	×
	8.8–10	×	×	×

The impact of the off-bias indicates that a transient overshoot can be avoided by applying a second positive pulse, slightly smaller than the first pulse but larger than the turn-on voltage of the device. This should be a logical approach as an applied electric field leads to the storage of charge carriers in an accumulation reservoir. Thus, we apply a set of two rectangular pulses above V_{on} as described before. Figure 3 shows the electrical pulse and the transient electroluminescence response of a triphenylamine capped QLED. The first pulse drives the devices regularly without showing a transient overshoot in the EL spectrum. After the bias drops to 0 V, a second, smaller bias pulse is applied and the EL decreases. At the end of the second pulse, an overshoot in the EL spectrum is seen. By applying a second pulse, an additional electric field prevents the accumulation of charges after the first pulse, and instead, the accumulation is shifted after the second pulse is turned off, charges diffuse and recombine under the formation of a spiky emission. The duration of the second bias (up to 500 ms) has no impact on the formation of the overshoot, indicating that charges are stored, rather than just accumulated. The delayed luminescence after the second voltage pulse further indicates that a difference between the two voltage pulses larger than 1 V is needed for the charges to diffuse and recombine. A large voltage difference between the first and the second pulse corresponds to a strong electric field change that finally pushes the stored charge to the QD core where they recombine. Equally, a downwards-stepping voltage pulse, with small electric field changes between each voltage step, removes the overshoot completely. Despite different device



(a) Change in pulse shape with variation in off voltage.

(b) Transient EL response due to different off voltages.

FIG. 2. An increased off voltage (a) reduces the transient overshoot and broadens its transient EL response in (b).

architectures and emissive materials, the QLEDs in this study and the OLEDs from Weichsel *et al.*[7] show strong similarities.

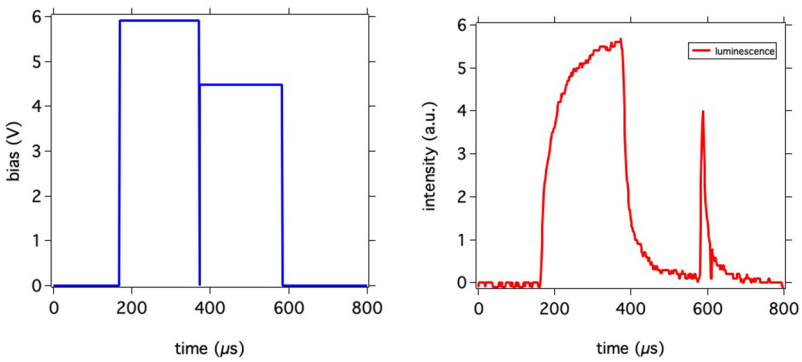
B. Charge trapping mechanism

In order to fully study the trapping of charges, we drive the device with a rectangular forward pulse followed by a rectangular reversed pulse (Fig. 4). We are thereby able to fill the trap states and consequently release the stored charges. During the first positive rectangular pulse, charges are injected from the electrodes into the active layer. The ligands surrounding the QDs limit the transport of charges, causing charges to accumulate and finally become trapped. Most of these charges may accumulate near the interface between the quantum dot and the ligand (region 1), with some located in shallow trap states on the ligand (region 2), while the few remaining charges are stored in deep trap states (region 3).

When the first pulse ends, the bias returns to 0 V and the electric field disappears. Charges close to the charge transport layers diffuse back to the electrode. Accumulated charges trapped in shallow states (located at the QD/ligand interface) are released and suddenly recombine, resulting in the spiky emission (region 2). Other than purely accumulated charges, trapped changes cannot be released in one step and instead their detrapping is facilitated by a reversed pulse.

Once the bias is reversed, the release of the trapped charges results in delayed luminescence (region 2). This luminescence depends on the applied bias before it is reversed: Fig. 5 shows that an increased off-bias leads to a decrease in the overshoot and instead the delayed luminescence is enhanced.

