

Investigating and Optimizing Charge Balance and Its Effect on Efficiency and Lifetime of QLEDs

by

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A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

Doctor of Philosophy

in

Electrical and Computer Engineering (Nanotechnology)

Waterloo, Ontario, Canada, 2024

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract:

Colloidal quantum dot light-emitting devices (QLEDs) have gained significant attention as next-generation display and solid-state lighting technologies, offering exceptional color purity, tunable emission wavelengths, high photoluminescence quantum yield (PLQY), and solution-processable fabrication techniques. The ability of quantum dots (QDs) to exhibit size-dependent optical properties through quantum confinement effects enables highly saturated red, green, and blue (RGB) emissions. Since their first demonstration in 1994, QLEDs have shown tremendous improvements in performance, achieving external quantum efficiencies (EQE) close to theoretical limits ($\sim 20\%$) and operational lifetimes ($T_{95}@100 \text{ cd/m}^2$) exceeding 300,000 hours.

Despite significant advancements, several unresolved challenges continue to limit the full commercial potential of QLEDs, particularly blue QLEDs (B-QLEDs), which exhibit notably lower electroluminescence (EL) stability compared to their red and green counterparts. A key factor impacting both device efficiency and lifetime is charge imbalance, which can lead to significant reduction in both performance metrics. This imbalance not only reduces the immediate efficiency of the device but also accelerates its long-term operational instability.

Additionally, while many developments have focused on red or single-color QLEDs, less attention has been given to conducting comparative studies that evaluate the performance differences among red, green, and blue QLEDs. This leaves gaps in understanding how charge dynamics and performance vary across these colors, particularly in B-QLEDs where the charge dynamics may differ due to changes in the QDs' bandgap. As a result, the exact mechanisms by which charge imbalance affects both efficiency and lifetime, especially in B-QLEDs, remain unclear. Therefore, further research is necessary to better understand these mechanisms and address the remaining challenges.

The primary goal of this thesis is to investigate and optimize charge balance in inverted QLEDs, with a focus on studying charge dynamics to better understand the electron and hole supply properties in red, green, and blue QDs. Additionally, this work explores the interactions between excitons and excess charges, examining how excess carriers, either electrons or holes, impact the EL performance of QLEDs. Based on the findings, new charge transport layers (CTLs) are explored to improve the device's charge balance. This research also investigates the EL loss mechanisms in upright B-QLEDs, which remain a major challenge for the commercialization of

QLED technology. Finally, new material systems are tested to enhance the EL stability of upright B-QLEDs.

To investigate whether commonly used HTLs in highly efficient upright structures can improve charge balance in inverted QLEDs, polymeric HTLs are employed in these devices. To address the challenge of HTL solvent erosion, a suitable recipe is developed for depositing polymeric HTLs on the QDs-EML. The fabricated inverted R-QLEDs exhibit relatively low efficiency, attributed to a poor interface between the QDs-EML and HTL, though not due to damage to the QDs-EML. However, the introduction of a wide bandgap interlayer between the QDs-EML and the HTL results in significant improvements in both efficiency and lifetime, primarily due to enhanced hole supply. Then, electron/hole supply properties of R, G, and B-QDs are investigated in single carrier devices. Results show that widening the bandgap of QDs increases hole supply efficiency but decreases electron efficiency.

To investigate their respective electron and hole supply efficiencies, a comparative study is conducted on inverted R, G, and B-QLEDs to explore charge injection characteristics. The findings reveal that in R-QLEDs, the e/h ratio in the QDs-EML is greater than 1, whereas in G- and B-QLEDs, the e/h ratio is less than 1, with charge balance conditions being significantly worse in the case of B-QLEDs. Additionally, photophysical measurements show that, compared to electrons, holes lead to a stronger Auger quenching effect, which is proposed as one possible reason for the poor efficiency and lifetime of B-QLEDs. Finally, by studying spontaneous electron transfer effect at the ETL/QDs-EML interface, it is observed that injecting electrons into the QDs-EML first, rather than holes, is more favorable for efficiency enhancement, suggesting that efficient electron supply is a prerequisite for achieving efficient QLEDs.

Based on the findings regarding the charge supply properties of each color, new CTLs are implemented to develop an inverted QLED structure with improved charge balance. The results from this structure show that employing a double ZnMgO ETL approach, where each ETL is annealed at different temperatures to enhance electron supply, along with an HTL featuring a relatively shallow lowest unoccupied molecular orbital (LUMO), leads to EQEs exceeding 23% for inverted R- and G-QLEDs. Additionally, doping the ZnMgO ETL with graphene QDs is proposed as another method to further enhance electron supply in inverted G-QLEDs, leading to improved device efficiency and extended lifetime due to enhanced charge balance.

Next, the EL loss mechanism in upright B-QLEDs is systematically studied using non-invasive marking layers at both HTL and ETL to detect charge leakage. The results indicate that electron injection is stronger than hole injection in upright B-QLEDs. Additionally, findings from EL and PL measurements confirm that, aside from some partially reversible deterioration in the PLQY of the QDs-EML, the rapid EL loss in upright B-QLEDs is primarily due to increased electron leakage across the HTL. This leakage causes damage to the hole injection layer (HIL) and diverts holes away from the QDs-EML, leading to a deterioration in hole supply to the QDs-EML.

Ultimately, the functional layers in upright B-QLEDs are modified to reduce electron supply and enhance hole supply. The results show that replacing the Al cathode with an Ag/Al electrode, featuring a deeper work function to limit electron injection, results in a 30X improvement in the device's EL stability. Additionally, introducing an insulating polymer layer between two ZnMgO layers to limit electron supply significantly extends the device lifetime by 12X. Furthermore, utilizing a new HTL to block electron leakage and improve hole supply leads to an 8X improvement in EL stability.

Acknowledgements

Completing my PhD has been a rewarding journey, filled with both exciting progress and difficult challenges. Although there were times when the obstacles felt overwhelming, looking back, these experiences helped me grow in patience and improve my research skills. I am especially thankful to my supervisor, Professor Hany Aziz, for his support, kindness, and knowledge. His guidance has inspired me to become both a better researcher and a better person, and for that, I am truly grateful.

I would like to acknowledge my advisory committee, Professor Dayan Ban, Professor Youngki Yoon and Professor Yuning Li for reviewing my work and their valuable comments and suggestions. I would also like to thank Professor Ayse Turak for accepting the role as my external PhD examiner.

I would like to thank Richard Barber and Czung-Ho Lee for their technical assistance and for making the Giga-to-Nano lab facilities a great working environment.

I would also like to thank my mom and my dad, Shokat and Ali, and my siblings, Goli, Golaftab, Leyla, Robabeh, Mahdi, and Majid; and all the rest of my extended family and friends for their love and support. I would not have been able to do it without you all.

I extend my heartfelt thanks to my parents-in-law, Ozra and Mehdi, for their kindness and support.

Lastly, I want to express my deepest gratitude to Shaghayegh, my best friend, soul mate, and loving wife. Her unwavering love and encouragement have been the driving force behind my achievements. I am forever grateful to her for being my constant support, my rock, and my inspiration. Thank you, Shaghayegh, for always being by my side.

Dedication

To my beloved parents, Shokat and Ali, whose unwavering support and love have been the foundation of all my achievements.

And to my dear wife, Shaghayegh, for her endless patience, encouragement, and belief in me throughout this journey.

Table of Contents

Examining Committee Membership	ii
Author's Declaration	iii
Abstract:.....	iv
Acknowledgements.....	vii
Dedication	viii
List of Figures	xii
List of Tables	xix
List of Abbreviations	xx
Chapter 1.....	1
1.1 Introduction	1
1.2 The rise of QLEDs in display technology.....	1
1.3 QDs Structure.....	3
1.4 Architectures and operational mechanism of QLEDs.....	6
1.5 Materials employed in cutting-edge devices.....	7
1.6 QLEDs Performance Metrics.....	8
1.6.1 Luminance.....	9
1.6.2 EL efficiency.....	9
1.6.3 EL stability.....	9
1.7 Current Challenges and motivation for this work.....	10
1.8 Thesis outline	11
Chapter 2. Literature review	13
2.1 Charge imbalance issue in QLEDs	14
2.1.1 Charge imbalance in QLEDs	14
2.1.2 Impact of charge imbalance on QLEDs.....	15
2.1.3 Approaches for enhancing charge balance in QLEDs	18
2.2 Root Causes of the Rapid EL Loss in B-QLEDs: Investigating the Role of Charge Balance	21
2.2.1 QDs PLQY Stability	22
2.2.2 HTL stability	22
2.2.3 ETL stability	24
2.3 Conclusion	24
Chapter 3. Research objectives and methodology	26

In this chapter, the research objectives are presented in Section 3.1, followed by the research rational described in Section 3.2. Finally, the research methodology and experimental details are explained in Section 3.3.....	26
3.1 Research objectives.....	26
3.1.1 Identifying the causes of the low efficiency in the inverted QLEDs with polymer HTL.	26
3.1.2 Investigating the degree of charge balance in inverted R, G and B-QLEDs and its influence on EL performance.	26
3.1.3 Exploring new ETL and HTL designs for optimizing charge injection and excitonic processes.	26
3.1.4 Investigating the degree of charge balance in upright B-QLEDs and its influence on EL performance	26
3.1.5 Exploring new ETL and HTL designs for optimizing charge injection and EL performance in upright B-QLEDs.....	27
3.2 Research Rational	27
3.2.1 Why Inverted QLEDs?.....	27
3.2.2 Why investigating the charge balance condition in inverted QLEDs?	27
3.2.3 Why investigating the charge balance and EL loss mechanism in upright B-QLEDs?	28
3.3 Research methodology and experimental details.....	29
3.3.1 Device layout.....	29
3.3.2 Device fabrication and material selection	30
3.3.3 Experimental measurements	32
Chapter 4. Identifying the causes of the low efficiency in the inverted QLEDs with polymer HTL	36
4.1 Finding an HTL solvent that minimizes damage to the QDs-EML in inverted QLEDs.....	37
4.2 Developing an architecture and fabrication recipe for inverted QLEDs that allows polymeric HTLs.	40
4.3 Investigating correlation between the QDs-EML bandgap and charge carrier (electron and hole) supply efficiencies.	45
Chapter 5. Investigating the degree of charge balance in inverted R, G and B-QLEDs and its influence on the EL performance.....	55
5.1 Differences in Electron and Hole Injection and Auger Recombination between Red, Green and Blue CdSe-based Quantum Dot Light Emitting Devices	55
5.1.1 Identifying the sequence of charge supply and the influence of excess carriers on the efficiency and lifetime of R, G, and B-IQLEDs by applying different conditions of electron and hole supplies.	56
5-1-2 Investigating the interaction of excess carriers with excitons in R, G, and B-IQLEDs by spectroscopic characterization	67
5.1.3 Conclusion	75

5-2 Differences in Spontaneous Electron Transfer in Red, Green and Blue Quantum Dots Light Emitting Devices and Its Benefits for Electroluminescence Efficiency	76
5-2-1 Comparing the EL performance of R, G, and B-QLEDs	78
5-2-2 Comparing the spontaneous electron transfer in R, G, and B-QLEDs.....	81
5.2.3 Simulation of spontaneous electron transfer effect.....	88
5.2.4 Conclusion.....	91
Chapter 6. Exploring new ETL and HTL designs for optimizing charge injection and improving EL performance in inverted QLEDs	92
6.1 Double Electron Transport Layer Approach for Efficiencies >23% in Quantum Dots Light Emitting Devices.....	92
6.1.1 Positive aging observation	93
6.1.2 Electron supply enhancement by Double ETL approach.....	99
6.1.3 Conclusion	102
6.2 Doping Graphene Quantum Dots in ETL to Improve Electron Supply in Inverted G-QLEDs.....	103
6.2.1 Double ETL QLEDs with Graphene QDs dopped ETL.....	103
6.2.2 Conclusion	105
Chapter 7. Investigating the degree of charge balance in upright B-QLEDs and its influence on the EL performance	107
7-1 Deciphering the Causes of the Rapid Electroluminescence Loss in Blue Quantum Dot Light-Emitting Devices.....	107
7.1.1 Observation of electron leakage.....	108
7.1.2 B-QLEDs stability test	113
7.1.3 Lifetime enhancement by electron supply reduction.....	119
7.1.4 Impact of electron leakage on HIL	121
7.1.5 Conclusion.....	124
7.2 Exploring new ETL and HTL designs for optimizing charge injection and EL performance in upright B-QLEDs.....	124
7.2.1 Modifying ETL in upright B-QLEDs	124
7.2.2 Modifying HTL in upright B-QLEDs.....	126
7-2-3 Conclusion	127
Chapter 8 Summary and Future Work.....	128
8.1 Summary of main conclusions	128
8.2 Future Work	129
References	132

List of Figures

Figure 1.1. Structure of QDs comprising a core, shell, and ligands. ¹	3
Figure 1.2. (a) Emission spectra of red/green/blue QD-LEDs compared with OLEDs. Reproduced with permission from ref. ² , and (b) color gamut comparison of four representative display techniques. ⁴	4
Figure 1.3 a. The variation of EL emission color with the size of CdSe QDs. ³ b.The variation of EL/PL emission color with changing the composition of QDs. ⁵	5
Figure 1.4 General utilization of the CTLs in QLEDs: (a) all-organic (Type I), (b) all-inorganic (Type II), and (c) hybrid (Type II). (d) Upright and (e) inverted architecture of the QLEDs.....	6
Figure 1.5 General device structure of inverted QLEDs.....	7
Figure 1.6 Energy levels of materials commonly used in the fabrication of QLEDs. ⁵	8
Figure 3.1 Schematic of the QLED substrate layout used in this study.	29
Figure 3.2 (a) PL, (b) absorbance spectra, and (c) core and shell size of R-QDs, G-QDs, and B-QDs.	30
Figure 4.1. Normalized PL spectra from Glass/R-QDs (12mg/mL) and Glass/R-QDs (12 mg/mL)/B-QDs (4 mg/mL) samples, initially and after rinsing with (a) Chlorobenzene, (b) 1,2-Dichlorobenzene, and (c) 1,4-Dioxane. The insets show the blue regions of the same spectra in logarithmic scale.	38
Figure 4.2. (a) J-V, (b) L-V and (c) EQE-J characteristics of devices A, B, C and D with structures as described in the text.	39
Figure 4.3. (a) Schematic diagram of the general device structure. (b) EQE versus B-QDs IL concentration of the inverted R-QLEDs, (c) J-V-L and (d) EQE-J characteristics of the inverted R-QLED without (W/O) an IL and with (W) G-QDs-IL or B-QDs-IL. Characteristics from an inverted R-QLED in which the QD-EML is rinsed with octane are also provided for comparison. (e) Normalized EL spectra of the same inverted R-QLEDs without (W/O) an IL and with (W) B-QDs-IL.	41
Figure 4.4: (a) J-V, (b) L-V, (c) EQE-J characteristics, and (d) normalized EL spectra of inverted R-QLED containing B-QDs-ILs made of solution of different concentrations (with different thicknesses). The 0 mg/mL curve represents a device without IL.	42
Table 4.2. Driving voltage, luminance, CIE values, and EQE at 20mA/cm ² of the devices without interlayer, rinsed with octane, and with G-QDs-IL, and B-QDs-IL.	43
Figure 4.5. (a) J-V-L, (b) EQE-J, and (c) normalized EL spectra characteristics of the inverted G-QLEDs without (W/O) and with (W) B-QDs-IL.	44
Figure 4.6 PL intensity of samples with the structure of Glass/R-QDs (A), Glass/R-QDs (A)/B-QDs(D), Glass/G-QDs (A), and Glass/G-QDs (A)/B-QDs(D). A and D show donor and acceptor. The thicknesses of acceptors and donor are about 32nm and 15nm, respectively.....	44

Figure 4.7. Schematic diagrams of the HODs with R-QDs, G-QDs, or B-QDs layers under (a) forward bias (FWB) and (b) reverse bias (RVB), HODs containing G-QDs-IL or B-QDs-IL on the R-QDs layer under (c) FWB and (d) RVB, HODs with R-QDs layer on G-QDs-IL and B-QDs-IL under (e) FWB and (f) RVB, HODs containing B-QDs-IL on the G-QDs layer under (g) FWB and (h) RVB, and HODs with G-QDs layer on B-QDs-IL under (i) FWB and (j) RVB..... 45

Figure 4.8. J-V characteristics of (a) HODs with R-QDs, G-QDs, or B-QDs layers (b) HODs containing G-QDs-IL or B-QDs-IL on either side of the R-QDs layer, (c) HODs containing B-QDs-IL on either side of the G-QDs layer, (d) EODs with R-QDs, G-QDs, or B-QDs layers, (e) EODs containing G-QDs-IL or B-QDs-IL on either side of the R-QDs layer, (f) EODs containing B-QDs-IL on either side of the G-QDs layer. 46

Figure 4.9. Schematic diagrams of the EODs with R-QDs, G-QDs, or B-QDs layers under (a) forward bias (FWB) and (b) reverse bias (RVB), EODs containing G-QDs-IL or B-QDs-IL on the R-QDs layer under (c) FWB and (d) RVB, and EODs containing B-QDs-IL on the G-QDs layer under (e) FWB and (f) RVB..... 48

Figure 4.10. (a) UPS spectra, (b) valance band level calculated from the secondary electron cutoff and Fermi-edge regions from UPS measurements, and (c) Tauc plots of R-QDs, G-QDs and B-QDs. 49

Figure 4.11. TRPL characteristics of samples with the structure of (a) Glass/R-QDs, Glass/R-QDs/TFB, and Glass/R-QDs/B-QDs-IL/TFB (collected at 633 nm), (b) Glass/R-QDs, Glass/TFB/R-QDs, and Glass/R-QDs/TFB (collected at 633 nm), (c) Glass/B-QDs and Glass/R-QDs/B-QDs (collected at 463 nm)..... 50

Table 4.3. τ and A components extracted from the tri-exponential decay curves for all the TRPL characteristics presented in Figure 4.11. 51

Figure 4.12. Cross-sectional TEM images of the (a) Glass/TFB/QDs and (b) Glass/QDs/TFB samples under different magnifications. 52

Figure 4.13. (a) Normalized luminance vs time and (b) Driving voltage vs time under 20 mA/cm² constant current driving of the R-IQLEDs without (W/O) and with (W) B-QDs-IL. The labels show the initial luminances in each case. 53

Figure 4.14. Schematic diagrams illustrating the differences in charge injection, electron leakage, radiative exciton recombination, and non-radiative exciton recombination (i.e. exciton quenching) between the devices without (a) and with (b) B-QDs-IL. 1 and 2 denote hole and electron injection from TFB and ZnO NPs, respectively; 3 denotes electron leakage to TFB; 4 and 5 denote radiative and non-radiative exciton recombination processes, respectively; and 6 represents surface defect trap states which can act as quenchers. The width of the arrow lines represents the relative magnitude of these processes in the two devices..... 54

Figure 5.1. (a) Schematic diagram and (b) J-V characteristics of EODs with R-QDs, G-QDs and B-QDs layers in which the ETL (ZnMgO) is annealed at 100°C (-↓) or 350°C (-↑). (c) Schematic diagram and (d) J-V characteristics of HODs with R-QDs, G-QDs and B-QDs layers in which the TCTA (+↓) or CBP (-↑) are used as the HTL. 57

Figure 5-2. (a) Schematic diagram of the device structure. J-V-L characteristics of the (b) R-QLEDs, (c) G-QLEDs, and (d) B-QLEDs under all charge injection scenarios. (e) EQE-J of the R-QLEDs (top), G-QLEDs (middle), and B-QLEDs (bottom) under all charge injection scenarios. (f) A comparison of EQE and lifetime (LT50 @ 100cd/m ²) of the R-QLEDs (top), G-QLEDs (middle), and B-QLEDs (bottom) under all charge injection scenarios.	59
Figure 5.3. Proposed schematic diagram illustrating the charge supply into R-QLEDs (left side), G-QLEDs (middle), and B-QLEDs (right side) in (a) the (+↑)(-↓) scenario and (b) the (+↓)(-↑) scenario. The numbers represent the valence band energy of the QD shells obtained from ultraviolet photoelectron spectroscopy measurements.	61
Figure 5-4. Simulation and experimental J-V characteristics of (a) R-QLEDs, (b) G-QLEDs, and (c) B-QLEDs. Electron (e) and hole (h) concentration in R-QLEDs (d and g), G-QLEDs (e and h), and B-QLEDs (f and i) simulated by SCAPS software under (+↓)(-↑) and (+↑)(-↓) charge supply scenarios, respectively. The number beside each trace represents the average carrier concentration (e or h) across the QDs-QML.....	63
Figure 5-5. Relative luminance vs time under 20 mA/cm ² constant current driving of (a) R-QLEDs, (b) G-QLEDs, and (c) B-QLEDs under different charge injection scenarios.	64
Figure 5-6. Normalized EL spectra of the (a) R-QLEDs, (b) G-QLEDs, and (c) B-QLEDs under all charge injection scenarios.	65
Table 5-2. Luminescence, V _{Th} , V _{On} , ΔV, EQE, LT50 @20mA/cm ² , and LT50 @100cd/m ² R, G and B-QLEDs under different charge injection scenarios as well as the standard deviation in the data obtained from 6 samples in each group.....	66
Figure 5-7. TrPL characteristics of R, G, and B-QLEDs with the charge supply scenarios (+↑)(-↓) depicted in (a-c) and (+↓)(-↑) depicted in (d-f), measured at different voltages from 0V to V _{On}	67
Figure 5-8. Steady state PL spectra of R, G, and B-QLEDs with the charge supply scenarios (+↑)(-↓) depicted in (a-c) and (+↓)(-↑) depicted in (d-f), measured at different voltages from 0V to V _{On}	68
Figure 5-9. Normalized TrPL overall lifetime (τ) (top) and normalized PL intensity (bottom) versus voltage of (a) R-QLEDs, (b) G-QLEDs, and (c) B-QLEDs measured from 0 V to V _{On} for (+↑)(-↓) and (+↓)(-↑) scenarios. Normalized TrPL overall lifetime (τ) versus current density of R-, G-, and B-QLEDs measured from 0 V to V _{On} for (d) the (+↓)(-↑) scenario and (e) the (+↑)(-↓) scenario. S represents the slope of the linear fit in each case.	69
Figure 5-10. PL peak position of (a) R-QLEDs, (b) G-QLEDs, and (c) B-QLEDs under charge supply scenarios of (+↑)(-↓) and (+↓)(-↑).	70
Table 5-4. Photophysical Properties of QLEDs Explored in This Work and What Is Already in the Literature.	73
Figure 5-12. Rise time (top) and EL at 40 μs (bottom) versus voltage of (a) R-QLEDs, (b) G-QLEDs, and (c) B-QLEDs measured above V _{On} for (+↑)(-↓) and (+↓)(-↑) scenarios.	74

Figure 5-11. TrEL measurements of R-QLEDs, G-QLEDs, and B-QLEDs for (+↑)(-↓) scenario in (a), (b), and (c) and for (+↓)(-↑) scenario in (d), (e), and (f), respectively.	74
Figure 5-14. Schematic energy level diagram of (a) QLEDs, (b) EODs, and (c) HODs.	79
Figure 5-13. (a) J-V-L, and (b) EQE-J of R, G, and B-QLEDs. J-V characteristics of (c) EODs and (d) HODs with R-QDs, G-QDs, or B-QDs layers.	79
Table 5-5. The voltages, luminance, and CIE, for R, G, and B-QLEDs measured at 20mA/cm ² as well as their maximum EQE.	80
Figure 5-15. TrPL characteristics of (a) R-QLEDs (collected at 628 nm), (b) G -QLEDs (collected at 526nm), and (c) B-QLEDs (collected at 462nm). (d) Average TrPL lifetime (τ_{ave}) versus voltage for all three colors. Steady state PL intensity of (e) R-QLEDs, (f) G-QLEDs, and (g) B-QLEDs. (h) Normalized PL intensity versus voltage for all three colors.	82
Figure 5-16. The TrPL characteristics of the G-QLEDs measured under 0V to -10V.	84
Figure 5-17. UV-Vis absorption of ZnMgO annealed at 100°C, 160°C, 270°C or 350°C. The Tauc plots of ZnMgO annealed at (b) 100°C, (c) 160°C, (d) 270°C and (e) 350°C.	86
Figure 5-18. The TrPL of (a-d) R-QLEDs (collected at 628nm), (e-h) G-QLEDs (collected at 526nm), and (i-l) B-QLEDs (collected at 462nm) in which the ZnMgO ETL is annealed at 100C°, 160C°, 270C°, and 350C° and biased under 0V or -5V. The TrPL overall lifetimes (τ) are provided in each graph.	87
Figure 5-20. Comparing the TrPL characteristics of (a) R-QLEDs, (b) G-QLEDs, and (b) B-QLEDs with TCTA and CBP HTLs biased under 0V or -5V.	88
Figure 5-19. Normalized TrPL overall lifetime (τ/τ_0) versus ETL annealing temperature of (a) R-QLEDs (collected at 628 nm), (b) G-QLEDs (collected at 526 nm), and (c) B-QLEDs (collected at 462 nm) under 0 or -5 V. τ_0 is the TrPL overall lifetime (τ) at 100 °C.	88
Figure 5-21. Electron concentration in the QDs-EML and ZnMgO ETL of (a) R-QLEDs, (b) G-QLEDs, and (c) B-QLEDs under 0 V (top) and -5 V (bottom). The electric field distribution in the QDs-EML and ZnMgO ETL of (d) R-QLEDs, (e) G-QLEDs, and (f) B-QLEDs under 0 V (top) and -5 V (bottom). The electron concentration in the ETL is changed from 10 ¹⁷ (1/cm ³) to 10 ¹⁸ (1/cm ³) associated with changing its annealing temperature from 100 to 350 °C, respectively.	89
Figure 6-1. a. Schematic diagram of the G-IQLEDs. b. J-V-L and c. EQE-J characteristics, and d EL spectra of the G-IQLEDs after fabrication (0h) and after positive aging (24h). d. EL spectra of the G-IQLEDs after fabrication and after positive aging. e. Changes in driving voltage and EQE for 300h. f. Normalized luminance (top) and driving voltage vs time under 20 mA/cm ² constant current driving of the G-IQLEDs.	94
Figure 6-2. Comparison of a. J-V, b. L-V, and c. EQE of G-IQLEDs with CBP or TCTA HTL.	94
Figure 6-4. a. J-V, b. L-V, and c. EQE of G-IQLEDs with TCTA HTL before and after rebuilding.	96

Figure 6-3 a Schematics of the G-IQLEDs rebuilding process. b The average EQE of rebuilt G-IQLEDs with TCTA HTL measured for the initial device at 0h and 24h, and for the rebuilt device at 0h and 24h. The energy band diagram of G-IQLEDs with c CBP and d TCTA HTL, respectively, showing the configurations before and after positive aging.	96
Figure 6-5. J-V, L-V, and EQE-J of G-IQLEDs in which ETL is annealed at (a-c) 100°C, (d-f) 150°C, (g-i) 220°C, (j-l) 350°C measured for 150h.	98
Figure 6-6. Changes in a current density at 14V, b driving voltage at 20 mA/cm ² , and c EQE at 20 mA/cm ² of the devices over time, where the ETL is annealed at different temperatures: 100°C (control), 150°C, 220°C, and 350°C. d. AFM images of ETL annealed at different temperatures: 100°C (control), 150°C, 220°C, and 350°C.....	99
Figure 6-7. a. AFM image of the double layers of ZnMgO. b. Schematic diagrams of the QLEDs with double ETL structure. JVL and EQE of G-IQLEDs (c and d), R-IQLEDs (e and f), and B-IQLEDs (g and h) with a double ETL structure. The counter plots of EQE under the variation of ETL thicknesses for i R, j G, and k B-IQLEDs with double ETL structure. l. EL spectra of R, G, and B-IQLEDs with double ETL.	100
Figure 6-8. Changes in EQE of the G-IQLEDs with a double ETL structure for 5 days.	101
Figure 6-9. The lifetime of R, G, and B-IQLEDs with double ETL measured under a constant current density of 20 mA/cm ²	102
Figure 6-10. a. Absorption and PL spectra of Graphene QDs. b. Schematic of EODs with a double ETL structure. c. J-V characteristics of EODs with a single ETL annealed at 100°C or 350°C, compared to a double ETL structure where the first ETL is doped with Graphene QDs.	103
Figure 6-11. a. Schematic illustration of the inverted G-QLEDs with double ETL structure in which the first ETL is doped by Graphene. b. J-V-L characteristics, c. EQE, d. EL spectra, and e. lifetime of the graphene-doped ZnMgO device with CBP HTL.....	104
Figure 6-12. a. J-V-L characteristics, b. EQE, c. EL spectra, and d. lifetime of the graphene-doped ZnMgO device with TCTA HTL.....	105
Figure 7-1. a Schematic diagram of the B-QLEDs structure. b J-V-L and c EQE-J characteristics of the B-QLEDs measured before electrical aging (labelled unaged) and after electrical aging (labelled aged) measured after working under a constant current density of 20 mA/cm ² for 60 min. e Normalized EL spectrum (on a logarithmic scale) of the B-QLED measured under a constant current density of 20 mA/cm ²	108
Figure 7-2. PL and EL characterization of B-QLEDs. a Comparison of EL spectrum of the B-QLEDs and PL spectra collected from samples made of various combinations of layers made of the same materials used in the device. All the films are deposited on glass substrates. b The EL spectra of the B-QLEDs measured at different voltages ranging from 2.04 to 2.18V, just below and above V _{ON} . c Schematic diagram of the experimental setup used to measure the EL intensity of the device under square voltage signals with different pulse widths of 425 ns to 450 ns, at a frequency of 2 MHz, and a constant amplitude of 3 V. d EL spectra as a function of pulse width	

signals with a constant amplitude of 3V. e The EL spectra of the B-QLEDs with MLs under voltages below and above V_{ON} (1.9 to 2.3V). f The EL spectra of the B-QLEDs with MLs under voltages of 2.4 to 3V. 109

Figure 7-3. a Schematic diagram of the B-QLEDs with MLs structure. b J-V-L and c EQE characteristics of the B-QLEDs with MLs. d PL spectrum collected from control device and B-QLEDs with MLs and the subtraction of the PL spectrum of the device with MLs from the PL spectra of control. e EL spectrum of control and B-QLED with MLs measured under a constant current density of 20 mA/cm². 113

Figure 7.4. EL and PL characterization of B-QLEDs after aging. a Normalized EL spectra of the B-QLEDs measured for 60 min under a constant current density of 20 mA/cm². b Normalized PL spectra of the B-QLEDs measured before (0 min) and after (60 min) aging. c TrPL characteristics of the QDs-EML before and after aging collected at 468nm. d TrPL characteristics of the TFB HTL before and after aging collected at 435nm. e The peak intensities of the EL, TFB PL, and B-QDs PL, normalized to their initial (pre-aging) values, collected from the device during aging and over the 3 hours after the bias is removed. f EL spectra of an aged B-QLEDs measured under low driving voltages of 2 to 2.4V. g Normalized EL spectra of the B-QLED with R-QDs ML at HTL side and G-QDs ML at ETL side under a constant current of 20 mA/cm² for 60 min. h EL spectra of the B-QLED with R-QDs ML at HTL side and G-QDs ML at ETL side measured under driving voltages of 1.9 to 2.3V. i EL spectra of the B-QLED with R-QDs ML at HTL side and G-QDs ML at ETL side measured under driving voltages of 2.4 to 3V..... 114

Figure 7-5. Deconvolution of the PL spectra of the B-QLED measured before (0 min) and after (60 min) aging. 115

Figure 7-6. a PL spectra of the B-QLED measured under bias (0 to 60 min) and resting time (62 to 240 min). b Voltage versus time of the B-QLED measured under a constant current density of 20 mA/cm². c current density versus time of the B-QLED. 116

Figure 7-7. a Schematic diagram of the structure of B-QLEDs with (W) ML placed at the HTL side. b Schematic diagram of the structure of B-QLEDs with ML placed at the ETL side. A comparison of c J-V-L and d EQE-J characteristics of the control device (W/O ML) with B-QLEDs with MLs placed at the HTL side or ETL side. e Normalized EL intensity of control and B-QLEDs with ML placed at the HTL side or ETL side measured under a constant current density of 20mA/cm². 117

Figure 7-9 Ag/Al and Al cathode comparison. a The JVL and b EQE-J characteristics of the B-QLEDs with Ag/Al and Al. c EL stability data of B-QLEDs with Ag/Al and Al cathode. 121

Figure 7-10. J-V characteristics of the EODs with Ag/Al and Al cathode. 121

Fig. 7-11 HIL damage verification. a Schematics of the B-QLEDs rebuilding process. b The average EQE of rebuilt B-QLEDs with Al cathode and with unaged and aged PEDOT:PSS. c J-V characteristics of the rebuilt B-QLEDs with Al cathode and with unaged and aged PEDOT:PSS. d The average EQE of rebuilt B-QLEDs with Ag/Al cathode and with unaged and aged PEDOT:PSS e J-V characteristics of rebuilt B-QLEDs with Ag/Al cathode and with unaged and aged PEDOT:PSS. f ATR-IR spectroscopy of unaged and aged PEDOT:PSS films. g Raman

Spectra of unaged and aged PEDOT:PSS films. h Schematic illustration of charge supply conditions in unaged and aged B-QLEDs..... 122

Figure 7-12 a. Schematic diagram of the B-QLEDs structure with PEI in the ETL side. A comparison of b. J-V-L, c. EQE-J, d. relative luminance vs time, and e. V-time of the B-QLEDs with PEI in the ETL and control device. The B-QLED lifetime is measured under a constant current density of 20 mA/cm². 125

Figure 7-13 a. Schematic diagram of the B-QLEDs structure with PF8Zc HTL. A comparison of b. J-V-L, c. EQE-J, d. EL spectra, e. relative luminance vs time, and f. V-time of the B-QLEDs with PEI in the ETL and control device. The B-QLED lifetime is measured under a constant current density of 20 mA/cm². 127

List of Tables

Table 4.1. The statistical averages and standard deviations of the devices voltages, luminances and EQEs at 20mA/cm ² for each set of devices of the same structure..	43
Table 4.2. Driving voltage, luminance, CIE values, and EQE at 20mA/cm ² of the devices without interlayer, rinsed with octane, and with G-QDs-IL, and B-QDs-IL.	43
Table 4.3. τ and A components extracted from the tri-exponential decay curves for all the TRPL characteristics presented in Figure 4.11.	59
Table 4.4 Comparison of the EL characteristics of the R-IQLED with a B-QDs-IL (this work) versus other R-IQLEDs with a solution processed HTL reported in the literature	61
Table 5-1. The material parameter utilized in the simulation extracted from the literature.	70
Table 5-2. Luminescence, V _{Th} , V _{On} , ΔV , EQE, LT50 @20mA/cm ² , and LT50 @100cd/m ² R, G and B-QLEDs under different charge injection scenarios as well as the standard deviation in the data obtained from 6 samples in each group	66
Table 5-3. Lifetime components of the TrPL results for all QLEDs extracted from the tri-exponential decay curves with the charge supply scenarios (+ $\uparrow$)(- $\downarrow$) and (+ $\downarrow$)(- $\uparrow$) measured at different voltages from 0V to V _{On} . τ_1 , τ_2 , and τ_3 are lifetime components and A ₁ , A ₂ , and A ₃ represent their respective weighing coefficients. τ shows the TrPL overall lifetime (1/e).	80
Table 5-4. Photophysical Properties of QLEDs Explored in This Work and What Is Already in the Literature.	73
Table 5-5. The voltages, luminance, and CIE, for R, G, and B-QLEDs measured at 20mA/cm ² as well as their maximum EQE.	80
Table 5-6. Lifetime components of the TrPL results for all QLEDs extracted from the two exponential decay curves measured at different voltages from 0V to -5V. τ_1 , and τ_2 are lifetime components and A ₁ and A ₂ represent their respective weighing coefficients. τ_{ave} shows the TrPL average lifetime.	91

List of Abbreviations

AR: Augmented Reality

ATR-IR: Attenuated Total Reflectance Infrared Spectroscopy

BLU: Backlight Unit

CBP: 4,4'-Bis(N-carbazolyl)-1,1'-biphenyl

CdS: Cadmium Sulfide

CdSe: Cadmium Selenide

CRT: Cathode Ray Tube

CTL: Charge Transport Layers

DCI-P3: Digital Cinema Initiatives P3

DOS: Density of States

EOD: Electron-Only Device

EL: Electroluminescence

EML: Emissive Layer

EQE: External Quantum Efficiency

FHD: Full High Definition

FRET: Förster Resonance Energy Transfer

FWHM: Full Width at Half Maximum

HD: High Definition

HIL: Hole Injection Layer

HOD: Hole-Only Device

HOMO: Highest Occupied Molecular Orbital

IQE: Internal Quantum Efficiency

ITO: Indium Tin Oxide

J-V: Current-Voltage

LCD: Liquid Crystal Displays

LiF: Lithium Fluoride

L-V: Luminance-Voltage

LT50: Time to 50% Luminance

ML: Marking Layer

MoO₃: Molybdenum Trioxide

OLEDs: Organic Light Emitting Diodes

PEDOT

: Poly(3,4-ethylenedioxythiophene)

PEIE: Polyethylenimine Ethoxylated

PF8Cz: Poly((9,9-dioctylfluorenyl-2,7-diyl)-alt-(9-(2-ethylhexyl)-carbazole-3,6-diyl))

PL: Photoluminescence

PLQY: Photoluminescence Quantum Yield

PMAH: Phosphomolybdic Acid Hydrate

Poly-TPD: Poly[N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine]

PVK: Poly(9-vinylcarbazole)

QDs: Quantum Dots

QLEDs: Quantum Dots Light Emitting Devices

sRGB: Standard Red Green Blue

TCTA: Tris(4-carbazoyl-9-phenyl) Amine

TEM: Transmission Electron Microscopy

TFB: Poly(9,9-dioctylfluorene-alt-N-(4-sec-butylphenyl)-diphenylamine)

TIPS-Pentacene: 6,13-Bis(triisopropylsilylethynyl)pentacene

TPBi: 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)

TrEL: Transient Electroluminescence

UHD: Ultra High Definition

UPS: Ultraviolet Photoelectron Spectroscopy

UV-Vis: Ultraviolet-Visible Spectroscopy

VOn: Turn-On Voltage

VTh: Threshold Voltage

VR: Virtual Reality

ZnMgO: Zinc Magnesium Oxide

Chapter 1

1.1 Introduction

In recent years, advancements in display technology have become a critical driving force behind the evolution of consumer electronics. From televisions to smartphones, the demand for superior visual quality has pushed researchers and industry leaders to explore new approaches that enhance the color purity, brightness, stability, flexibility, and efficiency of displays. This chapter introduces the concept of quantum dot light-emitting devices (QLEDs), a cutting-edge technology set to revolutionize display systems. By leveraging the unique properties of quantum dots (QDs), QLEDs offer enhanced color accuracy, wider color gamut, and improved efficiency compared to traditional display technologies like liquid crystal displays (LCDs) and organic light-emitting diodes (OLEDs).^{6, 7}

This chapter begins with an overview of the role of QLEDs in display technology, comparing them to existing technologies such as LCDs and OLEDs. It then explores the structure of QDs, detailing their core, shell, and ligands, which are crucial components that determine their optical and electronic properties. A detailed discussion of QLED architectures and operational mechanisms follows, along with an examination of the materials used in advanced QLED devices, highlighting ongoing efforts to optimize their performance for future optoelectronic applications. Then, it addresses key factors such as efficiency and stability, which are critical for the commercial success of QLEDs in high-performance display applications. The chapter also discusses the current challenges in QLEDs and outlines the primary motivations behind this research. Finally, it provides an overview of the thesis structure.

1.2 The rise of QLEDs in display technology

The display market has seen significant success with LCDs and OLEDs, which have outperformed other technologies. LCDs gained popularity in the early 2000s by overcoming the limitations of cathode ray tube (CRT) displays, offering high luminance, low operating voltage, and affordability.⁸ LCDs function by polarizing light through liquid crystals using a bias, requiring a backlight unit (BLU) for color creation, but suffer from slow response times, limited color purity, and the need for a BLU that prevents ultra-thin designs. In contrast, OLED displays address these issues with a self-emissive layer that enhances color quality and allows for thinner, larger displays without needing a BLU, finding widespread use across various applications.⁹ Today, LCDs and

OLEDs dominate the market for displays, including televisions, computer screens, and smartphones.

The merging of different technologies has turned traditional media into interactive formats, making visual content a regular part of daily life. As intelligent devices like mobile phones, tablets, Augmented Reality (AR), and Virtual Reality (VR) become increasingly integral, the display panel has emerged as a crucial interface, significantly influencing user experience. Resolution and color are key factors in display quality, with high-resolution displays such as High Definition (HD), Full High Definition (FHD), and Ultra High Definition (UHD) (4k/8k) now commonplace. However, as pixel sizes in these displays often exceed the human eye's detection limit at normal viewing distances, further resolution improvements yield diminishing returns. In contrast, enhancing color quality offers greater appeal, as displays with a wider color gamut deliver more vivid and accurate images. Despite advancements, current color standards like Recommendation 709 (Standard Red Green Blue, sRGB) and Digital Cinema Initiatives P3 (DCI P3) cover only 35.9% and 53.6% of the 1931 Commission Internationale de l'Éclairage (CIE) color space, respectively, indicating significant room for improvement. Researchers are now striving to achieve the Recommendation 2020 (Rec. 2020) standard, which encompasses 75.8% of the color space, promising a more immersive viewing experience.³

Although OLEDs offer decent color purity, there is still room for improvement in the color space of displays. To address these issues, inorganic QDs have emerged as a promising alternative for display devices. With nearly 100% photoluminescence quantum yield (PLQY), narrow emission spectra, and tunable emission wavelengths, QDs offer superior color purity, and an expanded color gamut compared to OLEDs using organic emitters.¹⁰⁻¹⁴ This has spurred efforts to integrate QDs into display technologies like LCDs and OLEDs. For instance, companies like Samsung have commercialized displays that use QDs in color conversion layers to enhance color saturation. However, current research is increasingly focused on incorporating QDs directly into the emission layer of self-emissive devices, leveraging their electroluminescence (EL) properties. Unlike LCDs and OLEDs, where light is partly absorbed by color conversion layers, QLEDs with QDs in the emission layer can achieve higher luminance, improved color purity, and a wider color gamut without needing additional conversion layers, making them a promising candidate for the next generation of display technologies.

1.3 QDs Structure

In General, QDs, as the emissive layer (EML) of QLEDs, are nanoparticles with a complex structure composed of a core, a shell, and ligands. Figure 1.1 shows the schematic structure of QDs. The core refers to the central part of the QDs and is typically made of II-VI semiconductor materials, such as cadmium selenide (CdSe)¹⁵⁻¹⁷. In some cases, III-V semiconductor materials, like indium phosphide (InP), are also used. The core is responsible for the unique optical and electronic properties exhibited by QDs, such as their ability to emit/absorb light of different wavelengths. The shell envelops the core and is composed of a material that has a wider bandgap than the core to provide a well for charge confinement in the core region. The shell can act as a protective layer, preventing the core from interacting with the environment and reducing degradation over time. Additionally, the shell can modify the QDs emission properties, such as improving quantum yield by passivating the surface of the core especially when there is a good lattice matching between the core and shell materials. Ligands are polymer chains that bind to the surface of the QDs, forming a protective layer to stabilize the QDs, prevent aggregation of particles, and maintain solubility in solvents. Ligands also help passivate surface defects and can influence the QDs electronic and optical properties. Different ligands can be used to tailor the QDs behavior, allowing for functionalization and customization for specific applications.

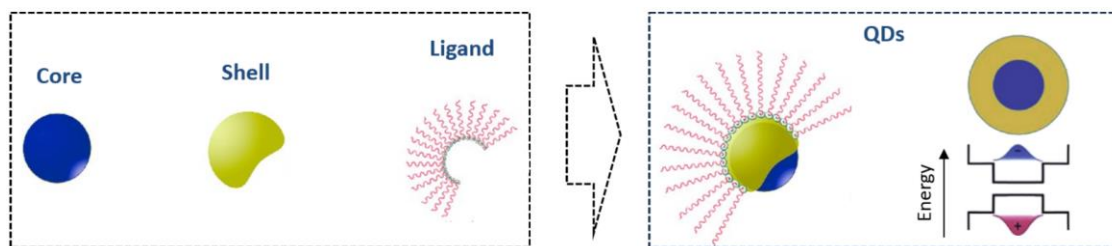


Figure 1.1. Structure of QDs comprising a core, shell, and ligands.¹

QDs possess substantial potential for revolutionizing the future of optoelectronic devices¹⁸. These materials exhibit unique features such as tunable bandgaps, high PLQY, excellent color purity, and suitability for low-cost manufacturing processes.^{16, 19, 20} Due to their exceptional optoelectronic properties, QDs are prominently featured in a wide range of applications such as solar cells, biological imaging and sensing, medical diagnostics, communication, and light-emitting devices for lighting and display technology.²¹⁻²⁴ Continued progress in controlling the optoelectronic properties of QDs, along with advancements in device architectures, have rendered them highly appealing for optoelectronic applications. Such advancements have led to the

development of highly efficient QLEDs that exhibit comparable performance to cutting-edge OLEDs. Compared to the organic semiconductors which their PLQY is limited due to triplet excitons, the PLQY of QDs is ideally 100 % owing to a negligible singlet-triplet energy splitting of Wannier-type excitons, providing internal quantum efficiency (IQE) of about 100 %²⁵. In addition, the narrower emission spectra of QDs results in higher color purity compared to organic materials used as the EMLs of OLEDs. Figure 1.2a compares the EL spectra of QLEDs and OLEDs. As shown, QLEDs exhibit narrower and more distinct emission peaks for blue, green, and red colors, indicating higher color purity compared to OLEDs. Additionally, Figure 1.2b compares the CIE values for LCDs, OLEDs, Quantum Dot LCDs (Q-LCDs), and QLEDs. As illustrated, QLEDs cover a broader color gamut than the other devices, allowing for more accurate and vibrant color reproduction, making them ideal for high-quality display applications.

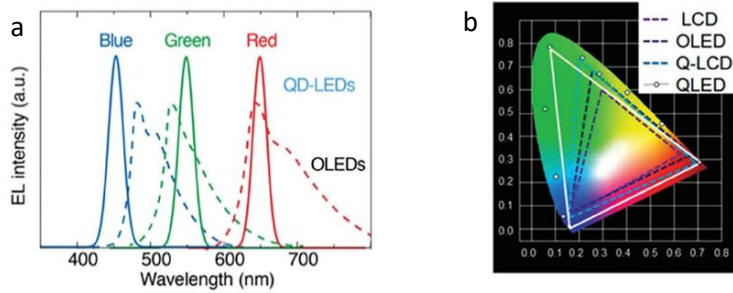


Figure 1.2. (a) Emission spectra of red/green/blue QD-LEDs compared with OLEDs. Reproduced with permission from ref. ², and (b) Color gamut comparison of four representative display techniques.⁴

The intrinsic properties of QDs are determined by factors, such as size, defect, composition, shape, and crystallinity, all of which must be precisely controlled during their synthesis. Figure 1.3a shows the EL spectra of QDs with various sizes. As illustrated, decreasing the size of QDs leads to significant changes in their optical emission and bandgap, primarily due to the quantum confinement effect, which becomes more pronounced at smaller sizes. Controlling the size of QDs allows for the tuning of material properties for specific applications. The quantum confinement effect becomes significant when the size of the particle is sufficiently small compared to the exciton Bohr radius. The Bohr model provides valuable insights into the exciton system, particularly regarding the exciton radius, which represents the distance between the electron and

hole within an exciton. This concept is analogous to the Bohr radius in the hydrogen atom. The exciton Bohr radius, r_B , is defined by the equation:^{18, 26}

$$r_B = \frac{4 \cdot \pi \cdot \epsilon \cdot \hbar^2}{q^2} \cdot \left(\frac{1}{m_e} + \frac{1}{m_h} \right) \quad (1.1)$$

where q is the elementary charge, ϵ is the materials dielectric constant, $\hbar$ is the reduced Planck constant, and m_e and m_h are the effective masses of the electron and hole, respectively. In the confinement regime, the motion of electrons and holes is spatially confined, forcing their energy states into discrete levels and widening the bandgap. As the confining dimension decreases, the energy levels become more discrete, and the bandgap increases. This quantization is governed by the Schrödinger equation within a three-dimensional spherical infinite potential well. Detailed solutions to this equation are discussed in the referenced literature. The confinement energy for the ground state ($n = 1$) is then expressed as:^{26, 27}

$$E_{n=1} = E_g - \frac{q^2}{2\epsilon \cdot r_B} + \frac{\pi^2 \cdot \hbar^2}{2m_{eff} \cdot r^2} \quad (1.2)$$

where E_g is the energy band gap. This equation describes how the energy states shift as the radius of the material changes. The quantum confinement effect (where $r_B > r$) influences the density of states (DOS) within the material, leading to the quantization of electronic states. In other words, quantum confinement is responsible for the increased energy difference between energy states and the widening of the bandgap. Some compound semiconductors include the anionic sulfur, selenium, and/or tellurium combined with the cations of zinc, cadmium and/or mercury are extensively employed in synthesizing QDs. Figure 1.3b shows the variation of EL/PL emission color with changing the composition of QDs. Among these compounds, CdSe-based QDs have demonstrated the highest PLQY to meet the demand for efficient QLEDs fabrication.