In a similar manner to the dual pulse operation, the application of a second pulse, smaller than the initial pulse, delays the accumulation of charges until the end of the second pulse. Interestingly, the amount of charge released from deep trap states when the reversed bias returns to 0 V does not change. We assume, therefore, that the amount of stored charges in deep trap states is independent of possible accumulated charge. When the negative bias returns to 0 V, a third delayed and much smaller luminescence signal from deeply trapped charges is seen (region 3). As the resulting luminescence is significantly smaller, independent of the ligand and the previous bias, we conclude that deeply trapped charges are less common than their accumulated counterparts.



(a) Electrical pulse shape

(b) Transient EL response.

FIG. 3. (a) The shape of a double rectangular pulse and (b) the resulting transient EL response. Note that the application of the double rectangular pulse avoids the storage of charges after the first pulse, instead leading to a delayed luminescence after the second pulse.

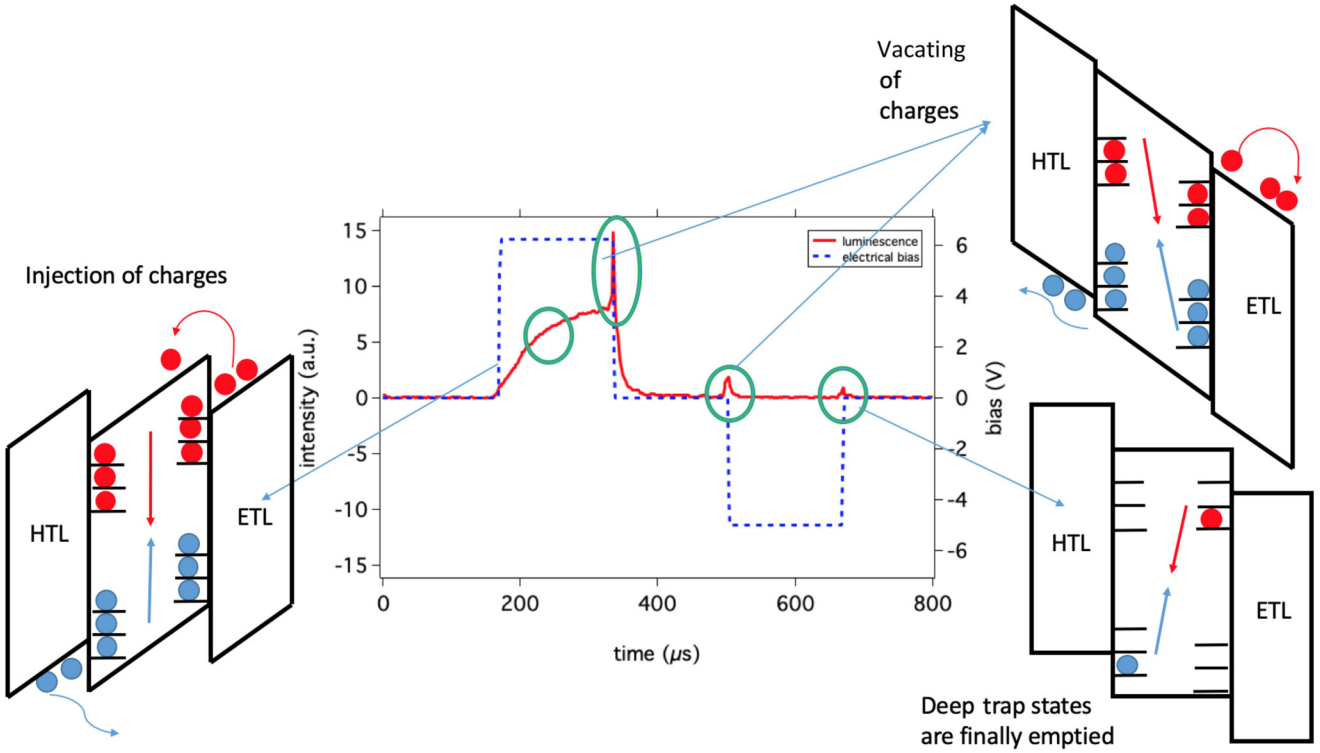
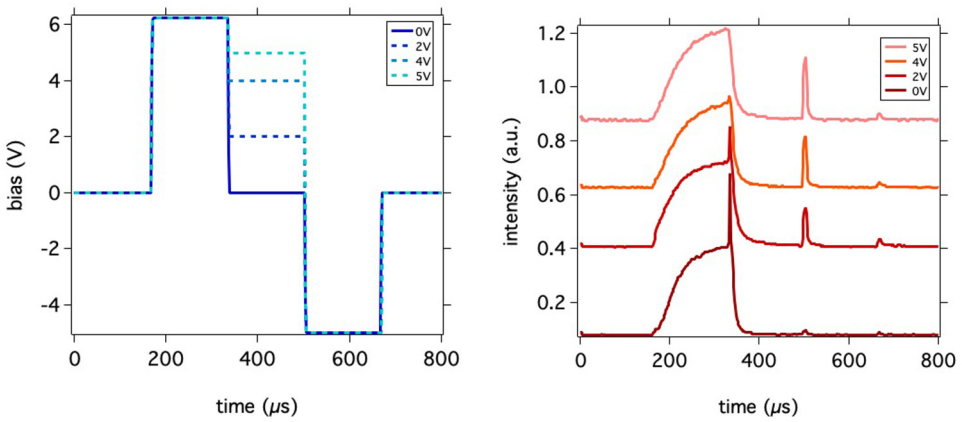