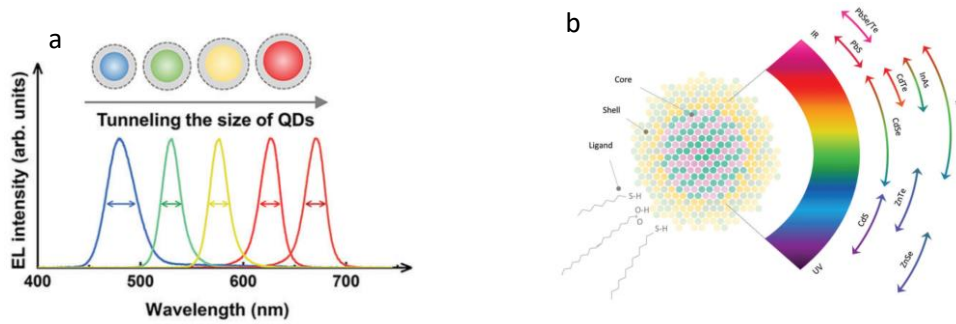


Figure 1.3 (a) The variation of EL emission color with the size of CdSe QDs.³ (b) The variation of EL/PL emission color with changing the composition of QDs.⁵

1.4 Architectures and operational mechanism of QLEDs

In addition to enhancing the optical and electrical properties of QDs discussed in the previous section, significant progress has been made in the development of QLEDs architecture to achieve high-performance devices. Generally, the architecture of QLEDs closely resembles that of OLEDs, consisting of an EML of QDs sandwiched between electron transport layers (ETLs) and hole transport layers (HTLs), respectively. Similar to OLEDs, ETLs and HTLs play a critical role in the performance of QLEDs by respectively supplying electrons and holes into the QDs-EML. Depending on the choice of the CTL materials, QLEDs can be categorized in three types, all-organic CTLs (Type I), all inorganic (Type II) CTLs, and hybrid structures (Type III). In 1994, the first QLEDs with a simple structure of metal/QDs-EML/metal and a low external quantum efficiency (EQE) of $\sim 0.01\%$ have been introduced¹⁰. To avoid the significant quenching effect by

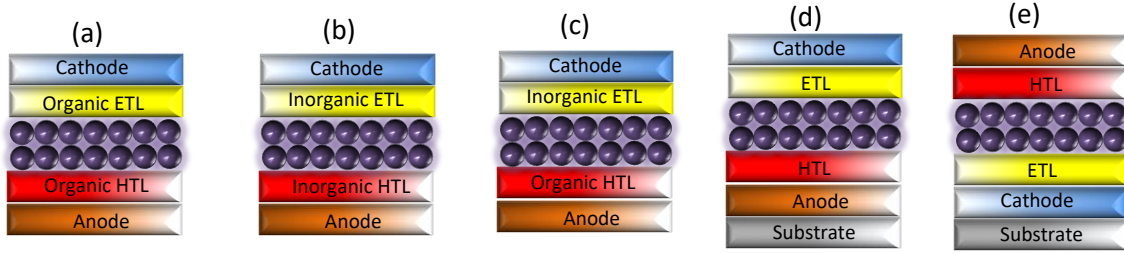


Figure 1.4 General utilization of the CTLs in QLEDs: (a) all-organic (Type I), (b) all-inorganic (Type II), and (c) hybrid (Type II). (d) Upright and (e) inverted architecture of the QLEDs.

metal electrodes, QLEDs with the structure of metal/organic HTL/QDs-EML/organic ETL/metal, referred to as Type I (Figure 1.4a), have been proposed, resulting in a record EQE of 0.5%. In 2005, a Type II QLED structure (Figure 1.4b) comprising Au/p-GaN/CdSe/n-GaN/In with an EQE of $\sim 1\%$ was reported²⁸. Since 2011, hybrid QLEDs (Type III-Figure 1.4c) have gained considerable attention due to their outstanding EQEs (exceeding the theoretical limit of 20%) for red (R)²⁹, green (G)³⁰, and blue (B)¹⁴-QLEDs. Since the introduction of ZnO and its derivatives as the ETL of QLEDs with a hybrid structure, significant progress in the lifetime, and efficiency of QLEDs have been achieved. All the categorized types can be utilized in QLEDs with both upright and inverted architectures. In the upright architecture (Figure 1.4d), the transparent electrode on the substrate serves as a hole-injecting contact, while in the inverted architecture (Figure 1.4e), it serves as electron injecting contact. Extensive investigations have been conducted in the literature on upright QLEDs, which feature a structure of ITO/hole injection layer (HIL)/HTL/QDs-EML/ETL/Al. All the layers in this structure are commonly deposited using a solution-coating

process. An accurate selection and optimization of both CTLs and QDs have resulted in the development of highly efficient and stable upright R, G, and B-QLEDs^{31, 32}. On the other hand, inverted QLEDs have the structure of ITO/ETL/QDs-EML/HTL/HIL/Al in which both HTL and HIL are commonly deposited by the thermal evaporation approach. Inverted QLEDs are highly advantageous for display technology, since the bottom transparent cathode can be directly connected to an n-channel metal oxide or amorphous silicon-based thin-film transistor (TFT) in the active-matrix back panel. This allows for efficient and simplified integration of the QLEDs, enabling the driving of large-sized and high-resolution displays^{33, 34}. Figure 1.5 shows the energy band diagram of hybrid inverted QLEDs which operate through three steps: i) charge injection (electron and hole injection into CTLs), ii) charge transport (carrier movement through CTLs to the QDs-EML), and iii) exciton formation and recombination (electron-hole pair interaction).

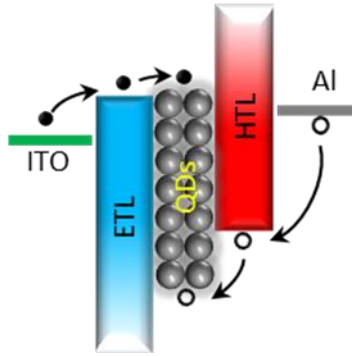


Figure 1.5 General device structure of inverted QLEDs.

1.5 Materials employed in cutting-edge devices.

In order to achieve highly efficient and stable QLEDs, careful selection of appropriate materials for the QDs-EML, ETL, HIL, and HTL is necessary. Figure 1.6 shows the energy levels of materials commonly used in the fabrication of QLEDs. Among the II-VI QDs used as the EMLs of QLEDs, the CdSe/ZnS core/shell QDs structure has gained significant attention due to its high PLQY^{35, 36}, coming from the minimum lattice mismatch at the interface of core/shell. Despite the attempts to replace Cd-based QDs with III-V QDs, which offer non-toxic properties, the challenges of low PLQY and the lack of a reliable synthesis method still need to be addressed³⁷.

In the case of ETL, ZnO and its derivatives are extensively employed as the ETL owing to their superior electron mobility, appropriate energy band alignment with QDs-EML for efficient electron injection, and chemical robustness. While alternative materials like 2,2',2''-(1,3,5-

Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) and TiO₂ have been tested as ETLs, their performance has been found to be poor and not comparable to that of the ZnO.

Poly(9,9-dioctylfluorene-alt-N-(4-sec-butylphenyl)-diphenylamine) (TFB), 4,4'-Bis(N-carbazolyl)-1,1'-biphenyl (CBP), and tris(4-carbazoyl-9-phenyl) amine (TCTA) are notable organic materials that have gained attention as HTLs in QLEDs³⁸⁻⁴⁰. Exhibiting excellent hole transport properties, these materials possess a deep highest occupied molecular orbital (HOMO) level, crucial for efficient hole injection into the QDs-EML. Moreover, there are some reports that poly(9-vinylcarbazole) (PVK)⁴¹ and poly[N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine] (poly-TPD)⁴² have also been explored as HTLs in QLEDs.

Poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) and molybdenum trioxide (MoO₃) are commonly used HIL for efficient hole injection from the anode into the HTL, in upright and inverted structure, respectively. There also some reports using phosphomolybdic acid hydrate (PMAH) as the HIL in inverted structure.³⁴

Indium tin oxide (ITO) is also used as the transparent electrode, while metals like Al and Ag are commonly used as the counter electrode in QLEDs structure.

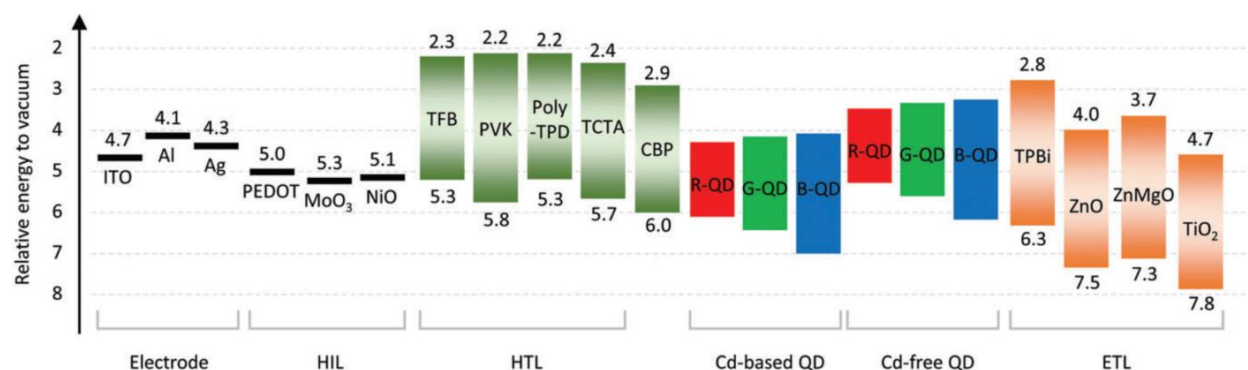


Figure 1.6 Energy levels of materials commonly used in the fabrication of QLEDs.⁵

1.6 QLEDs Performance Metrics

To evaluate the performance of QLEDs, two primary metrics are crucial: EL efficiency and EL stability. EL efficiency measures how effectively excitons form and undergo radiative recombination to emit photons, reflecting the overall quality of the photon emission from the device. EL stability, on the other hand, assesses the ability of the QLED to maintain its emission

characteristics over time, ensuring that efficiency is preserved during continuous operation and storage. Together, these metrics provide insights into the operational mechanism, endurance, and consistency of the QLED. This section offers an overview of the key performance parameters, including luminance, EL efficiency, and EL stability, that are used to assess QLED performance.

1.6.1 Luminance

Luminance refers to the luminous intensity emitted by a light source per unit area in a specific direction, within a given solid angle. It is a measure of how bright a surface appears to the human eye from a particular angle, accounting for the eye's sensitivity to different wavelengths of light. This parameter is used to gauge the perceived brightness of a light source, including both EL and PL. Luminance is expressed in candelas per square meter (cd/m^2). The candela (cd) quantifies the intensity of light, while the lumen (lm) measures the luminous power associated with the radiation.

1.6.2 EL efficiency

The EL efficiency can be quantified through EQE, defined as the ratio of photon emissions from the QLEDs to the number of injected carriers, is a critical parameter for evaluating the efficiency of QLEDs, which can be defined by the following equation:

$$EQE = \gamma \times \eta_{rc} \times \eta_{out} \quad (1)$$

where γ is the charge balance factor, η_{rc} denotes the ratio of radiatively recombined excitons under operational conditions, and η_{out} signifies the light out-coupling efficiency. Specifically, γ represents the impact of charge injection and transport, η_{rc} describes the quenching mechanism in QLEDs, and η_{out} quantifies the ratio of photon extraction within the device structure. η_{out} is influenced by various factors that limit photon extraction, including cavity effects, light reflection, and refraction within the multi-stacked layers.

1.6.3 EL stability

The stability of QLEDs is assessed by measuring their EL changes over time while applying a constant current density. In order to assess the lifetime of QLEDs, the literature commonly employs LT50, LT75, and LT95, which represent the time at which the device reaches 50%, 75%, and 95% of the initial luminance (L_0) of the QLEDs, respectively. Due to the variation

in L_0 and lifetime spans among QLEDs, the following equation is employed to convert the equivalent lifetime of QLEDs and extrapolate the results to the same initial luminance level:

$$(L_a)^n (t_{x\%}) = (L_b)^n (t'_{x\%}), \quad 1 < n < 2 \quad (2)$$

L_a and L_b represent two distinct initial luminance values, n signifies the exponential luminance dependence of the device luminance decay, and t represents the time required for the luminance to decrease from the initial luminance value to x percent of that value.

1.7 Current Challenges and motivation for this work

Over the past three decades, considerable efforts have been devoted to enhancing the performance of QLEDs, leading to significant improvements in both efficiency and lifetime. However, despite these advancements, the underlying working mechanisms and factors influencing both efficiency and EL stability remain poorly understood, primarily due to the complexity of identifying the precise contributors to device operation and degradation. One of the most critical factors affecting QLED performance is charge balance, which involves achieving the proper balance between electron and hole injection into the QDs-EML. Imbalances in charge injection can result in detrimental effects, such as non-radiative recombination and charge leakage, ultimately leading to reduced efficiency and shortened EL lifetime. Therefore, identifying the factors that impact charge balance and developing strategies to improve it are essential for optimizing overall performance and extending the operational lifetime of QLEDs.

Moreover, most research to date has primarily focused on R and G-QLEDs, while B-QLEDs remain less extensively studied and present distinct stability and performance challenges. As the bandgap of QDs increases, either by reducing their size or altering their material composition, several key differences arise. These changes result in a different material system, with higher bandgap materials requiring greater energy for charge injection, often leading to reduced injection efficiency. Additionally, B-QDs are more susceptible to surface defects and trap states, which contribute to exciton quenching and reduced EL stability. These differences suggest that the charge supply behavior and working mechanisms of the device change significantly as the QDs-EML shifts from R to G and B, further complicating device optimization across the full color spectrum.

While the EQE of B-QLEDs is now comparable ($>20\%$) to that of R and G-QLEDs, their operational lifetime remains far behind. Currently, T95 lifetimes ($@1000\text{ cd m}^{-2}$) for R and G-QLEDs of around 5000 hours have been achieved.⁴³ In contrast, the longest reported T95 lifetime for a B-QLED is only approximately 277 hours ($@1000\text{ cd m}^{-2}$),⁴⁴ with most B-QLEDs in the literature exhibiting even shorter lifetimes. This significant gap in lifetime performance, despite comparable EQE, highlights the unique stability challenges faced by B-QLEDs and the critical need for further research to enhance their long-term stability.

Most of the current knowledge on charge dynamics and device performance in QLEDs comes from studies focused on individual colors rather than direct comparisons between R, G, and B-QLEDs. While it is known that R-QLEDs generally exhibit better charge injection efficiency and stability compared to G- and B-QLEDs, and that B-QLEDs face more significant challenges due to larger bandgaps and charge imbalances, these insights are based on isolated studies. Moreover, most research has been performed on upright QLED structures, with relatively few studies exploring inverted structures. Direct comparisons of R, G, and B-QLEDs—evaluating charge balance, efficiency, and EL stability—are limited, leaving a gap in understanding how performance varies across the full color spectrum. This lack of comparative data highlights the need for more comprehensive research to optimize QLED performance across all colors and device architectures.

This thesis primarily investigates and compares the charge balance in inverted R, G, and B-QLEDs and its impact on EL performance, with the goal of developing new HTL and ETL designs based on these findings to improve charge balance, thereby optimizing overall device efficiency and lifetime. Additionally, it explores the degree of charge balance in upright B-QLEDs, provides insights into the underlying degradation mechanisms, and suggests novel approaches to enhance EL stability in these devices.

1.8 Thesis outline

The thesis is organized into eight chapters. Chapter 1 provides an introduction, while Chapter 2 offers a literature review on the charge imbalance issue in QLEDs. Chapter 3 outlines the objectives of the study and presents the methodology, including the materials, device configuration, and characterization techniques used. Chapters 4 through 7 form the main body of the thesis. Chapter 4 explains the causes of low efficiency in inverted QLEDs with polymer HTL.

Chapter 5 investigates the degree of charge balance in inverted R, G, and B-QLEDs and its impact on EL performance. Chapter 6 proposes new ETL and HTL designs to optimize charge injection and improve EL performance in inverted QLEDs. Chapter 7 explores the charge balance in upright B-QLEDs, its influence on EL performance, and suggests new ETL and HTL materials for enhancing charge injection and EL performance. Finally, Chapter 8 summarizes the main findings of this work and offers recommendations for future research.

Chapter 2. Literature review

Charge balance, the equilibrium between the injection of electrons and holes into the QDs-EML, is a critical factor in determining the performance of QLEDs. This balance ensures efficient exciton formation and minimizes non-radiative losses, directly impacting the efficiency and lifetime of the QLEDs.⁴⁵⁻⁴⁷ An imbalance in charge injection can lead to various detrimental effects, including reduced exciton formation, increased Auger recombination, and charge leakage and accumulation, all of which negatively affect device performance. Therefore, understanding and optimizing charge balance is essential for fabricating QLEDs with relatively high efficiency and long lifetime. Moreover, a thorough knowledge of charge balance is crucial for gaining deeper insights into the working mechanisms of QLEDs, enabling more effective strategies for improving device performance.

While R and G-QLEDs have both the efficiency and lifetime required for commercialization, B-QLEDs, despite achieving the necessary efficiency, still suffer from poor operational lifetimes, which remain a major obstacle to their commercial viability. Therefore, identifying the root causes of this rapid EL loss is crucial for developing strategies to enhance the stability and efficiency of B-QLEDs, thereby advancing their commercial viability in display technologies.

This chapter begins with an in-depth analysis of the charge imbalance issue in QLEDs, discussing the underlying factors that lead to charge imbalance. The effects of charge imbalance on the device, including reduced exciton formation, increased non-radiative losses, and faster degradation, are explored in detail. Various approaches for enhancing charge balance in QLEDs are then reviewed, focusing on strategies such as QDs-EML modifications, interface engineering, and improvements to charge transport layers to optimize electron and hole injection.

The chapter also addresses the root causes of rapid EL loss in B-QLEDs. The role of charge balance in B-QLED stability is investigated, highlighting how charge-induced defects, Auger recombination, and charge leakage contribute to rapid EL loss. The chapter concludes with potential solutions to mitigate these challenges and improve the operational lifetime of B-QLEDs, aiming to bridge the gap between their efficiency and stability.

2.1 Charge imbalance issue in QLEDs

The determination of charge injection and transport into the QDs-EML relies on three crucial factors: i) the charge injection barrier at the electrodes/CTLs, ii) the carrier mobility of the CTLs, and iii) the charge injection barriers at the CTLs/QDs-EML. Unbalanced charge injection, stemming from an uneven supply of electrons and holes, leads to a reduction in γ , as well as the accumulation of charge within QDs-EML and its interfaces with CTLs, along with charge carrier leakage from QDs-EML to the counter electrode. Generally, charge imbalance gives rise to detrimental effects including, poor exciton formation into the QDs-EML, Auger quenching, charge accumulation, Joule heating, and leakage current⁴⁸⁻⁵², all negatively affecting both the EQE and lifetime. Despite significant improvements, charge imbalance still continues to be a key bottleneck that limits the performance of the QLEDs.¹⁹ In this section, the charge imbalance issue is discussed in light of previous work available in the literature, emphasizing the ongoing challenges and advancements aimed at optimizing the efficiency and lifetime of QLEDs.

2.1.1 Charge imbalance in QLEDs

Charge imbalance issue in both conventional and inverted QLEDs has been extensively reported in the literature. Klimov et al.⁵³ demonstrated that in inverted R-QLEDs, where CdSe based QDs-EML has a simple core-shell structures, electron injection exceeds hole injection, leading to charge imbalance, which reduces device efficiency. Similarly, Keating et al.⁵⁴ proposed that electron injection is easier than hole injection in upright R-QLEDs utilizing TrEL measurements. Also, using electrically pumped single-nanocrystal spectroscopy, Deng et al.⁵⁵ found that in R-QDs, electrons are injected into the QDs-EML first, followed by holes. They proposed a working mechanism for the device, suggesting that the negatively charged state of the QDs enhances Coulomb interactions, which accelerates hole injection while limiting excessive electron injection. Moreover, Sun et al.⁵⁶ showed that inefficient hole injection is a critical issue in upright B-QLEDs, which causes device degradation and reduces operational stability. They verified that challenge lies in balancing the energy levels between ITO, HTLs, and QDs-EML, as mismatched energy levels lead to increased operating voltage, luminance decay, and irreversible PL loss. Additionally, Shen et al.⁵⁷ demonstrated in a comparative study on upright QLEDs that the electron supply in B-QLEDs is significantly lower than that of R- and G-QLEDs, as confirmed by TREL results. This imbalance was identified as the cause of the lower EL efficiency in B-QLEDs.

Moreover, the characterization of EL from CTLs to determine the majority carrier type, pinpoint the device recombination zone, and assess the possible presence of charge leakage caused by charge imbalance in QLEDs has been widely reported. For example, Ye et al.⁵⁸ proposed that electrons, as the majority carrier in upright R-QLEDs, bypass the QDs-EML and recombine in the HTL, verified by TFB EL emission, revealing inefficiencies in hole supply. Similarly, the EL emission from TFB HTL has shown that electrons act as the majority carriers in upright G- and B-QLEDs.^{58, 59} Moreover, Chung et al.⁶⁰ intentionally doped the CBP HTL with Flrpic in the R-QLED structure to identify and quantify the presence of excess electrons reaching the HTL, which was identified as the main cause of device lifetime deterioration. Qu et al.⁶¹ identified electron over-injection in B-QLEDs using R-QDs as a fluorescent sensor to study the exciton recombination zone. Their EL results showed that the exciton recombination zone in blue QLEDs is near the HTL and shifts toward the ETL as the applied bias increases.

Moreover, single-carrier devices have been extensively used to compare electron and hole supply properties of CTLs in QLEDs, serving as a method to identify the majority and minority carriers. For instance, Kim et al.⁶² using single carrier devices, showed that generally electron supply is stronger than hole supply in inverted G-QLEDs. Also, Yeom et al.⁶³ employed single carrier devices to assess charge transport in their InP based QLEDs. The findings showed that electron transport in the electron only devices (EODs) was more efficient than hole transport in the hole only devices (HODs). Moreover, in a comparative study, Chen et al.⁴⁰ verified that R-QDs exhibit efficient electron and hole injection, leading to balanced charge transport. G-QDs show moderately efficient injection, while B-QDs suffer from poor electron injection in EODs and higher hole currents in HODs, resulting in significant charge imbalance and faster degradation in real devices.

2.1.2 Impact of charge imbalance on QLEDs

Several studies have reported the negative effects of charge imbalance on different parts of QLEDs. In this section, the reported impacts of charge imbalance on the QDs-EML, HTL, and ETL are reviewed and discussed.

2.1.2.1 Impact of charge imbalance on QDs-EML

The detrimental effects of charge imbalance within the QDs-EML have been examined in several studies. Bae et al.⁴⁹ found that because of significant charging of R-QDs with extra electrons, Auger recombination greatly impacts both efficiency and the onset of efficiency roll-off

at high currents. In another work,⁶⁴ they demonstrated that simple core/shell QDs reduce hole trapping from the shell to the core, leading to a charge imbalance in the QDs-EML and increasing the likelihood of Auger quenching. Chang et al.⁶⁵ demonstrated that in R-QLEDs, the early stages of device degradation are caused by Auger recombination occurring in QDs, which become negatively charged due to excess electron injection. Notably, after cooling the device or allowing it to rest for a prolonged period, the PLQY drop is recovered. Oppositely, through a combination of EL and PL measurements, Shirasaki et al.⁶⁶ concluded that the primary cause of the efficiency loss is the electric-field-induced reduction in QDs luminescence efficiency, rather than Auger recombination. This reduction is attributed to the Stark effect, which affects the QDs' emission under high voltage, leading to the observed efficiency roll-off.

Additionally, the excitonic behavior of QDs in the presence of excess electrons or holes has been investigated in several reports. Galland et al.⁶⁷ revealed that negative and positive trions formed in charged QDs both lead to non-radiative Auger recombination, which significantly reduces PLQY. Using charged films of colloidal CdSe/CdS core/shell QDs, Jha et al.⁶⁸ measured the radiative and nonradiative decay rates of the negatively charged exciton (negative trion). The radiative rate of the negative trions was found to be approximately 2.2 times faster than that of the exciton, with an estimated radiative time of about 10 ns. The negative trion lifetime for the measured samples was around 0.7–1.5 ns, which is 7.5 times longer than the biexciton lifetime, proposing that excess electrons in the QDs-EML can significantly reduce the device efficiency. Wu et al.⁶⁹ employed a photochemical doping approach to create negatively and positively charged R-QDs. They demonstrated that the decay of negative trions is about an order of magnitude faster than that of neutral excitons and twice as long as that of positive trions, indicating that the PLQY of positively charged QDs can be quenched much more quickly than that of negatively charged QDs. Similarly, Park et al.⁷⁰ employed single-dot spectroscopy to study Auger recombination dynamics in QDs. They showed that the positive trion decays much faster than both the negative trion and the neutral exciton. The positive trion lifetime was around 1.5 ns, the negative trion about 10 ns, while the neutral exciton had a significantly longer lifetime of 86 ns. The shorter decay of positive trions was attributed to a higher density of deep hole states and stronger hole confinement.

Furthermore, recently, Lee et al.⁷¹ utilized the idea of using single carrier device to charge QDs with electrons and holes, aiming to explore the interaction of excess carriers with excitons.

To supply excess electrons and excess holes the structures of ITO/ZnO/R-QDs/TPBi/LiF/Al and ITO/TFB/R-QDs/CBP/MoOx/Al, are applied, respectively. Consistent with previous findings, it was observed that the PL decay of positive trions was found to be approximately two times faster than that of negative trions.

Additionally, Joule heating resulting from charge imbalance has been identified as a cause of degradation in the QDs-EML. Sun et al.⁵⁰ demonstrated that in QLED devices, carrier leakage occurs when injected charge carriers, particularly electrons, escape from their intended recombination regions. This leakage leads to energy dissipation as heat rather than light, contributing to Joule heating. The excess heat generation accelerates the debonding of surface ligands and creates trap states, which quench PL and reduce device efficiency, particularly at high current densities. Similar observations were reported by Lee et al.⁷² who used R-QDs in inverted structure.

2.1.2.2 Impact of charge imbalance on HTL

Ye et al.⁵⁸ showed that during the operation of upright R-QLEDs, leakage electrons trigger in situ electrochemical reduction reactions in the HTL. As a result, trap states are formed, which negatively affect the charge transport characteristics, resulting in the reduction of EL efficiency and lifetime. Xue et al.⁷³ also discovered that the stability of upright R-QLEDs is primarily affected by the interfaces between the QDs and HTL. Due to the aging process, some QDs remain in permanent dark states, potentially caused by the formation of nonradiative sites in the HTL. Electron leakage is likely responsible for the HTL degradation, resulting in increased resistance in the HTL and a higher operating voltage for aged devices. Similarly, Liu et al.⁷⁴ showed that electrons leaking from the QDs-EML are consistently injected into the HTL, triggering a reduction reaction. This reaction generates inter-band defects, which significantly reduce hole mobility and worsen the imbalance between electron and hole injection in the QLEDs. Wang et al.⁷⁵ reported that excessive electron injection causes electron leakage in inverted G-QLEDs with a CBP HTL, leading to HTL degradation and further reducing charge balance in the device.

2.1.2.3 Impact of charge imbalance on ETL

Chen et al.⁷⁶ showed that a large portion of holes leak from QDs-EML into the ETL through the defects of ZnMgO, originating from zinc hydroxide ($\text{Zn}(\text{OH})_2$) and/or oxygen vacancies (V_O), could serve as hole leakage channels. Also, Wang et al.⁷⁷ found that QLEDs suffered from significant hole leakage into the ETL, which negatively impacted device performance. Also,

Chung et al.⁷⁸ demonstrated that charge transfer occurs at the ZnO/QDs interface in R-QLEDs, producing positively charged states in ZnO, subsequently leading to luminance loss, a mechanism that contributes to EL loss.

2.1.3 Approaches for enhancing charge balance in QLEDs

As discussed in section 2.1, in QLEDs, achieving charge balance is critical for optimizing both efficiency and lifetime. Enhancing charge balance in QLEDs involves several strategies, including modifying the QDs-EML and the CTLs to ensure efficient electron and hole injection into the QDs-EML. This section explores key approaches such as QDs-EML composition tuning, suitable CTLs selection, interface engineering, and the use of insulating layers to improve charge balance.

2.1.3.1 QDs-EML modification

Shen et al.⁴³ doped throughout the CdSe/ZnSe core/shell regions in R, G, and B-QDs with Se to improve the hole injection by changing the conduction and valance band energy levels, resulting in balanced charge injection. Furthermore, Song et al.⁷⁹ enhanced hole injection into the QDs-EML by employing an intermediate ZnSe layer and an ultrathin ZnS outer layer as shell materials, in addition to surface modification with 2-ethylhexane-1-thiol. Moreover, by tailoring the energy band structure through gradient composition and shell thickness, Cao et. al.⁸⁰ were successfully synthesized high PLQY QDs with a ZnSe outer shell, resulting in reduced carrier injection barriers, especially for holes.

Bae et al.⁶⁴ introduced a $\text{CdSe}_x\text{S}_{1-x}$ alloy layer at the core-shell interface of CdSe/CdS R-QDs to enhance charge confinement effect and reduce nonradiative Auger recombination, thereby improving the PLQY of the QDs. Also, Park et al.⁸¹ showed that increasing the smoothness of the confinement potential affects Auger decay by examining a series of CdSe/CdS QDs, where the core and shell are separated by a $\text{CdSe}_x\text{S}_{1-x}$ alloy layer with 1 to 5 sublayers of radially varying composition. Single-dot measurements reveal that using a five-step composition gradient significantly reduces Auger decay for charged excitons.

Furthermore, Li et al.⁸² achieved significant improvements in charge carrier mobility and balance in QLEDs by replacing long-chain oleic acid ligands with chloride ligands through efficient chlorination. This process removed the insulating organic ligands and attached conductive chloride ions onto the surface of the QDs. As a result, charge injection was enhanced, and

recombination losses were reduced, leading to improved overall device performance. Also, Pu et al.⁸³ identified that carboxylate-based ligands on QDs tend to react with injected charge carriers, causing charge imbalance and luminescence quenching. To solve this, they replaced the carboxylate ligands with electrochemically stable ligands, such as primary amines. These ligands prevent unwanted reactions, stabilize the QD surface, and enable more efficient charge injection and balance, ultimately enhancing both device efficiency and lifetime. Also, Shen et al.⁸⁴ demonstrated that substituting the oleic acid ligands with shorter 1-octanethiol ligands doubles the electron mobility of the QD film and significantly enhances hole injection into the QD layer, thereby improving overall charge balance, as evidenced by a reduction in the V_{On} .

2.1.3.2 QDs-EML/CTL interface modification

Ding et al.⁸⁵ utilized PEI's insulating properties in inverted R-QLEDs to reduce electron injection and achieve charge balance by increasing PEI thickness to block excess electrons. PEI also suppressed QDs charging and improved surface morphology compared to ZnO, reducing leakage and enhancing charge balance. This optimization with a 15 nm PEI layer resulted in a 2.5-fold efficiency improvement over QLEDs without PEI. Oppositely, Cun et al.⁸⁶ used a PEI interlayer between the PVK and QDs-EML in inverted QLEDs to lower the vacuum level, reducing the hole-injection barrier and balancing charge carriers. Additionally, PEI's amine group passivates QD surface defects, suppressing fluorescence quenching, all resulting in EQE improvement. Additionally, Sun et al.⁸⁷ demonstrated that to suppress excess electron injection, a 13 nm $Zn_{0.85}Mg_{0.15}O$ interlayer with a higher conduction band edge and lower conductivity was inserted between the ZnO ETL and the R-QDs-EML. This improved charge injection balance by reducing electron supply and blocked non-radiative pathways, leading to enhanced device efficiency.

2.1.3.3 HTL modification

The use of a double HTL to improve hole injection has been extensively reported.^{88, 89} For instance, Chen et al.⁴¹ reported that using a double HTL significantly improved hole injection in B-QLEDs, leading to better charge balance and enhanced device performance. They employed PVK and TFB as the double HTLs, which formed a stepwise energy alignment for more efficient hole injection, reduced the hole injection barrier, promoted better charge balance, and improved surface morphology, ultimately boosting the EQE threefold compared to single-layer HTL devices.

Also, mixing HTLs has been proposed to enhance the hole supply in QLEDs.⁹⁰⁻⁹² For example, Fang et al. identified that mixing TFB with 20 wt % CBP as a HTL greatly improved

charge balance and hole injection in R-QLEDs. This optimized HTL mixture led to more efficient hole-electron recombination in the QDs-EML by reducing the hole injection barrier and balancing charge transport.

2.1.3.4 HIL modification

As mentioned in Section 1.4, PEDOT:PSS and MoO₃ are widely used as HILs in upright and inverted QLEDs, respectively. It has been extensively attempted to improve hole supply in inverted QLEDs.^{34, 93} Wu et al.⁹⁴ demonstrated that incorporating graphene oxide (GO) into the PEDOT:PSS significantly improved hole injection in inverted QLEDs. The GO-doped PEDOT HIL enhanced the wettability, increased the work function, and improved the conductivity of the HIL, which reduced the hole injection barrier. This modification promoted better hole injection from the Al anode into the PVK HTL, resulting in enhanced charge balance.

Also, several studies have reported improvements in hole supply in upright structures through modifications of the HIL.⁹⁵⁻⁹⁸ Cho et al.⁹⁹ demonstrated that utilizing a bilayer HIL consisting of VO₂ and PEDOT:PSS significantly enhanced hole injection by reducing the energy barrier between the ITO electrode and PEDOT:PSS. As a result, the device achieved an EQE of 18%, which is a marked improvement over the 13% EQE of devices using only PEDOT:PSS as the HIL. Li et al.⁴⁵ proposed that ionic liquid doping of the PEDOT:PSS using AgTFSI significantly improved charge balance and hole injection in R-QLEDs. The AgTFSI doping increased the hole concentration and work function of the PEDOT:PSS, leading to enhanced hole injection efficiency.

2.1.3.5 ETL modification

Alexandrov et al.¹⁰⁰ demonstrated that doping ZnO NPs with Al as an ETL significantly improved QLED performance. This enhancement was attributed to the improved electron mobility and reduced surface roughness of the Al-doped ZnO, which facilitated better electrical contact with the QDs-EML and improved charge balance, thereby boosting overall device efficiency. Kim et al. proposed that using size-controlled ZnO NPs as the ETL significantly improved charge balance and electron injection. By adjusting the particle size and trap energy level of ZnO NPs, they optimized electron transport, leading to enhanced device performance. Moreover, Pan et al.¹⁰¹ showed that the size of ZnO NPs used in the ETL plays a crucial role in improving electron injection and charge balance. By tuning the size of ZnO NPs from 5.5 nm to 2.9 nm, they enhanced electron mobility from $7.2 \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$ to $4.8 \times 10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$, which resulted in a significant

increase in current efficiency and EQE. Also, Kirkwood et al.¹⁰² demonstrated that the defect density and electron mobility of the ZnO significantly impact QLEDs efficiency by balancing electron and hole injection into the QD layer. ZnO nanoparticle films with tunable electron mobilities were achieved by annealing out defect states in ZnO nanoparticle suspensions before deposition, resulting in the enhancement of the device performance.

2.1.3.6 Charge leakage reduction

Zhang et.al.⁴⁸ sandwiched the QDs-EML of inverted R-QLEDs between Al₂O₃ insulating layers, effectively suppressing leakage current and leading to higher efficiency. Also, Kim et.al.¹⁰³ inserted polyethylenimine ethoxylated (PEIE) between the QDs-EML and HTL, improving charge balance by regulating hole injection and reducing leakage currents, ultimately enhancing device performance. Moreover, to reduce the electron leakage, HTLs with shallow LUMO such as TCTA that can block electrons efficiently, thereby decreasing leakage of current and enhancing luminance, has been proposed¹⁰⁴. Also, in some reports, the utilization of thermally activated delayed fluorescence (TADF) material in HTL has been suggested. In this structure, the leaked electrons can form excitons with the injected holes from the HTL, followed by energy transfer from the TADF material to the QD-EML, resulting in efficiency enhancement^{105, 106}.

2.2 Root Causes of the Rapid EL Loss in B-QLEDs: Investigating the Role of Charge Balance

Despite significant advancements in both QDs synthesis and device structure development, B-QLEDs still lag behind their red and green counterparts in performance, particularly in EL stability, which presents a major obstacle to their commercialization. Generally, EL stability in QLEDs is influenced by both external and internal factors. External factors, such as moisture, oxygen, and UV light, are typically addressed through engineering solutions like encapsulation.¹⁰⁷ Internal factors, however, involve degradation due to changes in the functional materials and interfaces, presenting a significant challenge in the device stability. Key degradation mechanisms reported include chemical or morphological changes in CTLs,^{58, 78} QD degradation (e.g., ligand detachment, QD charging),^{44, 59, 83} and trap/defect states at interfaces⁴⁰. These issues lead to quenching sites, leakage currents, and electrochemical reactions that damage the functional layers or interfaces. Degradation can occur spontaneously or be triggered by electrical stress, impacting QLEDs shelf life and stability. Most studies have focused on R-QLEDs. However, significant differences in electron and hole injection and confinement between R, G, and B-QDs make it

uncertain whether these findings apply to B-QLEDs, highlighting the need for specific studies on their degradation mechanisms. This section reviews the literature on the mechanisms behind the unstable EL properties of B-QLEDs from various perspectives identified in the research conducted to date, specifically the role of charge balance.

2.2.1 QDs PLQY Stability

The study by Gao et al.⁵⁹ verified that charge accumulation during operation can lead to the detachment of surface ligands, such as oleic acid, from QDs. This highlighted that accumulated electrons into the B-QDs-EML react with ligands, causing their detachment and leading to irreversible damage.

Lin et al.¹⁰⁸ report that the operational lifetime of B-QLEDs is negatively affected by the formation of hole traps within the QDs-EML, which leads to inefficient hole transport and increased trap-assisted recombination. The work used TrEL measurements to analyze the degradation mechanisms. The findings highlight the importance of improving charge balance within the device, as the presence of hole traps greatly reduces efficiency and accelerates degradation, presenting a critical challenge in the development of highly stable B-QLEDs.

Chen et al. reported that the lifetime of B-QLEDs is limited by significant surface-bulk coupling in QDs, where the interaction between surface states and the QDs core leads to charge-induced degradation, primarily due to electron accumulation. This electron accumulation exacerbates surface-bulk coupling, resulting in the formation of surface-localized charges that cause irreversible degradation of the QDs and reduce PL and EL stability over time. To address this, they designed B-QDs with a large core and a nonmonotonically-graded shell, which reduces surface-bulk coupling and mitigates electron-induced degradation without compromising charge injection. The resulting B-QLEDs achieved record-high operational lifetimes (T95) ranging from 75 to 227 hours at 1,000 cd/m², significantly surpassing existing benchmarks for B-QD-LEDs.

2.2.2 HTL stability

. The study by Zhang et al.¹⁰⁹ showed that oxidation at the B-QDs/HTL interface is a significant cause of degradation in B-QLEDs. They verified that severe hole accumulation at this interface makes the HTL prone to oxidation, leading to reduced device efficiency and lifetime. To mitigate this issue, an anti-oxidation transition layer, poly(p-phenylene benzobisoxazole) (PBO),

was introduced, which reduces oxidation, improves hole injection, and enhances overall device performance.

Kim et al.²⁰ reported that the lifetime of B-QLEDs is hindered by poor charge balance, especially a weak hole injection. To address this, double QDs-EML with a gradient chloride content is developed, which enhanced hole transport. The resulting device achieved efficiency near the theoretical limit, high brightness, and an extended operational lifetime.

Li et al.¹¹⁰ verified that the operational lifetime of B-QLEDs was significantly improved by developing a low-temperature cross-linked HTL using 4,4'-bis(3-(((4-vinylbenzyl)oxy)methyl)-9H-carbazol-9-yl)-1,1'-biphenyl (DV-CBP). This approach reduced the cross-linking temperature to 150°C and increased hole mobility to $1.01 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, leading to a substantial improvement in device performance. As a result, the B-QLEDs achieved a maximum EQE of 21.35% and extended the operational lifetime (T50) from 54.39 hours (for PVK-based devices) to 245.95 hours at 1000 cd/m².

Deng et al.³⁰ showed that the lifetime of B-QLEDs is negatively affected by electron leakage at the QD/HTL interface, which is further exacerbated by the energetic disorder of TFB HTLs. To address this issue, they developed a new HTL using poly((9,9-dioctylfluorenyl-2,7-diyl)-alt-(9-(2-ethylhexyl)-carbazole-3,6-diyl)) (PF8Cz), characterized by a shallower LUMO level and reduced energetic disorder. This structure minimized electron leakage and enhanced hole injection, resulting in B-QLEDs with a peak EQE of 21.9% and a significantly extended operational lifetime of 4,400 hours at 100 cd/m², marking a substantial advancement in the stability and efficiency of B-QLEDs.

Qu et al.⁶¹ reported that B-QLEDs are electron-dominated devices, as identified through impedance spectroscopy, which revealed more efficient electron injection compared to hole injection. This electron over-injection is confirmed by a lower built-in voltage for electron-only devices compared to hole-only devices. Additionally, they used R-QDs as a fluorescent sensor to demonstrate that the exciton recombination zone is near the HTL, further indicating electron dominance.

2.2.3 ETL stability

Chen et. al.⁴⁰ proposed that the degradation mechanisms in B-QLEDs differ significantly from those in red QLEDs, mainly due to charge accumulation at the QDs/ETL interface. In B-QLEDs, electrons excited in B-QDs tend to cross the junction between the QDs-EML and the ZnO ETL, leading to space-charge accumulation. This results in a rise in operating voltage and faster degradation compared to R-QLEDs. The charge imbalance, caused by inefficient electron injection, accelerates degradation, primarily at the QDs/ETL interface, where ZnO becomes unstable due to this accumulation. This process is further aggravated by charge transfer, which creates trap states that hinder electron injection and contribute to device EL loss.

Qu et al.¹¹¹ also reported that B-QLEDs suffer from insufficient electron injection due to the high potential barrier at the QDs/ZnO interface, leading to efficiency loss and reduced operational lifetime. To address this issue, they introduced an ultra-thin lithium fluoride (LiF) interfacial layer between the QDs-EML and the ZnO electron transport layer. This LiF layer facilitates electron tunneling, enhances electron injection, and suppresses exciton quenching at the QD/ZnO interface. As a result, the B-QLEDs achieved a maximum EQE of 9.8% and a current efficiency of 7.9 cd/A, both of which are significantly higher than those of the control devices, and the operational lifetime of the devices was doubled at an initial brightness of 1000 cd/m².

2.3 Conclusion

In summary, most studies in the literature have focused on upright QLEDs, leaving the investigation and optimization of inverted QLEDs, which are more compatible with oxide TFTs and OLEDs, largely unexplored. While charge imbalance has been identified as the primary factor contributing to poor efficiency in QLEDs, most research efforts have addressed this issue in single-color devices, particularly R-QLEDs, even though the charge supply properties of QDs may vary significantly with changes in the QDs bandgap. Additionally, although the interaction of excitons with excess carriers in QDs has been extensively studied in single-QDs systems or single-carrier devices, a significant knowledge gap remains regarding this effect within the QDs-EML structure in operational QLEDs, particularly in wide bandgap QDs. Moreover, while TFB HTL is commonly used in upright devices for all primary colors, inverted QLEDs still lack common HTLs that can be used across all colors while maintaining high efficiencies. Also, despite numerous efforts to improve charge balance in QLEDs by incorporating insulating interlayers, these additions increase the complexity of device fabrication, as their thickness must be precisely controlled.

Furthermore, numerous studies have investigated the degradation mechanisms in R and G QLEDs, but relatively few have focused on B-QLEDs. Although considerable advancements have been made in enhancing the EL stability of B-QLEDs through improvements in materials and design, its degradation mechanism is still not well understood. This is primarily due to the material and structural differences of B-QDs, which have wider bandgaps and more complex core-shell structures, leading to unique challenges in charge injection and recombination. Moreover, B-QDs tend to suffer from higher rates of charge accumulation, causing, Auger quenching, charge-induced defects, and surface degradation, further complicating their stability. Therefore, further research is crucial to gain a deeper understanding of these processes and develop strategies to significantly improve the EL stability of B-QLEDs.

Chapter 3. Research objectives and methodology

In this chapter, the research objectives are presented in Section 3.1, followed by the research rational described in Section 3.2. Finally, the research methodology and experimental details are explained in Section 3.3.

3.1 Research objectives

3.1.1 Identifying the causes of the low efficiency in the inverted QLEDs with polymer HTL.

- a) Finding an HTL solvent that minimizes damage to the QDs-EML in inverted QLEDs.
- b) Developing an architecture and fabrication recipe for inverted QLEDs that allows polymeric HTLs.
- c) Investigating correlations between the QDs-EML bandgap and charge carrier (electron and hole) supply efficiencies.

3.1.2 Investigating the degree of charge balance in inverted R, G and B-QLEDs and its influence on EL performance.

- a) Identifying the sequence of charge supply and the influence of excess carriers on the efficiency and lifetime of inverted R, G, and B-QLEDs by applying different conditions of electron and hole supplies.
- b) Investigating the interaction of excess carriers with excitons in inverted R, G, and B-QLEDs by spectroscopic characterization.
- c) Studying the impact of spontaneous electron transfer at the ETL/QDs-EML on the efficiency of inverted R, G, and B-QLEDs.

3.1.3 Exploring new ETL and HTL designs for optimizing charge injection and excitonic processes.

- a) Utilizing a double ETL approach to enhance the EQE and lifetime of inverted QLEDs.
- b) Doping the ETL to improve the electron supply into the QDs-EML in the inverted QLEDs.

3.1.4 Investigating the degree of charge balance in upright B-QLEDs and its influence on EL performance

- a) Identifying the sequence of charge supply and sensing electron and hole leakage by non-invasive marking layers.
- b) Characterizing EL and PL changes under electrical stress.

- c) Exploring the impact of charge leakage on device CTLs.

3.1.5 Exploring new ETL and HTL designs for optimizing charge injection and EL performance in upright B-QLEDs

- a) Limiting electron supply by modifying the cathode.
- b) Limiting electron supply by modifying the ETL.
- c) Enhancing hole supply by modifying the HTL.

3.2 Research Rational

3.2.1 Why Inverted QLEDs?

In order to achieve a large size and high-resolution display, an active-matrix driving scheme is essential. N-type metal-oxide semiconductors, such as ZnO and TiO₂, are potential candidates for the fabrication of thin film transistors (TFTs) in active-matrix back-panel owing to their superior electron mobility, chemical stability and robustness, film uniformity, and cost-efficient fabrication^{112, 113}. For the integration of QLEDs with an n-type TFT, the inverted device structure is preferred as the cathode of the inverted QLED can be directly connected to the drain of the TFT, thereby reducing the fabrication cost and increasing display resolution. Moreover, using an inverted architecture allows the modification of the ETL, such as annealing at high temperatures (>100°C) before depositing other device layers, which is necessary to achieve enhanced conductivity and improved ETL quality¹¹³.

3.2.2 Why investigating the charge balance condition in inverted QLEDs?

As previously discussed, the charge balance issue has primarily been studied in upright QLEDs. However, differences in the material systems between inverted and upright QLEDs result in differences in charge supply properties. Consequently, findings from upright QLEDs are unlikely to be directly applicable to inverted QLEDs, which must be studied independently. Furthermore, the charge imbalance issue has primarily been explored in single-color QDs, particularly in R-QLEDs, while G-QLEDs and B-QLEDs may exhibit different charge imbalance effects compared to R-QLEDs. Therefore, a comparative study of charge supply efficiencies across different colors is necessary. It is also well known that the primary consequence of charge imbalance is nonradiative Auger recombination. However, this effect has been widely studied in single QDs or single-carrier devices but not in real QLEDs. Hence, it is crucial to investigate this effect in real R-, G-, and B-QLEDs, as interactions between QDs and adjacent materials, such as

neighboring QDs and CTLs, can significantly affect it. This research could provide valuable insights, such as (i) determining the majority carrier type in inverted R-, G-, and B-QLEDs, (ii) assessing its impact on efficiency and EL stability, and (iii) exploring the interaction of majority carriers with excitons. Finally, based on these findings, new material systems will be implemented to optimize the performance of inverted QLEDs.

3.2.3 Why investigating the charge balance and EL loss mechanism in upright B-QLEDs?

Investigating the charge balance and EL loss mechanism in upright B-QLEDs is crucial due to their unique instability and degradation issues compared to R and G-QLEDs. B-QLEDs typically exhibit lower operational stability and efficiency, largely because of challenges related to charge imbalance and leakage, which accelerate degradation. By studying charge balance in upright B-QLEDs, one can better understand how electron and hole injection rates contribute to overall device performance. Moreover, this allows for the identification of failure mechanisms such as charge leakage through the CTLs, which leads to further performance degradation. Investigating these mechanisms is particularly important for improving device lifetime and maintaining stable EL performance. Understanding the EL loss mechanism is essential for developing strategies to mitigate degradation. This investigation will help pinpoint the exact causes of efficiency loss and enable the development of B-QLEDs with higher stability, pushing them closer to commercial viability.

3.3 Research methodology and experimental details

3.3.1 Device layout

The schematic overview of the fabricated devices is presented in Figure 3.1. The schematic highlights the coverage of the emissive and transport layers and the vertical overlap of the ITO and metal electrodes that define the device dimensions. Each device is manufactured on a 50.8 mm $\times$ 50.8 mm glass substrate with pre-patterned ITO electrodes that are approximately 100 nm thick and feature a resistivity of 20 Ω sq⁻¹. A total of 14 ITO electrodes (2 mm wide) are placed on opposite sides of the substrate to define one dimension of the device area. As the ITO pads approach the substrate edge, their width increases to 4 mm to ensure better contact with the test fixtures during measurement. On either side of the ITO sets, there are 7.4 mm thick ITO pads that serve as counter electrodes. These counter electrodes are connected by a 100 nm thick layer of Al, which defines the second dimension of the device. The overlap between the bottom ITO electrodes and the top Al electrodes results in devices with active areas measuring 2 mm $\times$ 2 mm. The B-QDs EML and CTLs are sandwiched between the two electrodes. A small rectangular feature on one of the ITO pads serves as a marker to indicate the orientation of the substrate. To explore different device structures, the substrate was segmented into four quarters, each containing three ITO pads. Consequently, in the statistics reported in this study, results are based on measurements from either two or four quarters, corresponding to a total of six or twelve devices, respectively.

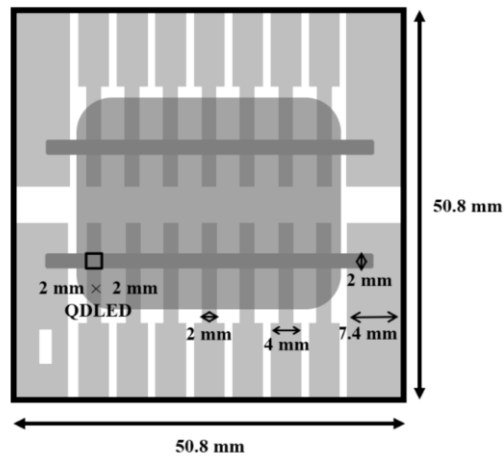


Figure 3.1 Schematic of the QLED substrate layout used in this study.

3.3.2 Device fabrication and material selection

This study focuses on inverted R, G, and B-QLEDs, as well as upright B-QLEDs, with the structures ITO/ETL/R, G, and B-QDs/HTL/HIL/Al for the inverted devices, and ITO/HIL/HTL/B-QDs/ETL/Al for the upright devices, respectively. The materials used, device fabrication process, and characterization techniques are thoroughly discussed in the subsequent sections.

3.3.2.1 CdSe/ZnS core/shell QDs-EML

In this work, Cd-based QDs are selected as the EML owing to their high PLQY and excellent chemical stability. All three colors (R, G, and B) of QDs which are dispersed in octane with the structure CdZnSe/CdZnS/ZnS for R and G, and CdZnSe/ZnSeS/ZnS for B-QDs, are purchased from Mesolight Inc. Figure 3.2a show the PL intensity, maximum PL (λ_{max}), PLQY, and full width at half maximum (FWHM) of R-QDs, G-QDs, and B-QDs films. Figure 3.2b shows their absorbance. In addition, Figure 3.2c compares the core and shell size of the QDs.

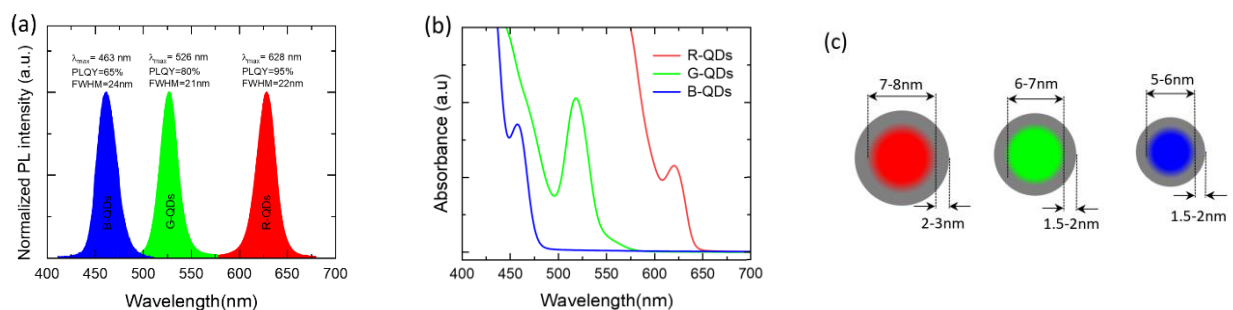


Figure 3.2 (a) PL, (b) absorbance spectra, and (c) core and shell size of R-QDs, G-QDs, and B-QDs.

3.3.2.2 ZnO and ZnMgO nanoparticle solution

In this study, ZnO and ZnMgO, purchased from SkySpring Nanomaterials, Inc and Mesolight Inc respectively, are employed as the ETL. Both are colloidal nano-sized particles dispersed in ethanol, deposited with solution-coating process. The solution-coating of ZnO and ZnMgO nanoparticles is carried out in a glove box with strict control over oxygen and moisture levels to ensure the optimal conditions for the coating process. After coating, ETL films should be annealed above 100°C in the glovebox. The annealing temperature is a factor that significantly affect the conductivity of ZnO and ZnMgO¹⁰², therefore annealing at high temperatures is used to improve the electron current supply.

3.3.2.3 HTL/HIL

CBP and TCTA small molecules and TFB polymer are used as the HTL in this work. CBP and TCTA are commonly used HTLs for hole injection in inverted QLEDs. CBP exhibits a deeper

HOMO and LUMO compared to the TCTA, proposing a more hole injection but less electron leakage blocking properties. The deposition of small molecules in this work is achieved through thermal evaporation performed in a high vacuum, which does not require any subsequent post-annealing process. Also, TFB as a polymeric HTL is coated using spin coating, followed by a baking process, both conducted under the controlled atmosphere of a glovebox filled with N₂. Also, three HIL materials, namely 1,4,5,8,9,11-Hexaazatriphenylene hexacarbonitrile (HAT-CN), MoO₃, and PEDOT:PSS are used in this study. HAT-CN and MoO₃ are deposited by using thermal evaporation under high vacuum conditions, while PEDOT:PSS is deposited by solution coating in ambient air.

3.3.2.4 Device fabrication.

Inverted QLEDs: The ITO-coated (100 nm) substrates are first cleaned with Micro 90 and sonicated with deionized water, then thoroughly rinsed with acetone and isopropanol, respectively. After drying with nitrogen gas, the substrates were treated with oxygen plasma for 5 min. Then, ETL (ZnO NPs or ZnMgO) dispersed in ethanol is spin-coated on the substrate at 3000 rpm for 60 sec (ZnO) or 40 sec (ZnMgO), followed by baking at 100-350 °C for 30 min. QDs dispersed in octane with a concentration of 12 mg/mL was deposited on the ETL as the EML at 3000 rpm for 60 sec. The deposited EML was baked at 50 °C for 30 min. The TFB with a concentration of 8 mg/mL was spin-coated at 4000 rpm for 40 sec, followed by baking at 120 °C for 15 min. The CBP, TCTA, MoO₃, HAT-CN, and the Al anode, were deposited using a thermal evaporation system (Angstrom Engineering) at 5×10^{-6} torr. The same recipes were followed in the fabrication of the single carrier devices. All the solution-coating and annealing steps are carried out in a nitrogen-filled glovebox.

Upright B-QLEDs: After cleaning the ITO substrate, the spin coating of PEDOT: PSS (filtered through a 0.22 µm PTFE filter) is performed at 5000 rpm for 60 s backed at 150 °C for 15 min in the air. Then, the substrates were moved to a glove box filled with nitrogen for the remaining steps of the device fabrication. The TFB HTL (8 mg mL⁻¹) dissolved in chlorobenzene was spin coated at 4000 rpm for 40 s followed by 20 min annealing at 120 °C. Afterward, the B-QDs (12.5 mg mL⁻¹) EML was spin coated at 3000 rpm for 60 s and annealed at 50 °C for 30 min. The ZnMgO NPs (25 mg mL⁻¹) layer dispersed in ethanol was spin coated at 3000 rpm for 40 s followed by 20 min of annealing at 100 °C. Then, 100 nm of the Aluminum (cathode) was subsequently deposited using a thermal evaporator (Angstrom Engineering) at a vacuum level of 5×10^{-6} Torr. For the

device with an Ag/Al cathode, the deposition process starts with 20 nm of Ag followed by 80 nm of Al. The encapsulation process is performed in a glove box by using an ultraviolet-curable resin. Finally, the devices were encapsulated using UV-curable resin glue and cover glass, cured under 365 nm UV radiation for 20 min. The active size of the QLEDs was 4 mm². Moreover, all the fabricated QLEDs exhibit a positive aging effect, i.e. the luminance is increased over time reached to its maximum value after 3 days. This process is known to occur in QLEDs encapsulated with a UV-curable acidic resin over time during storage.¹¹⁴

For the devices with QDs marking layer (ML) placed at the HTL side, QDs (4 mg mL⁻¹) layer was spin coated on the PEDOT:PSS layer at 3000 rpm for 60s with no subsequent annealing process before TFB deposition. Also, for the devices with QDs ML placed at the ETL side, the ZnMgO ETL is divided into two parts, with a QDs ML coated in between. The first ZnMgO (12.5 mg mL⁻¹) layer was spin coated at 4000 rpm for 40 s followed by annealing at 100 °C for 20 min. Then, the QDs (4 mg mL⁻¹) ML was spin coated, followed by the deposition of the second ZnMgO with a similar concentration and recipe as the first ZnMgO layer.

The rebuilding process in upright B-QLEDs was carried out on unencapsulated B-QLEDs in a nitrogen-filled glovebox. The Al cathode of a batch of devices, containing both unaged and aged B-QLEDs, was peeled off by Scotch tape. Then, the ZnMgO layer is washed off by spin coating (4000 rpm for 40 s) 200μL of ethanol. Subsequently, the B-QDs layer is washed off by spin coating (4000 rpm for 40 s) 150μL of octane. Finally, 200μL chlorobenzene was spun coated (3000 rpm for 60 s) to wash off the TFB layer. To rebuild the device, fresh layers of TFB, B-QDs-EML, ZnMgO, and Al were deposited and finally, the devices were encapsulated.

3.3.3 Experimental measurements

In this section, the measurement tools employed in this work will be introduced, along with a brief explanation of their purposes. Furthermore, an overview of the techniques utilized will be discussed.

3.3.3.1 Current density-voltage-luminance (J-V-L) measurement

The J-V-L measurement technique is employed to characterize the EL of QDLEDs by analyzing the relationship between current density (J), voltage (V), and luminance (L). This measurement provides valuable insights into the charge supply and transport behavior across the device and the overall EL efficiency.

3.3.3.2 PL and EL characterization

PL characterization measures the emitted photons from materials when they are optically excited. This technique helps to analyze the electronic transitions and photoluminescent properties of the QLEDs, providing valuable insights into their light emission behavior and optical characteristics. Also, EL in QLEDs is the process of light emission from the device when an electric current is applied. In QLEDs, this phenomenon occurs through carrier injection instead of optical excitation. EL characterization entails measuring the emitted photons and examining the electroluminescent properties of the QLEDs, such as their efficiency, color output, and spectral characteristics. Therefore, PL and EL emission spectra are measured to study the light emission properties of the materials used in QLEDs. PL spectra provide information about the photoluminescence of CTLs and QDs, while EL spectra reveal the electroluminescence behavior of QLEDs.

3.3.3.3 TrPL and TrEL

TrPL measurement is a technique used to study exciton decay rate and other dynamics in luminescent materials. It involves measuring the time-dependent decay of photoluminescence after excitation with a short pulse of light (375 nm wavelength). By analyzing the decay characteristics, such as the lifetime and intensity, valuable information about the radiative and non-radiative processes in the material can be obtained. TrPL measurements are particularly useful for investigating charge carrier recombination dynamics in QLEDs.

TrEL measurement is a technique used to study the transient behavior of light emission in electroluminescent materials. It involves measuring the time-dependent emission of photons under electrical excitation. By analyzing the emission characteristics, such as the intensity and response time, valuable insights into the charge carrier dynamics and recombination processes within the QLED device can be obtained. Therefore, both TrPL and TrEL techniques are utilized in this work to study the transient dynamics of the PL and EL.

3.3.3.4 Ultraviolet photoelectron spectroscopy (UPS)

UPS is a technique used to analyze the energy levels and electronic properties of materials. It involves shining ultraviolet light onto a sample, which causes the emission of photoelectrons. The energy distribution of these emitted electrons is measured, providing information about the electronic structure of the material. UPS can determine parameters such as the work function,

ionization potential, and valence band structure. In this work, UPS measurement is performed to identify the valence band level of the shell of the QDs.

3.3.3.5 UV-Vis spectroscopy

UV-Vis spectroscopy measures the absorption and transmission of ultraviolet (UV) and visible (Vis) light by a sample. It provides information about the electronic transitions and molecular structure of the sample. In this work, the bandgap of QDs is calculated using absorbance data.

3.3.3.6 Transmission electron microscopy (TEM)

TEM is an imaging technique that uses electrons to visualize the structure of materials at high resolution. It involves passing an electron beam through a thin specimen to generate an image, allowing for examination of the sample's morphology, size, shape, and crystal structure at the nanoscale. In this work, cross sectional TEM imaging is used to analyse the interface of QDs and TFB.

3.3.3.7 Raman Spectroscopy

Raman spectroscopy is a non-destructive analytical technique used to study the vibrational modes of molecules. It works by measuring the scattering of light from a laser when it interacts with the molecular vibrations, providing insights into the chemical structure, composition, and physical state of a material. To characterize the impact of electrical stress on PEDOT:PSS films in upright B-QLEDs, Raman spectroscopy measurements were performed.

3.3.3.8 Attenuated Total Reflectance Infrared (ATR-IR) spectroscopy

ATR-IR spectroscopy is a technique used to measure the infrared absorption of a sample. It involves directing infrared light through a crystal in contact with the sample, allowing the light to penetrate a few micrometers into the surface. This method is useful for analyzing surface properties and is commonly used for studying solids, liquids, and thin films without extensive sample preparation. In this work, ATR-IR spectroscopy is performed to explore the impact of electrical stress on PEDOT:PSS in upright B-QLEDs.

3.3.3.9 Device characterization

Device current–voltage–luminance (J–V–L) characteristics were measured using an Agilent 4155C semiconductor parameter analyzer connected to a silicon photodiode. The luminance of the QLEDs was collected with a Minolta Chroma Meter CS-100. To measure the EL and PL spectra, an Ocean Optics QE65000 spectrometer is used. A Newport 200 W xenon/mercury arc lamp excitation source and a monochromator were used for the PL measurements. An M6000PLUS

OLED lifetime test system was used to measure the QLEDs lifetime under a constant driving current of 20 mA/cm². TRPL measurements are performed using an Edinburgh Instruments FL920 spectrometer. The TEM images are obtained by a Thermo Scientific Talos 200X. UV–vis absorption measurements were performed with a Shimadzu UV-2501PC UV–vis spectrophotometer. The UPS measurements are carried out using a Thermo-VG Scientific ESCALab 250 microprobe equipped with Monochromatic Al K-alpha or Twin anodes (Mg or Al). To perform Raman spectroscopy, a Renishaw Raman microscope system with a laser at 632 nm is used.

Chapter 4. Identifying the causes of the low efficiency in the inverted QLEDs with polymer HTL

The material in this chapter is reprinted with permission from M. Azadinia et al. "Inverted solution-processed quantum dot light-emitting devices with wide band gap quantum dot interlayers", ACS Appl. Mater. Interfaces 2023, 15, 19, 23631–23641. Copyright 2024 American Chemical Society.

At the present time, most of the reported high-performance QLEDs have an upright architecture in which TFB and ZnMgO are utilized as HTL and ETL, respectively^{20, 43, 76}. In addition to its excellent hole mobility, $10^{-2}\sim 10^{-3}$ cm²/V.s, TFB has a suitable HOMO energy level of 5.5 eV, which facilitates hole injection into the QDs-EML^{91, 115, 116}. This together with excellent electron supply properties of ZnMgO has resulted in R, G, and B-QLEDs with upright structure and efficiencies above 20%^{30, 43}. On the other hand, to the best of our knowledge, inverted R, G, and B-QLEDs with a common ETL and HTL that demonstrate EQEs exceeding 20% have not been reported so far. Therefore, it is possible that the utilization of ZnMgO and TFB as CTLs in inverted structure QLEDs could yield efficiencies comparable to upright QLEDs. In addition, the ability to use a solution-coated material simplifies the device fabrication process and lowers the fabrication cost. Also, the capability to utilize cross-linkable polymers may provide additional advantages such as improving device stability. However, coating polymer HTLs on top of QDs-EMLs negatively affects them since most of the organic solvents used for coating these polymers can dissolve the hydrophobic QDs-EML^{41, 117}. To date, although many approaches have been attempted to address this issue, to the best of our knowledge, no previous studies have reported on high-performance inverted QLEDs utilizing TFB or other solution-coated materials as HTL that is directly deposited on the QDs-EML.

In this work, we find that the poor performance of inverted QLEDs with a polymer HTL arises primarily from electron leakage, inefficient charge injection, and significant exciton quenching at the HTL interface in the inverted architectures, and not due to solvent damage effects as is widely believed. We also find that using a layer of a wider bandgap QDs as an IL in between the HTL and the main QDs-EML can facilitate hole injection, suppress electron leakage, and reduce exciton quenching, effectively mitigating the poor interface effects and resulting in high EL performance. Using an IL in inverted QLED with a solution-processed TFB HTL improves the

efficiency 2.85X (from 3% to 8.56%) and prolongs the lifetime 9.4X (from 1,266 to 11,950 hours at 100 cd/m²), which, to the best of our knowledge, is the longest lifetime for an inverted R-QLED with a solution coated HTL. Measurements on single carrier devices reveal that while electron injection becomes easier as the bandgap of the QDs decreases, hole injection surprisingly becomes more difficult, indicating that EMLs of QLEDs are more electron rich in case of red devices and more hole rich in case of blue devices. UPS measurements verify that blue QDs have a shallower valence band energy than their red counterparts, corroborating these conclusions.

4.1 Finding an HTL solvent that minimizes damage to the QDs-EML in inverted QLEDs.

In an inverted QLED with a solution-coated HTL, damage to the QDs-EML by the HTL solvent during the coating process of the latter is a major consideration. Therefore, using a solvent that minimizes damage to the QDs layer is necessary. To this end, three commonly used organic solvents; chlorobenzene, 1,2-dichlorobenzene, and 1,4-dioxane, are investigated as possible HTL solvents, and their effect on the underlying QDs film is investigated. As any erosion or solvent damage to the QDs films will lead to a decrease in their PL output, QDs films are prepared and their PL spectra before and after rinsing with the solvents are compared. Two groups of QDs film samples were prepared and tested. In the first group, the samples consisted of only single R-QDs films, prepared using a 12 mg/mL QDs solution similar to those used in making QLED-EMLs, coated on glass substrates. In the second group, each sample additionally has a thin film of B- QDs coated using a 4 mg/mL solution on the R-QDs film. This layer is used as a marking layer for probing surface erosion during the solvent rinsing step.

Figure 4.1(a) depicts the PL spectra collected from the samples initially and after rinsing with chlorobenzene. As seen, by coating the B-QDs marking layers on the R-QDs, the R-QDs layer losses about 10% of its initial PL intensity (at 630nm) in the initial spectra while a blue band with a peak at 460nm appears as seen more clearly in the inset. This indicates that the deposition of the wide bandgap QDs material does not significantly damage the underlying R-QDs layer. After rinsing with chlorobenzene, the red bands in both samples (i.e. the samples without and with the B-QDs layer) decrease to about 60% of their initial intensities, and the blue band disappears indicating significant erosion by the solvent and the removal of the top layer. Rinsing the samples with 1,2-dichloroethane similarly damages the films, again leading to a significant decrease in the

red PL band and the disappearance of the blue band, as can be seen from Figure 4.1(b). Interestingly, 1,4-dioxane causes the least damage to the QDs films, evident from the retention of the blue band and the less than 10% decrease in the red band in this case as seen in Figure 4.1(c). Based on these results, 1,4-dioxane is selected as the TFB solvent for the fabrication of the QLEDs in this work.

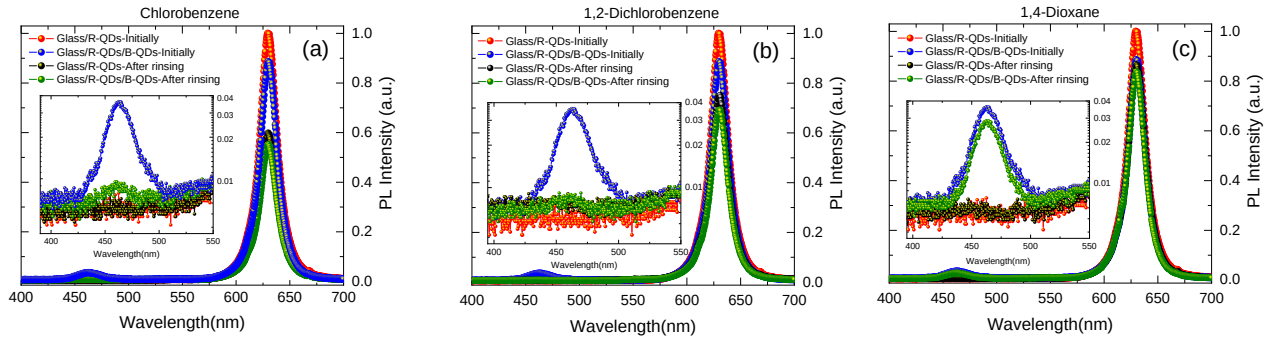


Figure 4.1. Normalized PL spectra from Glass/R-QDs (12mg/mL) and Glass/R-QDs (12 mg/mL)/B-QDs (4 mg/mL) samples, initially and after rinsing with (a) Chlorobenzene, (b) 1,2-Dichlorobenzene, and (c) 1,4-Dioxane. The insets show the blue regions of the same spectra in logarithmic scale.

Table 4.1. The statistical averages and standard deviations of the devices voltages, luminances and EQEs at 20mA/cm² for each set of devices of the same structure.

Device Structure	Driving Voltage	EQE	Luminance
Device A	4.03 ±0.14	2.97 ±0.12	810 ±34
Device B	2.83 ±0.063	12.89 ±0.74	3027 ±176
Device C	5.91 ±0.17	2.09 ±0.25	575 ±70
Device D	4.19 ±0.18	12.27 ±0.51	3375 ±140
R-IQLEDs W B-QDs-IL	5.75 ±0.19	8.8 ±0.73	2307 ±193
R-IQLED W G-QDs-IL	4.74 ±0.16	3.89 ±0.24	1072 ±66
R-IQLED Rinsed with octane	5.95 ±0.18	2.11 ±0.25	551 ±67
G-IQLED W/O-IL	2.96 ±0.16	0.23 ±0.05	193 ±47
G-IQLED W B-QDs-IL	3.31 ±0.17	1.4 ±0.1	1600 ±116

A group of six inverted R-QLEDs with the structure of ITO/ZnO NPs/R-QDs/TFB/HAT-CN/Al, referred to herein as device A, are fabricated and tested. The statistical averages and standard deviations of the devices voltages, luminances, and EQEs at 20 mA/cm² as well as of devices discussed later in this work are presented in Table 4.1. Figure 4.2 shows typical Current Density vs Voltage (J-V), Luminance vs Voltage (L-V), and EQE vs J characteristics of devices of this structure. As seen, the devices exhibit a maximum EQE of only 3% despite the use of 1,4-dioxane as the TFB solvent. Such a low EQE was unexpected given the limited solvent damage effect of the 1,4-dioxane on the QDs layer as established above, and suggested that additional

factors might be involved in the low efficiency. Therefore, in order to glean some insights into the causes of the lower efficiency, groups of devices of three other structures (B, C and D), each comprising six devices of the same structure, were also fabricated and their EL properties compared with A. Their structures were as follows:

- Device B: ITO/PEDOT:PSS/TFB/R-QDs/ZnO NPs/Al, essentially an upright device made of the same materials as A with the exception of the HIL which was made of PEDOT:PSS instead of HAT-CN since the latter is easily removed by the TFB solvent.
- Device C: ITO/ZnO NPs/R-QDs/TFB/MoO₃/Al, essentially a device of the same structure as A but with MoO₃ instead of HAT-CN as the HIL.
- Device D: ITO/ZnO NPs/R-QDs/CBP (vacuum deposited) /MoO₃/Al, essentially a device of the same structure as C in which the TFB layer is replaced by a vacuum-deposited layer of CBP.

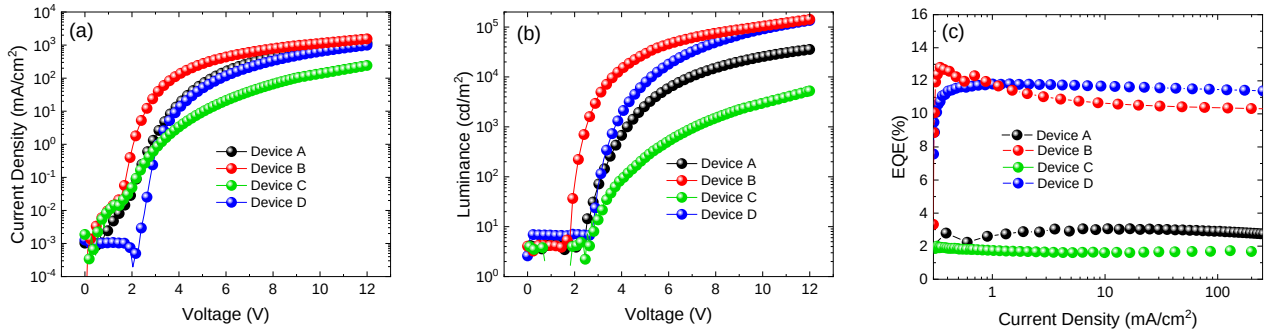


Figure 4.2. (a) J - V , (b) L - V and (c) EQE - J characteristics of devices A, B, C and D with structures as described in the text.

As can be seen, device B exhibits a maximum EQE of 12.8 %, more than 4X higher than that of device A. The high efficiency of device B rules out that the low EQE of device A might be due to any intrinsic limitations in the TFB, QDs or ZnO NP layers. Also, as seen from Device C, changing the HIL material has a very little effect on EQE ruling out the possibility that the low efficiency of device A could be due to poor hole injection into the TFB layer from HAT-CN, the latter being the only different material in device B versus A. In contrast, the maximum EQE of device D, with the vacuum deposited HTL, is ~12%, on par with that of device B with the upright architecture, indicating that the low efficiency of A can not be due to electron supply issues across the ZnO bulk or ZnO/EML interface in the inverted architecture. The stark difference in EQE between device D and A combined with the high EQE of device B conclusively point to differences in the QDs-EML bulk or QDs-EML/TFB interface in the inverted versus the upright architecture

being the main reason behind the low device efficiency of A. However, knowing that the TFB solvent (1,4-Dioxane) does not significantly affect the QDs-EML bulk (from Figure 4.1c), the results suggest that the differences are likely limited to the interface between the QDs-EML and the HTL indicating that differences between the QDs-EML/TFB interface (i.e. in the inverted architecture) and the TFB/QDs-EML interface (i.e. in the upright architecture) might be the culprit.

It should be noted that, due to the higher charge carrier mobility in ZnO relative to organic HTLs and the large energy offsets between the HTL materials HOMO (Highest Occupied Molecular Orbital) and the valence band of the QDs, electron-hole recombination in the QDs-EML will occur mostly near the interface with the HTL¹¹⁸⁻¹²⁰. Therefore, the quality of this interface, and whether it has a large number of sub bandgap states or other exciton quenching defects, can directly affect device EQE. Inserting interfacial layers (IL) at the QDs/TFB interface may therefore reduce such quenching effects and improve device efficiency.

4.2 Developing an architecture and fabrication recipe for inverted QLEDs that allows polymeric HTLs.

Inserting an insulating IL in between the QDs-EML and the HTL has been used in the past as an approach for protecting the QDs-EML from damage by HTL solvents^{86, 103, 121}. The use of insulating materials in ILs can however negatively affect charge injection, especially if their thickness is not kept to below 10 nm, a requirement that is often difficult to control. Therefore, instead of using an insulating material, we investigated the use of a wider bandgap QDs, in this case B-QDs, as an IL in between the R-QDs-EML and the TFB HTL. With its wider bandgap relative to the QDs-EML, one can expect a B-QDs-IL to function as an exciton blocking layer that reduces the quenching of excitons of the main QDs-EML (i.e. the R-QDs) by defects at the HTL interface. In addition, based on the PL results in Figure 4.1, coating B-QDs on top of R-QDs films does not lead to any significant damage to the latter suggesting that a B-QDs-IL can be a safe choice from a device fabrication standpoint.

Inverted R-QLEDs with B-QDs-ILs made of B-QDs solutions of different concentrations (0, 2, 4, 6, 8, 10 and 12 mg/mL) were therefore fabricated and tested. Figure 4.3a shows a schematic diagram of the general device structure. Figure 4.4 presents the J-V-L, EQE-J and the EL spectra of these devices along with characteristics from reference devices without the B-QDs-

IL (denoted to by 0 mg/mL in the legend) for comparison. As can be seen from the figure, using the IL significantly improves device efficiency, with a concentration of a 6 mg/mL (which produces an IL of a thickness of 15 nm, as verified by Dektak-150 profilometer) IL giving the highest EQE (8.56% versus only 3% in case of the reference). Also, as seen, by increasing the IL thickness, the J-V characteristics shift to higher voltages, causing the current density at any given voltage to decrease. Also, by inserting the IL, a blue band appears as can be seen in the normalized EL spectra, the magnitude of which correlates with the IL thickness, indicating that some electron-hole (e-h) recombination takes place in the IL. Seeing this band in the EL spectra again confirms that the TFB solvent (1,4-dioxane) does not significantly alter or erode the QDs layers (both the QDs-EML and the B-QDs-IL) or lead to intermixing between them (or else efficient energy transfer from the B-QDs to the R-QDs would have rendered observing EL from the B-QDs impossible). Figure 4.3 (b) depicts the changes in the maximum EQE with the IL concentration. As a 15nm thick IL (6mg/mL) gives the highest EQE, this IL thickness is considered to be optimum and used for the rest of this work. The J-V, EQE-J and EL spectral characteristics of the inverted R-QLEDs without (W/O) and with (W) the 15 nm thick B-QDs IL are provided in Figures 4.3 (c), (d) and (e), respectively, for comparison with other results later.

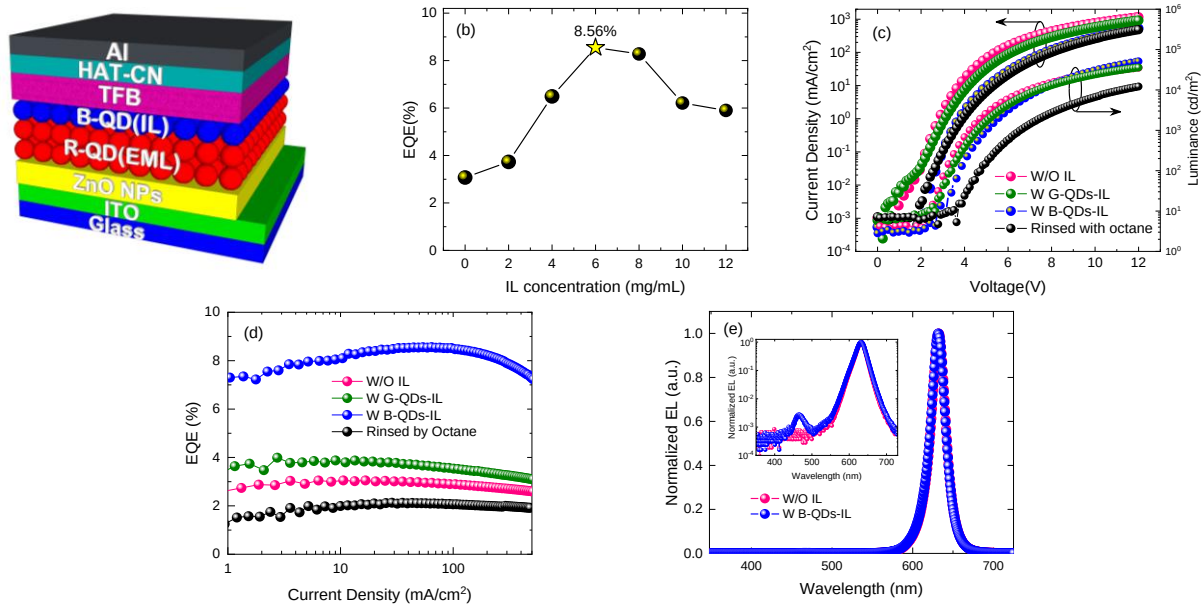


Figure 4.3. (a) Schematic diagram of the general device structure. (b) EQE versus B-QDs IL concentration of the inverted R-QLEDs, (c) J-V-L and (d) EQE-J characteristics of the inverted R-QLED without (W/O) an IL and with (W) G-QDs-IL or B-QDs-IL. Characteristics from an inverted R-QLED in which the QD-EML is rinsed with octane are also provided for comparison. (e) Normalized EL spectra of the same inverted R-QLEDs without (W/O) an IL and with (W) B-QDs-IL.

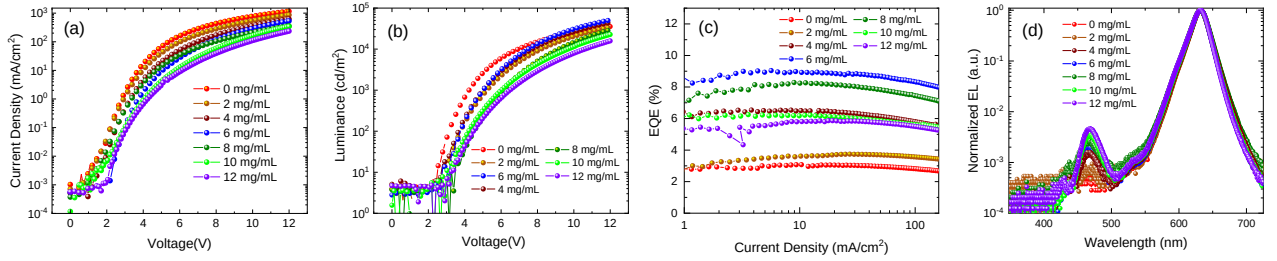


Figure 4.4: (a) J - V , (b) L - V , (c) EQE - J characteristics, and (d) normalized EL spectra of inverted R - $QLED$ containing B - QDs - ILs made of solution of different concentrations (with different thicknesses). The 0 mg/mL curve represents a device without IL .

Besides an expected reduction in exciton quenching at the HTL interface, the increase in EQE upon using the B - QDs - IL can also be attributed to two other possible roles for the IL ; i) a modification or reorganization in the QDs - EML by the B - QDs - IL solvent as both QDs materials (in the EML and IL) utilize the same solvent (octane), and/or ii) improving charge balance as a result of the differences in the conduction and valence bands of the B - QDs relative to the R - QDs , especially in view of the shift in the J - V characteristics towards higher voltages which may suggest that the IL reduces hole injection into, or electron leakage from, the QDs - EML , possibly leading to more favourable e/h concentrations in the QDs - EML . Therefore, to first investigate the impact of the IL solvent on the QDs - EML , an inverted R - $QLED$ without an IL but in which the R - QDs - EML is instead exposed to neat octane via spin following the same process used in coating the IL , before coating the TFB HTL, is fabricated and tested. Data from this device is included in Figures 4.3 (c) and 4.3(d), denoted to by “Rinsed with Octane”. As can be seen, subjecting the QD - EML to octane reduces the maximum EQE to about 2.1 % which is almost 30% lower than that of the device without the IL . This suggests that the exposure of the QDs - EML to octane is not a primary factor in the performance enhancement attained by using the IL . We also note a reduction in current density in case of the device rinsed with octane. This reduction may be attributed to a partial removal of organic ligands by the solvent which could increase QDs surface trap states or partially modify their surface energy, in turn affecting injection properties^{122 123}. Next, to explore the possible impact of the new energy barriers induced by the IL on electron leakage and hole injection, G - QDs , with a bandgap still wider than R - QDs - EML but smaller than the B - QDs , are utilized for the IL in another set of devices. One can expect the differences in their conduction and valence bands to lead to different energy barriers for both injecting holes into, and blocking electrons

leakage from, the QDs-EML. The J-V-L and EQE-J characteristics of these devices are also provided in Figures 4.3(c) and 4.3(d). As can be seen, the G-QDs-IL leads to a similar, albeit weaker, effect on device performance, again decreasing the device current density at any given voltage and increasing the EQE. Interestingly, a comparison of the characteristics of the devices with the G-QDs-IL and the B-QDs-IL suggests a correlation between the magnitude of the band gap and device performance may exist, with the wider bandgap leading to a higher EQE and a larger shift in the J-V characteristics. These observations suggest that the efficiency enhancement attained by the ILs results – at least in part - from a better charge balance in the devices due to the reduction of either the hole current (by decreasing the hole injection) or the electron current (by reducing the leakage of electrons to the HTL). The basic parameters of the devices under a constant current density of 20 mA/cm² are summarized in Table 4.2.

Table 4.2. Driving voltage, luminance, CIE values, and EQE at 20mA/cm² of the devices without interlayer, rinsed with octane, and with G-QDs-IL, and B-QDs-IL.

	Voltage (V)	Luminance (cd/m ²)	CIE		EQE (%)
			X	Y	
W/O IL	4.09	800	0.67	0.33	3
Rinsed with octane	5.93	550	0.67	0.33	2.1
W G-QDs-IL	4.72	1050	0.67	0.33	3.82
W B-QDs-IL	5.69	2250	0.66	0.33	8.56

To investigate if these observations and effects are specific to inverted R-QLEDs, green emitting inverted QLEDs (G-QLEDs) without and with B-QDs-IL were also fabricated and tested. Figure 4.5 shows the J-V-L, EQE-J, and normalized EL spectra characteristics of these devices. As seen, the use of the B-QDs-IL also leads to a significant improvement in the G-QLED performance. Similar to the R-QLEDs, the IL decreases the current density and increases the luminance at any given voltage (Figure 4.5(a)), resulting in a significant increase in device EQE (Figure 4.5(b)). An examination of the EL spectra again reveals the presence of a blue EL band in the devices with the IL (Figure 4.5(c)). Interestingly, in this case, the blue emission band was relatively stronger (3% of the height of the main EL band in the normalized spectra versus only 0.3% of the height of the main EL band in the case of the R-QLEDs in figure 4.3(e)). Such significant difference in the relative heights of the blue bands in the G-QLEDs versus the R-QLEDs suggests that a larger fraction of e-h recombination takes place in the IL in case of the G-QLEDs than in the R-QLEDs,

indicating that electron leakage from the QDs-EML to the IL, and therefore possibly also to the HTL, may be higher in the green devices. Alternatively, it could be due to different rates of exciton energy transfer from the B-QDs-IL to the R-QDs-EML versus the G-QDs-EML by the Förster process (FRET) which can be expected to be more efficient in case of the R-QD EML because of the smaller bandgap and therefore reduces the blue EL.

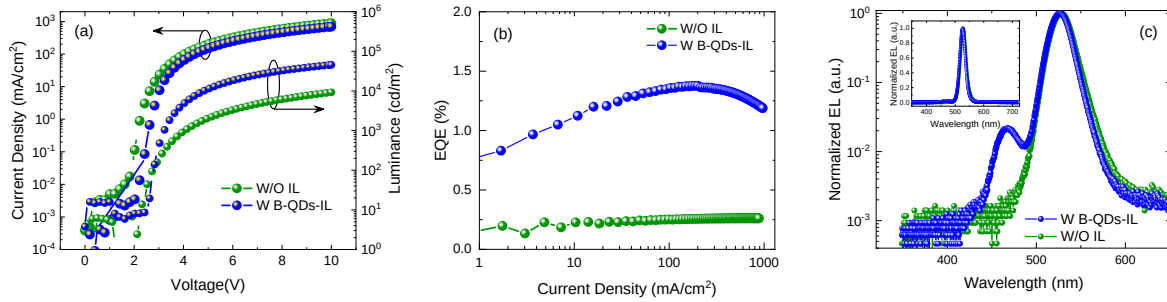


Figure 4.5. (a) *J-V-L*, (b) *EQE-J*, and (c) *normalized EL spectra characteristics of the inverted G-QLEDs without (W/O) and with (W) B-QDs-IL.*

To compare the rates of exciton energy transfer from the B-QDs-IL to the R-QDs-EML versus the G-QDs-EML by FRET, the PL intensity of the Glass/R-QDs (32nm)/B-QDs (0nm or 15nm) and Glass/G-QDs (32nm)/B-QDs (0nm or 15nm) are measured (Figure 4.6) and the FRET enhancement factor Q is calculated using the equation^{35, 124}:

$$Q = \frac{(PL_A(G-QDs) - PL_{DA}(G-QDs))}{(PL_A(R-QDs) - PL_{DA}(R-QDs))} \quad (1)$$

where PL_A and PL_{DA} are the PL intensity of the acceptor (G-QDs or R-QDs) in the absence and presence of the (B-QDs), respectively, in each case. The calculations give a $Q \sim 3.62$, confirming the lower FRET energy transfer rate to the G-QDs.

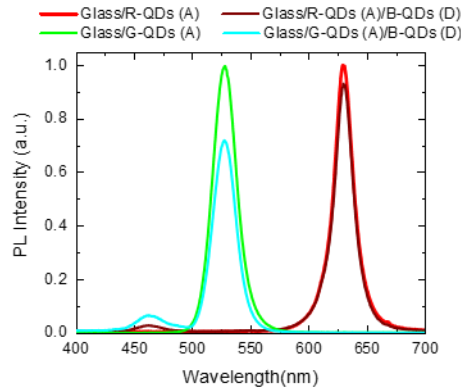


Figure 4.6 *PL intensity of samples with the structure of Glass/R-QDs (A), Glass/R-QDs (A)/B-QDs(D), Glass/G-QDs (A), and Glass/G-QDs (A)/B-QDs(D). A and D show donor and acceptor. The thicknesses of acceptors and donor are about 32nm and 15nm, respectively.*

4.3 Investigating correlation between the QDs-EML bandgap and charge carrier (electron and hole) supply efficiencies.

As mentioned earlier, one possible reason for the shift in the J-V characteristics towards higher voltages upon using the ILs is a reduction in hole injection. Therefore, in order to investigate how the insertion of the wide bandgap IL affects hole injection into the QDs-EMLs, a series of HODs with various QDs layers (R, G and B) with and without a wider band gap QDs-ILs as an additional layer are fabricated. Figures 4.7 (a-j) depict the energy band levels of the fabricated HODs, biased under both forward bias (i.e. with Al at a more positive bias relative to the ITO contact) and reverse bias conditions. First, HODs with only R-QDs, G-QDs, and B-QDs layers (of structure: ITO/PEDOT:PSS/TFB/QDs/TFB/HAT-CN/Al as depicted in Figures 4.7 (a) and (b) are tested. Figure 4.8a shows the J-V characteristics of this set of HODs under forward and reverse bias (FWB, and RVB, respectively). One can see a clear correlation, for both forward and reverse bias conditions, between the QDs bandgap and the magnitude of the hole current density, with the current at any given voltage becoming higher as the QDs bandgap increases suggesting that hole injection and transport becomes easier in the same direction. This conclusion is somewhat counterintuitive since it is generally assumed that QDs with wider bandgaps will have deeper valence bands which would make hole injection into them more difficult. This observation is however consistent with some recent reports^{125, 126}. Such observation suggests that using QDs with wider bandgaps relative to those in the QDs-EMLs as ILs in QLEDs may indeed facilitate hole injection into these QDs-EMLs.

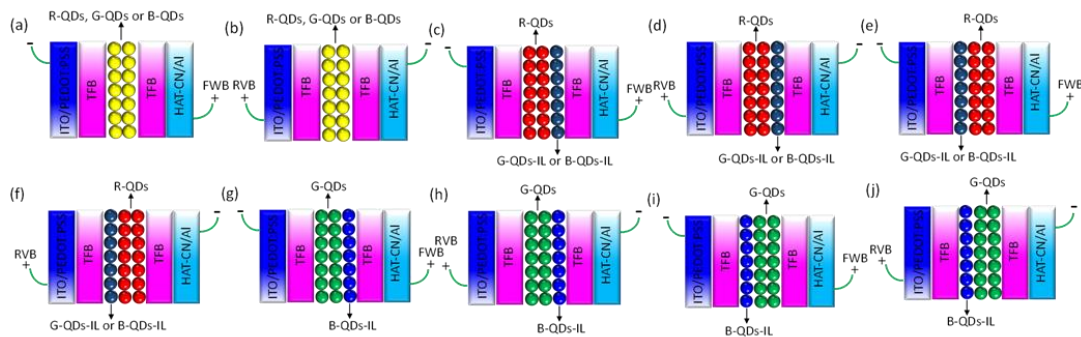


Figure 4.7. Schematic diagrams of the HODs with R-QDs, G-QDs, or B-QDs layers under (a) forward bias (FWB) and (b) reverse bias (RVB), HODs containing G-QDs-IL or B-QDs-IL on the R-QDs layer under (c) FWB and (d) RVB, HODs with R-QDs layer on G-QDs-IL and B-QDs-IL under (e) FWB and (f) RVB, HODs containing B-QDs-IL on the G-QDs layer under (g) FWB and (h) RVB, and HODs with G-QDs layer on B-QDs-IL under (i) FWB and (j) RVB.

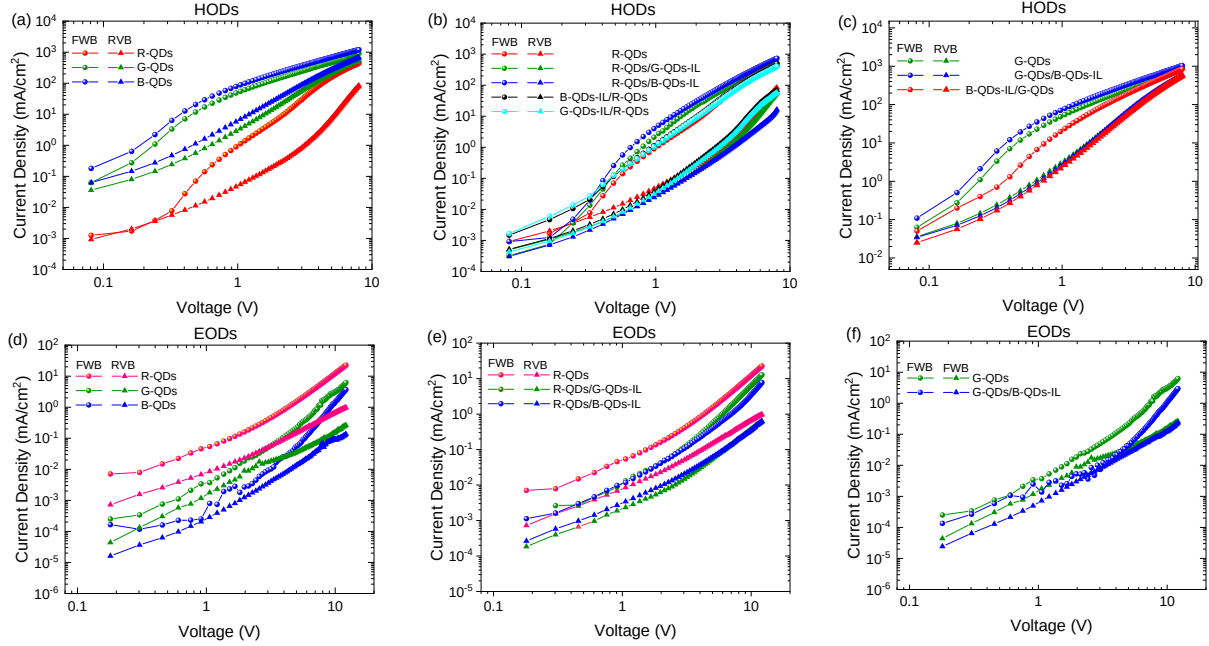


Figure 4.8. *J-V characteristics of (a) HODs with R-QDs, G-QDs, or B-QDs layers (b) HODs containing G-QDs-IL or B-QDs-IL on either side of the R-QDs layer, (c) HODs containing B-QDs-IL on either side of the G-QDs layer, (d) EODs with R-QDs, G-QDs, or B-QDs layers, (e) EODs containing G-QDs-IL or B-QDs-IL on either side of the R-QDs layer, (f) EODs containing B-QDs-IL on either side of the G-QDs layer.*

Therefore, to investigate this effect further, HODs with R-QDs layers that further contain B-QDs or G-QDs-ILs on either side of the R-QDs layers (i.e. of structures ITO/PEDOT:PSS/TFB/R-QDs/IL/TFB/HAT-CN/Al as depicted in figures 4.7 (c) and (d); and ITO/PEDOT:PSS/TFB/IL/R-QDs/TFB/HAT-CN/Al as depicted in figures 4.7 (e) and (f)) are fabricated and tested. The J-V characteristics of this set of HODs under forward and reverse biases are presented in Figure 4.8 (b). Interestingly, ILs located above the R-QDs layer (i.e. in the TFB/R-QDs/IL/TFB sequence with the ILs made of G- or B-QDs) increase the device hole current under forward bias condition, i.e. when the holes are injected into the R-QDs layer through them. In contrast, ILs located below the R-QDs layers (i.e. in the TFB/IL/R-QDs/TFB sequence with the ILs made of G- or B-QDs) do not have a similar current-enhancing effect when the holes are injected into the QDs layer through them (i.e. under reverse bias condition). This suggests that hole injection across the TFB/R-QDs interface (i.e. the case of upright QLEDs) is much more efficient than across the R-QLEDs/TFB interface (i.e. the case of inverted QLEDs) and therefore does not similarly benefit from the insertion of the wider band gap QDs-IL. Such an observation clearly shows that the order of the two layers significantly impacts the morphological and electronic properties of the interface and that the QDs-EML/TFB interface likely has much more

defects relative to the TFB/QDs-EML a phenomenon that must play a role in the lower EL performance of inverted QLEDs with solution coated HTLs than their upright counterparts. Such defects could possibly arise from morphological factors associated with differences in wetting properties and/or a partial removal of QD ligands by the TFB solvent and thus affect inverted devices^{122, 127, 128}. Using an IL made of a wider band gap QDs at this interface effectively mitigates some of the negative effects of these defects and improves hole injection across the interface. Conversely, the ILs have very little effect on J-Vs in all scenarios where holes are injected into the R-QDs layer first before reaching the IL, indicating that the wide bandgap ILs do not reduce the leakage of holes from the QDs-EML towards the counter electrode. Similar tests on HODs with G-QDs layers (instead of R-QDs layers) with and without ILs (in this case only B-QDs-IL) of structures as depicted in Figures 4.7 (g) through (j)) yield essentially the same results. The results from these devices are presented in Figure 4.8 (c).

Finding that the use of ILs made of wider bandgap QDs helps increase, rather than decrease, hole injection at the QDs-EML/TFB interface, it follows that the EQE enhancement observed in the inverted QLEDs upon using the ILs can not be due to a reduction in hole injection, indicating that the associated decrease in current observed in these inverted QLEDs must be due to other reasons, such as a reduction in electron leakage, imparted by the presence of the ILs. We therefore also test the ILs in EODs to investigate their effect on electron transport (i.e. with Al at a more positive bias relative to the ITO contact) and reverse bias conditions. EODs with the structures ITO/ZnO NPs/QDs/ZnO NPs/Al and ITO/ZnO NPs/QDs/IL/ ZnO NPs/Al as depicted in Figure 4.9 (a-f) are fabricated and tested under both forward and reverse bias conditions. In case of EODs, a forward bias corresponds to having a more positive potential on the Al relative to the ITO contact. The J-V characteristics of the EODs are presented in Figures 4.8 (d-f). From Figure 4.8 (d), it can be seen that, opposite to the HODs, the electron current density at any given voltage decreases as the bandgap of the QDs material increases (i.e. highest in case of the R-QDs and lowest in case of the B-QDs) in both forward and reverse bias conditions. We also note the lower currents at any given voltage in case of EODs relative to HODs which we attribute to the lower conductivity of the top ZnO layer which is annealed at a lower temperature in order to avoid damaging the underlying QDs layer. Seen in combination with observations from the HODs under forward and reverse bias one can make a conclusion that in QLEDs in general, whether inverted or upright, the EMLs will generally be more electron rich (i.e. have a high e/h ratio) in case of red

devices and more hole rich (i.e. have a lower e/h ratio) in case of blue devices, with green devices being somewhere in between. Here also, and again opposite from the case of the HODs, the insertion of an IL reduces currents at any given voltage under both forward bias (i.e. when the electrons are injected into the main QDs layer through the IL) and reverse bias (i.e. when the electrons are removed from the QDs layer through the IL) indicating that the use of a wide bandgap QDs-IL reduces both electron injection into, and electron leakage from, the main QDs layer, a behavior that can be readily attributed to their expectedly shallower conduction band minimum relative to that of the main QDs layer. In view of these results, we can attribute the higher EQE of the IQLEDs with the ILs - at least in part – to their role in reducing electron leakage from the QDs-EML to the TFB HTL, a phenomenon that is likely exacerbated by the poor hole injection at the QDs-EML/HTL interface in case of inverted devices.