FIG. 4. A schematic diagram illustrates the stored charges resulting in a transient overshoot and a delayed luminescence: Regions 1, 2, and 3 represent the injection and accumulation of charge carriers on the ligands, their trapping in shallow states and finally in deep trap states, respectively.

The accumulation and trapping of charge carriers on the ligands surrounding the QDs may increase nonradiative recombination, quench excitons, and clearly limit the performance of the QLED in terms of efficiency and lifetime. We can, therefore, use the transient electroluminescence measurements to elucidate the degradation pathway of purple QLEDs.

IV. APPROACH TO THE DEGRADATION MECHANISM

In order to study degradation, we measure the 90% rise time of the ligand-dependent transient electroluminescence signal of a virgin device and compare it to a device that has been exposed to a bias 1 V below its turn-on voltage. In the second step, the devices are turned on at lowest brightness (usually 3 cd/m^2) corresponding



(a) Electrical pulse (b) Transient EL response

FIG. 5. Effect of the variation of the off-bias (a) on the release time of accumulated charge carriers. This variation has no impact on the EL response of stored charge carriers in deep trap states (b).

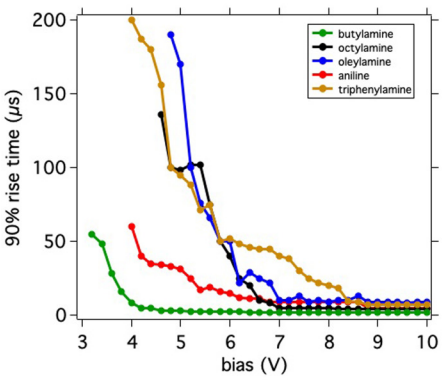
to a current of 100 μA. The initial current is maintained by increasing the applied bias. In both cases, the devices are exposed to bias for 1 h. We believe that a flow of current causes greater damage than a high voltage, which is why a rather small current is applied to drive the QLED.