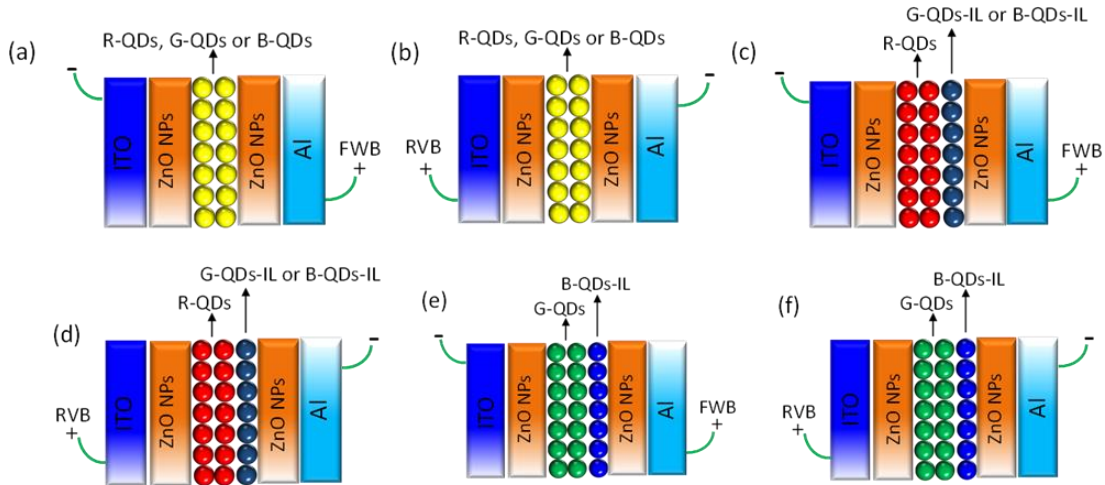


Figure 4.9. Schematic diagrams of the EODs with R-QDs, G-QDs, or B-QDs layers under (a) forward bias (FWB) and (b) reverse bias (RVB), EODs containing G-QDs-IL or B-QDs-IL on the R-QDs layer under (c) FWB and (d) RVB, and EODs containing B-QDs-IL on the G-QDs layer under (e) FWB and (f) RVB.

In order to further verify this conclusion, UPS measurements using a monochromatic He I light source are employed for probing and compare the energies of the valance band edge in the R, G, and B-QDs. 30nm thick films of R, G, and B-QDs were coated on ITO coated glass and transferred to the UPS chamber without exposure to air. Figure 4.10a shows the secondary electron cutoff and Fermi-edge regions from UPS measurements for the QDs. As can be seen, the binding energy of valance electrons decreases in the order, R, G, and B-QDs. By considering a photon energy of 21.2 eV for excitation, the calculated valance band levels are 7.21 eV, 7.07eV and 6.92eV for R, G, and B-QDs respectively, confirming that the B-QDs have the shallowest valance energy

level and R-QDs the deepest as depicted in Figure 4.10b. We have also carried out optical absorption measurements on the three materials as shown in figure 4.10c. From the shallower valance band level of the B-QDs, and its larger bandgap relative to the R-QDs, it also follows that the conduction band energy of the B-QDs must be much shallower than that of the R-QDs, thus confirming the conclusion that the interlayer can also effectively block the electron leakage.

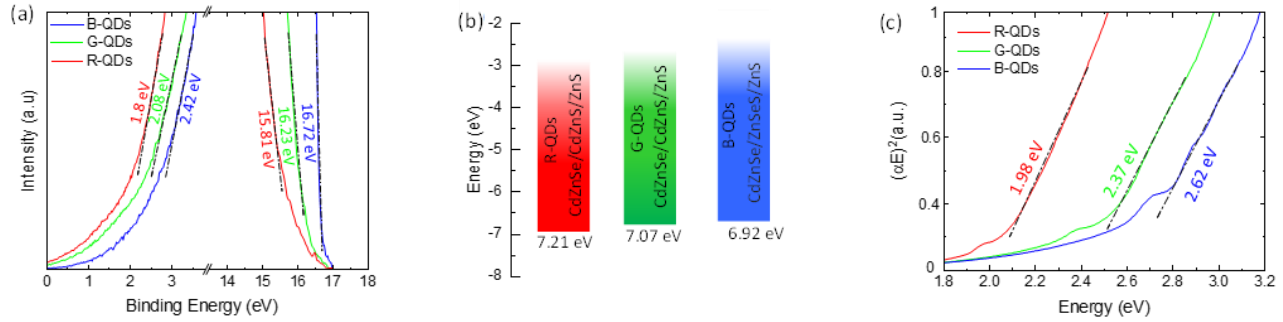


Figure 4.10. (a) UPS spectra, (b) valance band level calculated from the secondary electron cutoff and Fermi-edge regions from UPS measurements, and (c) Tauc plots of R-QDs, G-QDs and B-QDs.

Next, transient PL (TRPL) measurements are used to investigate if the presence of the IL may also be reducing exciton quenching at the TFB interface, as was also suggested earlier, an effect that may also be contributing to the EQE enhancement. Three different film samples on glass substrates are prepared: Glass/R-QDs(32nm), Glass/R-QDs(32nm)/TFB(25nm), and Glass/R-QDs(32nm)/B-QDs-IL(15nm)/TFB (25nm), and their TRPL characteristics at 633nm, using 330nm excitation, are collected. As shown in Figure 4.11a, the R-QDs exciton lifetime becomes shorter when the TFB is coated on it, pointing to some exciton quenching at the QDs/TFB interface. It is also observed that using an IL substantially reduces this quenching effect, maintaining the exciton lifetime near its original value. This can be attributed to the role of the wider band gap QDs in the IL in blocking the diffusion of excitons from the main QDs layer to the TFB interface where they can get quenched. Therefore, in addition to their role in reducing the leakage of electrons from the QDs-EML, reducing exciton quenching at the QDs-EML/TFB may also be a factor in the higher EQE of IQLEDs with ILs.

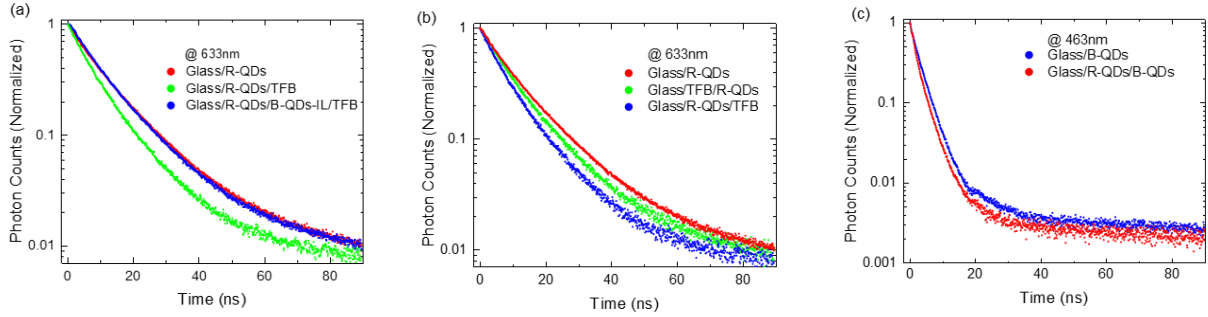


Figure 4.11. TRPL characteristics of samples with the structure of (a) Glass/R-QDs, Glass/R-QDs/TFB, and Glass/R-QDs/B-QDs-IL/TFB (collected at 633 nm), (b) Glass/R-QDs, Glass/TFB/R-QDs, and Glass/R-QDs/TFB (collected at 633 nm), (c) Glass/B-QDs and Glass/R-QDs/B-QDs (collected at 463 nm).

In addition, to further investigate the impact of the layers order on the quality of the interface, and if the QDs-EML/TFB interface might indeed have more quenching defects in comparison to the TFB/QDs-EML interface, we also test and compare the TRPL characteristics of film samples of Glass/R-QDs(32nm), Glass/R-QDs(32nm)/TFB(25nm), and Glass/TFB(30nm)/QDs(35nm). The results are provided in Figure 4.11b. As seen, while the affect exciton lifetime is shorter in the two samples where TFB is present in comparison to the R-QDs only sample which indicates that some exciton quenching occurs at the TFB interfaces in both cases, the exciton lifetime was shorter in case of Glass/R-QDs/TFB versus Glass/TFB/R-QDs pointing to more quenching in the first, verifying that the order of coating the layers indeed affects the quality of the interface and that the QDs-EML/TFB interface (in inverted devices) has more quenching defects relative to that in upright devices. This may also explain why hole injection from the TFB to the QDs-EML is less efficient in the inverted devices versus their upright counterparts as seen from the HODs results above. These observations perhaps provide important insights into the reasons of the lower performance of inverted QLEDs with solution coated HTLs in general. TEM cross sectional images of Glass/TFB (20 nm) /QDs (22 nm) and Glass/QDs (15 nm) /TFB (14 nm) samples taken under different magnifications (in Figure 4.12) show that both the TFB and QDs layers are less uniform in the Glass/QDs/TFB samples than in the Glass/TFB/QDs samples, further corroborating these conclusions. The larger non-uniformities in layers thicknesses when TFB is coated on QDs-EMLs can negatively affect the electric field distribution across the layers and increase current leakage, hence reduce device EQE. This may also explain why the use of ILs effectively improves the EL performance in the inverted devices.

We also tested the changes in TRPL characteristics of B-QDs, collected at 463nm, when put in contact with R-QDs. As can be seen in Figure 4.11c, the exciton lifetime of the B-QDs decreases but not significantly when in contact with R-QDs. The small decrease in the exciton lifetime points to limited energy transfer from B-QDs to R-QDs.

The τ values extracted from tri-exponential decay fits for all the TRPL characteristics presented in Figure 4.11 are provided in Table 4.3.

Table 4.3. τ and A components extracted from the tri-exponential decay curves for all the TRPL characteristics presented in Figure 4.11.

Sample	τ_1	A_1	τ_2	A_2	τ_3	A_3
Glass/R-QDs (@ 633)	6.64	0.44	6.22	0.18	16.32	0.34
Glass/TFB/R-QDs (@ 633)	5.11	0.41	6.65	0.15	14.68	0.4
Glass/R-QDs /TFB (@ 633)	4.5	0.35	9.92	0.59	26.43	0.04
Glass/R-QDs /B-QDs IL/TFB (@ 633)	5.92	0.39	7.91	0.17	17.13	0.33
Glass/B-QDs (@ 463)	1.93	0.43	2.37	0.31	13.14	0.23
Glass/R-QDs/B-QDs (@ 463)	1.66	0.47	3.66	0.27	18.35	0.24

Lastly, we also test and compare the EL stability of the R-IQLEDs devices without and with the B-QDs-IL. Figure 4.13 shows the changes in Luminance (normalized to the initial luminance) and driving voltage of these devices over time under a constant current driving of 20mA/cm². At this current, the initial luminance was 800 cd/m² and 2250 cd/m² for without and with IL, respectively. As can be seen, the use of the IL extends the device lifetime LT₅₀ (the time it takes for the luminance to decrease to 50% of the initial value) from 29 h to 44h. While the increase seems modest at first sight, given the different initial luminance values, these lifetimes translate to 1220 h and 11950 h, respectively, for an initial luminance of 100 cd m⁻², using the widely used scaling law and an accelerator factor of 1.8¹²⁹. To the best of our knowledge, this is the longest lifetime for a R-IQLED with a solution-coated HTL. Table 4.4 compares the EQE and LT₅₀ of the R-IQLED devices with the B-QDs of this work with other R-IQLEDs with solution-coated HTLs from published reports. One possible reason for the stability improvement is the better charge balance attained by using the IL (via reducing electron leakage and facilitating hole injection at the QDs-EML/TFB interface), which reduces the increase in non-radiative Auger recombination over time. Another reason could be the reduction in electron leakage and subsequent exciton formation in the HTL which can otherwise induce degradative processes in the HTL material in turn negatively impact device efficiency^{119, 130-132}.

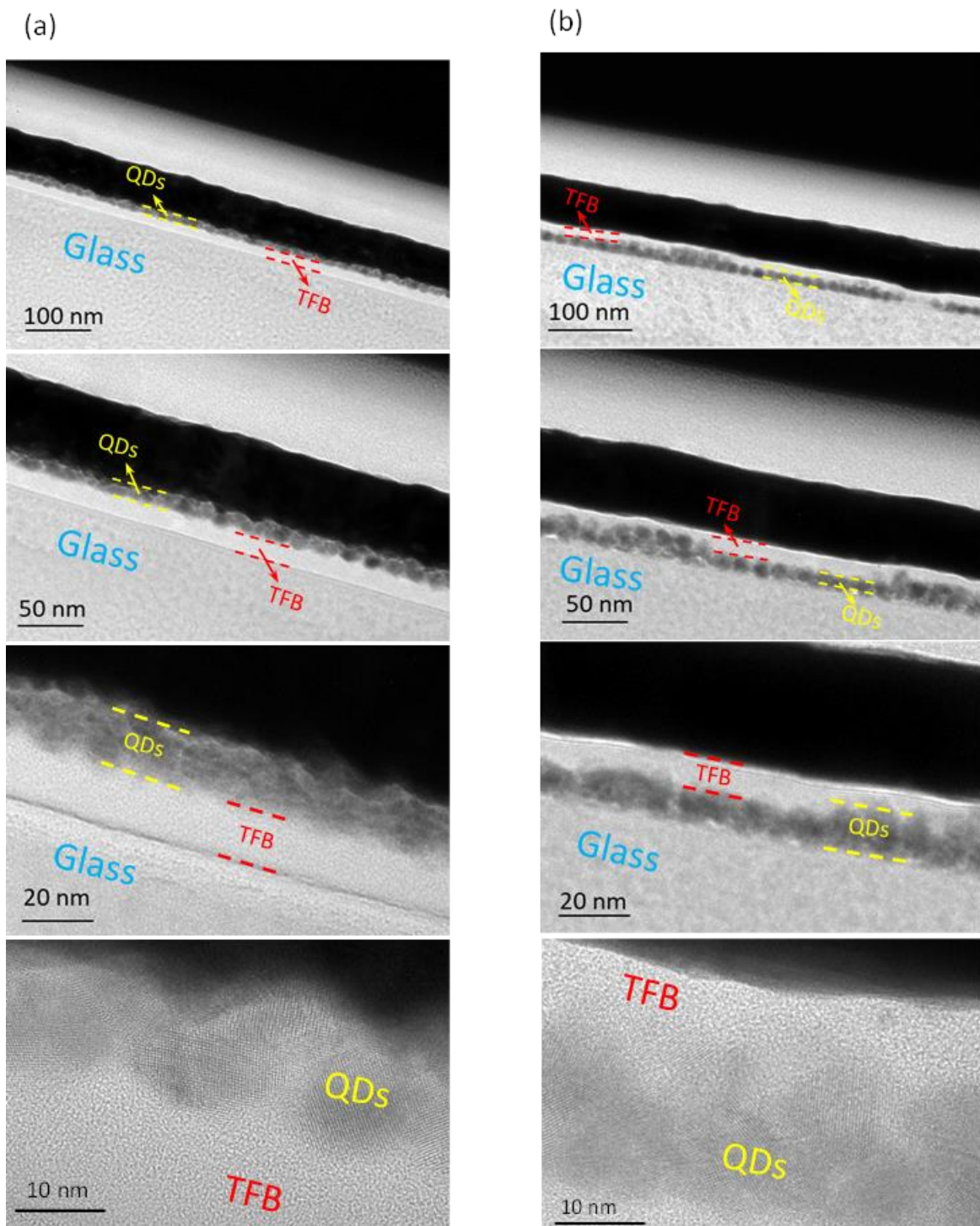


Figure 4.12. Cross-sectional TEM images of the (a) Glass/TFB/QDs and (b) Glass/QDs/TFB samples under different magnifications.

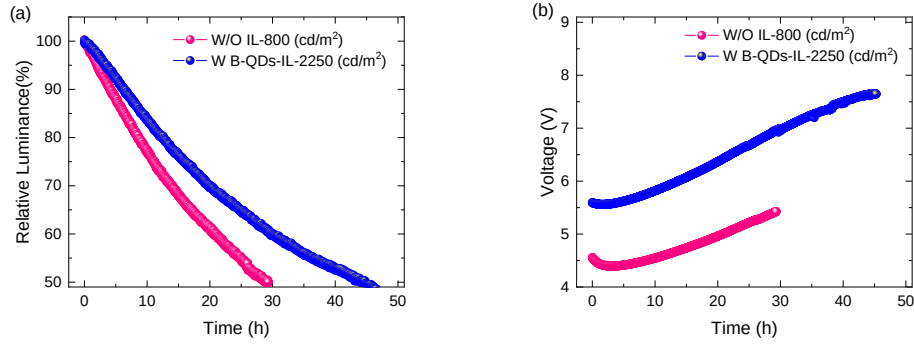


Figure 4.13. (a) Normalized luminance vs time and (b) Driving voltage vs time under 20 mA/cm² constant current driving of the R-IQLEDs without (W/O) and with (W) B-QDs-IL. The labels show the initial luminances in each case.

Table 4.4 Comparison of the EL characteristics of the R-IQLED with a B-QDs-IL (this work) versus other R-IQLEDs with a solution processed HTL reported in the literature.

Structure	EQE (%)	EL λ max (nm)	T ₅₀ @ 100 cd/m ²	Year	Ref
ITO/ZnO NPs/R-QDs/B-QDs/TFB/HAT-CN/Al	8.56	633	11950 @100 cd/m ²	-	This work
ITO/ZnO/TmPyPB/QDs/PVK/TFB/PMMAH/Al	11.6	629	-	2021	¹³³
ITO/ZnO/QDs/PVK:2CzPN/TFB/PMMAH/Al	9.82	639	-	2020	¹³⁴
ITO/ZnO/QDs/PVK:TAPC/HAT-CN/Al	12.6	-	11.26 @1000 cd/m ²	2020	¹³⁵
ITO/ZnO/QDs/PEI/PVK/PEDOT:PSS/Al	20.6	628	8253 @100 cd/m ²	2020	¹³⁶
ITO/ZnO/PEI/QDs/PVK/PEDOT:PSS/Al	20.74	624	127 @100 cd/m ²	2018	¹³⁷
ITO/ZnO NPs/QDs/PVK/TFB/PMMAH/Al	12.7	618	260 @100 cd/m ²	2018	¹³⁸
ITO/ZnO:Cs ₂ CO ₃ /QDs/p-TPD/PEDOT:PSS/Al	3.1	622	-	2018	¹³⁹
ITO/ZnO/QDs/PVK/PEDOT:PSS/Al	2.72	630	-	2016	¹⁴⁰
ITO/AZO:Cs ₂ CO ₃ /QDs/p-TPD/PEDOT:PSS/Al	1.3	-	-	2014	¹⁴¹
ITO/PEI/QDs/PVK/PEDOR:PSS/Al	0.18	633	-	2014	¹⁴²

Based on the above findings that i) electron injection in R-QDs-EMLs is generally much easier than hole injection, rendering them predominantly electron-rich, ii) the QDs-EML/TFB interface has a larger number of quenching defects than the same interface in upright architecture, and iii) the use of the IL helps a) facilitate hole injection from the TFB into the QDs-EML as well as suppress electron leakage in the opposite direction, and b) reduce exciton quenching at the TFB interface, we can attribute the poor performance of the IQLEDs without the IL to the high electron leakage, poor hole injection and significant exciton quenching at the QDs-EML/TFB interface. Figure 4.14 illustrates the differences between the devices without and with the IL, and provides an energy band model for explaining the role of the IL in suppressing electron leakage while facilitating hole injection, supported by results from the UPS and optical measurements.

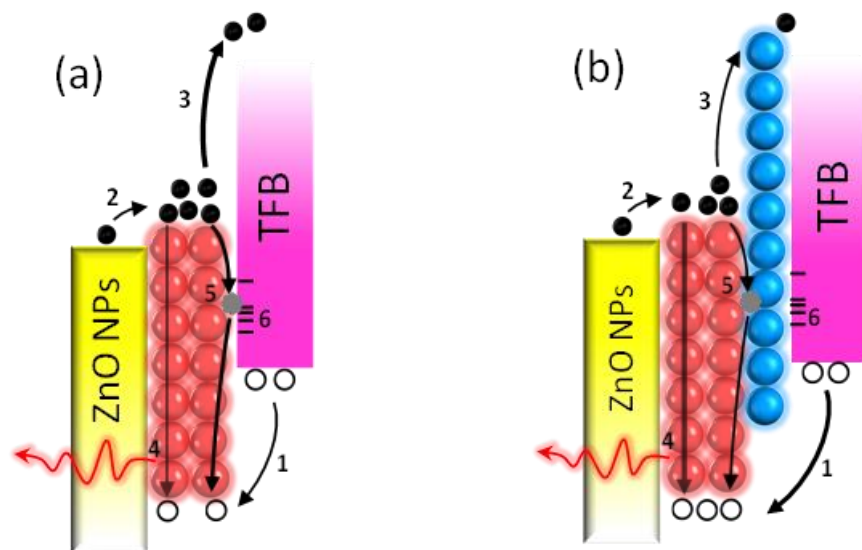


Figure 4.14. Schematic diagrams illustrating the differences in charge injection, electron leakage, radiative exciton recombination, and non-radiative exciton recombination (i.e. exciton quenching) between the devices without (a) and with (b) B-QDs-IL. 1 and 2 denote hole and electron injection from TFB and ZnO NPs, respectively; 3 denotes electron leakage to TFB; 4 and 5 denote radiative and non-radiative exciton recombination processes, respectively; and 6 represents surface defect trap states which can act as quenchers. The width of the arrow lines represents the relative magnitude of these processes in the two devices.

4.4 Conclusion

In summary, our studies on IQLEDs with a solution-coated HTL dissolved in an orthogonal solvent (1,4-dioxane) confirm the existence of a poor interface at QDs-EML/TFB, resulting in inefficient charge injection and significant exciton quenching. The utilization of a QDs-IL with a band gap wider than that of the QDs-EML in between the HTL and the QDs-EML improves the efficiency by 2.85X (from 3 to 8.56%) and prolongs the lifetime by 9.4X (from 1266 to 11,950 h at 100 cd/m²), which is, to the best of our knowledge, the longest lifetime among the R-IQLEDs with a solution-coated HTL. The performance improvement can be ascribed to multiple roles played by the QDs-IL, which include facilitating hole injection, suppressing electron leakage, and reducing exciton quenching. Observations from single-carrier devices show that, unlike the low band gap QDs, wide band gap QDs exhibit a lower electron injection but a higher hole injection, suggesting that QLEDs with R-QDs EML are more electron-rich, but QLEDs with B-QDs-EML are more hole-rich. UPS measurements verify that blue QDs have a shallower valence band energy than their red counterparts, corroborating these conclusions. The findings propose the utilization of a QDs-IL to obtain high-performance IQLEDs with a solution-coated HTL and present the dependence of the charge transport and injection on the QDs' band gap when the HTL is coated on either side of the QDs layer in an inverted or upright architecture.

Chapter 5. Investigating the degree of charge balance in inverted R, G and B-QLEDs and its influence on the EL performance

5.1 Differences in Electron and Hole Injection and Auger Recombination between Red, Green and Blue CdSe-based Quantum Dot Light Emitting Devices

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Despite the significant progress that has been made in recent years in improving the performance of QLEDs, the effect of charge imbalance and excess carriers on excitons in red (R) vs green (G) vs blue (B) QLEDs has not been compared or systematically studied. Recently, there has been an increasing body of work that investigates the interactions of charges and excitons in QDs utilizing spectroscopic techniques.^{65, 70, 143} However, most investigations of the influence of excess charges have been conducted on single QDs or on ensembles of QDs in single-carrier devices, and therefore do not accurately represent the conditions in QLEDs. In previous chapter,¹⁴⁴ it is found that significant differences in electron and hole injection efficiencies between R, G, and B-QDs exist due to differences in their conduction and valence band levels. It is therefore expected that R, G, and B-QLEDs will experience different extents and polarities of charging, resulting in differences in the level of interactions between excess charges and excitons, and therefore in Auger recombination efficiency. To the best of our knowledge, there have been no reports thus far that investigate the charge supply efficiency in R, G, and B-QLEDs in a comparative fashion or examine the impact of differences in carrier type and concentration on the EL performance of QLEDs during operation.

In this part, various CTL configurations that lead to different levels of electron/hole (e/h) ratios in the QDs-EML are utilized in R, G, and B-QLEDs based on CdSe, the most widely used material system and the one used in almost all state-of-the-art devices, for the purpose of investigating the sequence of charge injection (electrons or holes first) as well as identifying the type of the excess carriers within the QDs-EML in each case. Current–voltage–luminance (J–V–L), EQE-J, EL stability measurements, and EL spectral measurements reveal that as the bandgap of the QDs becomes wider, the efficiency of electron injection into the QDs-EML decreases

whereas that of holes increases. As a result, electrons are the excess carriers (*i.e.* $e/h > 1$) in the QDs-EMLs of R-QLEDs, whereas the opposite is true for G- and B-QLEDs (*i.e.* $e/h < 1$), with the latter being overwhelmingly rich in holes (*i.e.* $e/h \ll 1$). The observations also reveal that positive trions are more detrimental to both EQE and EL stability compared to negative trions, and are more effective in quenching excitons, more severely affecting both exciton lifetime and PL intensity. A comparison between QLEDs with the highest concentration of positive trions and those with the highest concentration negative trions (*i.e.* between B-QLEDs with CTLs that give the lowest e/h ratio and R-QLEDs with CTLs that give the highest e/h , respectively) reveals that the exciton lifetime and PL intensity decrease much faster upon increasing current in the first. In addition, transient electroluminescent (TrEL) measurements show a fast (reversible) decrease in the EL intensity of QLEDs that occurs in the first few microseconds after applying the bias, and that the magnitude of this decrease correlates with the relative concentration and of excess carrier in the QDs-EML and their type.

5.1.1 Identifying the sequence of charge supply and the influence of excess carriers on the efficiency and lifetime of R, G, and B-QLEDs by applying different conditions of electron and hole supplies.

To investigate the relative e/h ratios and compare the influence of the resulting trion species on the performance of inverted R, G, and B-QLEDs, it is essential to first study charge injection and transport characteristics of the inverted QLEDs in order to determine the sequence of charge injection (*i.e.* whether electron or hole injection occurs first as the external bias is increased) and the polarity of the predominant (excess) carriers in the QDs-EML for each case (*i.e.* for B vs G vs R). One approach to determine that is by changing the e/h charge supply ratio to the QDs-EML, which can be achieved by altering the CTLs properties. Therefore, in this work, two different ETLs and two HTLs that each provide different electron or hole supply levels (low and high) are employed. ZnMgO NPs annealed at either 100°C and 350°C, is used for the ETLs to respectively provide low or high electron supply levels (denoted here by the symbols $-\downarrow, -\uparrow$). Similarly, TCTA or CBP is used for the HTLs to respectively provide low or high hole supply levels (denoted here by the symbols $+\downarrow, +\uparrow$).

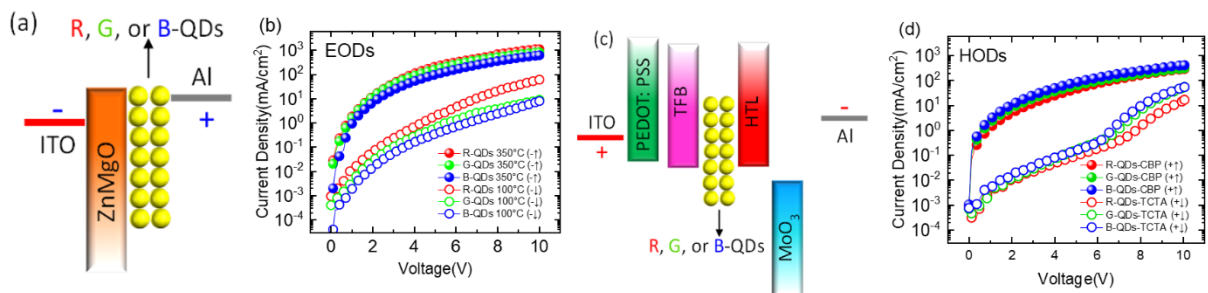


Figure 5.1. (a) Schematic diagram and (b) J-V characteristics of EODs with R-QDs, G-QDs and B-QDs layers in which the ETL (ZnMgO) is annealed at 100°C (-↓) or 350°C (-↑). (c) Schematic diagram and (d) J-V characteristics of HODs with R-QDs, G-QDs and B-QDs layers in which the TCTA (+↓) or CBP (-↑) are used as the HTL.

To verify the validity and effectiveness of these CTL choices, we first investigate the impact of the ZnMgO annealing temperatures on altering the electron transport properties. EODs with the structure of ITO/ZnMgO/QDs/Al, in which the ZnMgO ETLs are annealed at either 100 or 350°C, are fabricated and their J-V characteristics are measured. Figure 5-1a and 5-1b show the general device structure and the J-V data, respectively. As can be seen from the results, increasing the annealing temperature from 100°C to 350°C results in an increase in electron currents at any given voltage by about two orders of magnitude in all EODs regardless of the QD material used (R, G and B-QDs), which can be attributed to the possible role of the higher annealing temperature in increasing crystallinity as well as oxygen vacancies, which would increase the mobility and concentration of charge carriers.¹⁴⁵⁻¹⁴⁷ It is also worth pointing to the progressive decrease in current at any given voltage as the bandgap of the QDs increases for each annealing temperature, pointing to electron injection becoming increasingly more difficult in the same direction, consistent with our recent findings.¹⁴⁴ Similarly, the choice of CBP for the high hole supply scenario (+↑) HTL is based on its higher hole mobility, which is approximately $10^{-3} \text{ cm}^2/\text{v.s}$,¹⁴⁸ about an order of magnitude higher than that of TCTA ($\sim 10^{-4} \text{ cm}^2/\text{v.s}$)¹⁴⁸, the material utilized for the (+↓) scenario HTL. CBP also has a deeper HOMO than TCTA (6 eV versus 5.7 eV,¹⁴⁹ respectively) which additionally facilitates hole injection. The higher hole supply capacity of CBP versus TCTA is verified using HODs of the structure ITO/ PEDOT:PSS/TFB/QDs/HTL/MoO₃/Al, with CBP or TCTA as the HTL material, as depicted in Figure 5-1c. In these devices, PEDOT:PSS/TFB layers are utilized in order to block electron injection. As can be seen from the J-V characteristics of these HODs in Figure 5-1d, the CBP-based HODs exhibit hole currents approximately 10^1 - 10^2 X higher than their TCTA-based counterparts, showing that the use of CBP indeed allows for increasing the supply of holes to all QDs. Also, here again we see that the hole

supply becomes progressively easier as the band gap of the QDs increases, consistent with recent findings.¹⁴⁴

Having verified the low and high supply efficiencies of each of the selected HTL and ETL configurations for all three QDs, we move on to investigate the effect of the different e/h charge supply ratios on the performance of the R, G, and B QLEDs. Given the need to use high annealing temperatures for one of the ETL scenarios, an inverted device architecture of the structure ITO/ETL/R, G, or B-QDs/HTL/MoO₃/Al is used in this work. A schematic diagram of the general device structure is presented in Figure 5.2a.

Figure 5.2b shows the J-V-L characteristics of the R-QLEDs for the four scenarios resulting from the four possible combinations of electron and hole supply levels described earlier, namely; low holes-low electrons ((+↓)(-↓)), low holes-high electrons ((+↓)(-↑)), high holes-low electrons ((+↑)(-↓)), and high holes-high electrons ((+↑)(-↑)) [which correspond to the use of the following HTL and ETL combinations, respectively; TCTA + 100°C, TCTA + 350°C, CBP + 100°C, and CBP + 350°C]. As can be seen, the V_{On} (the voltage at which the device begins to emit electroluminescence, here taken as reaching an electroluminescence intensity of 1cd/m²) is higher than the V_{Th} (the voltage at which charge injection starts to increase rapidly and marked by the abrupt change in the slope of the J-V characteristics) for all devices, indicating that only one of the carriers (electrons or holes) is injected first (*i.e.* at V_{Th}) with the counter carrier not injected until V_{On} is reached, in turn indicating that, for voltages in between V_{Th} and V_{On} the conduction across the QDs-EML must be predominantly unipolar and therefore the QDs-EMLs must have highly unbalanced e/h ratios. The magnitude of the difference between V_{Th} and V_{On}, ΔV, was however different for the four scenarios. In the (+↓)(-↓) scenario, ΔV was 0.76V. Increasing electron supply without increasing hole supply (the (+↓)(-↑) scenario) reduces V_{Th} and increases current but does not appreciably affect V_{On}, causing the ΔV to increase to 1.2V and the device current density to increase by an order of magnitude. Given that the increase in electron supply does not result in a change in V_{On}, it is likely that, in the two charge supply scenarios, electrons are injected at V_{Th}, followed by hole injection at V_{On}, indicating that V_{On} may be limited by hole supply rather than electron supply. Also, the EQE-J characteristics of the devices (Figure 5-2e-top) reveal that an increase in electron supply leads to a reduction in EQE from 10.28% to 8.05%. This is consistent with the presence of

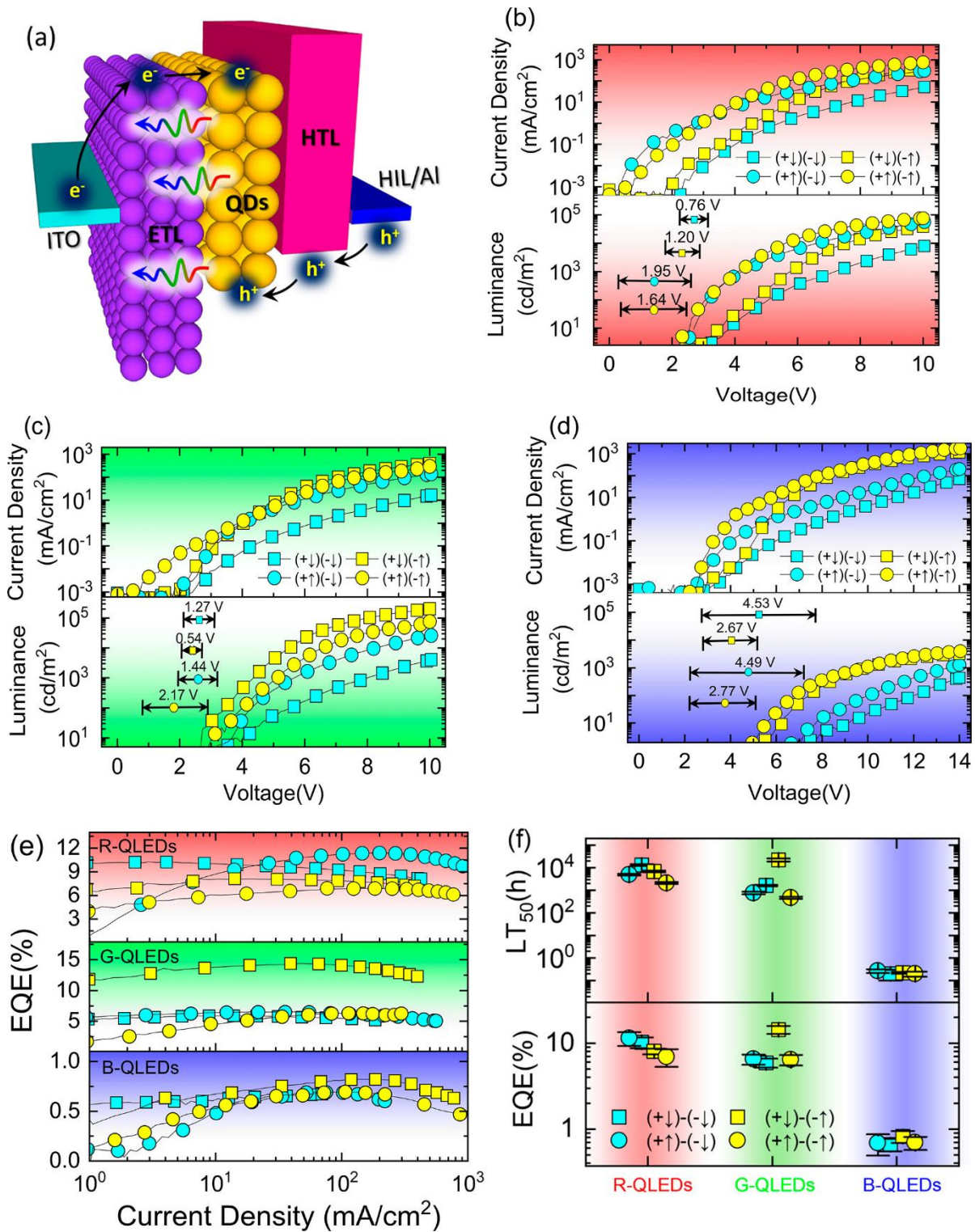


Figure 5-2. (a) Schematic diagram of the device structure. J-V-L characteristics of the (b) R-QLEDs, (c) G-QLEDs, and (d) B-QLEDs under all charge injection scenarios. (e) EQE-J of the R-QLEDs (top), G-QLEDs (middle), and B-QLEDs (bottom) under all charge injection scenarios. (f) A comparison of EQE and lifetime (LT_{50} @ $100\text{cd}/\text{m}^2$) of the R-QLEDs (top), G-QLEDs (middle), and B-QLEDs (bottom) under all charge injection scenarios.

excess electrons in the QDs-EML in the $(+\downarrow)(-\uparrow)$ scenario. These excess electrons are responsible for the decrease in the device efficiency, likely due to increasing nonradiative Auger recombination involving negative trions or electron leakage from the QDs-EML to the HTL. Comparing the $(+\uparrow)(-\downarrow)$ scenario relative to the $(+\downarrow)(-\downarrow)$ scenario, it can be seen that increasing the hole supply alone not only increases the current but also reduces V_{On} by 0.66V. It also increases the maximum EQE from 10.28% to 11.38%. These observations clearly show that in R-QLEDs, device performance is limited by hole injection, indicating that electrons must be the excess carriers (*i.e.* $e/h > 1$) resulting in the formation of negative trions in the R-QDs EML. This conclusion is further confirmed by observations from $(+\uparrow)(-\uparrow)$ scenario where the increased electron supply in this case reduces the device EQE to 6.85%. An overall comparison of all charge supply scenarios shows that reducing electron supply (*i.e.* all $(-\downarrow)$ scenarios) improves EQE for any given hole supply level. One can also conclude that although e/h is > 1 in R-QLEDs in general, for both high electron current scenarios $(-\uparrow)$, especially the $(+\downarrow)(-\uparrow)$ scenario, the number of electrons is likely to be much higher than holes. In contrast, among the four scenarios, the $(+\uparrow)(-\downarrow)$ scenario must give the lowest e/h ratio (the one closest to $e/h = 1$, the ideal ratio for charge balance), hence also the highest EQE. One can therefore also expect the formation of negative trions in R-QLEDs to be the highest in case of the $(+\downarrow)(-\uparrow)$ scenario and the lowest in case of the in the $(+\uparrow)(-\downarrow)$ scenario. Given the generally $e/h > 1$ ratio in these devices one can also expect the formation of positive trions to be insignificant in R-QLEDs. As illustrated in the schematic diagram in Figure 5-3, while the EMLs of R-QLEDs generally have e/h ratios > 1 , the ratio will be expectedly higher for $(+\downarrow)(-\uparrow)$ (Figure 5-3a-left side) than for $(+\uparrow)(-\downarrow)$ (Figure 5-3b-left side), causing more negative charging and negative trion formation in the earlier scenario.

Turning the attention now to the G-QLEDs, one can see from Figure 5-2c that there is a larger ΔV for the $(+\downarrow)(-\downarrow)$ scenario in comparison to that for its red counterpart (ΔV of 1.27V for G-QLED vs only 0.76V for the R-QLED). The larger ΔV indicates a larger difference between the onsets of injection for electrons and holes and therefore suggests a more significant charge imbalance which may explain the relatively lower EQE (only 5.87%). Interestingly, upon increasing the electron supply, *i.e.* the $(+\downarrow)(-\uparrow)$ scenario, the device EQE exhibits a notable improvement, reaching 14.38% and V_{On} becomes lower, reducing ΔV to 0.54V. This significant enhancement in the EQE, coupled with the reduction in V_{On} , indicates that increasing electron

supply substantially improves charge balance. This trend is opposite to that in the R-QLEDs, where increasing electron

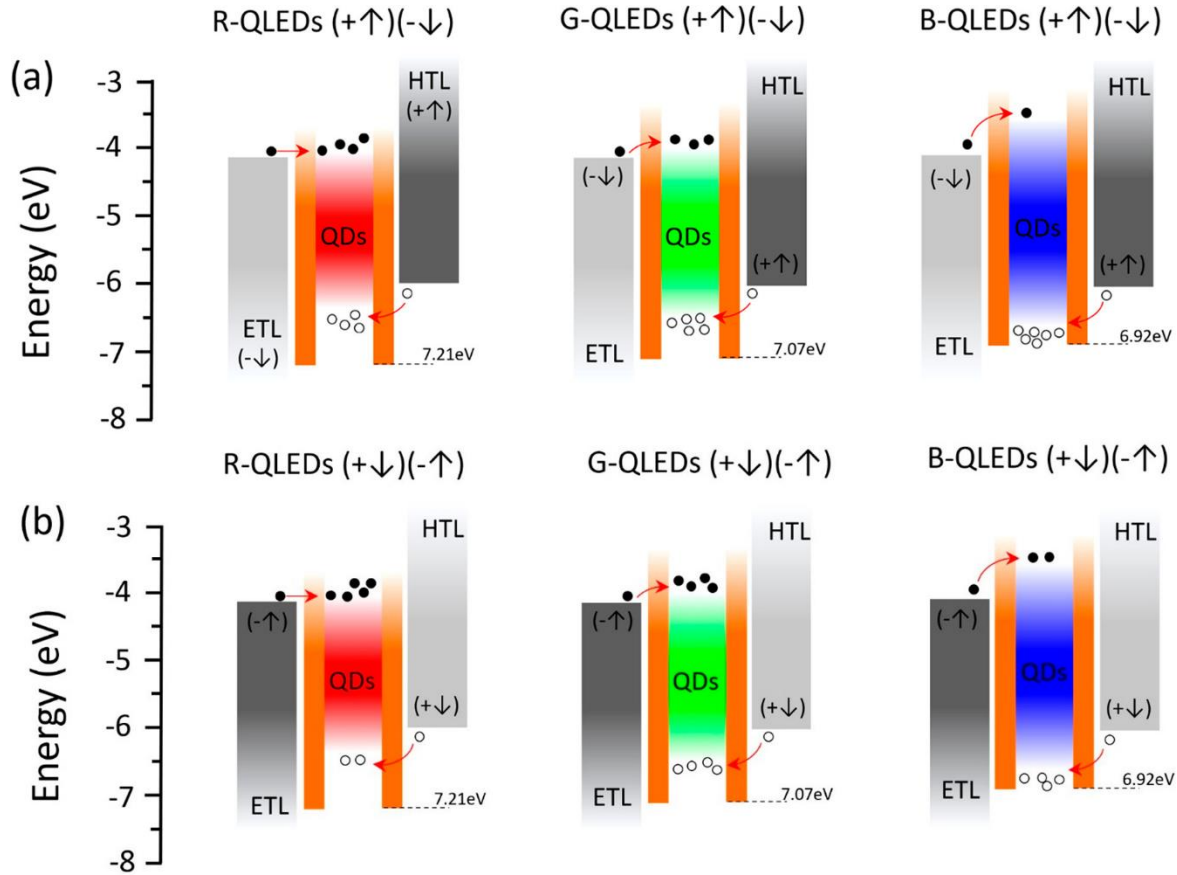


Figure 5.3. Proposed schematic diagram illustrating the charge supply into R-QLEDs (left side), G-QLEDs (middle), and B-QLEDs (right side) in (a) the (+↑)(-↓) scenario and (b) the (+↓)(-↑) scenario. The numbers represent the valence band energy of the QD shells obtained from ultraviolet photoelectron spectroscopy measurements.

supply instead reduced EQE. These results show that – contrary to R-QLEDs - holes are the excess carrier in the G-QLEDs, and that the device efficiency benefits from increasing electron supply and e/h ratio. The very similar performance of devices of the (+↑)(-↑) and the (+↑)(-↓) scenarios suggests that the e/h is much smaller than 1 and therefore small alterations to electron supply do not appreciably alter the e/h ratio in the QDs-EML or device EQE. As a result, one can also expect the (+↑)(-↓) scenario to produce the largest concentration of positive trions in case of G-QLEDs whereas the (+↓)(-↑) scenario to produce the least. Also, given the $e/h < 1$ ratio, one can expect the formation of negative trions to be generally negligible in G-QLEDs. Therefore, while the e/h ratio in the EMLs of G-QLEDs is generally < 1 , one can expect the ratio to be smaller for (+↑)(-↓) than for (+↓)(-↑), resulting in more positive charging and therefore a higher concentration

of positive trions in case of the earlier scenario as illustrated in the middle diagrams of Figures 5-3a and 2e.

Finally, looking at the results from the B-QLEDs (presented in Figures 5-2d and e (bottom part)), one can see that although the V_{Th} values for all charge supply scenarios are comparable to those of the R and G-QLEDs, the ΔV s tend to be much larger, pointing to a much larger charge imbalance. Here again, we see that increasing electron supply reduces ΔV , indicating that the onset of EL is limited by electron injection, in turn indicating that holes are injected more easily and thus are again the excess carriers. Here we see that although increasing electron supply reduces V_{On} and ΔV , indicating improved charge balance, it does not appreciably affect EQE. This suggests that the charge imbalance remains too large and the EQE continues to be limited by very low electron supply (*i.e.* $e/h \ll 1$). The much smaller e/h ratio in B-QLEDs implies that the conditions in B-QDs are extremely favorable for the formation of positive trions and for the leakage of holes to the ETL, which may explain the generally lower EQE of these devices relative to their R and G counterparts despite the comparable PLQY values of the QDs involved.^{31, 116} Like in the case of G-QLEDs, here again one can expect the e/h ratio to be smaller for $(+\uparrow)(-\downarrow)$ than for $(+\downarrow)(-\uparrow)$, with the e/h ratios generally smaller as illustrated in the right hand side diagrams of Figure 5-3b.

Table 5-1. The material parameter utilized in the simulation extracted from the literature.

	QDs ^{82, 144, 150}	ZnMgO ¹⁵¹	CBP ¹⁵²	TCTA ¹⁵²
Thickness (nm)	15	50	60	60
E _g (eV)	2-2.6	3.5	3.1	3.3
X (eV)	3.5-4	4	2.9	2.4
ϵ/ϵ_0	6.2	9	6	6
N_c (cm ⁻³)	$5 \times 10^{+18}$	$4 \times 10^{+18}$	$1 \times 10^{+19}$	$1 \times 10^{+19}$
N_v (cm ⁻³)	$1.8 \times 10^{+19}$	$1 \times 10^{+19}$	$1 \times 10^{+19}$	$1 \times 10^{+19}$
μ_e (cm ² /Vs)	1×10^{-4}	100	3×10^{-4}	1×10^{-8}
μ_h (cm ² /Vs)	1×10^{-4}	25	2×10^{-3}	3×10^{-4}
N_D (cm ⁻³)	$1 \times 10^{+16}$	$1 \times 10^{+16}$ - $1 \times 10^{+17}$	$1 \times 10^{+5}$	$1 \times 10^{+5}$
N_A (cm ⁻³)	$1 \times 10^{+5}$	$1 \times 10^{+5}$	$1 \times 10^{+17}$	$1 \times 10^{+17}$
V_e (cm/s)	$1 \times 10^{+7}$	$1 \times 10^{+7}$	$1 \times 10^{+7}$	$1 \times 10^{+7}$
V_h (cm/s)	$1 \times 10^{+7}$	$1 \times 10^{+7}$	$1 \times 10^{+7}$	$1 \times 10^{+7}$

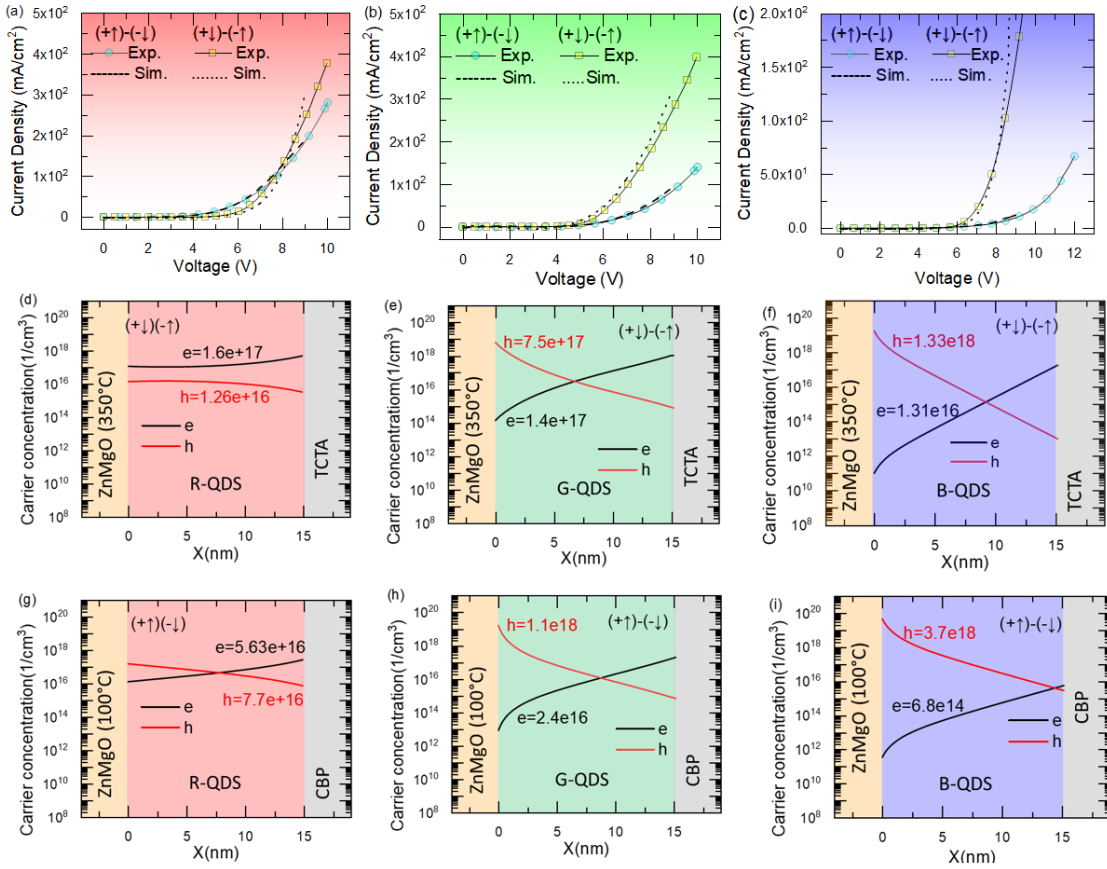


Figure 5-4. Simulation and experimental J-V characteristics of (a) R-QLEDs, (b) G-QLEDs, and (c) B-QLEDs. Electron (e) and hole (h) concentration in R-QLEDs (d and g), G-QLEDs (e and h), and B-QLEDs (f and i) simulated by SCAPS software under $(+\downarrow)(-\uparrow)$ and $(+\uparrow)(-\downarrow)$ charge supply scenarios, respectively. The number beside each trace represents the average carrier concentration (e or h) across the QDs-QML.

To further corroborate the above conclusions about the e/h ratios in the various QLEDs, one-dimensional SCAPS-1D software (Solar Cell Capacitance Simulator One dimension) was used to simulate charge injection and transport in them in order to estimate the concentrations of each of the electrons and holes in the QDs-EML in each case^{82, 151}. Table 5-1 shows the parameters utilized in the simulations. Figures 5-4 a-c compares the numerically simulated J-V characteristics and the experimentally measured ones, showing their close resemblance thus verifying the accuracy of the simulations. Figures 5-4d-i show the e and h concentrations across the QDs-EML for all devices. The average carrier concentration across the QDs-EML is also calculated and provided next to each trace to facilitate comparisons. As can be seen, the simulations give two orders of magnitude higher concentrations for holes versus electrons in B-QLEDs, corroborating the conclusion above. They also show that the e/h ratio increases as we go from B to G and then

to R, and also as we go from $(+\uparrow)(-\downarrow)$ to $(+\downarrow)(-\uparrow)$ scenarios, leading to an e/h ratio >1 for R-QLEDs of the $(+\downarrow)(-\uparrow)$ scenario. For the $(+\uparrow)(-\downarrow)$ R-QLED, the simulations predict a e/h ratio of ~ 1 (within only a 30% deviation, well within the known error/approximation margins of such simulations) in full agreement with the conclusions from the experimental results.

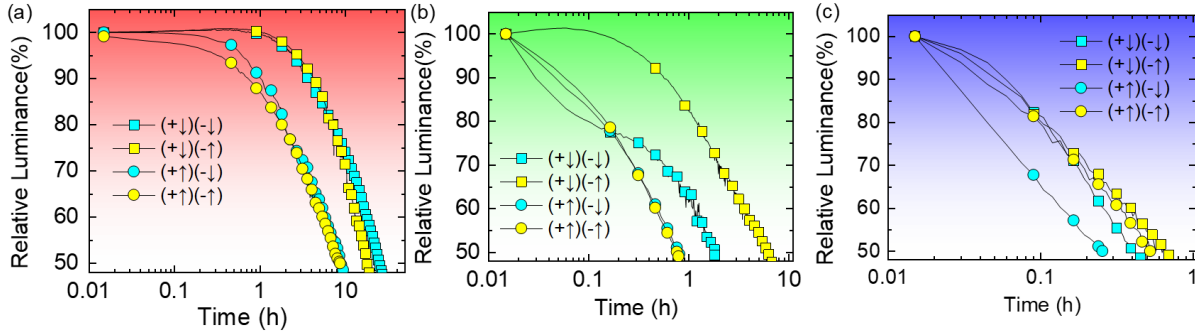


Figure 5-5. Relative luminance vs time under 20 mA/cm² constant current driving of (a) R-QLEDs, (b) G-QLEDs, and (c) B-QLEDs under different charge injection scenarios.

To also determine how the changes in hole and electron supply to the QDs EML may affect the EL performance over time, the EL stability of the R, G, and B-QLEDs with the same four charge supply scenarios are also tested and compared. Device EL lifetime (LT_{50}) data, defined as the time elapsed until the EL decreases by 50% of the initial value under a constant driving current, in this case 20mA/cm², is measured and presented in Figures 5-5a, b, and c, respectively. Figure 5-2f compares the projected LT_{50} for 100 cd/m² initial luminance using the widely used scaling law $(L_0)^n (LT_{50}) = \text{constant}$ with $n = 1.8$ ²⁸ (top) and EQE (bottom) of the R-QLEDs (left side), G-QLEDs (middle), and B-QLEDs (right side). As can be seen, for the R-QLEDs, devices of both $(-\downarrow)$ scenarios exhibit longer lifetimes compared to their $(-\uparrow)$ counterparts suggesting that reducing electron supply improves EL stability. In contrast, for the G-QLEDs, increasing electron supply improves stability, perhaps most evident in the 15X longer lifetime of the $(+\downarrow)(-\uparrow)$ versus the $(+\downarrow)(-\downarrow)$ G-QLEDs. These results can be readily explained in terms of the opposite e/h ratios of the R and G QLEDs ($e/h > 1$ and $e/h < 1$, respectively) and the known benefits of improving charge balance (hence the changes that bring e/h closer to 1) for device stability.^{60, 80, 87, 118, 119, 153} Quite notably, and similar to the EQE behavior, the LT_{50} at 100cd/m² values of B-QLEDs under all charge supply scenarios are approximately the same, around 0.2h in all cases. Obviously, there is a significant difference between the EQE and lifetime of the B-QLEDs and those of the R and G-QLEDs (Figure 5-2f), which might be closely connected with the highly unbalanced e/h ratios (*i.e.* $e/h \ll 1$), that makes the formation of positive trions in the QDs EML very efficient and allows

for the leakage of a large number of holes to the ETL, both of which can reduce device EL stability.^{40, 60, 154, 155} Table 5-2 shows the Luminescence (at 20mA/cm²), V_{Th} , V_{On} , ΔV , EQE, LT₅₀ (at 20mA/cm²), and LT₅₀ at 100cd/m² of R, G, and B-QLEDs under different charge injection scenarios as well as the standard deviation in the data obtained from 6 samples in each group.

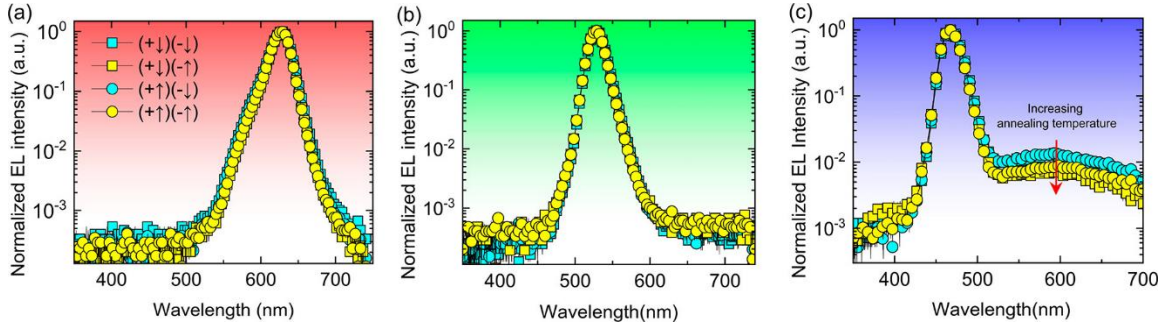


Figure 5-6. Normalized EL spectra of the (a) R-QLEDs, (b) G-QLEDs, and (c) B-QLEDs under all charge injection scenarios.

Figures 5-6a-c present normalized EL spectra (on a logarithmic scale) of the QLEDs for the different charge supply scenarios discussed above. As can be seen, the EL spectra of the R-QLEDs (Figure 5-6a) shows the characteristic QD emission band with no additional features, indicating that almost all e-h recombination occurs within the QDs-EML, with negligible contributions from the CTLs, regardless of the charge supply scenarios. In contrast, in the B-QLEDs (Figure 5-6c) and, but to a much lesser extent, in the G-QLEDs (Figure 5-6b), the spectra show a broad emission band (or an elevated background) on the longer wavelength side of the QDs emission. This band can be ascribed to emission from ZnMgO ETL intragap states^{87, 156, 157}. The appearance of the band shows that in these devices a significant fraction of holes indeed leaks across the QDs EML, allowing for some e-h recombination to take place within the ZnMgO ETL. Notably, in the B-QLEDs where this band is more visible, the height of this band in both (-↓) scenarios (*i.e.* devices in which ZnMgO is annealed at 100°C) is greater than that in their (-↑) counterparts (*i.e.* devices in which ZnMgO is annealed at 350°C). The lower intensity of this EL in the (-↑) devices can be attributed to either i) the higher concentration of electrons and e/h ratio in the QDs-EML which would increase e-h recombination within the layer and thereby reduce the leakage of unrecombined holes to the ETLs, or ii) increased passivation of ZnMgO intragap trap states due to the higher annealing temperature. While it is possible that a similar effect occurs in the devices of the two other colors, especially in the G-QLEDs, the fact that this band is much stronger in the B-QLEDs - making it possible for us to discern these variations - gives direct

evidence of the very high concentrations of excess holes in the QDs-EML of B-QLEDs (*i.e.* $e/h \ll 1$), allowing for a significant fraction of unrecombined holes to reach the ETL, as concluded previously. Knowing that the presence of holes in the ZnO-based ETLs can lead to luminescence degradation in QLEDs, one can expect the leakage of such a significant fraction of them to the ETL in case of B-QLEDs to play a major role in the low stability of these devices.¹⁴⁴

Table 5-2. *Luminescence, V_{Th} , V_{On} , ΔV , EQE, LT50 @20mA/cm², and LT50 @100cd/m² R, G and B-QLEDs under different charge injection scenarios as well as the standard deviation in the data obtained from 6 samples in each group.*

Device	HTL	ETL	Luminescence (cd/m ²)*	V_{Th} (V)	V_{On} (V)	ΔV (V)	EQE (%)	LT50 (h) @20mA/cm ²	LT50 (h) @100cd/m ²
R-QLED	(+↓)	(-↓)	3,270 ±450	2.26 ±0.18	3.02 ±0.31	0.76 ±0.14	10.28 ±1.4	24.8 ±2.34	13,200 ±1,250
	(+↓)	(-↑)	2,750 ±216	1.73 ±0.21	2.93 ±0.41	1.20 ±0.21	8.05 ±0.63	17.8 ±1.45	6,900 ±570
	(+↑)	(-↓)	3,350 ±618	0.41 ±0.09	2.36 ±0.42	1.95 ±0.26	11.38 ±2.1	9 ±0.74	5,000 ±430
	(+↑)	(-↑)	2,150 ±375	0.64 ±0.14	2.28 ±0.15	1.64 ±0.19	6.85 ±1.2	8.5 ±0.76	2,130 ±190
G-QLED	(+↓)	(-↓)	4,050 ±483	2.12 ±0.31	3.39 ±0.17	1.27 ±0.24	5.87 ±0.7	1.82 ±0.16	1,420 ±120
	(+↓)	(-↑)	9,600 ±920	2.08 ±0.29	2.62 ±0.22	0.54 ±0.11	14.38 ±1.5	6.1 ±0.92	22,500 ±3,400
	(+↑)	(-↓)	4,460 ±609	1.91 ±0.14	3.35 ±0.31	1.44 ±0.15	6.52 ±0.89	0.83 ±0.15	770 ±98
	(+↑)	(-↑)	3,600 ±516	0.62 ±0.18	2.79 ±0.24	2.17 ±0.23	6.27 ±0.9	0.75 ±0.08	475 ±55
B-QLED	(+↓)	(-↓)	105 ±17	2.96 ±0.25	7.49 ±0.46	4.53 ±0.36	0.67 ±0.11	0.42 ±0.04	0.2 ±0.02
	(+↓)	(-↑)	122 ±13	2.84 ±0.27	5.51 ±0.41	2.67 ±0.39	0.82 ±0.13	0.57 ±0.05	0.22 ± 0.02
	(+↑)	(-↓)	60 ±16	2.42 ±0.19	6.91 ±0.39	4.49 ±0.26	0.68 ±0.19	0.25 ±0.04	0.27 ±0.04
	(+↑)	(-↑)	65 ±11	2.38 ±0.31	5.15 ±0.46	2.77 ±0.41	0.70 ±0.12	0.52 ±0.07	0.2 ±0.03

5-1-2 Investigating the interaction of excess carriers with excitons in R, G, and B-IQLEDs by spectroscopic characterization

Finding a clear correlation between the extent of charge imbalance in a device and a deterioration in its EL performance, it becomes critical to understand the influence of altering the e/h ratios on excitons in the QLEDs examined above as a way to understand how the charge imbalance affects device efficiency and its loss over time. Towards this objective, we systematically study the effect of altering the e/h ratios on both optically and electrically generated excitons, by studying their effect on the PL (both steady state and transient) and EL (transient) characteristics, respectively in the R, G and B-QLEDs in order to glean insights into the influence of charge imbalance and excess carriers on their efficiency behavior.

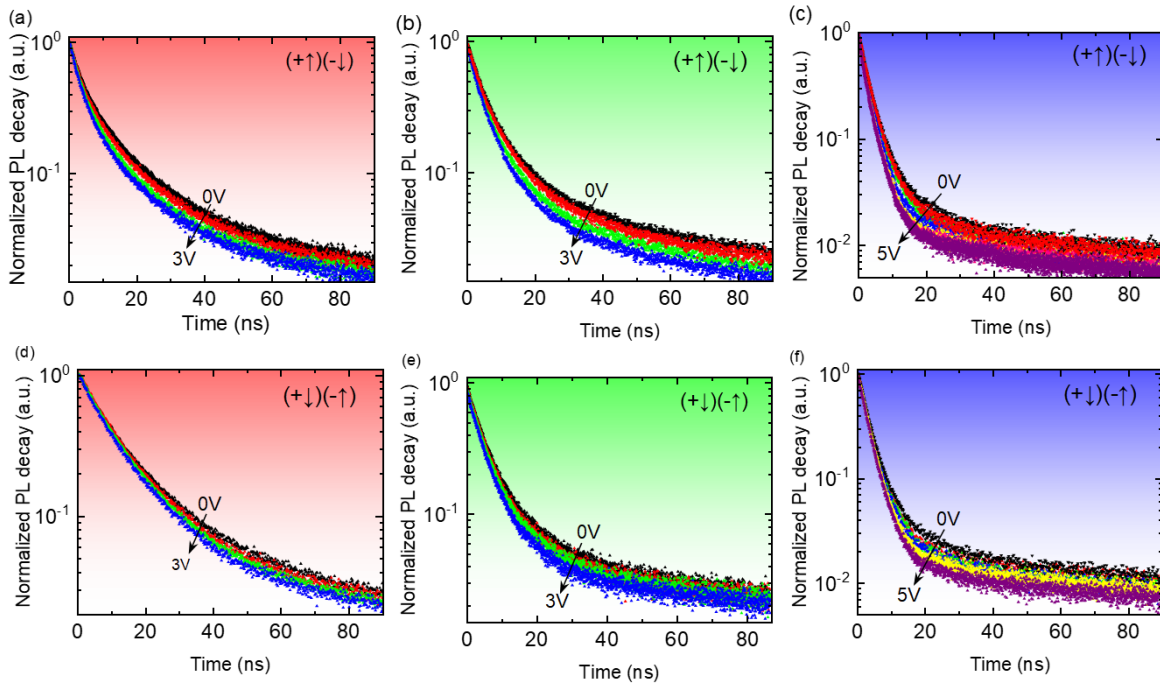


Figure 5-7. TrPL characteristics of R, G, and B-QLEDs with the charge supply scenarios $(+\uparrow)(-\downarrow)$ depicted in (a-c) and $(+\downarrow)(-\uparrow)$ depicted in (d-f), measured at different voltages from 0V to V_{On} .

For PL characterization, changes in both the steady state PL intensity and the transient PL(TrPL) decay rate are measured under different bias levels from 0 to V_{On} approximately (PL measurements at voltages $>V_{On}$ are not possible due to strong electroluminescence from the devices at these voltages). Different from previous studies where EOD and HOD are usually utilized for such PL measurements, we here do the PL measurements on the full QLEDs in order to ensure that the tests more accurately represent e/h conditions in the QDs-EMLs of actual QLEDs and with the HTLs and ETLs both being present. At 0 volts, the QDs-EMLs will expectedly have

low carrier concentrations. As the voltage increases and reaches V_{Th} , the concentration of only one of the carriers will increase rapidly (electrons in case of R QLEDs and holes in case of G- and B-QLEDs), allowing us to investigate the effect of that carrier on the PL behavior. In order to simplify the study, the measurements are limited to QLEDs of the two most extreme charge supply scenarios, $(+\uparrow)(-\downarrow)$ and $(+\downarrow)(-\uparrow)$, which respectively produce the lowest and highest e/h ratios.

Figures 5-7 and 5-8, respectively, show the TrPL decay characteristics and the steady state PL spectra of R, G, and B-QLEDs with the charge supply scenarios $(+\uparrow)(-\downarrow)$ and $(+\downarrow)(-\uparrow)$, measured at different voltages from 0V to V_{On} . As can be seen, the TrPL characteristics show a slower decay rate for the $(+\downarrow)(-\uparrow)$ scenario versus $(+\uparrow)(-\downarrow)$ for each color. The slower TRPL decay rate representing a longer TrPL overall lifetime (τ), the latter defined as the time until the TrPL intensity decreases to 0.36 ($=1/e$) of its initial value assuming an exponential decay rate, and can be attributed to the lower defect density in the higher temperature-annealed ZnMgO, which reduces its quenching effect on the QDs.^{102, 158} Figure 5-9a-c show the changes in τ (top) and in the steady state PL intensity (bottom), the latter from changes in the PL peak height, both normalized to

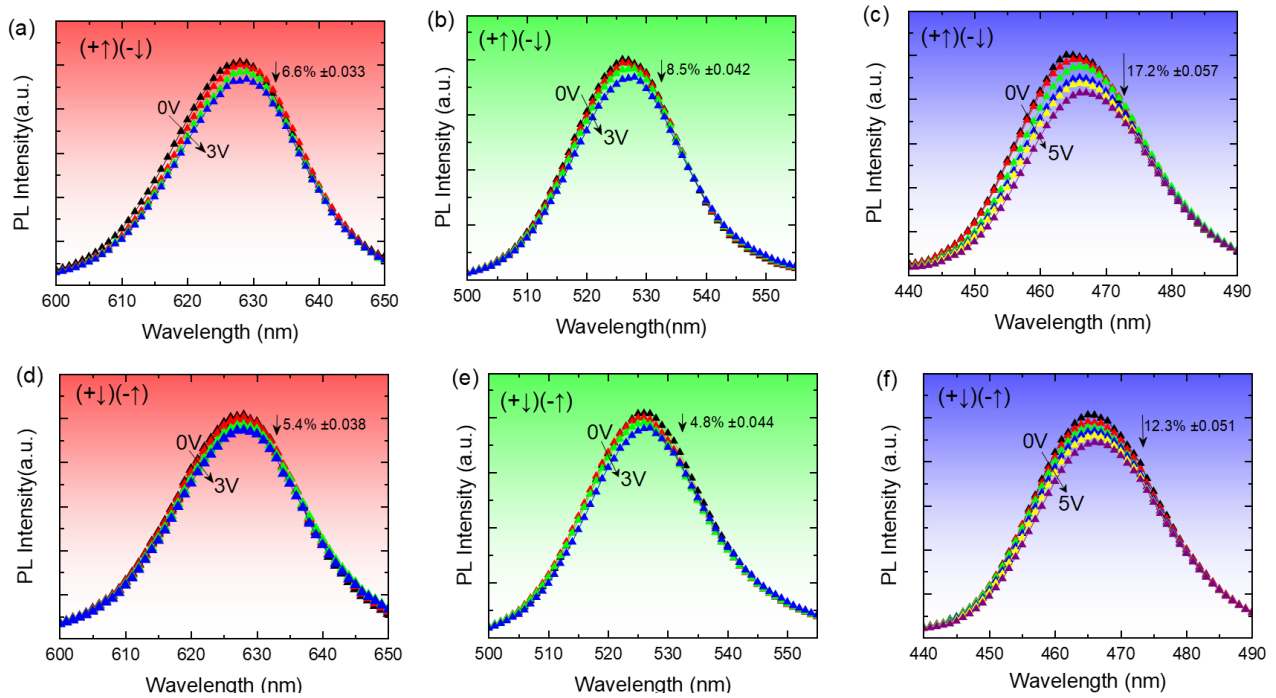


Figure 5-8. Steady state PL spectra of R, G, and B-QLEDs with the charge supply scenarios $(+\uparrow)(-\downarrow)$ depicted in (a-c) and $(+\downarrow)(-\uparrow)$ depicted in (d-f), measured at different voltages from 0V to V_{On} .

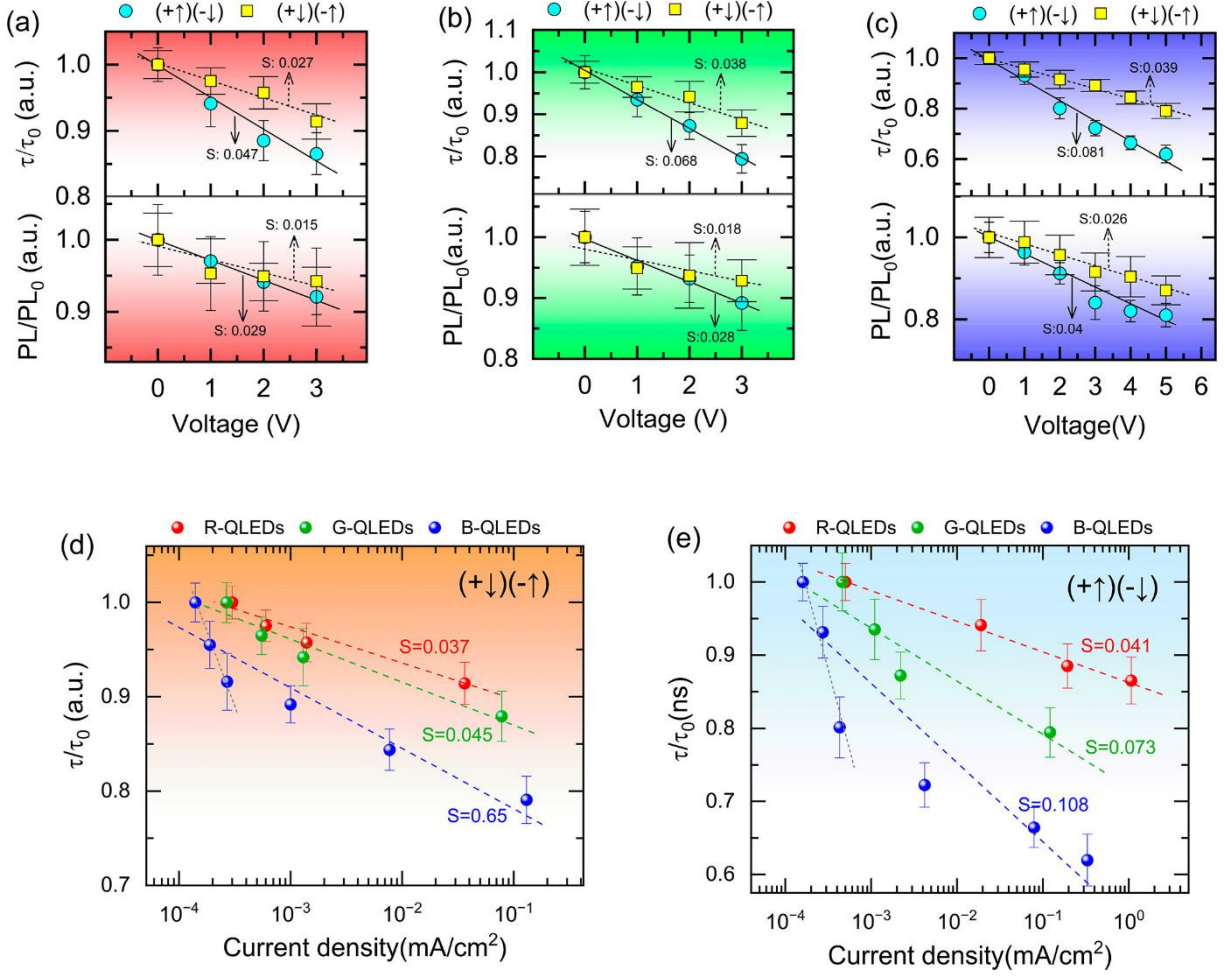


Figure 5-9. Normalized TrPL overall lifetime (τ) (top) and normalized PL intensity (bottom) versus voltage of (a) R-QLEDs, (b) G-QLEDs, and (c) B-QLEDs measured from 0 V to V_{On} for (+↑)(-↓) and (+↓)(-↑) scenarios. Normalized TrPL overall lifetime (τ) versus current density of R-, G-, and B-QLEDs measured from 0 V to V_{On} for (d) the (+↓)(-↑) scenario and (e) the (+↑)(-↓) scenario. S represents the slope of the linear fit in each case.

their values at 0 V (*i.e.* τ/τ_0 and PL/PL_0 , with τ_0 and PL_0 representing the values at $V=0$) versus the applied bias extracted from the data in Figures 5-7 and 5-8. Linear fits of the data and their slopes are also included. As can be seen, increasing the bias leads to a progressive decrease in both τ and PL intensity. The decrease in PL intensity and τ with increased voltage can be attributed to an increase in Auger quenching as more carriers (electrons in case of R-QLEDs and holes in case of G- and B-QLEDs) get injected into the QDs-EML. The decrease can also be attributed to Stark effects or electric field induced dissociation of excitons which would also increase with voltage. In order to confirm that the observed changes are not due to Stark effects, we have measured changes in PL peak position under the different bias conditions. This data is

provided in Figure 5-10. As the data shows, the changes in PL peak position are essentially the same for the

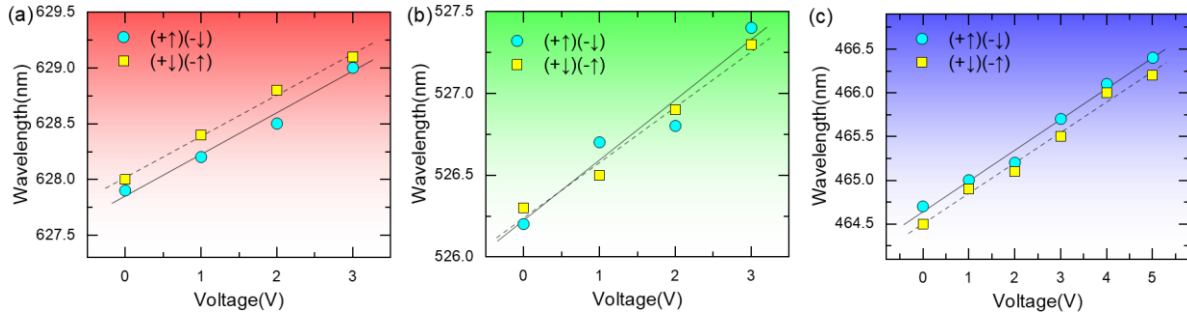


Figure 5-10. PL peak position of (a) R-QLEDs, (b) G-QLEDs, and (c) B-QLEDs under charge supply scenarios of (+↑)(-↓) and (+↓)(-↑).

two e/h ratios scenarios for each material, indicating that Stark effects are essentially the same and, therefore, do not account for the changes in the TrPL characteristics observed for the different e/h scenarios. Additionally, the different slopes of the trends for the (+↑)(-↓) and (+↓)(-↑) scenarios suggest that the quenching effect is not primarily caused by electric field induced quenching (where changes in voltage would produce proportional changes in fields and therefore the slopes for the same ΔV would be expected to be similar). The different slopes therefore suggest that the increase in quenching is predominantly from the increase in charges (*i.e.* Auger quenching) as opposed to being primarily from electric field quenching. To further investigate this point, the changes in τ , again normalized to their values at 0V, are also plotted as a function of current density. Figures 5-9d and e present this data for both charge supply scenarios, respectively, for the same QLEDs. As can be seen, the slopes of the PL output versus current become progressively steeper in the order: R-QLEDs $\rightarrow$ G-QLEDs $\rightarrow$ B-QLEDs for both charge supply scenarios suggesting a progressive increase in Auger quenching effect in the same order. Also notably, in both the G- and B-QLEDs, where the e/h ratio is <1 and holes are the excess carriers, the (+↑)(-↓) scenario devices show steeper slopes than their (+↓)(-↑) scenario counterparts, indicating that increasing hole concentrations (*i.e.* making the e/h even smaller) results in a significant increase in Auger quenching, and that the differences in the slopes are larger in case of the B-QLEDs, where the hole concentrations are highest. In contrast, in the R-QLEDs where the e/h is >1 and electrons are the excess carriers, the slopes are somewhat similar for the two charge supply scenarios. We also note that in case of the G and B-QLEDs, the τ/τ_0 versus J fits exhibit steeper slopes at $J < 10^{-3} \text{ mA/cm}^2$. Although the origins of this effect are not clear, the steeper slopes may perhaps be associated with

the very efficient injection of holes in these materials which results in a rapid increase in the number of positive trions (even at low voltages). As the electric field across the QDs layers increases further, the mobility of holes starts to increase, reducing the residence time of the holes on the QDs thereby reducing the slopes. The stronger PL quenching effect of excess holes compared to that of excess electrons can be attributed to the high density of valence band states and the smaller hole localization radius which accelerate non-radiative Auger recombination and make quenching by positive trions more effective.^{70, 71, 159}.

To further investigate and analyze the origins of the decrease in τ upon increasing the current, the TRPL characteristics are fitted using triexponential fits and the constituting individual lifetime components (τ_1 , τ_2 and τ_3 with τ_1 representing the fastest component) are extracted, along with their respective weighing coefficients (A_1 , A_2 and A_3). Table 5-3 presents this data for all QLEDs at each voltage. As can be seen, the obtained τ_1 values in all devices are in the range of 2-4 ns, typical of radiative trion lifetimes, indicating that the fastest components of the TrPL characteristics are dominated by trions, either positive or negative depending on the type of excess carriers in each device. In contrast, the slower components τ_2 and τ_3 , often attributed to neutral exciton lifetimes, with the first dominated by quenching effects at ETL^{82, 160}, varied significantly among the three colors, especially τ_3 , and were consistent with typical exciton lifetimes reported in the literature for CdSe/CdS QDs of the respective colors. The analysis also shows that as the voltage (and therefore current) increases, the value of A_1 increases, pointing to a clear increase in trion concentration, as expected. The non-zero value of A_1 at $V=0$ suggests the presence of a non-negligible concentration of trions even without bias which could be due to spontaneous charge transfer at the ETL/QDs-EML interface⁴⁹ and/or other fast quenching phenomena. Also notable is the generally larger value of A_1 in case of B-QLEDs versus the other colors pointing to the higher concentrations of trions in these devices consistent with the conclusions made above. Table 5-4 summarizes typical values of exciton (τ_x), negative trion (τ_{x-}) and positive trion (τ_{x+}) lifetimes reported in the literature, together with the values obtained in this work (from the analysis above). Calculated radiative and non-radiative (Auger) components of negative (positive) trions ($\tau_{r,x-}$ ($\tau_{r,x+}$), $\tau_{A,x-}$ ($\tau_{A,x+}$)) are also included in the table.

Table 5-3. Lifetime components of the TrPL results for all QLEDs extracted from the tri-exponential decay curves with the charge supply scenarios $(+\uparrow)(-\downarrow)$ and $(+\downarrow)(-\uparrow)$ measured at different voltages from 0V to V_{On} . τ_1 , τ_2 , and τ_3 are lifetime components and A_1 , A_2 , and A_3 represent their respective weighing coefficients. τ shows the TrPL overall lifetime ($1/e$).

QLED	Charge scenario	Voltage (V)	A_1	τ_1	A_2	τ_2	A_3	τ_3	τ
R-QLEDs	$(+\uparrow)(-\downarrow)$	0	0.39	3.45	0.44	9.52	0.16	26.23	6.28
		1	0.45	3.01	0.41	9.93	0.13	25.45	5.91
		2	0.47	2.89	0.37	7.47	0.14	26.61	5.62
		3	0.48	2.79	0.37	6.51	0.13	25.28	5.43
R-QLEDs	$(+\downarrow)(-\uparrow)$	0	0.28	4.10	0.52	11.18	0.2	28.17	11.28
		1	0.28	4.07	0.48	9.67	0.23	29.49	11.02
		2	0.29	3.78	0.49	9.84	0.21	28.26	10.81
		3	0.31	3.71	0.51	10.68	0.20	29.11	10.35
G-QLEDs	$(+\uparrow)(-\downarrow)$	0	0.38	2.82	0.36	6.12	0.25	14.10	5.11
		1	0.41	2.80	0.39	4.24	0.19	13.32	4.76
		2	0.43	2.42	0.35	4.01	0.21	12.98	4.44
		3	0.46	2.18	0.36	3.76	0.18	13.92	4.05
G-QLEDs	$(+\downarrow)(-\uparrow)$	0	0.31	3.41	0.42	7.33	0.27	15.27	5.56
		1	0.33	3.19	0.44	6.81	0.23	16.14	5.36
		2	0.32	3.11	0.45	6.63	0.21	14.91	5.23
		3	0.35	2.88	0.48	6.24	0.16	16.46	4.88
B-QLEDs	$(+\uparrow)(-\downarrow)$	0	0.43	2.55	0.38	5.15	0.17	9.24	2.92
		1	0.42	2.37	0.41	4.93	0.16	8.88	2.72
		2	0.42	1.98	0.44	4.34	0.14	10.82	2.34
		3	0.44	1.54	0.42	4.74	0.13	10.21	2.11
		4	0.48	1.52	0.42	4.96	0.11	10.13	1.93
		5	0.49	1.32	0.42	4.63	0.09	9.42	1.81
B-QLEDs	$(+\downarrow)(-\uparrow)$	0	0.48	3.02	0.40	4.11	0.11	10.41	3.33
		1	0.47	2.79	0.38	4.53	0.14	11.36	3.17
		2	0.52	2.68	0.33	4.82	0.13	11.48	3.05
		3	0.51	2.46	0.35	5.23	0.15	10.15	2.96
		4	0.54	2.34	0.31	5.12	0.14	11.86	2.81
		5	0.57	2.13	0.33	4.97	0.11	11.46	2.63

Table 5-4. Photophysical Properties of QLEDs Explored in This Work and What Is Already in the Literature.

PL peak (nm)	τ_X (ns) ^d	τ_X^- (ns) ^e	τ_X^+ (ns) ^f	τ_{RX^-} (ns) ^g	τ_{AX^-} (ns) ^h	τ_{RX^+} (ns) ⁱ	τ_{AX^+} (ns) ^j	Reference
622	19	2.7	1.6	NA	NA	NA	NA	⁴²
650	28.7	3	1.6	NA	NA	NA	NA	³⁶
660	29	3.1	1.5	17	3.8	14.5	1.7	⁴³
644	25	5.8	NA	NA	NA	NA	NA	⁴⁴
660	22.9	4.1	NA	13.7	4	NA	NA	¹²
628 ^a	29.1	3.7	NA	14.5	4.9	NA	NA	This work
526 ^b	13.9	NA	2.2	NA	NA	6.9	3.2	This work
463 ^c	9.4	NA	1.3	NA	NA	4.7	1.8	This work

^aR-QLEDs under charge supply scenario of (+↓)(-↑) and bias of 3V. ^bG-QLEDs under charge supply scenario of (+↑)(-↓) and bias of 3V. ^cB-QLEDs under charge supply scenario of (+↑)(-↓) and bias of 5V. ^dNeutral exciton lifetime. ^eNegative trion lifetime. ^fPositive trion lifetime. ^gRadiative lifetime of negative trion. ^hAuger lifetime of negative trion. ⁱRadiative lifetime of positive trion. ^jAuger lifetime of positive trion. $\tau_{RX^\pm}(X^\pm)$ are calculated from $\frac{\tau_X}{2}$.^{11,44} Also, radiative and Auger component of trions are calculated from $\frac{1}{\tau_{X^-(X^+)}} = \frac{1}{\tau_{A,X^-(X^+)}} + \frac{1}{\tau_{R,X^-(X^+)}}$.^{11,45,46}

In order to further investigate the impact of excess carriers on the EL performance of the R, G, and B-QLEDs, comparative TrEL measurements are also conducted on the devices with the (+↑)(-↓) and (+↓)(-↑) charge supply scenarios of each color by applying a square voltage signal with a pulse width of 40 μ s at a frequency of 10 kHz. The normalized TrEL results collected at various voltages (above V_{On}) are shown in Figure 5-11. As can be seen, increasing the bias shortens the EL rise time (the time it takes for the output signal to rise from 10% to 90%), making the advanced part of the TrEL signal more “square”. Notably, the EL intensity does not remain constant over the pulse duration afterwards. Rather, it decreases, and the rate of decrease becomes faster as the bias voltage increases.

Figure 5-11 presents the EL signal rise time (top) as well as the relative EL intensity before the pulse ends normalized to the peak EL intensity during the same pulse (bottom) for the different bias magnitudes. As can be seen, the EL rise time is generally shortest for the R-QLEDs and longest for the B-QLEDs suggesting there is a correlation between the EL rise time and the bandgap of the QDs-EML where a narrower bandgap helps the EL reach its peak value sooner. One possible reason for the slower EL response in the wide bandgap QLEDs can be the differences in the injection barrier for the second charge to be injected (*i.e.* for hole injection in case of R-

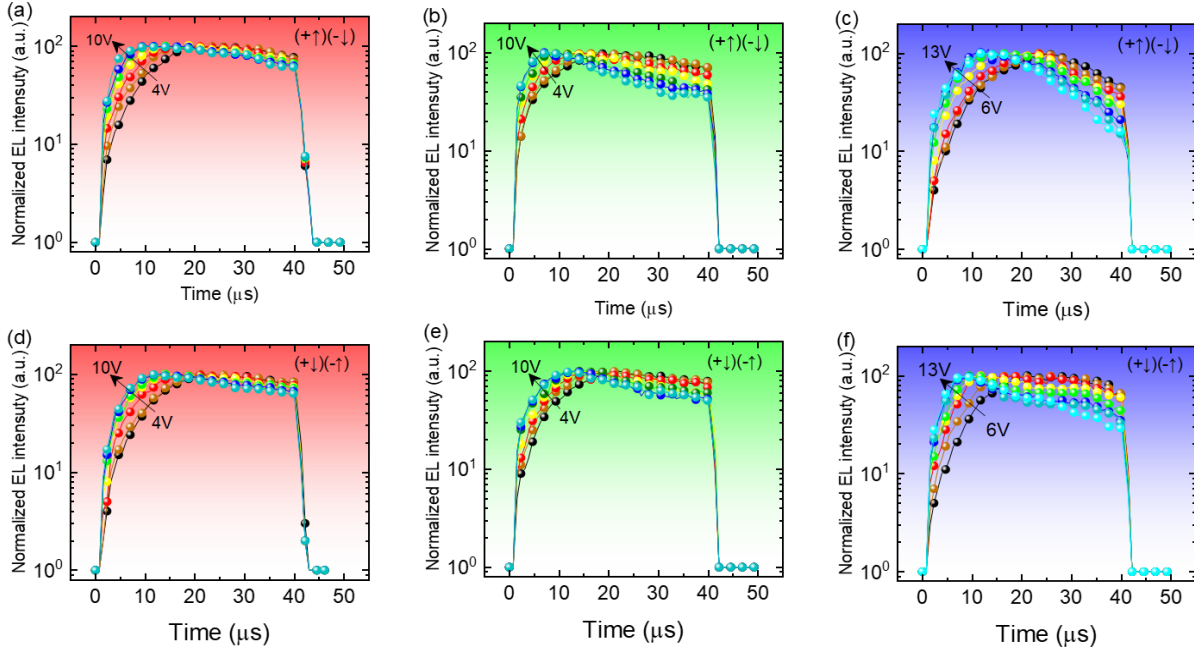


Figure 5-11. TrEL measurements of R-QLEDs, G-QLEDs, and B-QLEDs for $(+\uparrow)(-\downarrow)$ scenario in (a), (b), and (c) and for $(+\downarrow)(-\uparrow)$ scenario in (d), (e), and (f), respectively.

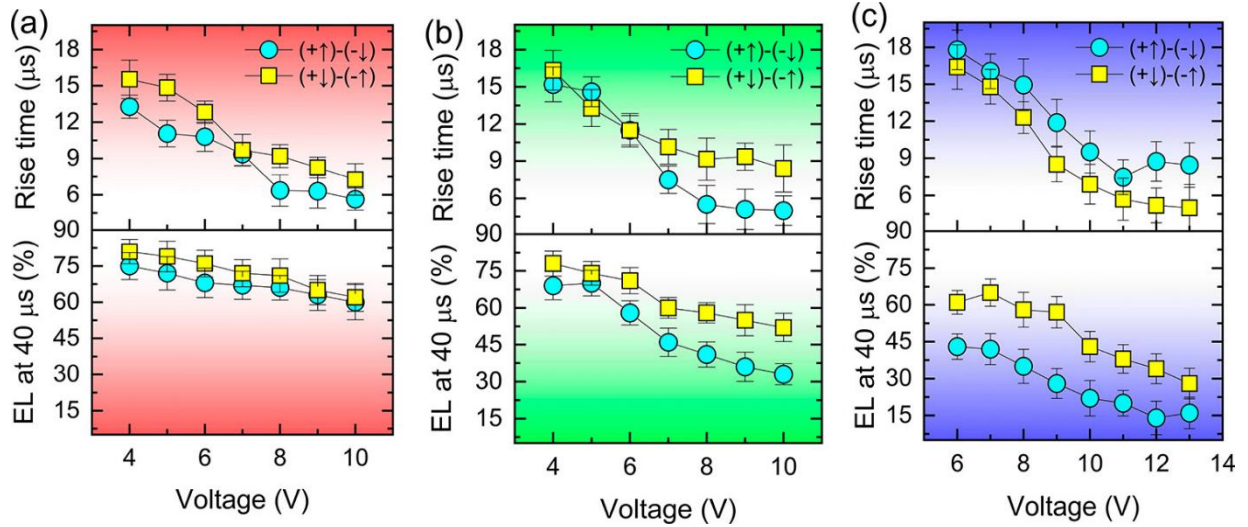


Figure 5-12. Rise time (top) and EL at 40 μ s (bottom) versus voltage of (a) R-QLEDs, (b) G-QLEDs, and (c) B-QLEDs measured above V_{ON} for $(+\uparrow)(-\downarrow)$ and $(+\downarrow)(-\uparrow)$ scenarios.

QLEDs, and for electron injection in case of G- and B- QLED) which can affect the speed by which the EL reaches its peak value.¹⁶¹⁻¹⁶³ Looking at the dependence of EL rise time on the charge supply rates for each color, one can see (from Figure 5-12a (top)) that in the R-QLEDs, the $(+\uparrow)(-\downarrow)$ scenario gives a faster rise time when compared to $(+\downarrow)(-\uparrow)$, which can be attributed to the higher rate of hole supply, in full agreement with the conclusion that hole injection is the

efficiency limiting (and speed-limiting) step in QLEDs of this color. In contrast, for B-QLEDs (in Figure 5-12c) the opposite is observed, again proving that electron injection is the limiting step in devices of this color. In G-QLEDs (Figure 5-12b-top), one can see that both charge injection scenarios give very similar rise times over the 4-6 V range, indicating that G-QLEDs lie in between the two other colors in that respect. In these devices the faster rise times of the $(+\uparrow)(-\downarrow)$ scenario at voltages $>6\text{V}$ suggests a possibly stronger field-dependent mobility in ZnMgO when annealed at the lower temperature.

Turning the attention now to the relative EL intensity at 40 μs data in Figure 5-12 (bottom), *i.e.* the EL intensity at the end of the pulse relative to the peak EL intensity during the same pulse one can see a correlation between the reduction in EL intensity over the pulse duration and the band-gap of the QDs-EML, with the R-QLEDs showing the smallest reduction and the reduction becoming increasingly larger with the QDs band-gap. In general, such a reversible reduction in EL over the pulse duration can be ascribed to gradual changes in charge concentrations and e/h ratios within the QDs-EMLs over the duration of the pulse. The reduction in EL intensity suggests that the changes in charge concentrations must be tilting the e/h ratios further away from 1 (*i.e.* increased charging occurs), resulting in a higher probability for trion formation and subsequent Auger recombination, and/or increased leakage of the excess carriers towards the counter CTL and electrode. The larger EL reduction in the case of the G and B- QLEDs indicates that this charging effect occurs much more readily in these devices relative to their R-QLEDs counterparts. Also notable is the larger dependence of the EL reduction rate (*i.e.* the charging rate) on the charge supply scenario in case of G- and B-QLEDs where $(+\uparrow)(-\downarrow)$ scenario brings about larger EL reductions in comparison to $(+\downarrow)(-\uparrow)$. Although it is possible that the smaller dependence in case of R-QLEDs is due to a generally better charge balance in these devices which makes altering electron supply ratios only marginally affect efficiency, the larger EL intensity reductions upon increasing hole supply in the other two colors may be due to the more efficient Auger recombination by positive trions versus negative trions consistent with results from EL measurements.

5.1.3 Conclusion

In conclusion, comparative systematic investigations of inverted R, G, and B-QLEDs reveal significant differences in electron and hole injection between the three colors, resulting in significant differences in e/h ratios and charge balance among them. In general, R-QLEDs have

electrons as excess carriers (*i.e.* $e/h > 1$) in their EMLs, whereas in both G- and B-QLEDs, the EMLs generally have excess holes (*i.e.* $e/h < 1$) with charge balance conditions being significantly worse in case of B-QLEDs (*i.e.* $e/h \ll 1$). Comparative TrPL and steady state PL measurements under current flow show that excess holes are more detrimental to QDs luminescence than electrons, revealing that Auger quenching by holes is more efficient. In addition, TrEL measurements under pulsed electrical driving uncover a rapid reversible decrease in the EL intensity that starts to occur within a few microseconds of applying the bias pointing to charging effects in the EMLs that further reduce charge balance and increase Auger quenching in them. This effect is also found to be stronger when holes are the excess carriers in the EML, and strongest in case of B-QLEDs, pointing to the more detrimental effect of holes on QLEDs EL output in general, and their significant role in the low efficiency and stability of B-QLEDs in particular. Results also show that a larger fraction of unrecombined holes reach the ETLs in case of B-QLEDs, a phenomenon that likely also plays a role in the lower efficiency and stability of these devices. The results provide insights into the differences in the efficiency behavior of R-G- and B-QLEDs and uncover the role of excess holes and poor charge balance in the lower efficiency and EL stability of B-QLEDs. While this study focuses primarily on CdSe-based QDs, the methodologies and approaches introduced here can be used for investigating and studying other material systems including perovskite QDs, carbon QDs, and InP QDs in future research endeavors.

5-2 Differences in Spontaneous Electron Transfer in Red, Green and Blue Quantum Dots Light Emitting Devices and Its Benefits for Electroluminescence Efficiency

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Differences between hole and electron injection efficiencies at the HTL and ETL interfaces are known to affect the sequence of charge injection process (*i.e.* whether holes or electrons are injected first into the QDs-EML) and therefore affect the Auger recombination, which, in turn, affects device efficiency and stability.⁶⁵ Auger recombination occurs when the QDs are charged with excess carriers, leading to the formation of either negative trions (two electrons-one hole) or positive trions (one electron-two holes) on them, depending on the type of excess carriers.^{27, 164} It has been reported that positive trions are generally

more detrimental to the luminescence efficiency of the CdSe-based QLEDs than negative trions because of the high density of valence band states and the smaller hole localization radius.^{71, 159} Therefore, the sequence of charge injection into the QDs-EML, which is primarily governed by the energy barriers at the charge injection layers (CTLs) interfaces, can play a critical role in determining the majority trion type, and, therefore, impact the performance of QLEDs. Yu et al. demonstrated that injecting an electron before a hole into a QD results in a higher electroluminescence efficiency than with the reverse sequence, a behavior that is attributed to a lower Auger recombination rate in negative trions compared to positive trions.¹⁵⁵ Also, Deng et al. observed that, while hole injection into neutral QDs is typically inefficient, the presence of negative charges in QDs-EML assists hole injection by enhancing Coulomb interactions and therefore benefits efficiency.⁵⁵ Moreover, Bae et al. reported that spontaneous electron injection, without the application of bias, can occur from the ZnO ETL into R-QDs,⁴⁹ charging the QDs-EML negatively and increasing the likelihood that electrons will be the majority carriers during device operation under bias. While most studies have focused almost exclusively on R-QDs, it is known that increasing the QDs-EML bandgap (i.e. going from R-QDs to G, and B-QDs) affects the energy barriers at the CTLs/QDs-EML interfaces, thereby influencing charge injection efficiency into the QDs-EML.¹⁴⁴ Considering the significant impact of charge injection efficiency on the sequence of charge injection into the QDs-EML, it is crucial to undertake a comparative study examining the order of charge injection into the QDs-EML of R, G, and B-QLEDs. This investigation will help determine the type of excess carrier in each color and its role in their EL efficiencies.

Here, we report on the importance of spontaneous electron transfer that is known to occur from the ETL into the QDs-EML under zero bias, resulting in the negative charging of the QDs-EML, on the EL efficiency of QLEDs. Our PL measurements, simulation results, and tests on both full devices and single carrier devices reveal a reduction in the magnitude of spontaneous electron transfer as the bandgap of the QDs-EML increases. We find that, in the R-QLEDs, which exhibit a stronger spontaneous electron transfer versus G and B-QLEDs, the sequence of charge injection into the QDs-EML is "electron first, hole next". This sequence increases the likelihood that electrons serve as the majority carriers during device operation, therefore, increasing the probability of negative trion formation. Conversely, in case of G and B-QLEDs, specifically B-QLEDs, with a weaker spontaneous electron transfer compared to R-QDs, the charge injection sequence into the QDs-EML is "hole first, electron next", suggesting a probability of holes being the majority carriers and positive trion formation during device operation. Comparing the maximum EQE of three colors, (8.91%, 6.59%, and 0.77% for R, G, and B-QLEDs, respectively), we propose that charging the QDs-EML with electrons first, as opposed to holes first, can be more favorable for EL efficiency enhancement due to the lower Auger recombination effect of negative trions versus positive trions.