Figure 6 shows the 90% rise time of the QLEDs capped with the five ligands of this study. For all ligands, the 90% rise time decreases with increased bias, indicating that with a higher bias, more charges are injected and recombine. The shorter ligands, butylamine and aniline, show a short rise time after turn-on, indicating that charges do not accumulate and instead recombine quickly. Together with the ligand length, the 90% rise time of the QLED increases before it decreases with increased bias. Compared to the short ligands, octylamine, oleylamine, and triphenylamine exhibit a rise time that is three to four times higher. A slower rise time is attributed to the increased ligand size and the reduced electrical conductivity in the case of octylamine and oleylamine. However, for a sufficient bias, all devices attain a 90% rise time within less than 10 μs.

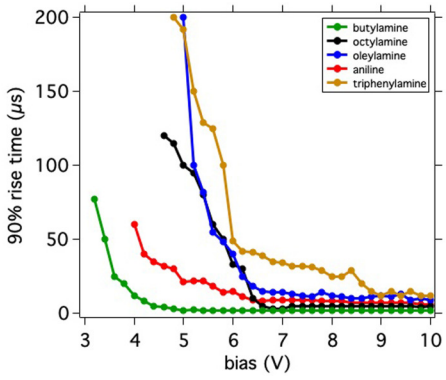
If the devices are exposed to a bias below their turn-on voltage for 1h and are turned on afterward to measure the transient EL, the 90% rise time does not change significantly [Fig. 6(b)]. The shortest ligand (butylamine) shows the quickest rise time, whereas the longer ligands are characterized by a slower rise time. With an almost identical rise time for the remaining four ligands, we assume that a bias below turn-on has no impact on the stability of the device and does not lead to degradation of the QLED.

Once the devices are turned on and driven for 1 h at low brightness, the transient rise time increases strongly [Fig. 6(c)]. Besides an increase in the turn-on voltage for all devices, the rise time increases significantly (Table II). Whereas the QLEDs with the short ligands initially have a quick rise time of less than 100 μs at turn-on, the rise time after the device has been operated for an hour doubles. The very short ligand length of butylamine does not sufficiently protect the QD and enhances the degradation of the QLED. The QLEDs with long ligands maintain their initial rise time; however, the applied bias required to turn on the device has increased by almost 3V, indicating that the device becomes more resistive. With increasing bias, the amount of injected charges increases and the rise time, therefore, decreases.

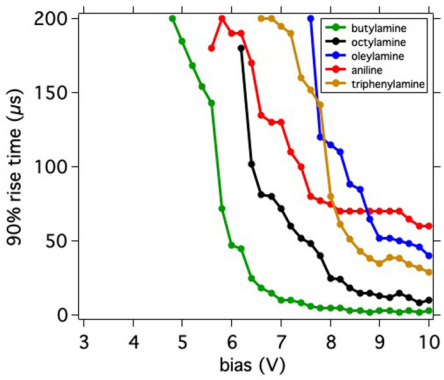
Table II summarizes the typical 50 μs as a 90% rise time for the QLEDs capped with different ligands. With a rise time of 50 μs,



(a) Transient EL rise time for a virgin device.



(b) Transient EL rise time for a device exposed to a bias below turn-on and then turned on afterwards.



(c) Transient EL rise time for a device operated at lowest brightness.

FIG. 6. 90% rise time of the transient EL for a virgin device (a), a device exposed to bias stress below (b), and above turn-on voltage (c).

TABLE II. Summary of the increased bias needed for a rise time of 50 μs.