5-2-1 Comparing the EL performance of R, G, and B-QLEDs

Figure 5-13a shows the J-V-L characteristics of the R, G, and B-QLEDs, while the schematic energy level diagram of the QLEDs is depicted in Figure 5-14a. From J-V-L results, it is evident that as the QDs-EML bandgap increases, the QLEDs exhibit higher threshold (V_{Th}) and turn-on (V_{On}) voltages, which correspond to the voltages for the onset of charge injection and for EL, here taken as reaching an EL intensity of 1cd/m^2 , respectively. The difference between V_{Th} and V_{On} arises from differences between the voltages at which one of the carriers (either electron or hole) is first injected and that at which the counter carrier starts to get injected allowing for electron-hole recombination and EL to start to be observed.¹⁶⁵ As can be seen, the difference between the V_{Th} and V_{On} becomes larger as we go from R-QD to G-QD and then to B-QDs, exhibiting a correlation with the size of the bandgap of QDs. This suggests that increasing the QDs-EML bandgap likely worsens charge balance in the QLEDs which can be attributed to the charge injection barriers at the CTL interfaces that will expectedly become larger. Figure 5-13b depicts the EQE of devices, with R, G, and B-QDs, exhibiting PLQY values of 90%, 80%, and 65%, respectively, while assuming equal out-coupling efficiency for all QLEDs. As can be seen, the EQE of the R-QLEDs remains nearly constant ($\sim 8\%$) across a broad range of current densities ($0.2\text{-}1000\text{mA/cm}^2$), indicating that the R-QLEDs effectively sustain favorable charge balance conditions even as the applied electric field intensity rises. On the other hand, while exhibiting a relatively poor EQE of about 2% at low current densities ($< 1\text{mA/cm}^2$), the EQE of the G-QLEDs increases by increasing the device current density, reaching a maximum EQE of 6.59% at $\sim 200\text{ mA/cm}^2$. This proposes that the G-QLEDs charge balance improves under higher electric fields. In other words, a type of carrier, either electron or hole, requires a higher electric field versus the counter type carrier to be injected into the G-QDs-EML. It should be noted that the efficiency of the R and G-QLEDs starts to decrease at about 1000mA/cm^2 , which can be ascribed to either a reduction in charge balance or to electric field-induced exciton quenching effects.^{53, 166, 167} In case of B-QLEDs, the device EQE is below 1% for the whole range of current density, indicating a poor charge balance in the device, even as charge injection increases. Based on the J-V-L and EQE-J results for all three colors, it can be concluded that, as the QDs-EML bandgap increases, the injection of one of the two carriers (either electron or hole) may become harder. Therefore, to investigate the difference in charge balance conditions in the QLEDs, electron and hole supply efficiencies into the QDs-EML need to be compared. The voltage, luminance, CIE (International Commission on Illumination), and EQE of R, G, and B-QLEDs measured at 20 mA/cm^2 are presented in Table 5-5.

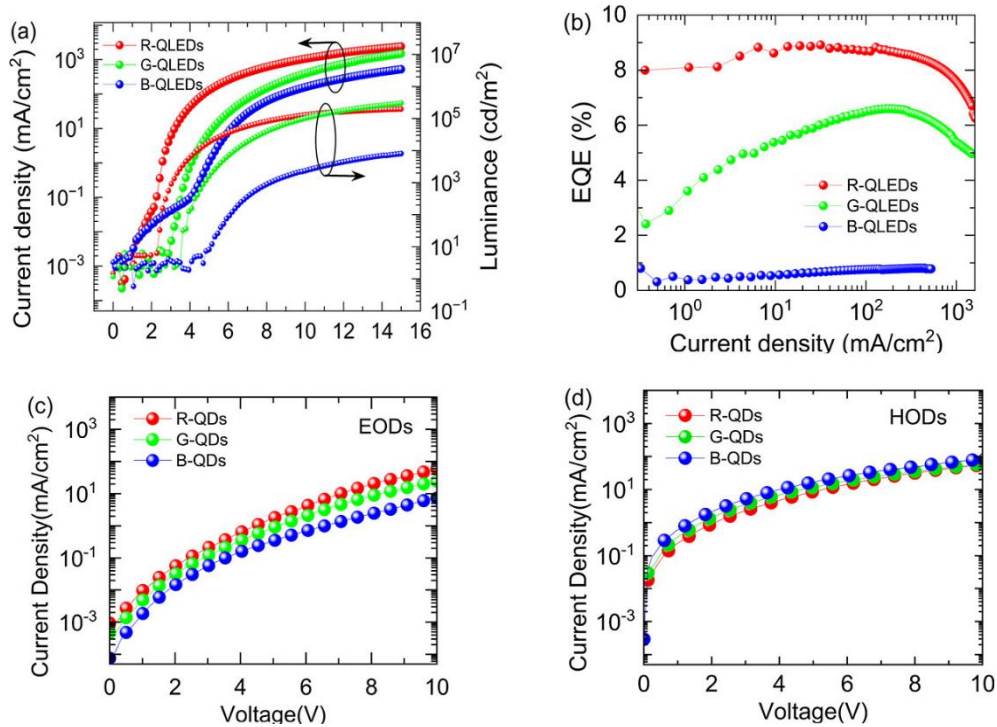


Figure 5-13. (a) J - V - L , and (b) EQE - J of R, G, and B-QLEDs. J - V characteristics of (c) EODs and (d) HODs with R-QDs, G-QDs, or B-QDs layers.

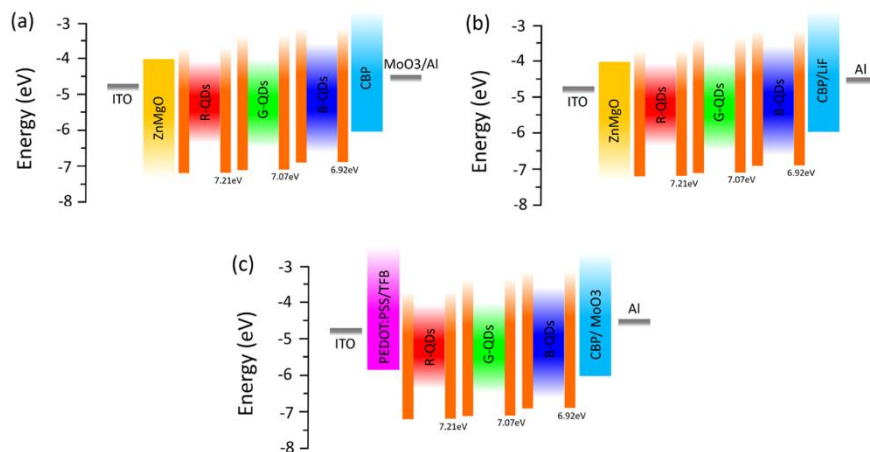


Figure 5-14. Schematic energy level diagram of (a) QLEDs, (b) EODs, and (c) HODs.

Table 5-5. The voltages, luminance, and CIE, for R, G, and B-QLEDs measured at 20mA/cm² as well as their maximum EQE.

Device	Voltage (V)	Luminance (cd/m ²)	CIE		Max EQE (%)
			X	Y	
R-QLEDs	3.55	2900	0.66	0.33	8.91
G-QLEDs	5.67	4700	0.16	0.79	6.59
B-QLEDs	6.82	250	0.14	0.06	0.77

In order to find which carriers, whether electrons or holes, get injected first into the QDs-EML of each device and likely act as the excess carriers during device operation, single carrier devices are fabricated containing QDs-layers of each of the three colors, and their J-V characteristics are compared. The schematic energy level diagram of electron only devices (EODs) and hole only devices (HODs) are illustrated in Figures 5-14b and c, respectively. The J-V characteristics of EODs with the structure of ITO/ZnMgO/R, G, or B-QDs/CBP/LiF/Al are shown in Figure 5-13c. As is evident, the electron current in the EODs at any given voltage decreases as the bandgap of the QDs increases, proposing that electron supply efficiency becomes more difficult as we go from R-QDs to G-QDs and then to B-QDs. Conversely, HODs with the structure of ITO/ PEDOT:PSS/TFB/R, G, or B-QDs/CBP/MoO₃/Al show that widening the QDs-EML bandgap from B-QDs to G-QDs and then to R-QDs results in a higher hole current density in HODs at any given voltage (Figure 5-13d). These observations are consistent with our recent findings.^{144, 165} Consequently, one can conclude that electrons are the carriers that their injection into the QDs-EML becomes harder as the QDs-EML bandgap becomes wider in the QLEDs as discussed above. Moreover, based on the single carrier devices data, it becomes evident that changing the QDs-EML bandgap can indeed influence the sequence of charge injection into the QDs-EML. Specifically, in the case of lower bandgap QDs-EML (R-QDs), electrons are injected first followed by holes, whereas in instances of wide bandgap QDs-EML (G and B-QDs-EML), holes are injected first followed by electrons. This suggests that the R-QDs-EML and B-QDs-EML are already negatively and positively charged, respectively, before the onset of EL. Moreover, the QDs-EML can be charged even without bias due to spontaneous charge transfer at the interface of CTLs and QDs-EML.^{158, 160, 168} As charging the QDs-EML before starting EL can affects the

performance of the QLEDs, it is necessary to investigate the occurrence of spontaneous charge transfer from CTLs into the QDs-EML for each color and explore how it can affect the efficiency of QLEDs.

5-2-2 Comparing the spontaneous electron transfer in R, G, and B-QLEDs

After finding the influence of the QDs-EML bandgap on the charge injection properties of QLEDs under forward bias, it is critical to investigate whether spontaneous charge transfer from the CTLs into the QDs-EML occurs before the onset of the EL. As charging of the QDs can significantly influence their photophysical properties,^{69, 70, 143, 165} testing and comparing their PL performance under zero bias and reverse bias (where bias-induced injection is not possible) can be useful for probing the presence of pre-existence of charges in the QD-EML due to spontaneous charging phenomena.

Figure 5-15 shows the transient PL (TrPL) and steady-state PL performance collected from the three QLEDs as the voltage is varied from 0 to -5V. Table 5-6 shows the lifetime components of the TrPL results for the QLEDs extracted from two exponential decay curves measured at different voltages from 0V to -5V. τ_1 , and τ_2 are lifetime components and A_1 and A_2 represent their respective weighing coefficients. Also, τ_{ave} shows the TrPL average lifetime. The TrPL lifetime, collected at 628nm, and the PL intensity of R-QLEDs are shown in Figures 5-15a and e, respectively.

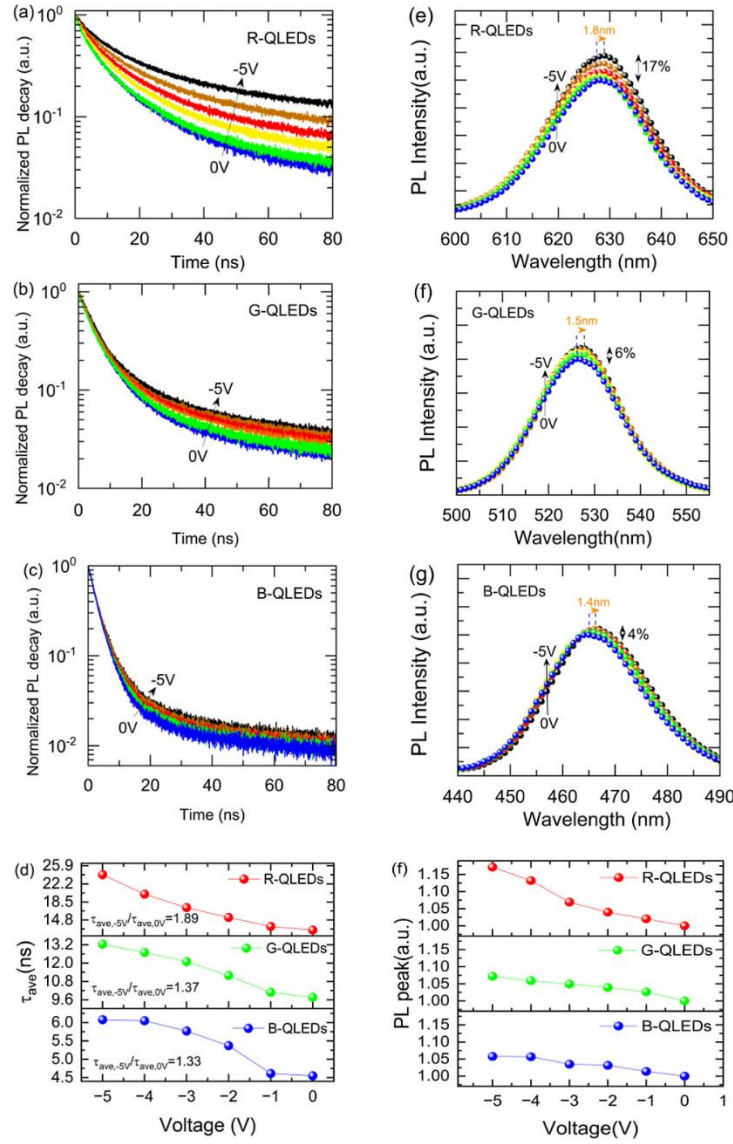


Figure 5-15. TrPL characteristics of (a) R-QLEDs (collected at 628 nm), (b) G-QLEDs (collected at 526nm), and (c) B-QLEDs (collected at 462nm). (d) Average TrPL lifetime (τ_{ave}) versus voltage for all three colors. Steady state PL intensity of (e) R-QLEDs, (f) G-QLEDs, and (g) B-QLEDs. (h) Normalized PL intensity versus voltage for all three colors.

As can be seen, both τ_{ave} (Table 5-6) and the PL intensity increase as the negative bias increases. This observation points to the presence of carriers (either electrons or holes) into the QDs-EML under zero bias conditions as a result of spontaneous injection of carriers that act as PLQY quenchers due to Auger recombination. When a reverse bias is applied, these charges are removed from the QDs-EML, leading to the observed increase in both the τ_{ave} and the PL intensity. As shown in Figure 5-16, when the TrPL of a G-QLEDs is measured from 0V to -10V, there is a

Table 5-6. Lifetime components of the TrPL results for all QLEDs extracted from the two exponential decay curves measured at different voltages from 0V to -5V. τ_1 , and τ_2 are lifetime components and A_1 and A_2 represent their respective weighing coefficients. τ_{ave} shows the TrPL average lifetime.

Device	Voltage	A_1	τ_1	A_2	τ_2	τ_{ave}
R-QLEDs	0V	0.51	3.57	0.44	15.24	12.74
	-1V	0.52	3.63	0.41	16.26	13.47
	-2V	0.49	4.1	0.44	18.16	15.33
	-3V	0.49	4.65	0.44	20.54	17.34
	-4V	0.46	5.29	0.44	23.58	20.1
	-5V	0.44	6.06	0.43	28.07	24.08
G-QLEDs	0V	0.72	3.88	0.22	14.52	9.75
	-1V	0.71	3.99	0.23	15.07	10.08
	-2V	0.7	4.05	0.21	16.89	11.18
	-3V	0.68	4.19	0.2	18.27	12.1
	-4V	0.69	4.26	0.18	19.69	12.69
	-5V	0.68	4.45	0.17	20.94	13.44
B-QLEDs	0V	0.92	2.59	0.08	10.18	4.55
	-1V	0.91	2.65	0.07	10.45	4.61
	-2V	0.87	2.64	0.1	11.05	5.37
	-3V	0.86	2.66	0.1	11.8	5.77
	-4V	0.84	2.71	0.12	12.13	6.05
	-5V	0.83	2.79	0.14	12.22	6.08

small change in the TrPL from -7V to -10V, proposing that the TrPL lifetime of the device approaches a limited value as the reverse bias increases. Also as seen, the reverse bias affects the PL intensity less in case of G-QLEDs (Figures 5-15b collected at 526nm and 5-15f) and B-QLEDs (Figures 5-15c collected at 462nm and 5-15g), indicating that quenching by preexisting is less in turn indicating that spontaneous charge transfer must also be relatively less in them by comparison. It is known that the presence of excess carriers in QDs-EML can result in the formation of trions which can be verified by analyzing the τ_1 and A_1 of TrPL results.¹⁶⁵ Looking at TrPL components in Table 5-6, in all cases, increasing the reverse bias improves τ_1 but reduces A_1 , both indicating that the density of charged species into the QDs-EML is reduced by increasing the reverse bias. Also, in all three colors, there is a red-shift in the PL spectra by increasing the reverse bias which can be attributed to Stark effects.^{166, 169} Figures 5-15d and f, respectively, compare τ_{ave} and PL peak intensity changes under reverse bias for all three colors. As shown in Figure 5-15d, the ratio of $\tau_{ave, -5V} / \tau_{ave, 0V}$ in R-QLEDs, G-QLEDs, and B-QLEDs are 1.89, 1.37, and 1.33, respectively, suggesting that the PL performance enhancements, that is observed because of charged species removal under reverse bias, is larger in the R-QLEDs compared to those of the G and B-QLEDs. Moreover, a similar

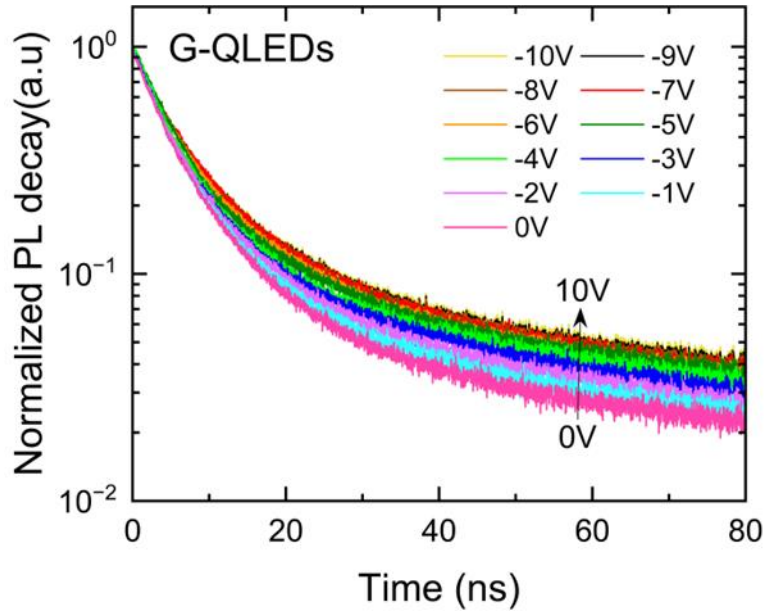


Figure 5-16. The TrPL characteristics of the G-QLEDs measured under 0V to -10V.

trend is observed when the PL peaks for all three colors are compared as shown in Figure 5-15f. These observations suggest that the spontaneous transfer of charges into the QDs-EML is stronger in the R-QLEDs versus G, and B-QLEDs.

In general, the presence of charges in the QDs-EML in the absence of bias will originate from spontaneous charge transfer from one or both CTLs, driven by differences in their Fermi levels. Therefore, to investigate whether the observations above are arising from charge transfer from the ETL or the HTL, we change each of the ETL and HTL one at a time and test for corresponding changes in the observed PL behavior. For this purpose, we first use a series of QLEDs in which the ETLs are annealed at different temperatures (100°C, 160°C, 270°C, and 350°C) while keeping the CBP unchanged as the HTL in all of them. Changing the annealing temperature of ZnMgO is known to passivate defects thus changing the density of states (DOS) in ZnMgO^{147, 170} which would affect any spontaneous charge transfer at the ZnMgO/QDs interface and therefore also the PL behavior of the devices under reverse bias. To find how changing the annealing temperature can affect the ZnMgO properties, the UV-Vis absorption of ZnMgO films coated on quartz substrate and annealed at different temperatures (100°C, 160°C, 270°C, and 350°C) are measured, as shown in Figure 5-17a. As can be seen, elevating the annealing temperature shifts the absorption onset toward shorter wavelengths, indicating that the optical bandgap of the samples reduces as the annealing temperatures increase. The Tauc plot of the samples (Figures 5-17 b to e) shows that the increasing of the annealing temperature reduces the optical bandgap of ZnMgO from 3.51 eV (for 100°C) to 3.42 eV (for 350°C), indicating that ZnMgO films become more crystalline by increasing the annealing temperature, thereby enhancing the density of states in ZnMgO.

Figure 5-18 shows the effect of changing the annealing temperature of the ZnMgO ETL (100°C-350°C) on the TrPL characteristics of QLEDs of the three colors measured at 0V or -5V. For comparison, the TrPL overall lifetimes (τ), defined as the time until the TrPL intensity decreases to 0.36 ($=1/e$) of its initial value, is provided beside each measurement. The normalized TrPL overall lifetime (τ/τ_0), where τ_0 represents the TrPL overall lifetime at 100°C, of each device is extracted from Figure 5-18 and compared as shown in Figure 5-19. Figure 5-19a shows that elevating the annealing temperature of the ETL from 100°C to 350°C in the R-QLEDs results in a gradual increase in the τ of the TrPL measured at 0V (by 1.18X) but a decrease in the τ of the TrPL measured at -5V (by 1.33X). The increase in τ can be explained by the passivation of the intrinsic defects in the ZnMgO ETL, a factor strongly influenced by the selected annealing temperature, as noted earlier.^{147, 170} The decrease in τ (at -5V) shows that more carriers are transferred into the QDs-EML in case of ZnMgO with high annealing temperatures, suggesting that electrons are the type of carrier that are transferred from the ETL into the R-QDs-EML spontaneously. The spontaneous (at 0V) electron transfer into the R-QDs-EML can occur because the QDs conduction-band level is located in energetic proximity to the Fermi level of the ZnMgO ETL.^{49, 171} Looking at the (τ/τ_0) of the G-QLEDs (Figure 5-19b) and B-QLEDs (Figures 5-19c), one can see that increasing the ZnMgO annealing temperature leads to a lower reduction in the τ under -5V compared to that of the R-QLEDs. This indicates that the concentration of spontaneously transferred electrons into the G, and B-QDs must be lower

versus R-QDs, which in turn suggests that spontaneous electron transfer decreases as the bandgap of the QDs increases. This can be readily attributed to the conduction band minimum (CBM) becoming shallower.

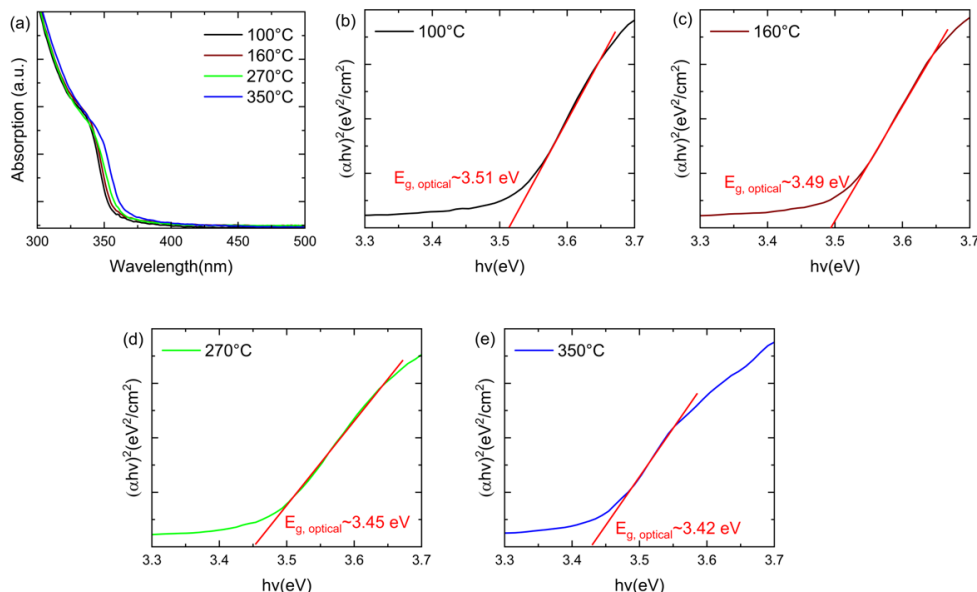


Figure 5-17. UV-Vis absorption of ZnMgO annealed at 100°C, 160°C, 270°C or 350°C. The Tauc plots of ZnMgO annealed at (b) 100°C, (c) 160°C, (d) 270°C and (e) 350°C.

Seeing that changing the ZnMgO annealing temperature influences the PL behavior indicating that spontaneous charge transfer must be occurring at the ETL/QDs interface and also seeing that it is more efficient in case of R-QLEDs than in G or B-QLEDs, we also similarly test the effect of changing the HTL while keeping the ETL unchanged. For this, we tested the effect of replacing CBP with TCTA. The results are presented in Figure 5-20. As is evident from the figure, altering the HTL negligibly affects the TrPL behavior in all three devices, suggesting that spontaneous charge transfer at the HTL interface is negligible for all three colors. Furthermore, this proposes that spontaneous electron transfer can significantly influence the performance of the QLEDs by determining the type of excess carrier in the QDs-EML before and even during the QLEDs operation.

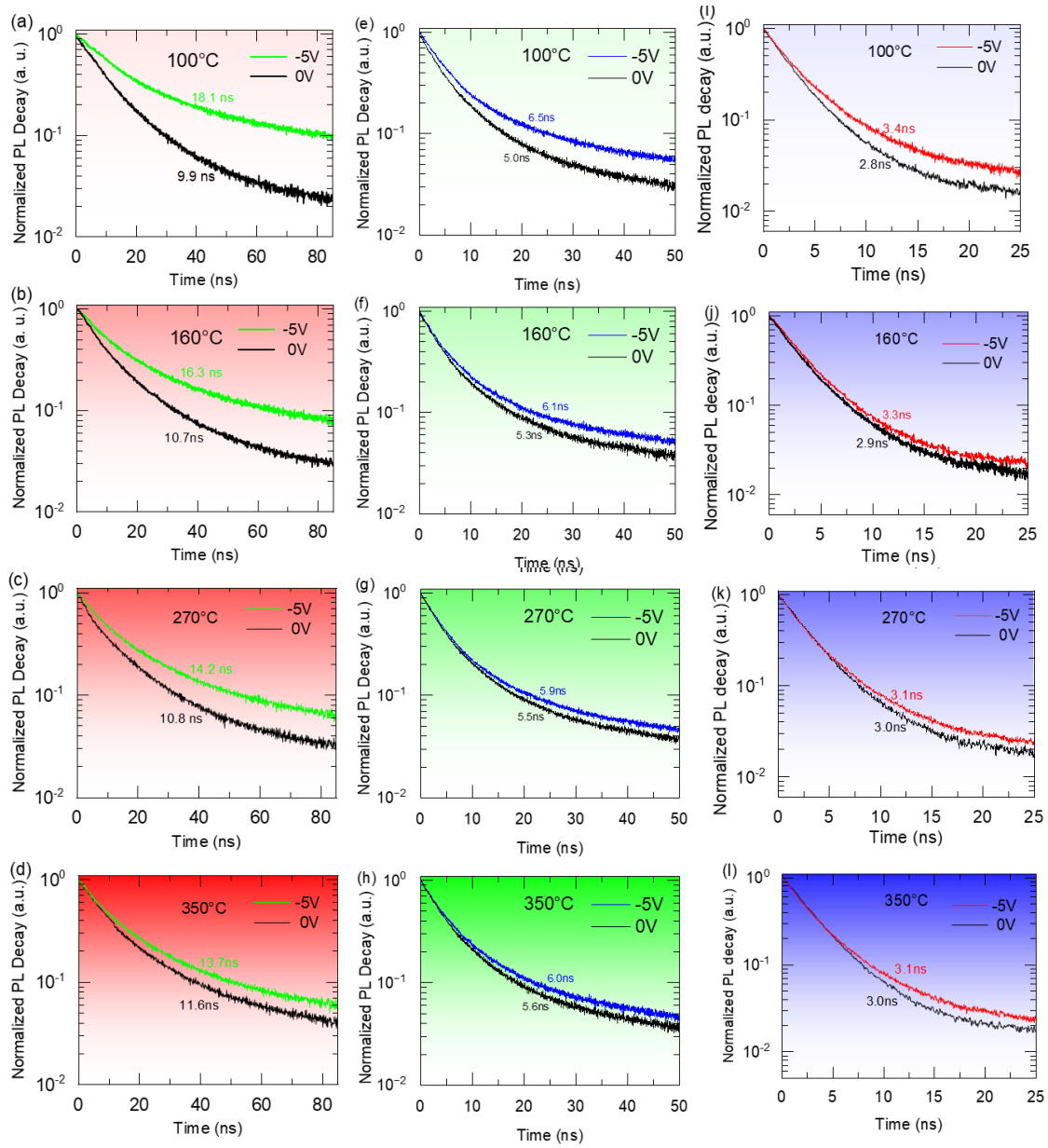


Figure 5-18. The TrPL of (a-d) R-QLEDs (collected at 628nm), (e-h) G-QLEDs (collected at 526nm), and (i-l) B-QLEDs (collected at 462nm) in which the ZnMgO ETL is annealed at 100°C, 160°C, 270°C, and 350°C and biased under 0V or -5V. The TrPL overall lifetimes (τ) are provided in each graph.

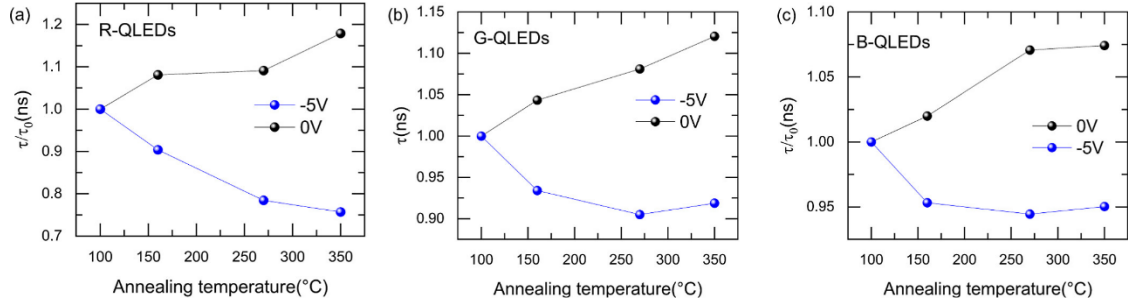


Figure 5-19. Normalized TrPL overall lifetime (τ/τ_0) versus ETL annealing temperature of (a) R-QLEDs (collected at 628 nm), (b) G-QLEDs (collected at 526 nm), and (c) B-QLEDs (collected at 462 nm) under 0 or -5 V. τ_0 is the TrPL overall lifetime (τ) at 100 °C.

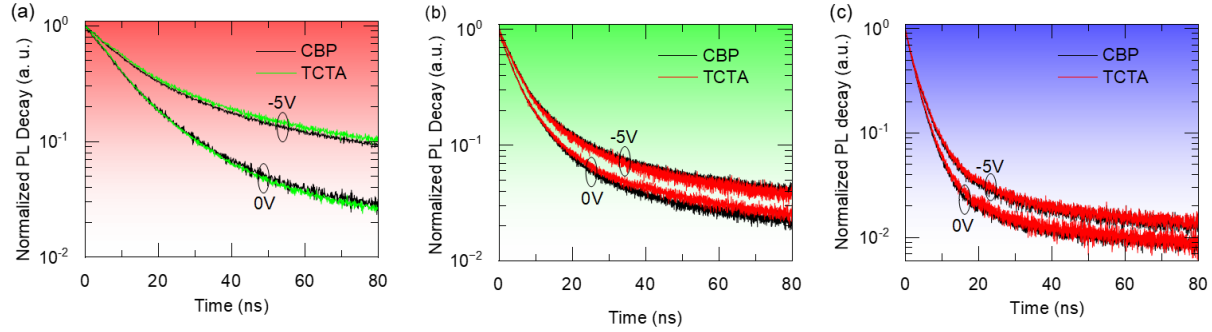


Figure 5-20. Comparing the TrPL characteristics of (a) R-QLEDs, (b) G-QLEDs, and (c) B-QLEDs with TCTA and CBP HTLs biased under 0V or -5V.

5.2.3 Simulation of spontaneous electron transfer effect

In order to further investigate and better understand how electrons may be spontaneously transferred into the QDs-EML, a one-dimensional SCAPS-1D software^{82, 151} is used to simulate the performance of the QLEDs. As a useful software to accurately simulate the characteristics of optoelectronic devices, the SCAPS is used in this work to calculate the concentration of electrons in the ZnMgO ETL and QDs-EML as well as the electric field distribution across the layers under 0V and -5V. The calculation relies on differential equations, including Poisson, drift-diffusion, and carrier continuity. It is known that the crystallinity and the typical crystallite size of ZnO derivatives increase with annealing temperature, thereby increasing the DOS and carrier concentration.^{145, 172, 173} Therefore, here the electron concentration in the ZnMgO is assumed to vary from 10^{17} to 10^{18} 1/cm³ as the annealing temperature increases from 100 to 350°C. Figure 5-21 shows the simulation results for the electron concentration and electric field distribution in the QDs-EML and ZnMgO ETL of all three colors under both 0V and -5V. As shown in Figure 5-21a, at zero bias (top), the simulations predict a smoothly varying electron concentration across both the ZnMgO

and the QDs-EML with a gradient in electron concentration within the R-QDs-EML, characterized by a higher concentration at the QDs-EML/ZnMgO interface and a decreasing concentration as one moves away from this interface. This clearly suggests significant electron diffusion from the ETL into the R-QDs-EML that occurs spontaneously under 0V, causing the electron concentration to be higher at the interface. Increasing the concentration of the electrons in the ETL (via increasing the annealing temperature) leads to a higher concentration of electrons in the QDs layer, which can be attributed to increased spontaneous electron transfer into the R-QDs-EML, in line with the aforementioned observation. Under -5V (Figure 5-21a, bottom), the accumulated electrons are swept away from the R-QDs-EML toward the ITO electrode by the applied electric field, leading to a reduction in the PLQY quenching effect of these charges observed under zero bias. In case of G and B-QLEDs (Figure 5-21b and c), in contrast, the electron concentration across the two layers changes abruptly at the interface and is significantly different in the two layers. The

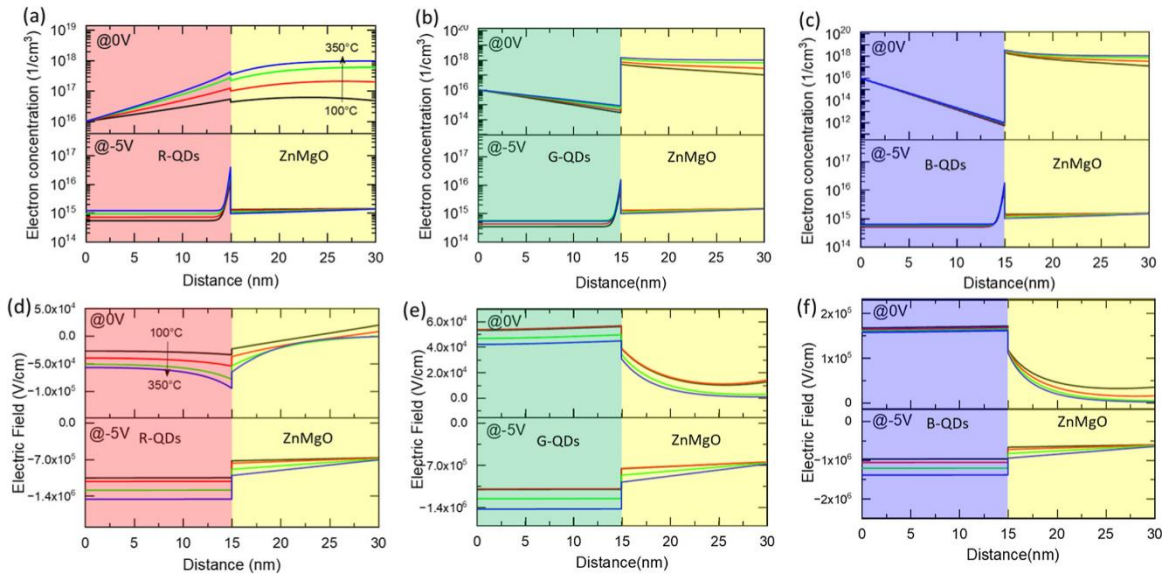


Figure 5-21. Electron concentration in the QDs-EML and ZnMgO ETL of (a) R-QLEDs, (b) G-QLEDs, and (c) B-QLEDs under 0 V (top) and -5 V (bottom). The electric field distribution in the QDs-EML and ZnMgO ETL of (d) R-QLEDs, (e) G-QLEDs, and (f) B-QLEDs under 0 V (top) and -5 V (bottom). The electron concentration in the ETL is changed from 10^{17} (1/cm³) to 10^{18} (1/cm³) associated with changing its annealing temperature from 100 to 350 °C, respectively.

electron concentration across the QDs-EML also has an opposite gradient with lower electron concentrations near the interface with ETL in case of the B-QDs versus the G-QLEDs. Also looking at the electron concentration gradients across the ETLs, one can see that they are also opposite in case of G- and B-QLEDs versus the R-QLEDs, showing a slightly higher electron concentration near the interface in the first two, suggestive of charge accumulation in the ZnMgO at the interface (a Schottky-type barrier). The large differences in the electron distributions between the R-QLEDs and the G- and B-QLEDs are in line

with spontaneous injection of electrons from the ETL into the QDs-EML being limited in case of the G and B-QLEDs. This can be attributed to the shallower CBM of the G-QDs and B-QDs versus R-QDs, hence the larger activation energy barrier for spontaneous electron transfer. Comparing all three colors, the electron concentration in the QDs-EML at the ETL interface decreases by approximately five orders of magnitude, as one goes from R-QDs to B-QDs, dropping from around 10^{17} to 10^{12} ($1/\text{cm}^3$). These results are in line with the observations suggesting that the QDs-EML of R-QLEDs are generally negatively charged with spontaneously transferred electrons from the ETLs before applying bias, indicating that the formation of positive trions will necessarily be very limited in R-QLEDs since the arrival of holes on the R-QDs when a forward bias is applied is always preceded by electrons making the charge injection sequence in them “electron first, hole next”. In contrast, as spontaneous electron transfer is negligible in case of the G- and B-QLEDs, and, from the HOD results, hole injection under forward bias is very efficient in them, the charge injection sequence in them will necessarily be “hole first, electron next”, thus promoting the formation of positive trions. Therefore, one possible reason for the lower efficiency of the wider band gap QLEDs in general, and of B-QLEDs in particular can be the “hole first, electron next” charge injection sequence in them which promotes the formation of positive trions which are known to be more effective in Auger quenching.^{27, 155, 165}

Furthermore, Figures 5-21d to f illustrate the electric field density established in the QDs-EML and ETL under both 0V and -5V conditions. As depicted in Figure 5.21d, the negative electric field on the QDs-EML side is greater than that on the ETL side, and this difference becomes more pronounced as the electron concentration in the ETL increases. In case of G-QLEDs (Figure 5.21e), a positive electric field is formed at the QDs-EML, showing the lack of spontaneous electron transferring from the ETL into the QDs-EML. This electric field has the potential to enhance the likelihood of exciton dissociation in the G-QDs-EML by exerting a Coulombic force, directing holes toward the trap states in the ETL. The intensity of this electric field becomes more pronounced in B-QLEDs, where a larger barrier hinders electron injection. As a result, a stronger electric field versus G-QLEDs forms, thereby amplifying the potential for exciton quenching by ETL trap states. Under reverse bias (-5V), the electric field shapes are almost flat across the layers in all cases, indicating the layers are essentially depleted in this condition. It's worth noting that the exciton quenching effect may become even more pronounced during device operation, as the externally applied electric field aligns with the electric field established within G and B-QLEDs under zero bias conditions. This can be considered as a cause of the low performance of wide bandgap QLEDs. More importantly, the established electric field at zero bias can accelerate the Auger quenching effect by assisting holes to leave the core of the QDs and move toward the ETL. Therefore, the spontaneous electron injection from the ETL into the QDs-EML can play a critical role in the efficiency of QLEDs by determining the sequence of charge injection into the QDs-EML as well as the PL quenching effect at the QDs-EML-ETL interface.

5.2.4 Conclusion

In conclusion, our study reveals that the spontaneous electron transfer from the ETL into the QDs-EML of QLEDs weakens with increasing in the bandgap of the QDs-EML (i.e. going from R-QDs to G, and B-QDs). Furthermore, our comprehensive analysis involving both experimental and simulation results demonstrates a correlation between the magnitude of spontaneous electron transfer and the sequence of carrier injection into the QDs-EML, with "electron first, hole next" and "hole first, electron next" in R-QDs and B-QDs, respectively. The disparities in the spontaneous electron transfer and charge injection sequences are accompanied with a substantial difference in the EQEs, with R-QLEDs exhibiting 8.91% and B-QLEDs showing 0.77%. This shows that the charge injection sequence of "electron first, hole next", rather than "hole first, electron next", can be more favorable for enhancing efficiency.

Chapter 6. Exploring new ETL and HTL designs for optimizing charge injection and improving EL performance in inverted QLEDs

6.1 Double Electron Transport Layer Approach for Efficiencies >23% in Quantum Dots Light Emitting Devices

In this chapter, new ETL and HTL designs are developed to improve the charge balance of inverted QLEDs. Although the inorganic ETLs exhibit better thermal and chemical stability compared to the organic HTL, they demonstrate some changes over time and under electrical stress, which can affect their properties and those of the adjacent material, thereby significantly impacting the performance of QLEDs.¹⁷⁴⁻¹⁷⁶ It has been widely reported that encapsulation increases the efficiency of QLEDs immediately and also gradually over time that latter is a phenomenon termed positive aging.^{76, 114, 177, 178} Acharya et al. showed that positive aging is due to the interaction between the encapsulation resin and ZnO, leading to carbonate formation that reduces ZnO defect densities.¹¹⁴ Also, Su et al. demonstrated that a multi-day interfacial reaction between ZnMgO and Al forms AlO_x, which is believed to enhance electron injection and reduce exciton quenching at the ZnMgO/Al cathode interface.¹⁷⁸ According to Chen et al., the positive aging is mainly occur due to enhanced electron injection across the QD/ZnMgO interface.¹⁷⁷ Generally, positive aging in QLEDs show improved efficiency and longer operational lifetimes, due to enhanced electron injection and reduced exciton quenching, though the exact cause remains unclear. Recently, we have found that the inverted IQLEDs tend to have higher hole (h)/electron (e) ratio, especially for green and blue.^{179, 180} Therefore, it is highly desirable to investigate whether positive aging could occur in inverted QLEDs and result in an improvement in electron supply, thereby enhancing charge balance in the device (i.e., achieving an h/e ratio close to 1).

In this part, it is observed that a significant positive aging occurs in inverted QLEDs even without encapsulation, indicating that the phenomena does not primarily happen due to the encapsulation resin as is widely believed. Experiments on devices that certain layers were replaced by fresh ones verify that changes in the ETL or its interface with the cathode result in the gradual increase in electron supply over time. The results also reveal that for positive aging to occur in I-QLEDs, a prerequisite is that this increased electron supply be injected uniformly into the QDs-EML, along with efficient electron blocking properties in the HTL. Modified devices with a double ETL, simultaneously enhancing electron supply and uniform injection, show immediate high

efficiencies and accelerate the positive aging process, resulting in EQEs of 24.4% and 23.1% for red (R) and green (G)-QLEDs, respectively.

6.1.1 Positive aging observation

First, to investigate whether the positive aging effect occurs in inverted QLEDs, inverted G-QLEDs with the structure of ITO/ZnMgO/G-QDs/TCTA/MoO₃/Al are fabricated and characterized. To avoid significant damage to the organic HTL in inverted QLEDs caused by encapsulation—where a glass cover is sealed to the device substrate using ultraviolet (UV)-curable resin glue—the device is not encapsulated. Figure 6-1a depicts the device structure. After fabrication, the devices are stored in a nitrogen-filled glovebox and their performance is measured overtime. Figure 6-1b shows the J-V-L characteristics of the device just after fabrication (i.e. 0h) and after 24h. As shown, after 24h, the current density increases significantly, suggesting that the supply of one type of carrier (i.e. electrons or holes) or both increases during this period. This enhancement in current density results in improved luminance and a reduced turn-on voltage (the voltage at the onset of EL, here defined as reaching an EL intensity of 1 cd/m² and necessarily requiring the presence of both electrons and holes in the G-QDs-EML), decreasing from about 4V to 3V. Figure 6-1c shows the device EQE. As seen, the changes in current density and luminance results in a 2.4X improvement in EQE, proposing that such changes observed after 24h improves the device charge balance, indicating the occurrence of a positive aging effect in the G-IQLEDs even without encapsulation. This effect does not cause any change in the shape of the EL spectrum (Figure 6-1d). Figure 6-1e shows the changes in EQE and driving voltage during the first 300 hours after the device fabrication. The device was not biased during this period, except for short intervals (< 5 sec) every few hours to collect J-V-L and EQE measurements. As can be seen, the EQE reaches to its maximum value after 24h, then start to show some negative shelf aging effect. In contrast, the device driving voltage shows a gradual reduction, indicating that the charge supply improves with increased current density during positive aging. Figure 6-1f presents the device lifetime, showing relative luminance on the top and driving voltage on the bottom, measured under a constant current density of 20 mA/cm². As observed, positive aging leads to an about 35X longer lifetime which can be attributed to the enhancement of the device charge balance. Therefore, it can be concluded that the enhancement in either electron supply, hole supply, or both improves the

charge balance and consequently results in the positive aging effect in inverted G-QLEDs even without encapsulation, thereby significantly improving their efficiency and lifetime.

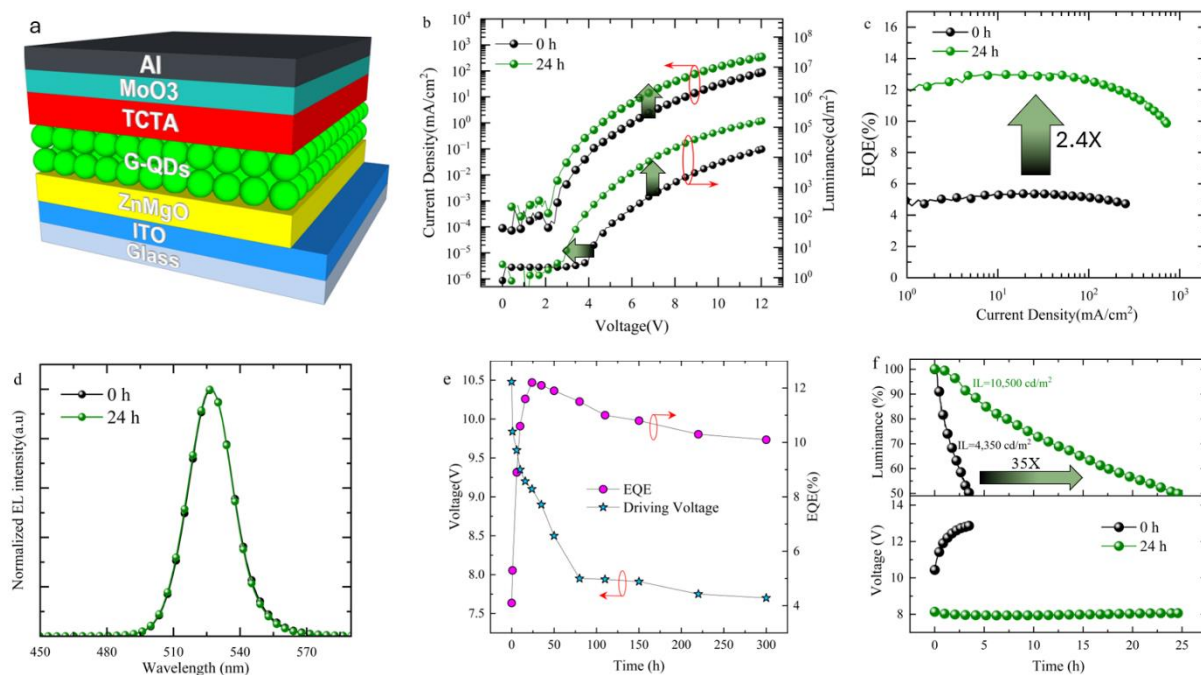


Figure 6-1. (a) Schematic diagram of the G-IQLEDs. (b) J-V-L and (c) EQE-J characteristics, and (d) EL spectra of the G-IQLEDs after fabrication (0h) and after positive aging (24h). (e) Changes in driving voltage and EQE for 300h. (f) Normalized luminance (top) and driving voltage vs time under 20 mA/cm² constant current driving of the G-IQLEDs.

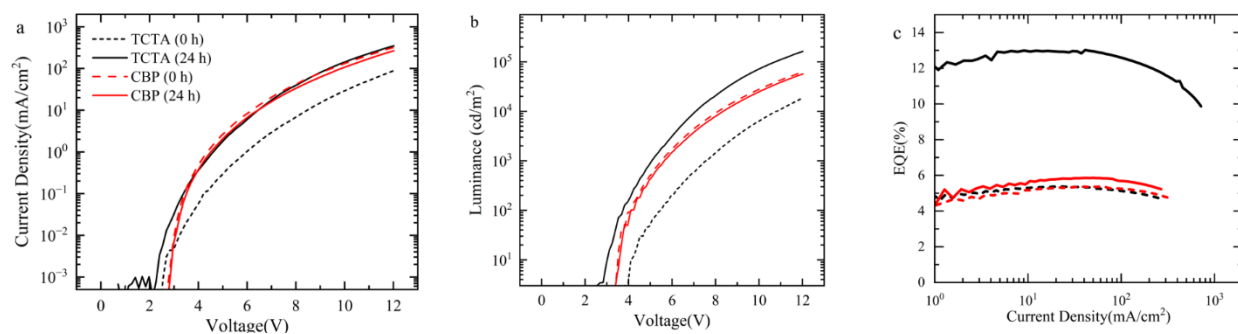


Figure 6-2. Comparison of (a) J-V, (b) L-V, and (c) EQE of G-IQLEDs with CBP or TCTA HTL.

To explore whether an increase in hole supply efficiency contributes to the efficiency improvement during the first 24 hours, another set of devices was tested using CBP as the HTL instead of TCTA, as CBP is known to supply more holes compared to TCTA.^{119, 179} Figure 6-2a compares the J-V characteristics of the devices with CBP and TCTA after fabrication (0h) and after 24h. As can be seen, the current density of the device with CBP at 0h is comparable with that of the TCTA at 24h, suggesting that the utilization of the CBP increases the device current density, which is likely due to an increase in the hole current density. However, the EQE of the device (Figure 6-2c) at 0h is comparable with that of TCTA at 0h. These results suggest that the increase in hole supply does not improve device efficiency, indicating that hole supply is not the limiting factor, and that positive aging may instead be associated with an increase in electron supply.

To investigate if electron supply is behind the positive aging behaviour, we investigate the effect of replacing all layers above the ZnMgO layer in inverted G-QLEDs with fresh ones after the positive aging behaviour has been experienced. In this experiment, all layers above the ZnMgO ETL in an inverted G-QLEDs with TCTA HTL are removed as described in the experimental section and schematically illustrated in Figure 6-3a. After that, fresh layers of G-QDs, TCTA, MoO₃, and Al are deposited to rebuild the device. Figure 6-4a, b, and c, respectively, show the J-V, L-V, and EQE-J characteristics of the device before and after rebuilding, referred to here as the initial device and rebuilt device, respectively. The average EQE of the initial device and rebuilt device, based on measurements on a group of twelve devices in each case, is shown in Figure 6-3b. As seen, the EQE of the rebuilt device at 0h remains comparable with that of initial device at 24h. Noticeably, after 24h, the rebuilt device does not show a significant change in the EQE, showing that no positive aging occurs in this device. Importantly, these results also propose that the positive aging effect happens at the ETL, which is the only unchanged layer in the rebuilt devices. This indicates that the enhancement of electron current, resulting from changes either at the ITO/ZnMgO interface or within the ZnMgO layer, is responsible for the positive aging effect. It has been known that oxygen vacancies (V_O) from intrinsic lattice defects occur during synthesis of ZnMgO, potentially acting as deep charge traps that negatively affect electron transport.^{76, 175} Therefore, the reduction of these trap states in the ZnMgO layer likely explains the enhanced electron current and the resulting positive aging.

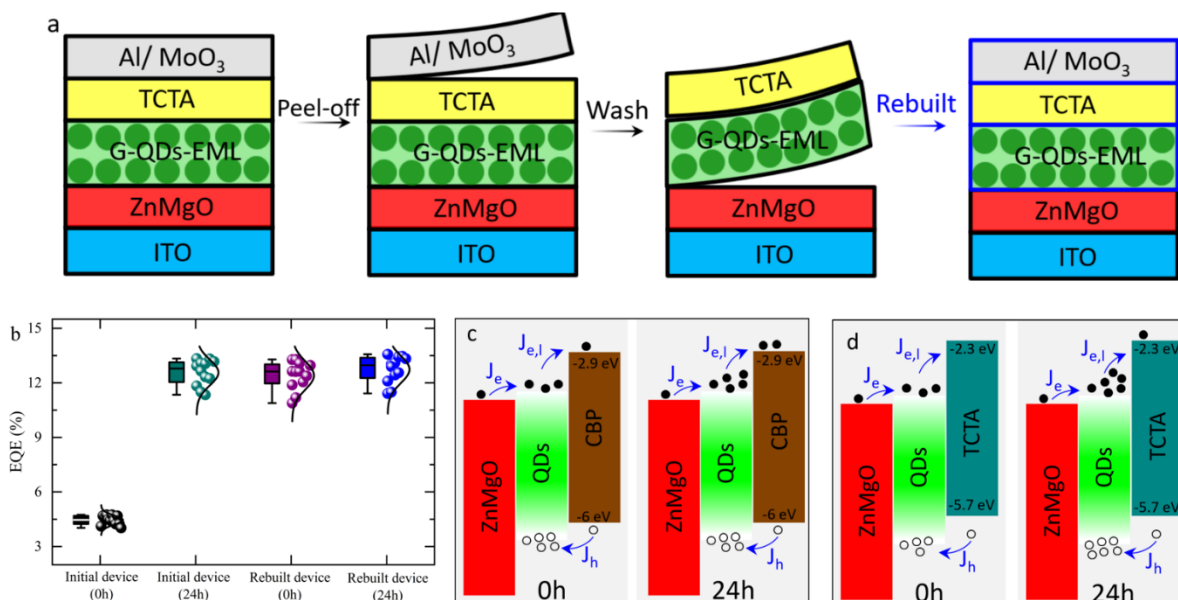


Figure 6-3 (a) Schematics of the G-IQLEDs rebuilding process. (b) The average EQE of rebuilt G-IQLEDs with TCTA HTL measured for the initial device at 0h and 24h, and for the rebuilt device at 0h and 24h. The energy band diagram of G-IQLEDs with (c) CBP and (d) TCTA HTL, respectively, showing the configurations before and after positive aging.

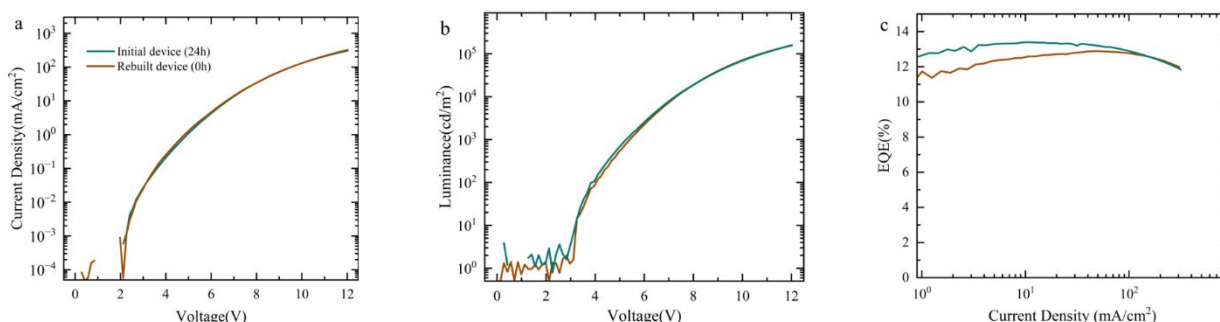


Figure 6-4. (a) J-V, (b) L-V, and (c) EQE of G-IQLEDs with TCTA HTL before and after rebuilding.

To explain why positive aging occurs in devices with TCTA but not in those with CBP, the energy band diagrams of the devices before and after positive aging are compared. Figures 6-3c and d show the energy band diagrams of inverted G-QLEDs with CBP and TCTA as the HTL, respectively, showing the conditions before (0h) and after positive (24h) aging. As can be seen, there is 0.6eV difference between the lowest unoccupied molecular orbitals (LUMO) of TCTA (i.e. -2.3eV) and CBP (i.e. -2.9eV),¹⁴⁹ indicating that TCTA provides a larger barrier to limit electron leakage from QDs-EML into the HTL. In case of CBP (Figure 6-3c), before positive aging, the hole supply (J_h) is more than electron supply (J_e), resulting in an electron to hole (e/h) ratio of <1 into the QDs-EML, as we previously reported.^{179, 180} In this condition, it is likely that some

electrons leak ($J_{e,l}$) into the CBP due to its relatively deep LUMO level. After positive aging, when the electron supply increases, the leakage current also increases, resulting in a reduction of device charge balance. In case of TCTA (Figure 6-3d), before positive aging, while hole supply is stronger than electron supply, electron leakage is limited by a large energy barrier at the QDs/HTL interface. After positive aging, the increased electron injection into the QDs-EML improves the device charge balance, bringing the e/h close to 1. One can conclude that the simultaneous increase in electron and hole supply in G-IQLEDs with a TCTA HTL is responsible for positive aging, whereas devices with a CBP HTL do not exhibit this effect due to the deeper LUMO level of CBP causing electron leakage and reduced charge balance.

Finding that the electron supply enhancement occurs due to some changes either in the ZnMgO ETL or its interface with ITO during positive aging, resulting in a significant EQE enhancement in devices with TCTA, we test the effect of increasing the annealing temperature of ZnMgO ETL which would increase electron supply.¹⁸¹ Figure 6-5 shows the changes in J-V, L-V, and EQE-J characteristics of G-IQLEDs over time, where the ETL is annealed at different temperatures: 100°C (control), 150°C, 220°C, and 350°C. Figures 4-6a and b show the changes in current density (measured at 14V) and driving voltage (measured at 20 mA/cm²) of the devices, respectively, over a period of 300 hours for devices with the different annealing temperature, extracted from the data in Figure 6-5. As seen at 0h, higher annealing temperatures lead to an instant increase in current density and a corresponding decrease in driving voltage of the devices, consistent with an instant increase in the device electron supply. Increasing the annealing temperature also reduces the changes in current density over time, thereby suppressing the positive aging behavior. Surprisingly, however, the EQE (Figure 6-6c) does not change significantly at 0h, contrary to the expectation that the instant increase in electron supply would lead to an instant increase in EQE. Consistent with the current density, the positive aging behavior is also slowed by increasing the annealing temperature. The fact that an increase in annealing temperature does not lead to an instant enhancement in EQE and also suppresses changes in ZnMgO over time suggests that this temperature rise induces effects in ZnMgO that reduce the EQE.

To test if the increase in annealing temperature can change the morphological properties of ZnMgO, a factor that can significantly affect the uniformity of electron supply, we examine its surface morphology using Atomic Force Microscopy (AFM). Figure 6-6d illustrates the surface

morphology of ZnMgO layers deposited on Glass/ITO substrates, which were annealed at different temperatures ranging from 100°C to 350°C. As observed, the surface roughness of the ZnMgO layers generally increases with the annealing temperature. At 100°C (control), the surface exhibits relatively smooth characteristics with a root mean square (RMS) roughness of 1.87 nm. However,

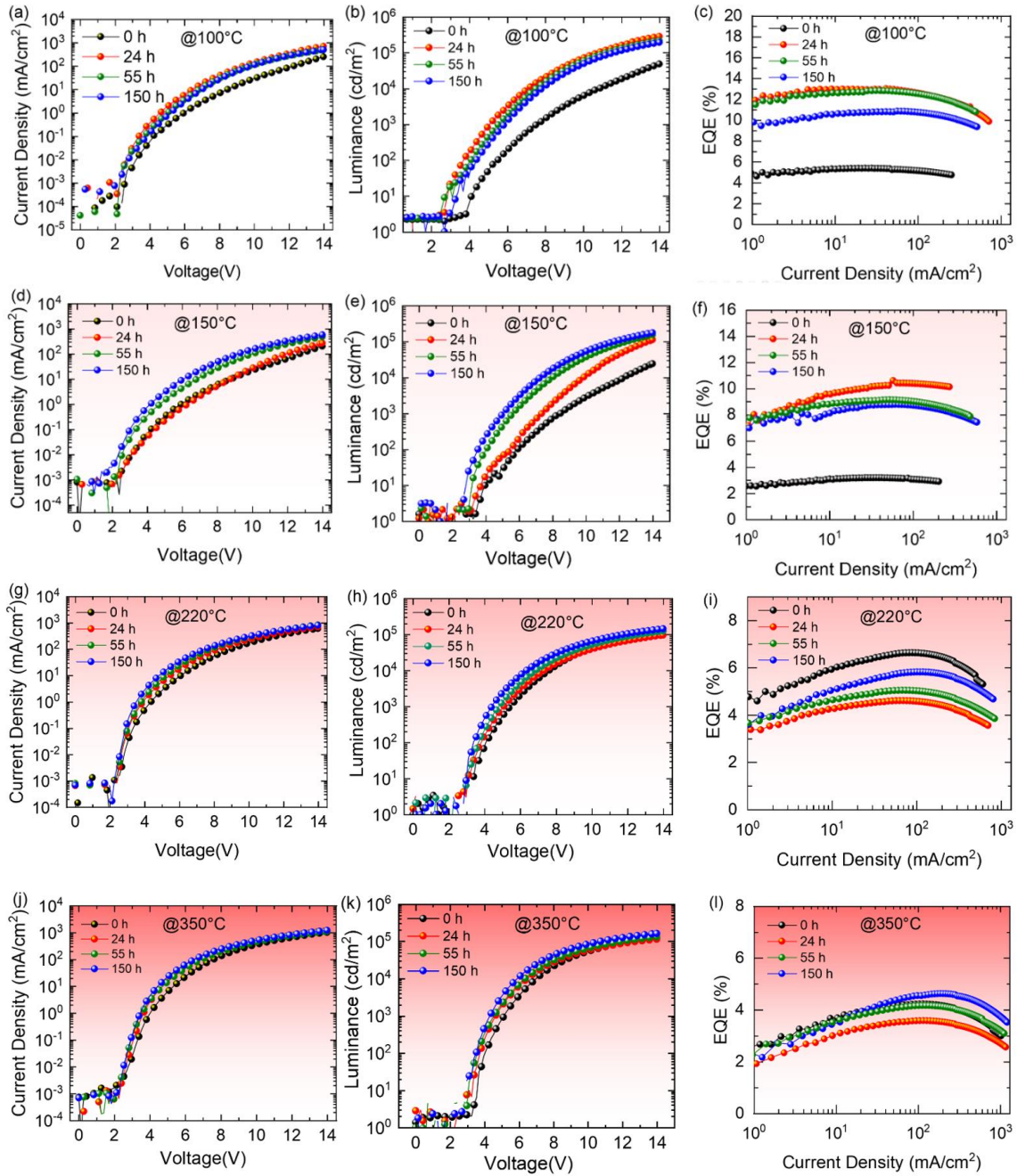


Figure 6-5. J-V, L-V, and EQE-J of G-IQLEDs in which ETL is annealed at (a-c) 100°C, (d-f) 150°C, (g-i) 220°C, (j-l) 350°C measured for 150h.

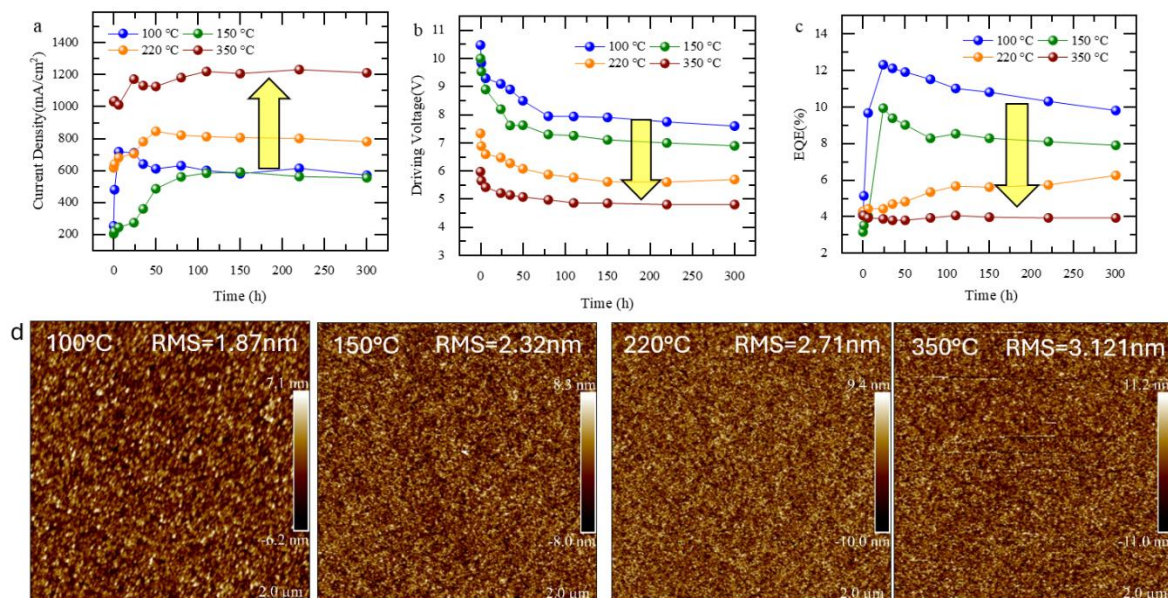


Figure 6-6. Changes in (a) current density at 14V, (b) driving voltage at 20 mA/cm², and (c) EQE at 20 mA/cm² of the devices over time, where the ETL is annealed at different temperatures: 100 °C (control), 150 °C, 220 °C, and 350 °C. (d). AFM images of ETL annealed at different temperatures: 100 °C (control), 150 °C, 220 °C, and 350 °C.

as the temperature increases to 150 °C and 220 °C, the roughness increases to 2.32 nm and 2.71 nm, respectively, as indicated by the height scale variations. At the highest annealing temperature of 350 °C, the surface becomes significantly more textured, showing the largest RMS roughness of 3.12 nm. This increase in surface roughness with higher annealing temperatures suggests changes in the ZnMgO crystallinity or grain structure. The increased roughness in the ZnMgO layer could cause non-uniform electron injection into the QDs EML, with more electrons being injected from the tips of the sharper regions relative to other area. Moreover, the heightened roughness of the ZnMgO layer can increase the roughness of the overlying QDs-EML layer, which may also negatively affect the device's EQE. Therefore, one can conclude that the high roughness of the ZnMgO ETL, resulting from high annealing temperature, is likely to limit the EQE enhancement.

6.1.2 Electron supply enhancement by Double ETL approach

Finding that the increasing the ZnMgO annealing temperature enhances the electron current supply, a prerequisite for improving the EQE, but leads to non-uniform electron supply – ultimately not increasing the EQE of the G-IQLEDs - we test the double ETL approach. In this approach, the ZnMgO is divided into two layers annealed at different temperatures: i) the first

ETL, coated on the ITO and annealed at 350°C, leverages the benefit of increasing the electron supply, and ii) the second ETL, coated on the first ETL and annealed at 100°C, ensures uniformity

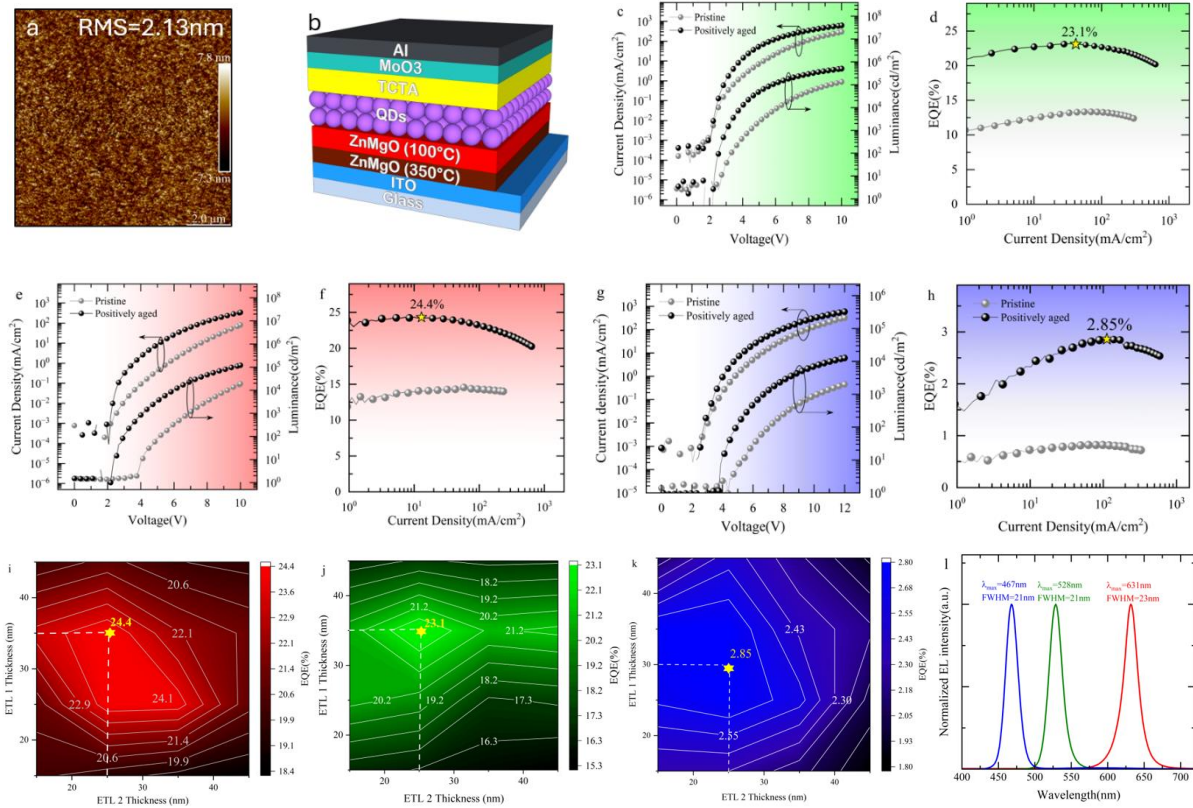


Figure 6-7. (a) AFM image of the double layers of ZnMgO. (b) Schematic diagrams of the QLEDs with double ETL structure. JVL and EQE of G-IQLEDs (c and d), R-IQLEDs (e and f), and B-IQLEDs (g and h) with a double ETL structure. The counter plots of EQE under the variation of ETL thicknesses for i R, j G, and k B-IQLEDs with double ETL structure. l. EL spectra of R, G, and B-IQLEDs with double ETL.

in the electron supply into the QDs-EML. Figure 6-7a presents the AFM image of the double layers of ZnMgO, showing a similar roughness to a single ZnMgO annealed at 100°C (Figure 6-7d), the double ETL does not significantly change the film morphology, making it suitable for providing a uniform electron supply into the QDs-EML. Figure 6-7b depicts the schematic diagram of the QLEDs with double ETL. Figure 6-7c, and d show the J-V-L and EQE-J characteristics of the G-QLEDs with the double ETL. As seen, the current density, luminance, and EQE of the device measured just after fabrication (pristine) are comparable with those of a device with a single ETL experienced positive aging (Figure 6-1b and c), indicating that using the double ETL immediately enhances both the current density and EQE. Surprisingly, the device with a double ETL also demonstrates significant positive aging, similar to the device with a single ETL, which further

enhances the device current density, resulting in an EQE of 23.1%. Figure 6-8 shows changes in EQE of the G-IQLEDs with a double ETL structure for 5 days. As can be seen, the positive aging process and reaching to maximum EQE in double ETL structure is about 2X faster than single ETL (Figure 6-1e). Regardless of changes in which part of the ETL, whether the ITO/ETL or within the ETL, leads to positive aging in G-IQLEDs, the double ETL data indicate that the increase in electron current density with a uniform supply into the QDs-EML as well as convenient electron blocking properties of TCTA results in a significant EQE enhancement.

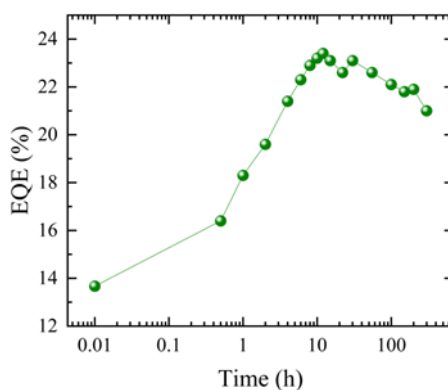


Figure 6-8. Changes in EQE of the G-IQLEDs with a double ETL structure for 5 days.

To test whether the double ETL approach can also work in other colors, red (R) and blue (B)-IQLEDs with double ETL are fabricated. Figure 6-7e and f illustrate the JVL and EQE of R-IQLEDs, respectively, while Figure 6-7g and h illustrate the JVL and EQE of B-IQLEDs. As can be seen, both R and B-IQLEDs exhibit significant positive aging, similar to G-IQLEDs. For R-IQLEDs, the EQE reaches 24.4% after positive aging, which, to the best of our knowledge, is among the highest reported EQEs in the literature.^{43, 72, 182, 183} In case of B-IQLEDs, the EQE improves about 3.5X, increasing from 0.82% to 2.85%. One possible reason for the lower EQE of B-IQLEDs compared to R or G-IQLEDs could be the higher electron leakage, which is likely to occur due to the shallower conduction band level of B-QDs compared to R and G-QDs. Generally, the double ETL approach results in a significant improvement in the EQE of IQLEDs for all primary colors. To find the optimum thickness of ETLs, the thickness of the first ETL (i.e. ETL1) and second ETL (i.e. ETL2) are manipulated. Figures 6-7i-k show the counter plots of EQE under the variation of ETL thicknesses for R, G, and B-IQLEDs with double ETL. As seen, the optimum thickness is almost similar for all three primary colors, suggesting the feasibility of integrating R, G, and B-IQLEDs on the same ETL structure to achieve RGB functionality. Figure 6-7l shows the EL spectra of the devices with a double ETL structure. As seen, the devices exhibit maximum

emission ($\lambda_{\max}$) at 631 nm, 528 nm, and 467 nm, with full width at half maximum (FWHM) of 23 nm, 21 nm, and 21 nm for R, G, and B-IQLEDs, respectively.

Lastly, the EL stability of the devices with a double ETL structure is tested. Figure 6-9 shows the changes in the luminance of the R, G, and B-IQLEDs over time under a constant current density of 20 mA/cm². At this current, the initial luminance of the devices is 6,020, 15,300, and 435 cd/m² for R, G, and B-IQLEDs, respectively. Using the lifetime scaling equation:

$$(L_0)^n \times T_{50} = \text{constant} \quad (1)$$

where L_0 is the initial brightness, n is the acceleration factor, taken to be 1.8¹⁵³, and T_{50} is the time for luminance dropping to 50% of the initial value (L_0). The device LT_{50} (@100 cd/m²) value are 399,000, 78,400, and 5h for R, G, and B-IQLEDs, respectively.

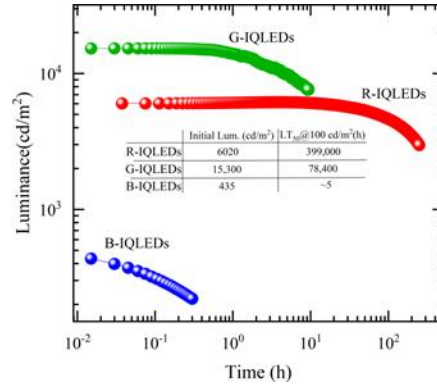


Figure 6-9. The lifetime of R, G, and B-IQLEDs with double ETL measured under a constant current density of 20 mA/cm².

6.1.3 Conclusion

In summary, it is observed that a significant positive aging occurs in inverted G-QLEDs without encapsulation. Experiments on devices that certain layers were replaced by fresh ones verify that changes in the ETL or its interface with the cathode result in the gradual increase in electron supply over time. The results reveal that the increase in electron supply with a uniform injection into the QDs-EML, along with efficient electron blocking properties in HTL, causes the positive aging in inverted G-QLEDs. Modified devices with a double ETL, simultaneously enhancing electron supply and uniformity, show immediate high efficiencies and accelerate the positive aging process, resulting in EQEs of 24.4% and 23.1% for red (R) and green (G)-QLEDs, respectively.

6.2 Doping Graphene Quantum Dots in ETL to Improve Electron Supply in Inverted G-QLEDs

6.2.1 Double ETL QLEDs with Graphene QDs doped ETL

As an extension of the double ETL approach and to overcome the challenges associated with the high annealing temperature of the first ETL, Graphene QDs were doped into the ETL of inverted G-QLEDs to further enhance electron injection efficiency and stability. The rationale behind this approach stems from the favorable electrical properties of graphene, particularly its high electron mobility, which can potentially improve the conductivity and electron transport properties of the ETL.

Figure 6.10a shows the absorption and PL spectra of Graphene QDs. It exhibits a peak PL at 675 nm with a FWHM of 24 nm and a PLQY of 32%. The relatively low PLQY suggests that using this material as a dopant in the ETL may not significantly contribute to color emission. To evaluate the effectiveness of graphene doping in enhancing electron transport through the ETL, it was incorporated into the first ETL of EODs. As shown in Figure 6.10b, the EOD structure consists of a layer of ZnMgO doped with Graphene QDs (ZnMgO:QDs at a 75%:25% weight ratio) placed on an ITO substrate, followed by a regular layer of ZnMgO, the G-QDs emitting layer, and finally the Al cathode. Both ETLs were annealed at 100°C. The J-V measurements (Figure 6.10c) reveal a significant increase in electron current at any given voltage for devices with double ETL structure in which the first ETL is doped by Graphene (graphene-doped ZnMgO). The current density is approximately two orders of magnitude higher than that of EODs with an ETL annealed at 100°C, and it is comparable to that of devices annealed at 350°C. This demonstrates that graphene doping effectively enhances electron injection, even at relatively low annealing temperatures.

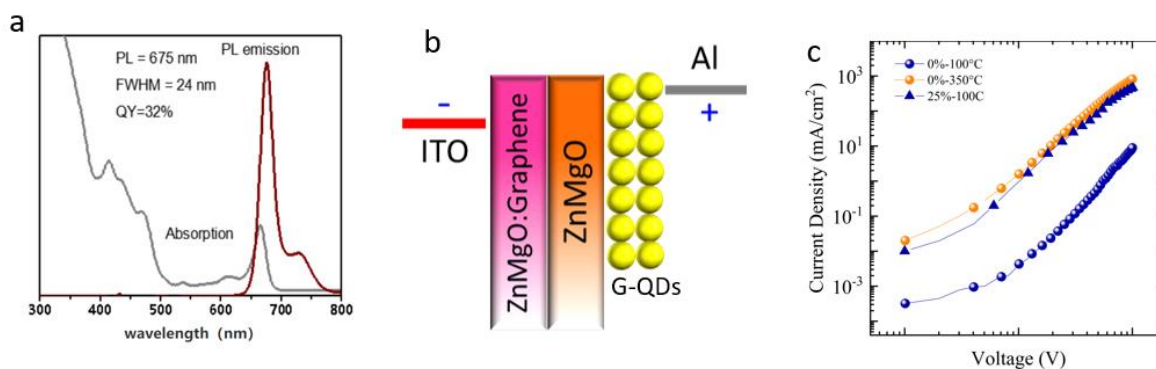


Figure 6-10. (a) Absorption and PL spectra of Graphene QDs. (b) Schematic of EODs with a double ETL structure. (c) J-V characteristics of EODs with a single ETL annealed at 100°C or 350°C, compared to a double ETL structure where the first ETL is doped with Graphene QDs.

To test whether the enhancement of electron supply through Graphene doping can improve the performance of G-QLEDs, inverted G-QLEDs with a Graphene-doped structure are fabricated. Figure 6-11a presents a schematic illustration of the device. Both CPB and TCTA HTLs were tested within this structure. Figure 6-11b shows the J-V-L characteristics of CPB-based inverted QLEDs, where Graphene QDs were doped into the first ETL at varying concentrations of 0%, 10%, 25%, and 50%. As the dopant concentration increased, both the device current density and luminance showed a corresponding rise. However, there was no significant improvement in device EQE (Figure 6-11c) as a result of ETL doping. This aligns with the double ETL results, where an increase in electron current did not lead to EQE enhancement in CBP based devices due to the relatively deep LUMO energy level of CPB which causes electron leakage. Additionally, the EL spectra (Figure 6-11d) indicate that no additional peak appears due to the presence of Graphene QDs. Furthermore, as shown in Figure 6-11e, doping with Graphene did not significantly affect the device lifetime.

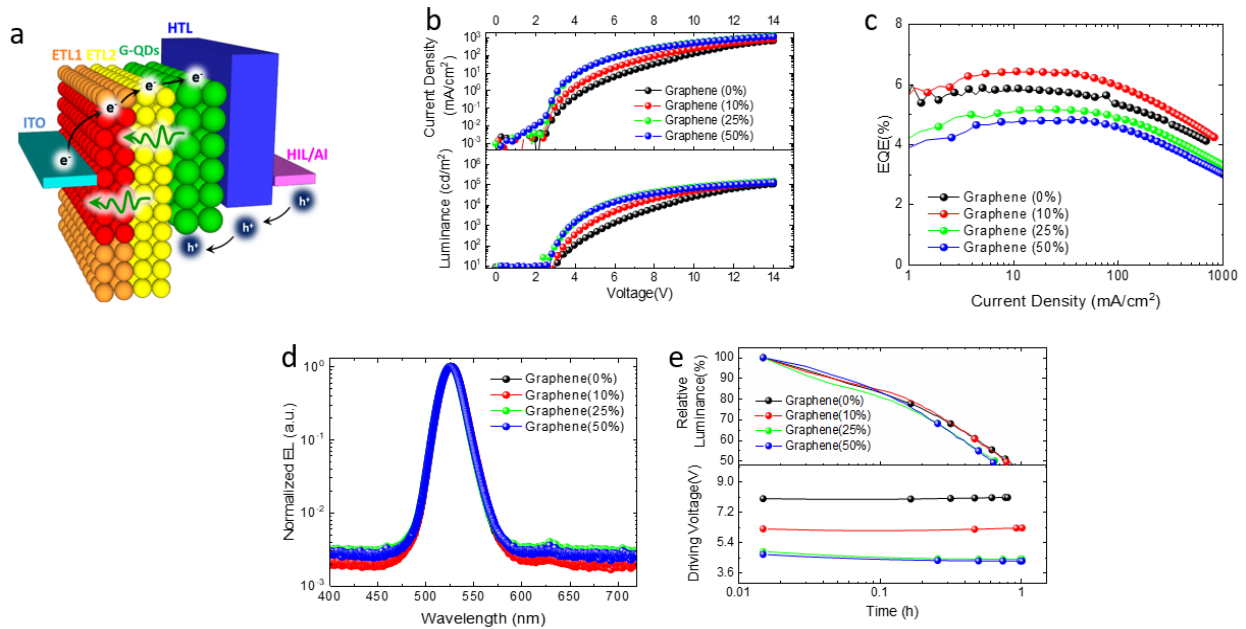


Figure 6-11. (a) Schematic illustration of the inverted G-QLEDs with double ETL structure in which the first ETL is doped by Graphene. (b) J-V-L characteristics, (c) EQE, (d) EL spectra, and (e) lifetime of the graphene-doped ZnMgO device with CBP HTL.

Figure 6-12a shows the J-V-L characteristics of TCTA-based inverted QLEDs with a Graphene-doped structure. Similarly, Graphene QDs is doped into the first ETL at varying concentrations of 0%, 10%, 25%, and 50%. As the dopant concentration increased, both the device

current density and luminance increase. As a result of these enhancements, the device EQE (Figure 6-12b) increase about 2X when the Graphene QDs concentration is 10%. Again, this is aligned well with the double ETL results, where an increase in electron current results in the efficiency enhancement when the HTL is TCTA. Moreover, the EL spectra (Figure 6-11c) indicate that no additional peak appears due to the presence of Graphene QDs. However, as shown in Figure 6-12d, doping with Graphene leads to a significant improvement in the device lifetime.

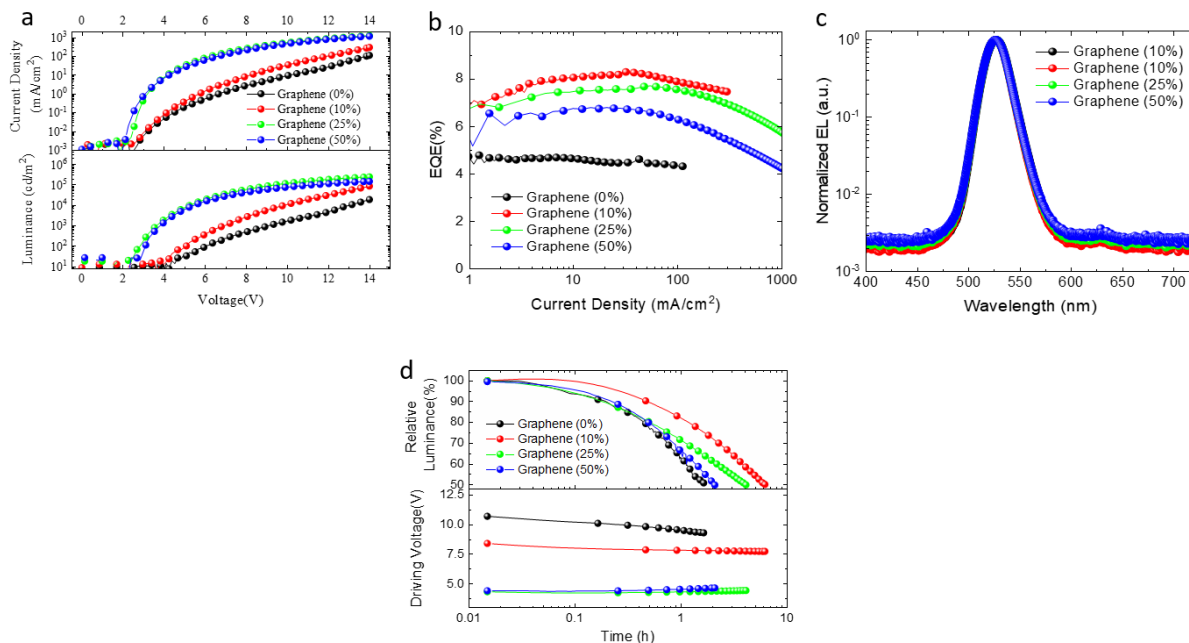


Figure 6-12. (a) J-V-L characteristics, (b) EQE, (c) EL spectra, and (d) lifetime of the graphene-doped ZnMgO device with TCTA HTL.

It should be noted that in devices where EQE improved due to electron current enhancement, the EQE trends show a larger efficiency roll off at high current densities (i.e. $>100 \text{ mA}/\text{cm}^2$). One possible reason is increased Auger quenching, where the higher voltages may exacerbate charge imbalance, resulting in non-radiative recombination processes.^{50, 184} Increased electric field induced quenching could be another factor.⁶⁶ However, since the devices fabricated in this study are intended for display applications that primarily operate at current densities below the onset of efficiency roll-off, this effect was not explored here.

6.2.2 Conclusion

In summary, doping Graphene QDs into the first ETL of inverted G-QLEDs significantly enhances electron injection at relatively low annealing temperatures. This improvement in electron

supply was evident across both CPB- and TCTA-based devices. In the case of TCTA-based devices, the increase in electron injection due to GQDs doping resulted in a notable improvement in EQE, approximately doubling when the dopant concentration was optimized at 10%. Additionally, Graphene QDs doping contributed to a marked improvement in device lifetime without introducing any new emission peaks, affirming its potential to enhance device stability and performance. However, in CPB-based devices, the deeper LUMO level limited the impact of increased electron injection on EQE due to electron leakage, though current density improvements were still observed. Therefore, doping graphene quantum dots into the ETL presents a promising approach to further optimizing the charge balance and stability of inverted G-QLEDs, particularly when paired with suitable hole transport layers like TCTA.

Chapter 7. Investigating the degree of charge balance in upright B-QLEDs and its influence on the EL performance

7-1 Deciphering the Causes of the Rapid Electroluminescence Loss in Blue Quantum Dot Light-Emitting Devices

EL loss mechanisms in QLEDs, especially blue (B) emitting ones, remain unclear. Currently, T_{95} (@1000 cd m^{-2}) lifetimes for red (R) and green (G)-QLEDs around 5000 h are now possible^{30, 43, 183}. The longest reported T_{95} lifetime for a blue (B)-QLED is only ~ 277 h (@1000 cd m^{-2})⁴⁴ however, and most B-QLEDs reported in the literature have much shorter lifetimes. The root causes of the limited electroluminescence (EL) stability of B-QLEDs remain not well understood. Devising effective strategies for improving the lifetime B-QLEDs, requires attaining a better understanding of the various degradation mechanisms at play.

In QLEDs, electrical stress induces a gradual decrease in EQE manifested in a decrease in EL intensity not different from that observed in organic light-emitting diodes (OLEDs)^{185, 186}. Studies of degradation mechanisms in QLEDs have ascribed the behavior to HTL decomposition^{58, 73, 130}, QDs-EML degradation^{44, 59, 83}, and/or QDs-EML/ETL interface deterioration⁴⁰. Most of those studies however were conducted on R-QLEDs^{60, 65, 74}. With recent findings of significant differences in the injection and confinement of electrons and holes between R, G, and B-QDs due to differences between core and shell conduction and valence band levels,^{144, 179} the applicability of these findings to B-QLEDs becomes less certain, necessitating conducting mechanistic studies to elucidate degradation mechanisms in B-QLEDs specifically.

Here, EL and PL measurements are systematically conducted on B-QLEDs based on the widely used CdSe/CdS QD material system that contain marking layers (MLs) placed in certain locations in order to investigate changes in charge injection and transport during device aging and their correlations with the rapid EL loss. Results show that – aside from some partially reversible deterioration in the photoluminescence quantum yield (PLQY) of the QDs-EML - the rapid EL loss in these devices is caused mainly by an increase in electron leakage across the HTL and a subsequent damage to the hole injection layer (HIL), resulting in a deterioration in hole supply to the QDs EML. Electron supply to the QDs-EML is found to be easier than hole supply in B-QLEDs in general, causing the electron (e)/hole (h) to be >1 and significant electron leakage to the HIL,

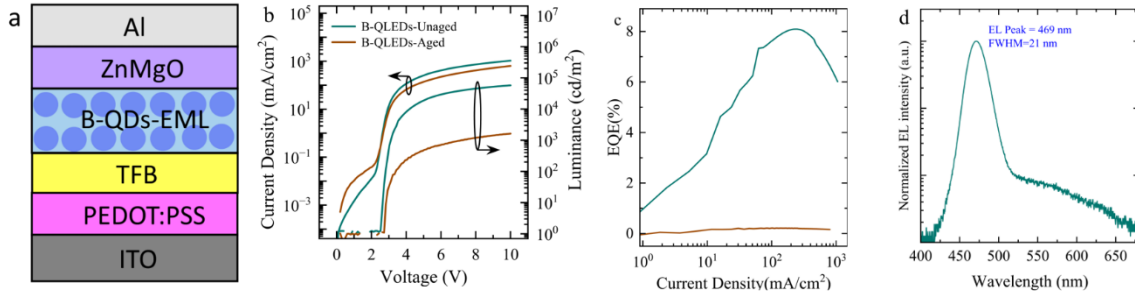


Figure 7-1. (a) Schematic diagram of the B-QLEDs structure. (b) J-V-L and (c) EQE-J characteristics of the B-QLEDs measured before electrical aging (labelled unaged) and after electrical aging (labelled aged) measured after working under a constant current density of 20 mA/cm² for 60 min. (d) Normalized EL spectrum (on a logarithmic scale) of the B-QLED measured under a constant current density of 20 mA/cm².

even in fresh devices. Under electrical stress, this electron leakage increases further, causing the charge imbalance in the QDs-EML to deteriorate further and more electrons to reach the HIL. Experiments on devices that were electrically aged and then later had certain layers replaced by fresh ones verify the HIL changes and the role of electrons in inducing them. Modified devices with reduced electron supply show 30X longer EL lifetime, proving the role of excess electrons in the rapid EL loss in blue QLEDs.

7.1.1 Observation of electron leakage

First, to investigate the charge injection behaviour in B-QLEDs and test for charge leakage in them, devices of the widely used structure indium tin oxide (ITO)/PEDOT:PSS/TFB/B-QDs/ZnMgO/Al are fabricated and their EL characteristics are studied. Figure 7-1a depicts the device structure. The J-V-L and EQE-J characteristics of the B-QLEDs measured before (Unaged) and after (Aged) being subjected to electrical stress - in this case by keeping under electrical bias to maintain a constant current density of 20 mA/cm² for 60 minutes - are presented in Figures 7-1b and c, respectively. For the unaged device, the J-V characteristics show an increase in the sub-threshold current density by about two orders of magnitude as the applied bias increases from 0 to ~2.2V. As this current flow occurs at voltages below V_{ON} it arises predominantly from one of the two charge carriers, either electrons or holes, being injected at one of the two electrodes and collected at the counter electrode before the onset of injection of the counter charge carriers. Also for this device, the EQE increases with current density from ~1% at 1 mA/cm², reaching its maximum of 8.2% at 250 mA/cm². An increase in EQE with current will generally result from reaching more balanced e/h ratios in the B-QDs-EML, which suggests that one of the carriers, again either electrons or holes, requires a higher electric field for its concentration in the B-QDs-

EML to become comparable to that of the other carrier, in turn suggesting the charge balance must be very limited at the lower voltages. Figure 7-1d shows the normalized EL spectrum (on a logarithmic scale) of the B-QLEDs. As can be seen, the spectrum shows the typical B-QDs band with a peak at 469 nm and a full width at half maximum (FWHM) of 21 nm. It additionally shows a broad emission band spanning from ~520 nm to 650 nm. This band can be attributed to emission from charge transport layers (CTLs), a sign that a portion of the charge carrier/s are not confined within the EML and therefore leak into the CTLs. To determine which layer is responsible for this broad emission band, the EL spectrum is compared with PL spectra collected from samples made of various combinations of layers made of the same materials used in the device, as shown in Figure 7-2a. As seen, the PL spectrum from the glass/B-QDs sample shows only the narrow 469 nm band without any significant emission in the 520-650 nm, suggesting that the B-QDs-EML is

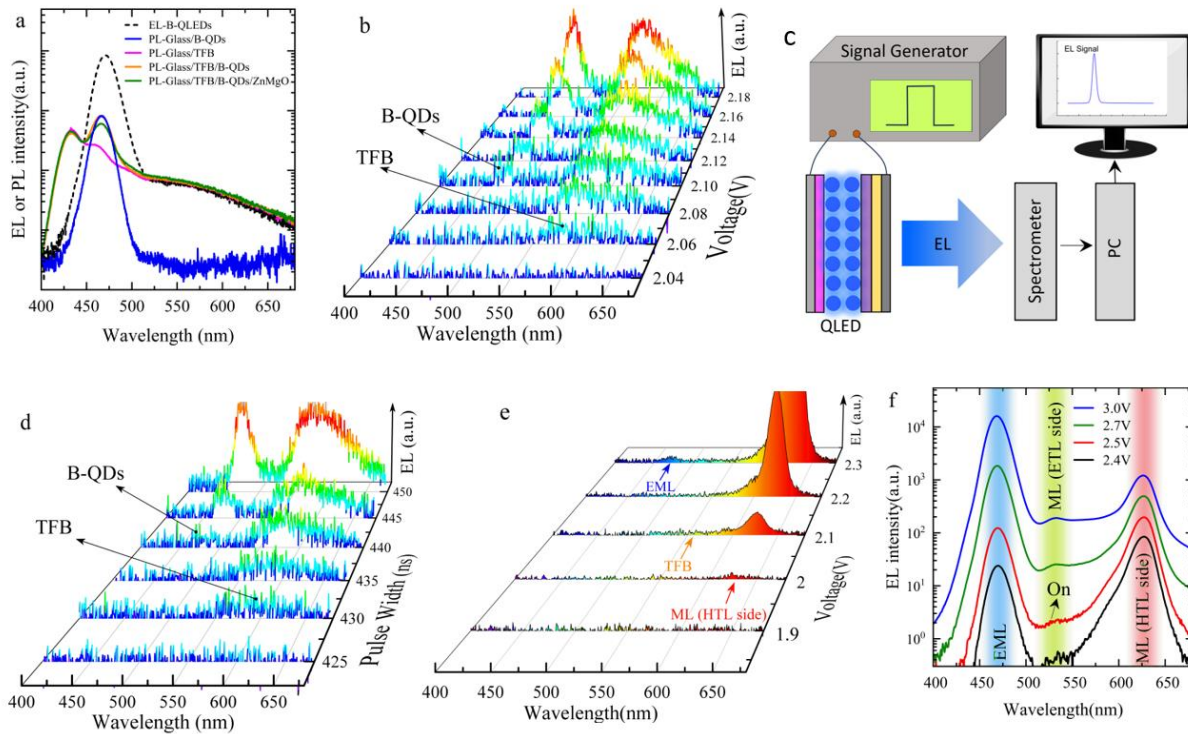


Figure 7-2. PL and EL characterization of B-QLEDs. (a) Comparison of EL spectrum of the B-QLEDs and PL spectra collected from samples made of various combinations of layers made of the same materials used in the device. All the films are deposited on glass substrates. (b) The EL spectra of the B-QLEDs measured at different voltages ranging from 2.04 to 2.18V, just below and above V_{ON} . (c) Schematic diagram of the experimental setup used to measure the EL intensity of the device under square voltage signals with different pulse widths of 425 ns to 450 ns, at a frequency of 2 MHz, and a constant amplitude of 3 V. (d) EL spectra as a function of pulse width signals with a constant amplitude of 3V. (e) The EL spectra of the B-QLEDs with MLs under voltages below and above V_{ON} (1.9 to 2.3v). (f) The EL spectra of the B-QLEDs with MLs under voltages of 2.4 to 3V.

not responsible (at least solely) for the broad band in the EL spectra. In contrast, the PL spectrum from the glass/TFB sample clearly shows that the TFB exhibits a broad emission band that well matches that in the EL spectrum. Notably, depositing additional device layers on the TFB (i.e. glass/TFB/B-QDs and glass/TFB/B-QDs/ZnMgO samples), produces no new features, indicating that the broad emission band in the EL spectrum is primarily from TFB. One possible reason for TFB emission (in the EL spectrum) could be from Förster resonance energy transfer (FRET) process, where excitation energy in the B-QDs-EML can cause the formation of excitons in the TFB HTL. However, the smaller bandgap of the B-QDs (2.6 eV)¹⁴⁴ compared to that of TFB (2.9 eV)¹⁸⁷ would make the process very inefficient. Notably, the opposite scenario is well-documented in the literature, where exciton transfer from the HTL to the QDs-EML is often observed.^{188, 189} Apart from having a wider bandgap, the fact that the height of the broad band is essentially the same in both the glass/TFB and glass/TFB/B-QDs samples also indicates that energy transfer from B-QDs to TFB must be negligible. In the absence of efficient energy transfer, one can conclude that electron leakage into the HTL, allowing for e-h recombination to occur within it, must be behind this TFB emission. Such leakage can be due to the poor electron-blocking properties of TFB or/and much easier electron injection into the QDs-EML compared to holes, leading to high e/h ratios in the QDs-EML.

To further explore this possibility, we conduct EL spectral measurements on the QLEDs at different voltages in order to investigate if emission from the B-QDs-EML and HTL starts at different voltages and thus determine whether electrons reach the HTL or holes reach the B-QDs-EML first as the voltage is slowly increased. Figure 7-2b shows the EL spectra measured at different voltages ranging from 2.04 to 2.18V, just below and above V_{ON} . As seen, while no EL is observed at 2.04 V, EL from TFB appears first as the voltage is increased to 2.06V, followed by EL from the B-QDs-EML at 2.1V. Such sub-bandgap turn-on voltage of 2.1 V in B-QDs can be attributed to field-assisted¹⁹⁰ and thermally-assisted charge injection¹⁹¹. That e-h recombination occurs within the TFB first indicates that electrons must be present in the B-QDs-EML and are able to reach the TFB before holes start to get injected into the B-QDs-EML (the latter at 2.1 V). It follows that electron injection into the B-QDs-EML must be easier than hole injection, at least at voltages near V_{ON} , resulting in an electron (e)/hole (h) ratio of >1 in the B-QDs-EML, and allowing for the possibility that electron leakage into the HTL can occur at these voltages.