	50 μs as 90% rise time		
Amine	Bias virgin device (V)	Bias below turn-on (V)	Bias above turn-on (V)
Butylamine	3.4	3.4	7.8
Octylamine	5.8	5.8	7.6
Oleylamine	5.8	5.8	9.4
Aniline	4.2	4.1	9.4
Triphenylamine	5.8	6	8.4

we assume that all trap states are filled and the device operates efficiently. It confirms that a bias below its turn-on voltage has hardly any impact on the bias for a typical rise time of 50 μs. Instead, after the device has been turned on, the bias needed for a 50 μs response increases strongly, typically between 2.5 and 5 V. Whereas the bias after turn-on increases for QDs capped with a long ligand (octylamine, oleylamine, and triphenylamine) by roughly half, it more than doubles for the QDs with a short ligand (butylamine and aniline). The presence of the longer ligands induces trap states that prevent the accumulation of charges in shallow trap states, which can easily be released with the return of the bias. As the shorter ligands show less accumulation in a virgin device, such devices require a much stronger increase in the bias after turn-on. We assume that deeper trap states cause a built-in potential and an increased resistivity and potentially enhance non-luminescent recombination pathways.

Interestingly, the formation of a transient overshoot for the longer ligands (octylamine, oleylamine, and triphenylamine) is not affected by a bias stress below turn-on; however, if the device is operated, the transient overshoot disappears completely. With its disappearance, we have found a method to qualitatively measure the degradation of QLEDs.

It appears that the ligands surrounding the QDs limit the efficient and long lasting operation of a purple/blue QLED. Short and conductive ligands show the best performance in terms of a quick rise time, improved device stability after turn-on, and an efficient injection of charges into the QD without storing them. This leads to no overshoot once the bias is turned off. Possibly, accelerated electrons cause damage when injected into the active layer.

Because three ligands exhibit a transient overshoot after the bias is turned off, we have identified the storage of charges on the ligands as the primary origin of device instability. Our findings suggest that the charges are not stored equally over the ligands but instead accumulate and are stored at the quantum dot-ligand interface. The height and the width of the transient overshoot are not ligand dependent but can be decreased by a second bias that enables the stored charges to be released in the form of delayed luminescence. In the case of a forward and reversed pulse shape (Fig. 5), the delayed luminescence from deep trap states, region 3 where a negative bias is increased to 0 V, does not change. This finding indicates that a bias above turn-on affects the accumulation and the shallow trap states and has little impact on the deep trap states. A longer and less conductive ligand requires an increased bias to drive the QLED and also results in a slower response time to a rectangular pulse. When charges accumulate, a higher bias is required to operate the device and nonluminescent recombination pathways become more likely, reducing the device efficiency.

We anticipate that further research on novel, more stable inorganic ligands with mediocre electrical conductivity or the advent of ligand-free device architectures could potentially reduce the accumulation of charges and thereby enhance both the stability and life time of purple QLEDs.

V. CONCLUSIONS

Purple quantum dot light emitting diodes with five different ligands of various lengths and electrical conductivity were studied for the first time with transient electroluminescence measurements. For QDs capped with short ligands (butylamine and aniline), a short response time to a rectangular pulse was measured. For their long counterparts (octylamine, oleylamine, and triphenylamine), an overshoot was detected when the bias was turned off. In addition, their response time to a rectangular pulse was increased, almost by a factor of 4. The transient overshoot can be avoided by applying a second, smaller pulse, which avoids the accumulation of charges and instead leads to a delayed luminescence. In order to fill trap states, a rectangular forward pulse is applied. In order to release the trapped charges, a reverse-bias rectangular pulse is applied. We find that the accumulated charges lead to a delayed luminescence, while deeply trapped charges generate a third, smaller luminescence signal when released from their trap states. Since overshoot and delayed luminescence behavior have no impact on the ligand length, we assume that charges are stored at the QD-ligand interface before they recombine when the bias is turned off.

Once the devices are turned on for an hour, the applied bias required to drive the device increases by 2–3 V, indicating that the active layer becomes more resistive. With an increased response time and the disappearance of the transient overshoot, we believe that the organic ligands surrounding the QDs are a major obstacle for the realization of a stable and efficient purple quantum dot LED.

SUPPLEMENTARY MATERIAL

See the supplementary material for spectroscopic characterization of the QDs after ligand exchange and voltage-current-luminescence as well as spectral emission data of the QLEDs.

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