To investigate if electrons are again injected first into the B-QDs EML when higher voltages, typical of those used during normal device operation (i.e., ≥ 3 V), are used, we also study the EL spectral characteristics of the devices at higher voltages. However, as at voltages above V_{ON} both bands will always be present, we use pulsed driving in this case (instead of DC driving) and study changes in EL spectra as the pulse width is varied. A square pulsed voltage with different pulse widths ranging from 425 ns to 450 ns, at a frequency of 2MHz, and a constant amplitude of 3V are applied on the device, as schematically depicted in Figure 7-2c. Figure 7-2d shows the collected EL spectra as a function of pulse width. As can be seen, here again, EL from only TFB appears first, at pulse widths in the of 430 ns and 435 ns range, with no EL from the B-QDs-EML until the pulse width reaches 440 ns. This clearly indicates that even at these high voltages electrons are injected into the B-QDs-EML first whereas holes require more time to reach the B-QDs-EML and produce EL from it. Therefore, for typical QLED driving conditions, one can again expect e/h ratios in the B-QDs-EML to be >1 , thus again allowing for the possibility that electron leakage into the HTL to occur. The easier injection of electrons into the QDs-EML relative to holes, at both the lower and higher voltages, can be attributed to the well-matched conduction band level of ZnMgO and QDs^{49, 192} and/or higher charge mobility in ZnMgO versus TFB^{160, 193}. Therefore, based on these experimental results, the electron leakage from the B-QDs-EML into the TFB can be ascribed to an easier electron supply relative to the hole supply in B-QLEDs with an upright structure.

Having verified the easier injection of electrons (vs holes) into the B-QDs-EML and also that electrons reach the TFB and get injected into it more readily, evident in the lower onset of EL from TFB vs the B-QDs-EML at both bias levels, we next investigate i) the depth of electron penetration into the TFB and whether they (i.e. the electrons) can cross (i.e. leak through) the layer to the HIL, and ii) if holes may similarly also leak into the ETL which would indicate poor confinement of both charges. For this, we fabricate B-QLEDs with luminescent MLs in the HTL and ETL. Different from other studies where organic luminescent materials are usually utilized for marking layers, we here use QDs (of other colours) in those layers instead. This approach is taken in view of recent findings that charge injection into QDs is generally very efficient, which minimizes perturbations to charge injection or transport across the device layers due to the inclusion of the marking layers. Figure 7-3a depicts the device structure. One marking layer of red QDs (R-QDs) is introduced in between the HIL and HTL and another marking layer of green QDs

(G-QDs) is placed in the middle of the ZnMgO layer, as described in the device fabrication section. The J-V-L and EQE-J of these devices are shown in Figure 7-3b and c, respectively. As seen, compared to the control device, introducing the MLs does not significantly change the shape or the J-V-L characteristics verifying that their inclusion negligibly affects charge injection and transport across the devices. They also negligibly affect EQE indicating that they (i.e. the MLs) do not significantly affect the concentrations of excitons within the B-QDs-EML or their kinetics. Figure 7-3d shows a PL spectrum collected from the same device, as well as a trace representing the difference between this spectrum and that of the control device (with no MLs) obtained by subtracting the PL intensity value at each wavelength of the later from it. As seen, the spectrum shows clear PL bands, at 525 nm and 630 nm, from the R-QDs and G-QDs, respectively, confirming the presence of the MLs in the HTL and ETL. The EL spectrum of this device (Figure 7-3e) measured at 20 mA/cm² (~3V) shows the same two bands, indicating that both electrons and holes leak through the HTL and ETL, respectively, towards the counter electrodes. Notably however, the height of the R-QDs ML band (on the HTL side) is about an order of magnitude higher than the G-QDs ML band (on the ETL side); an opposite trend from that observed in the PL spectra where the G-QDs ML band is higher (by about ~2.7X). The relatively lower EL intensity of G-QDs ML vs R-QDs ML must therefore be due to a relatively smaller number of holes that leak through the ETL in comparison to the number of electrons that leak through the HTL and not because of a stronger quenching effect by the ZnMgO. The observations also indicate that a significant number of electrons can reach the PEDOT:PSS. Generally speaking, one can expect such significant electron leakage to undermine hole supply into the device, limiting the number of holes that reach the B-QDs-EML.

To test whether the leakage of electrons or holes starts at a lower voltage again in this case, the EL spectra of the B-QLEDs with the MLs are measured at different voltages starting just below V_{ON}. Figure 7-2e shows the collected EL spectra. EL from the R-QDs ML (on the HTL side) starts first at 2V, showing that electrons can easily cross the entire TFB layer and reach the HIL even at these low voltages where they meet with holes. By increasing the applied bias, the TFB starts to emit at 2.1V, followed by the B-QDs-EML at 2.3V. Finally, emission from the G-QDs ML on the ETL side starts to appear at 2.5V (Figure 7-2f). The lower voltage onset of EL from the R-QDs ML again points to electron supply (injection and transport) being much easier than hole supply,

consistent with the conclusions made earlier. The results also show that leaked electrons can traverse the TFB layer and reach the PEDTOT:PSS layer at low voltages (i.e. $\leq 2\text{V}$).

7.1.2 B-QLEDs stability test

Finding out that a significant fraction of electrons can reach the PEDOT:PSS HIL, and that the supply of holes to the B-QDs-EML is generally more difficult (requires higher voltages), we next investigate if changes in charge injection and/or transport (charge supply) occur when the devices are under electrical stress. Toward this objective, B-QLEDs are driven under a constant current, in this case 20 mA/cm^2 , for 60 min, and their EL spectra are continuously measured.

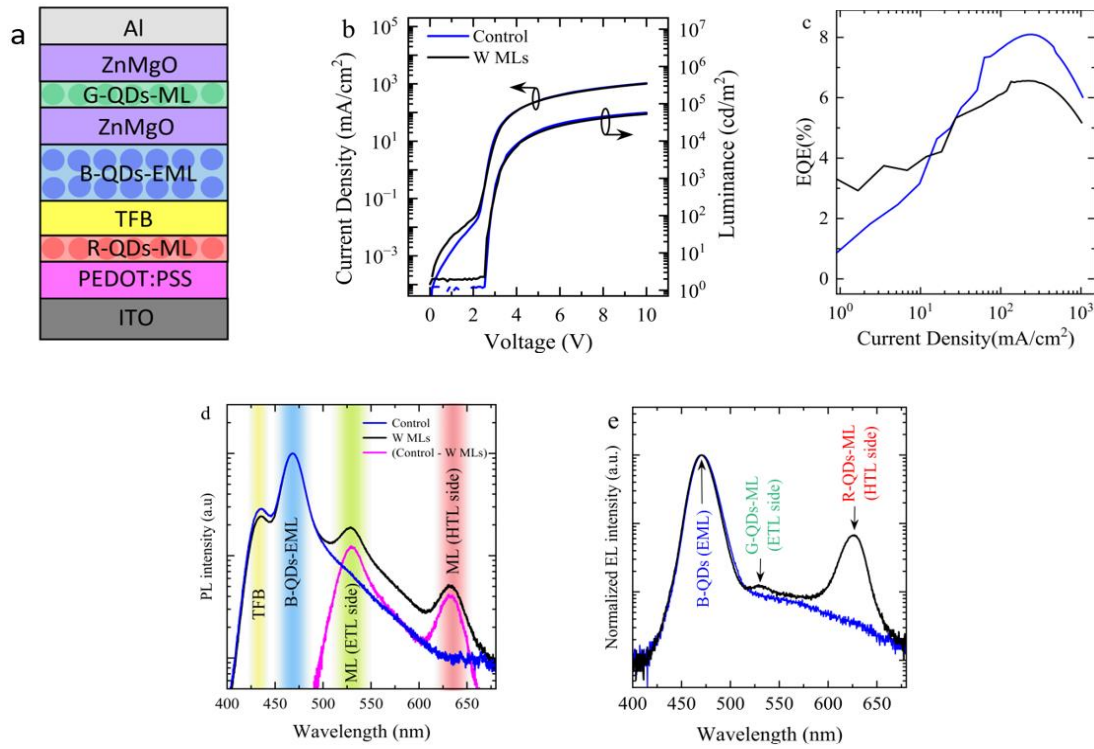


Figure 7-3. (a) Schematic diagram of the B-QLEDs with MLs structure. (b) J-V-L and (c) EQE characteristics of the B-QLEDs with MLs. (d) PL spectrum collected from control device and B-QLEDs with MLs and the subtraction of the PL spectrum of the device with MLs from the PL spectra of control. (e) EL spectrum of control and B-QLED with MLs measured under a constant current density of 20 mA/cm^2 .

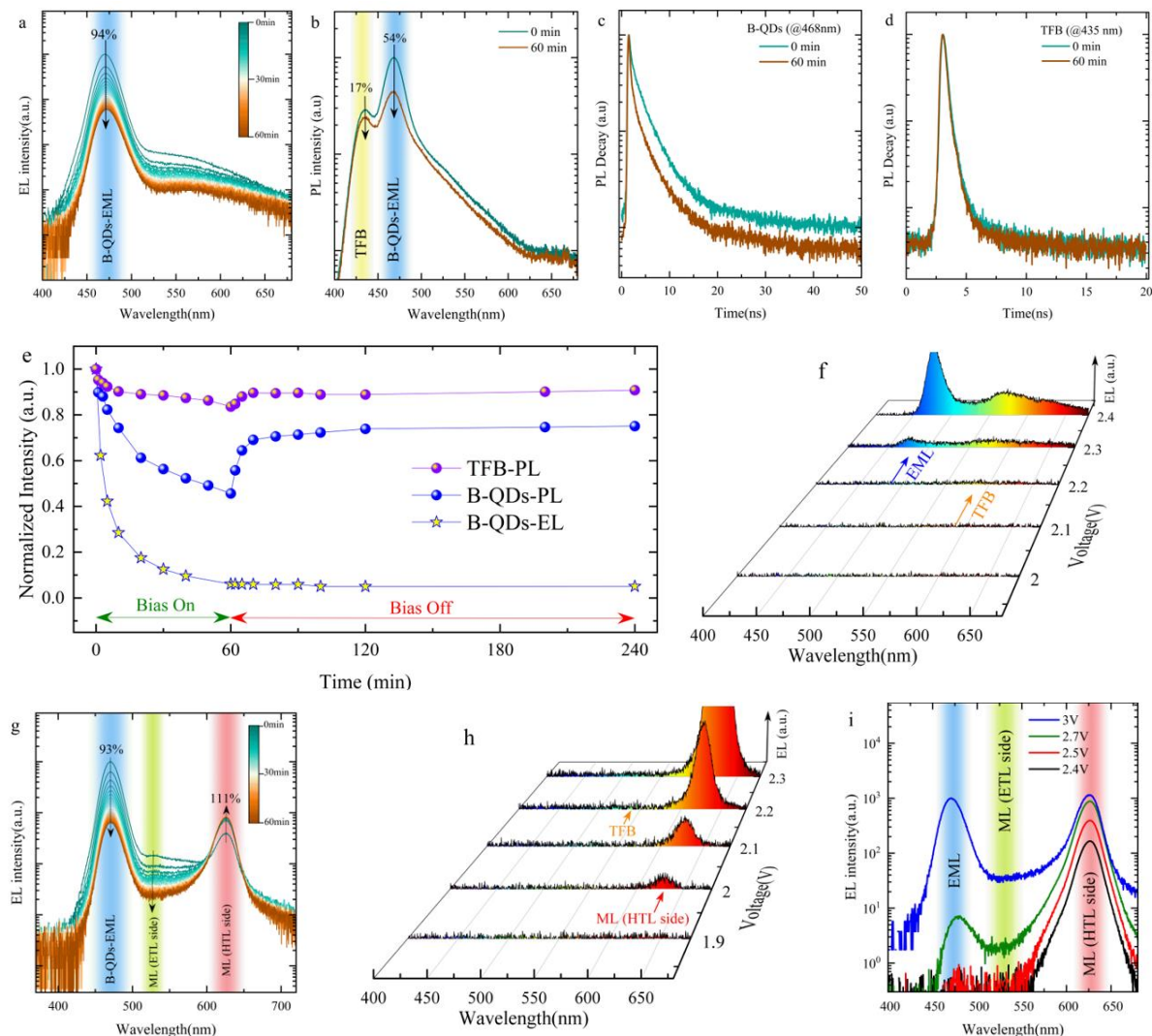


Figure 7.4. EL and PL characterization of B-QLEDs after aging. (a) Normalized EL spectra of the B-QLEDs measured for 60 min under a constant current density of 20 mA/cm². (b) Normalized PL spectra of the B-QLEDs measured before (0 min) and after (60 min) aging. (c) TrPL characteristics of the QDs-EML before and after aging collected at 468nm. (d) TrPL characteristics of the TFB HTL before and after aging collected at 435nm. (e) The peak intensities of the EL, TFB PL, and B-QDs PL, normalized to their initial (pre-aging) values, collected from the device during aging and over the 3 hours after the bias is removed. (f) EL spectra of an aged B-QLEDs measured under low driving voltages of 2 to 2.4V. (g) Normalized EL spectra of the B-QLED with R-QDs ML at HTL side and G-QDs ML at ETL side under a constant current of 20 mA/cm² for 60 min. (h) EL spectra of the B-QLED with R-QDs ML at HTL side and G-QDs ML at ETL side measured under driving voltages of 1.9 to 2.3V. (i) EL spectra of the B-QLED with R-QDs ML at HTL side and G-QDs ML at ETL side measured under driving voltages of 2.4 to 3V.

Figure 7-4a shows the EL spectra. As seen, the EL intensity decreases by 94% of its initial value after aging. Figure 7-4b compares the PL intensity of the device initially (0 min) and after (60 min) electrical aging, the latter normalized to the initial value. One can see that the PL intensity of the B-QDs-EML decreases by 54 % after aging, pointing to a deterioration in the QDs PLQY by the

electrical stress^{59, 65}. Measurements of transient PL (TrPL) decay rate of the B-QDs EML, collected at 468 nm (Figure 2c), also show a significant decrease in QDs exciton lifetime pointing to increased quenching effect after aging. While these changes in the QDs PLQY and exciton lifetime can be due to phenomena within the QDs themselves, such as charge trapping and/or chemical changes, they can also be induced by changes in the HTL, where leaked electrons can cause chemical degradation and/or get trapped, possibly creating quenching centers.^{59, 60, 80, 194} Looking at the 435 nm band in the PL spectra, which corresponds to TFB emission, while it shows a 17% lower intensity after aging, deconvoluting the spectra in order to remove contributions from the B-QDs-EML reveals a smaller decrease in TFB PL intensity (only ~10%, in Figure 7-5), and TrPL measurements show negligible changes in decay rates at this wavelength (Figure 7-4d). These observations suggest that the QDs PLQY reduction is unlikely to be due to the formation of quenching defects in TFB.

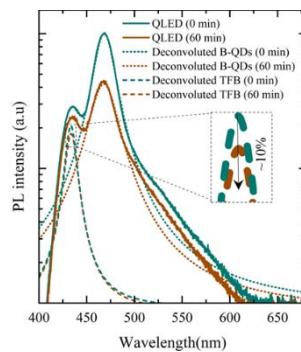


Figure 7-5. Deconvolution of the PL spectra of the B-QLED measured before (0 min) and after (60 min) aging.

We also continue to monitor changes in PL and EL intensities for a period of 3 hours after the bias is turned off in order to check for any recovery behavior upon electrical resting. Figure 7-4e shows the peak intensities of the EL, TFB PL (435nm), and B-QDs PL, normalized to their initial (pre-aging) values, collected from the device during aging (i.e. when the bias is on) and over the 3 hours after the bias is removed (during which no bias is applied except for brief applications of bias (<2sec) every 10-20 min for measuring the EL intensity). The full TFB and B-QDs PL spectra are given in Figure 7-6a. As seen in Figure 7-4e, the intensity of the PL from both the B-QDs-EML and the TFB recovers to a large extent when the bias is turned off. This recovery is fast initially, but the trend slows down and eventually saturates after recovering to ~75% and ~90% of its initial (pre aging) levels for the B-QDs and TFB, respectively. This recovery suggests that the PL intensity reduction during electrical aging arises primarily from charge trapping effects, rather

than being the result of chemical changes (decomposition), especially for TFB. Interestingly, different from the PL behavior, no recovery in EL is observed. The different EL and PL behaviors under resting indicates that the QDs PLQY reduction during electrical stress is not the primary factor behind the rapid EL loss.

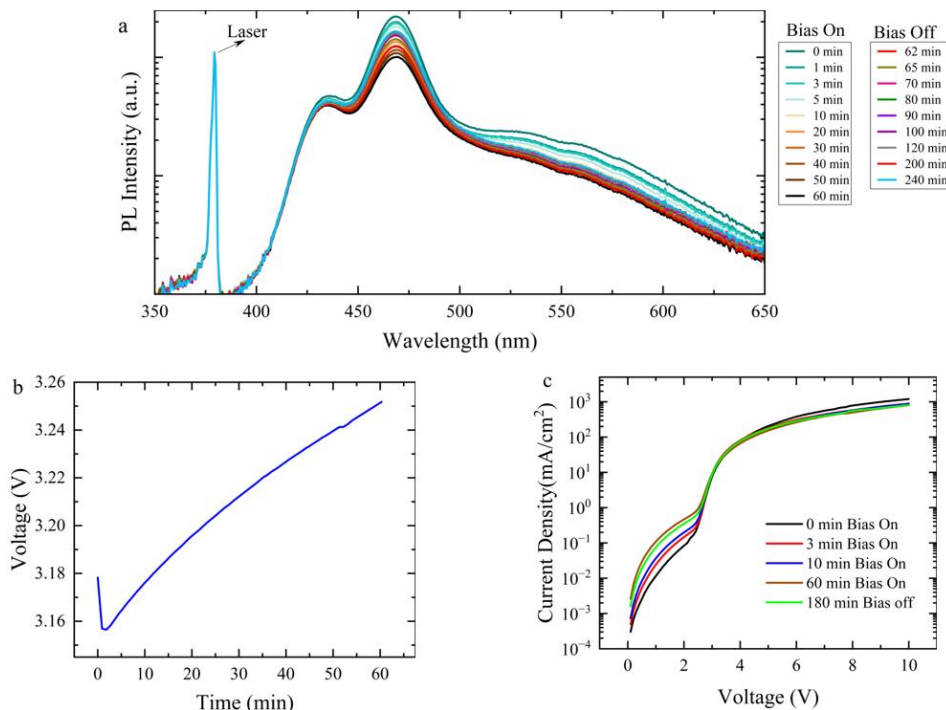


Figure 7-6. (a) PL spectra of the B-QLED measured under bias (0 to 60 min) and resting time (62 to 240 min). (b) Voltage versus time of the B-QLED measured under a constant current density of 20 mA/cm². (c) Current density versus time of the B-QLED.

Knowing that hole supply is more difficult than electron supply (needs higher voltages to reach its onset) and that e/h is >1 in the B-QDs-EML, one may expect any further deterioration in hole supply to further increase the charge imbalance, thus significantly negatively affect EQE. To investigate this possibility, changes in EL spectra with bias in the aged device are also studied. Figure 7-4f shows the EL spectra at different voltages just below and above V_{ON} . As seen, EL from the B-QDs-EML starts at 2.3V, ~ 0.2 V higher than before aging (Figure 7-2b), and the current density at V_{ON} is also lower (Figure 7-1c), indicating that charge injection of at least one of the two carriers is becoming more difficult. To investigate this further, we study the changes in the electrical characteristics of the devices during electrical aging (at 20 mA/cm² constant current driving). Figure 7-6b shows the changes in the device driving voltage over the aging time. As can be seen, the voltage goes down initially, but then it starts to increase gradually. Figure 7-6c shows

the changes in the J-V characteristics, showing a progressive increase in subthreshold currents during aging, with negligible recovery afterwards. Since, as shown earlier, subthreshold currents in these devices arise primarily from electron leakage, the observations suggest a progressive, irreversible increase in electron leakage during device aging. In contrast, currents at voltages above V_{ON} decrease with aging, in agreement with the observed increase in driving voltage over time. This observation, signifying charge injection and/or transport becoming more difficult over time, can therefore be ascribed to the deterioration in hole supply concluded earlier.

To further investigate how these changes affect the EL behavior, we similarly aged a device with MLs under a constant current of 20 mA/cm^2 for 60 min, and periodically measured its EL spectra during that time. Figure 7-4g shows the EL spectra from this device. As seen, in contrast to EL from the B-QDs-EML and G-QDs ML (located on the ETL side) which decreases progressively, the EL intensity of the R-QDs ML (located on the HTL side) significantly increases. This increase indicates an increase in electron leakage, causing more electrons to reach the R-QDs-ML, where they recombine with holes to produce EL. Remarkably, this increase happens mostly

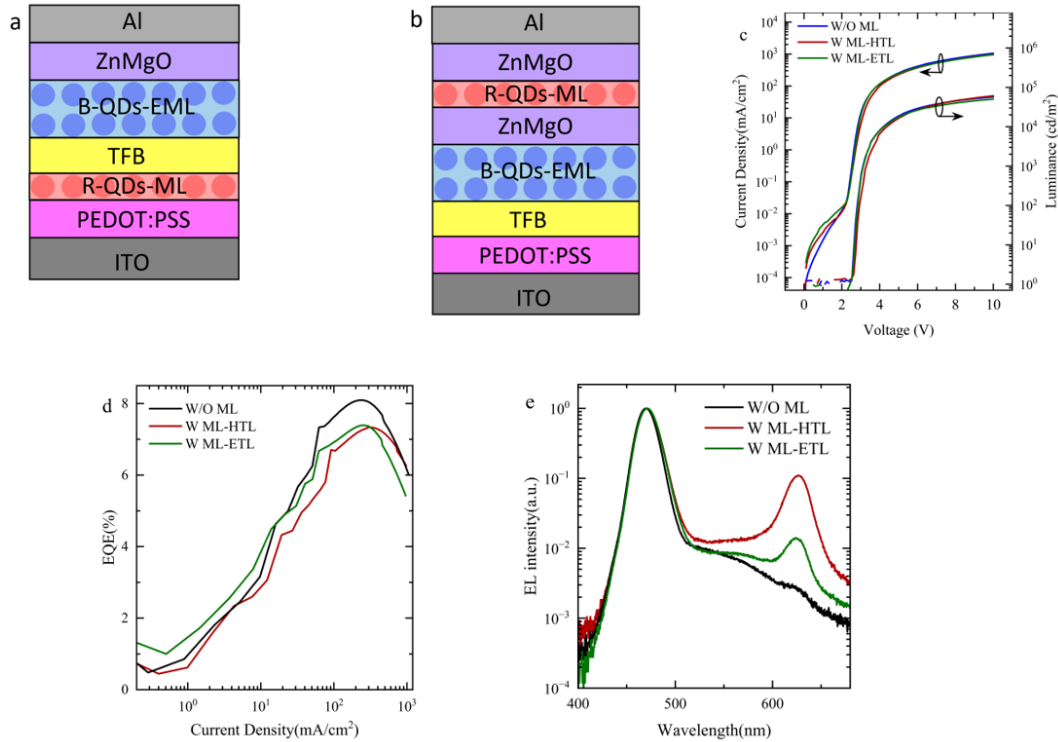


Figure 7-7. (a) Schematic diagram of the structure of B-QLEDs with (W) ML placed at the HTL side. (b) Schematic diagram of the structure of B-QLEDs with ML placed at the ETL side. A comparison of (c) J-V-L and (d) EQE-J characteristics of the control device (W/O ML) with B-QLEDs with MLs placed at the HTL side or ETL side. (e) Normalized EL intensity of control and B-QLEDs with ML placed at the HTL side or ETL side measured under a constant current density of 20 mA/cm^2 .

during the first few minutes of aging, the same time frame during which the voltage decreases in case of figure 7-6b. Such increase in electron leakage and in e-h recombination near the PEDOT:PSS will inevitably reduce hole supply to the other device layers, reducing the number of holes that will reach the B-QDs-EML and the G-QDs ML, hence the fast decrease in their EL. We also conduct EL spectral measurements on them at various voltages just below and above the V_{ON} in order to compare them with those collected before aging. Figure 7-4h presents the EL spectra

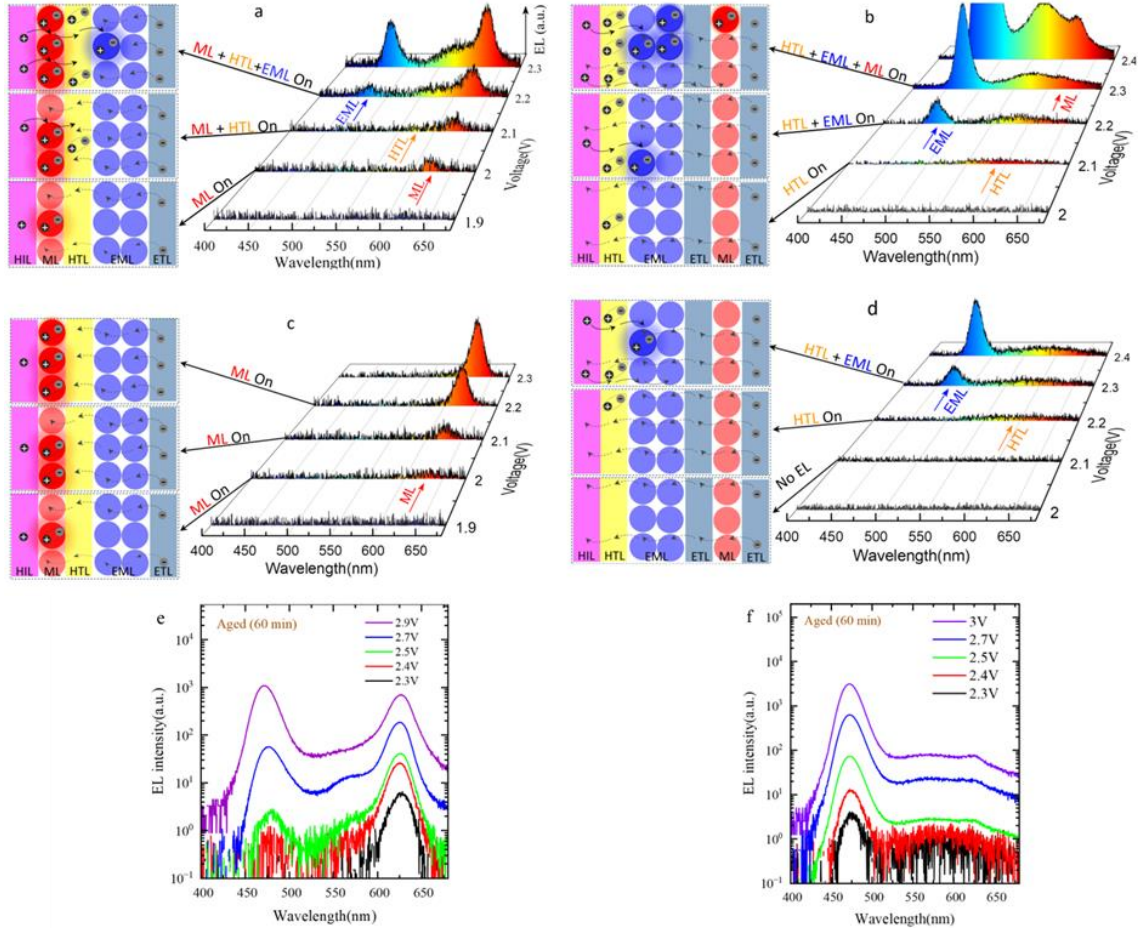


Figure 7.8. EL characterization of B-QLEDs with ML at HTL side or ETL side before and after aging. EL spectra of B-QLED with (a) ML placed at the HTL side and (b) ML placed at ETL side measured before aging. EL spectra of B-QLED with (c) ML placed at the HTL side and (d) ML placed at ETL side measured after aging under a constant current density of $20\text{mA}/\text{cm}^2$ for 60 min. (e) EL spectra of B-QLED with ML placed at the HTL side measured from 2.3 to 2.9V after aging under a constant current density of $20\text{mA}/\text{cm}^2$ for 60 min. (f) EL intensity of B-QLED with ML placed at the ETL side measured from 2.3 to 3V after aging under a constant current density of $20\text{mA}/\text{cm}^2$ for 60 min.

after aging. As shown, compared with before aging, no change is observed in the voltage at which EL from the R-QDs ML (on the HTL side) starts to be detectable (the data for the unaged device

is in Figure 7-2e). In contrast, EL from the B-QDs-EML now starts at 2.7V (Figure 7-4i), $>0.4V$ higher than before. This suggests that holes now need a higher voltage to reach and get injected into the B-QDs-EML, consistent with hole supply becoming more difficult. We can therefore conclude that a deterioration in hole supply efficiency is the primary factor responsible for the increase in the devices V_{ON} after aging, and is perhaps a primary factor in the rapid EQE loss in B-QLEDs under electrical stress. Notably, after aging, no EL from the G-QDs ML (on the ETL side) is observed even at 3V (Figure 7-4i). This suggests that hole leakage into the ETL is significantly suppressed after aging, again in line with the reduced hole supply after aging. One can therefore conclude that an increase in electron leakage and a decrease in hole supply occur in the B-QLEDs under electrical stress. Knowing that initially the e/h in the devices is >1 , these changes would exacerbate the charge imbalance and cause significant EQE losses which would cause - or at least contribute significantly to - the rapid EL degradation in these devices.

Tests on B-QLEDs with only a single ML (instead of two) of R-QDs placed in either the HTL or the ETL were also conducted and found to corroborate these conclusions. Results from these devices are provided in Figures 7-7 and 7-8).

7.1.3 Lifetime enhancement by electron supply reduction

Finding that in B-QLEDs the $e/h > 1$, a significant fraction of electrons leaks through the HTL, and the hole supply decreases further by electrical stress inevitably exacerbating the charge imbalance in the devices, we next investigate if reducing electron supply would improve the device EL stability. Therefore, we test the effect of using Ag/Al instead of Al as the cathode. Due to its deeper work function ($4.7eV$)¹⁹⁵ relative to Al ($4.3eV$)¹⁹⁶, using Ag would lead to a higher energy barrier for electron injection at the cathode/ZnMgO and therefore would make electron injection more difficult. Figure 7-9a compares the J-V-L characteristics of the B-QLEDs with the Ag/Al and Al cathodes. As seen, the use of the Ag reduces the subthreshold currents (i.e. currents at $V < V_{ON}$) showing that the use of Ag/Al helps reduce electron leakage. Figure 7-9b compares the EQE of the B-QLEDs with Ag/Al and Al. As seen, the Ag/Al does not change the EQE significantly. The little effect on EQE suggests that the e/h in the B-QDs-EML is $\gg 1$ and therefore a small decrease in it does not appreciably affect EQE. Comparisons between Al and Ag/Al in electron only devices (EODs) also show (Figure 7-10) that the Ag/Al reduces electron current at any given voltages, further corroborating that Ag reduces the electron supply into the B-QLEDs.

Figure 7-9c presents the EL stability data of the devices with these two cathodes. The Ag/Al and Al devices show initial luminance of 920 cd/m² and 950 cd/m², respectively, under a constant current density of 20 mA/cm². As can be seen the use of Ag/Al significantly slows down EL degradation rate, decreasing by 50% of its initial value in 6 hrs instead of only a few minutes in case of Al at this current density. Using the lifetime scaling equation:

$$(L_0)^n \times T_{50} = \text{constant} \quad (1)$$

where L_0 is the initial brightness, n is the acceleration factor, taken to be 1.8¹⁵³, and T_{50} is the time for luminance dropping to 50% of the initial value (L_0), using Ag/Al improves the device LT_{50} (@100 cd/m²) from 11h to 332h. These results clearly show the role of excess electrons in the rapid EL loss in blue QLEDs. Considering that both devices still have comparable EQEs initially (which suggests no significant differences in Auger quenching phenomena in the B-QDs-EML, a common suspect in device degradation), and knowing that hole supply tends to decrease over time under electrical stress, one naturally wonders if the reduced electron leakage by the Ag/Al helps retain hole supply levels, and hence the higher EL stability. This, in turn, raises a question as to whether electron leakage to the PEDOT:PSS may be affecting it, further contributing to the deterioration in hole supply.¹⁹⁷

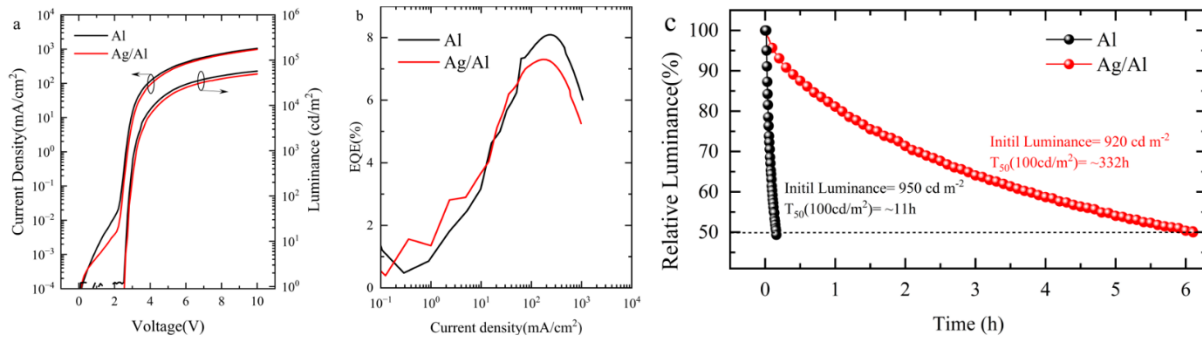


Figure 7-9 Ag/Al and Al cathode comparison. (a) The JVL and (b) EQE-J characteristics of the B-QLEDs with Ag/Al and Al. (c) EL stability data of B-QLEDs with Ag/Al and Al cathode.

7.1.4 Impact of electron leakage on HIL

To find out if changes in the PEDOT:PSS contribute to the deterioration in hole supply efficiency and if electron leakage plays a role in this phenomenon, we investigate the effect of replacing all layers above the PEDOT:PSS in B-QLEDs with Al or Ag/Al cathodes that have been previously electrically aged with fresh ones. In this experiment, we take unencapsulated devices that were electrically aged for 3 hrs under 20 mA/cm² (resulting in a decrease in EL intensity by 95% and 35% for devices with the Al and Ag/Al cathodes, respectively, over that period). All layers above the PEDOT:PSS HILs are then removed as described in the experimental section and schematically illustrated in Figure 7-11a. After that, fresh layers of TFB, B-QDs, ZnMgO, and Al or Ag/Al are deposited, and the rebuilt B-QLEDs are encapsulated. For comparison, this process is also performed for identical devices that were not electrically stressed to be used as control. The average EQE of the rebuilt devices, based on measurements on a group of six devices in each case, is shown in Figure 7-11b. As seen, the EQE of the Al devices with the pre-stressed PEDOT:PSS is about 20% lower than the unstressed ones, indicating that some changes happen in the PEDOT:PSS

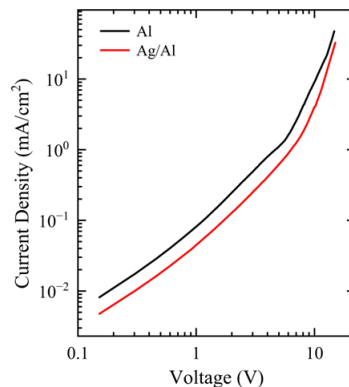


Figure 7-10. J-V characteristics of the EODs with Ag/Al and Al cathode.

layer (or at the ITO interface) after aging. Also, Figure 7-11c shows the J-V characteristics of the rebuilt devices. As can be seen, devices with the pre-stressed PEDOT:PSS show higher

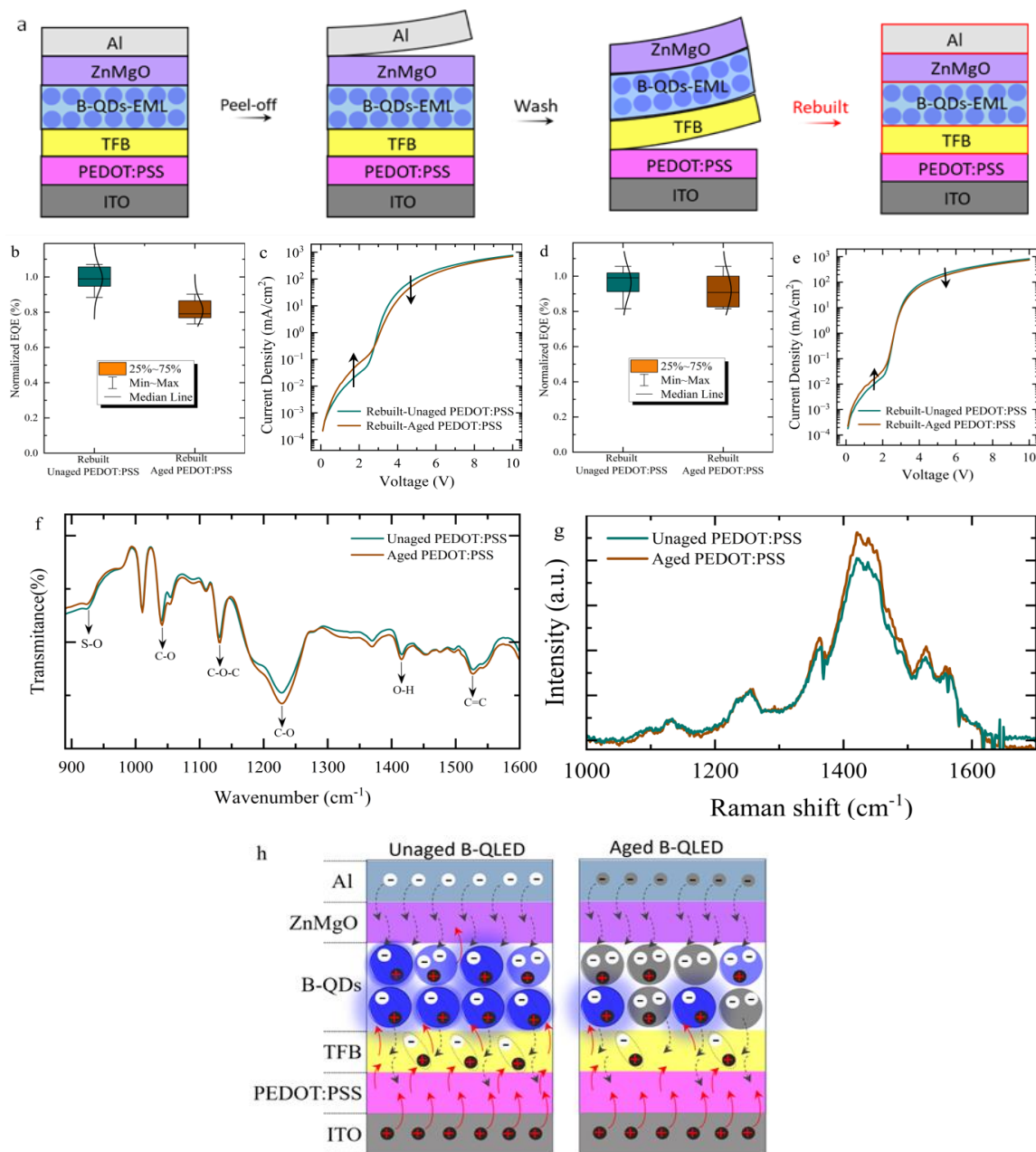


Fig. 7-11 HIL damage verification. (a) Schematics of the B-QLEDs rebuilding process. (b) The average EQE of rebuilt B-QLEDs with Al cathode and with unaged and aged PEDOT:PSS. (c) J-V characteristics of the rebuilt B-QLEDs with Al cathode and with unaged and aged PEDOT:PSS. (d) The average EQE of rebuilt B-QLEDs with Ag/Al cathode and with unaged and aged PEDOT:PSS. (e) J-V characteristics of rebuilt B-QLEDs with Ag/Al cathode and with unaged and aged PEDOT:PSS. (f) ATR-IR spectroscopy of unaged and aged PEDOT:PSS films. (g) Raman Spectra of unaged and aged PEDOT:PSS films. (h) Schematic illustration of charge supply conditions in unaged and aged B-QLEDs.

subthreshold currents (currents below the V_{ON}) but lower currents at higher voltages compared to their counterparts with the unstressed PEDOT:PSS, resembling the behaviour in the aged B-QLEDs (Figures 7-1c and 7-6c). The lower current density in the devices with the pre-stressed PEDOT:PSS indicates that the hole supply reduction that occurs in B-QLEDs during electrical stress is associated with changes in the PEDOT:PSS HIL or its interface with ITO. Figures 7-11d and e show the corresponding data from the Ag/Al devices. As seen, here the EQE of the rebuilt devices is only 10% lower than the control. The J-V plots also show smaller differences. These results clearly indicate that the PEDOT:PSS changes less during electrical stress in case of the Ag/Al devices, convincingly proving that electron leakage to the PEDOT:PSS is driving those changes and contributing to the deterioration in hole supply.¹⁹⁷

Finding that the hole supply reduction occurs due to some changes in the PEDOT:PSS layer or its interface with ITO, we use Attenuated Total Reflectance-Infrared (ATR-IR) and Raman spectroscopy measurements to try to detect and investigate changes in PEDOT:PSS layers after electrical aging. Figure 7-11f shows ATR-IR spectra from PEDOT:PSS layers from aged and unaged devices, where all layers above the PEDOT:PSS layer are removed, similar to the procedure described in the previous section. As can be seen, only small changes are observed in this case suggesting that chemical changes in PEDOT:PSS are unlikely to be a major factor. Figure 7-11g shows the Raman spectra collected from the same PEDOT:PSS. As can be seen, the band between 1350 to 1500 cm^{-1} , which corresponds to the PEDOT,¹⁹⁸⁻²⁰⁰ increases after aging, suggesting that the PEDOT becomes more crystalline. This suggests possible aggregation in PEDOT pointing to possible phase separation between PEDOT and PSS which would reduce conductivity in the PEDOT:PSS HILs hence the reduced hole supply.

The changes in charge supply conditions in the unaged and aged B-QLEDs are illustrated in Figure 7-11h. As can be seen, before aging (Figure 7-11h-left side), the electron supply (black dashed arrows) is easier than the hole supply (red arrows), resulting in an $e/h > 1$ into the B-QDs-EML and the formation of the device recombination zone close to the HTL interface. In this case also significant electron leakage across the HTL occurs. In contrast, hole leakage to the counter electrode is much less. Under electrical stress, the electron leakage increases over time, and the hole supply decreases. The leaked electrons also negatively affect the PEDOT:PSS, causing the hole supply efficiency to deteriorate further overtime, hence also the number of holes that get

injected into the B-QDs-EML, exacerbating the charge imbalance in the B-QDs-EML (i.e. e/h becomes $\gg 1$), resulting in increased trion formation and Auger quenching, hence the decrease in device EQE and the reversible QDs PLQY losses.^{49, 53} The grey speheres symbolize quenched QDs due to trion formation, and the increase in their numbers after aging (Figure 7-11h-right side). Since the increase in electron leakage and reduced hole supply are permanenet, the EL losses are not reversible.

7.1.5 Conclusion

In conclusion, an increase an electron leakage and electron-induced damage to the hole injection layer (HIL) that leads to a deterioration in hole supply are found to play a key role in the rapid EL loss in B-QLEDs. EL and PL measurements on B-QLEDs, fabricated with and without luminescent MLs, show that the electron supply is easier than the hole supply, resulting in an electron e/h ratio >1 in the B-QDs-EML and significant electron leakage into the HTL and to the HIL. Under electrical stress, electron leakage increases and hole supply deteriorates further causing charge imbalance to increase, and, as a result, the EQE decereas. Unlike the PLQY losses that occur during device aging, which are mostly reversible, the EL losses are therefore irreversible. Modified devices with a reduced electron supply demonstrated a 30X increase in lifetime, showing that the excess electron supply is a major factor in the rapid EL loss observed in these devices. This work gives novel insights into the causes of the rapid EL loss in B-QLEDs and provides new strategies for improving their stability.

7.2 Exploring new ETL and HTL designs for optimizing charge injection and EL performance in upright B-QLEDs

In this section, based on the observations from the previous section, both the ETL and HTL parts of the device are modified with the aim of reducing the electron supply and enhancing the hole supply in upright B-QLEDs.

7.2.1 Modifying ETL in upright B-QLEDs

As concluded in the previous section, the electron supply is stronger than the hole supply in upright B-QLEDs. Therefore, limiting the electron supply is likely to improve both the device efficiency and lifetime. In this section, to limit the electron supply, a thin layer of PEI (1 mg/mL) insulating material is incorporated in the middle of the ZnMgO ETL, as shown schematically in Figure 7.12a. Figure 7.12b compares the J-V-L characteristics of the PEI-based device with the

control (without PEI). As seen, the PEI-based device exhibits a lower current density compared to the control device, suggesting that the incorporation of PEI likely reduces the electron current. Looking at the EQE data (Figure 7.12c), the PEI-based device shows a higher EQE at low current densities ($< 30 \text{ mA/cm}^2$) compared to the control, indicating that the use of PEI leads to better charge balance within this current range.

To assess the impact of reducing the electron supply using PEI on the device's lifetime, the EL stability was measured under a constant current density of 20 mA/cm^2 . Figures 7-12d and e compare the relative luminance and voltage changes between the PEI-based device and the control. As shown, the use of PEI improves the device lifetime by approximately 12 times, which can be attributed to the reduction in electron supply and, consequently, the improvement in charge balance. One can conclude that, the electron supply reduction by PEI insulating material is an effective approach to increase the EL lifetime of B-QLEDs.

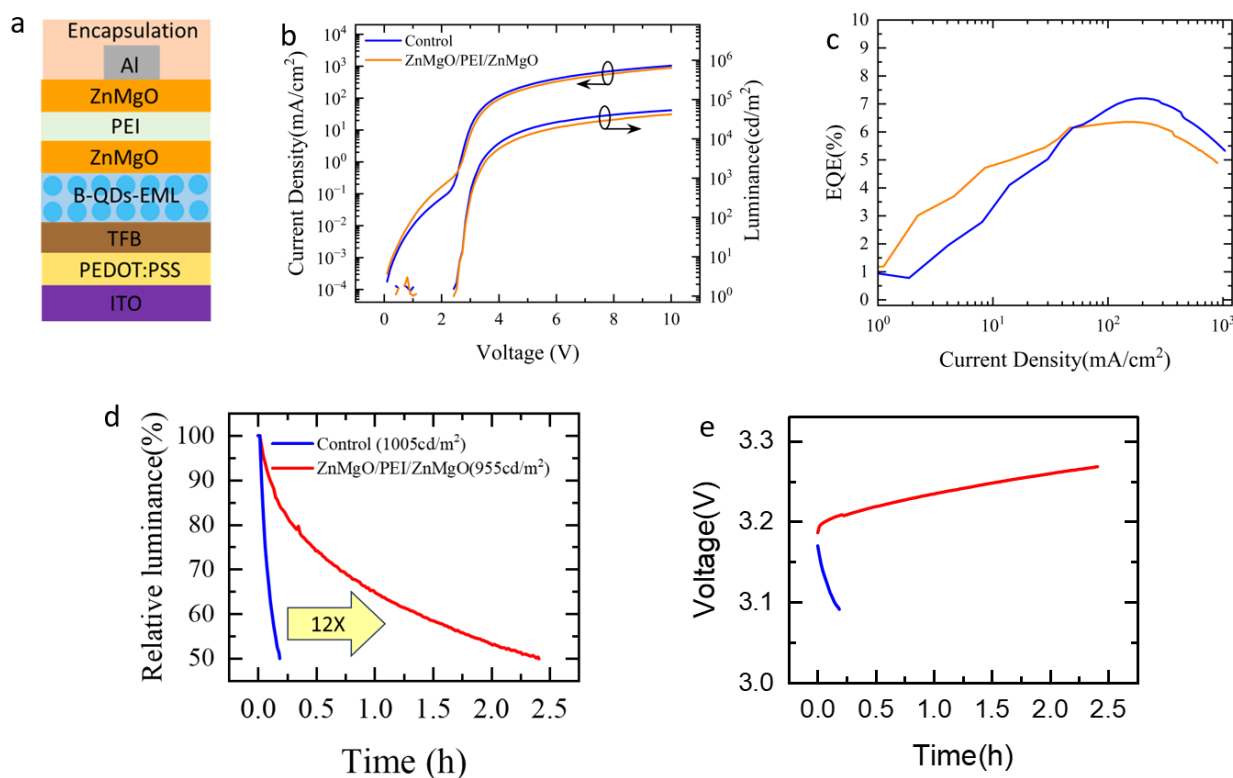


Figure 7-12 (a) Schematic diagram of the B-QLEDs structure with PEI in the ETL side. A comparison of (b). J-V-L, (c) EQE-J, (d). relative luminance vs time, and (e) V-time of the B-QLEDs with PEI in the ETL and control device. The B-QLED lifetime is measured under a constant current density of 20 mA/cm^2 .

7.2.2 Modifying HTL in upright B-QLEDs

As outlined in Section 7.1, in addition to the relatively weaker hole supply, electrons are prone to leaking into the TFB HTL due to its relatively deep LUMO level. Consequently, employing a new HTL that offers both efficient hole injection and effective electron-blocking properties is anticipated to enhance the performance of B-QLEDs. Recently, Deng et al.³⁰ proposed PF8Cz as an efficient HTL, mitigating electron leakage at the organic/inorganic interface due to its low electron affinity and reduced energetic disorder, resulting in a significant improvement in efficiency and lifetime of G and B-QLEDs. Therefore, in this section, PF8Cz is incorporated into the B-QLED structure as a replacement for TFB.

Figure 7.13a illustrates the schematic of the device structure, while Figure 7.12b compares the J-V-L characteristics of devices using PF8Cz and TFB. As shown, the use of PF8Cz results in a lower current density at any given voltage, while the devices exhibit comparable EQEs (Figure 7.12c). This is accompanied by a reduction in sub-threshold current, leading to higher EQEs at lower current densities. These observations suggest that the charge balance in the device is likely improved due to the reduction in electron leakage. However, it does not have a significant effect on the device efficiency.

Figure 7.13d compares the EL spectra of devices based on TFB and PF8Cz. As observed, PF8Cz emits light in the 500-700 nm range, suggesting that electrons still leak into the HTL. This could explain why PF8Cz does not significantly affect the EQE (Figure 7.12a). However, the PF8Cz-based device demonstrates a longer EL lifetime (8x), as shown in Figure 7.13e. The extended lifetime can be attributed to reduced electron leakage current. In summary, while PF8Cz enhances the device lifetime, it does not significantly improve overall performance, suggesting that although PF8Cz has relatively good electron-blocking properties, it may not effectively enhance hole supply efficiency.

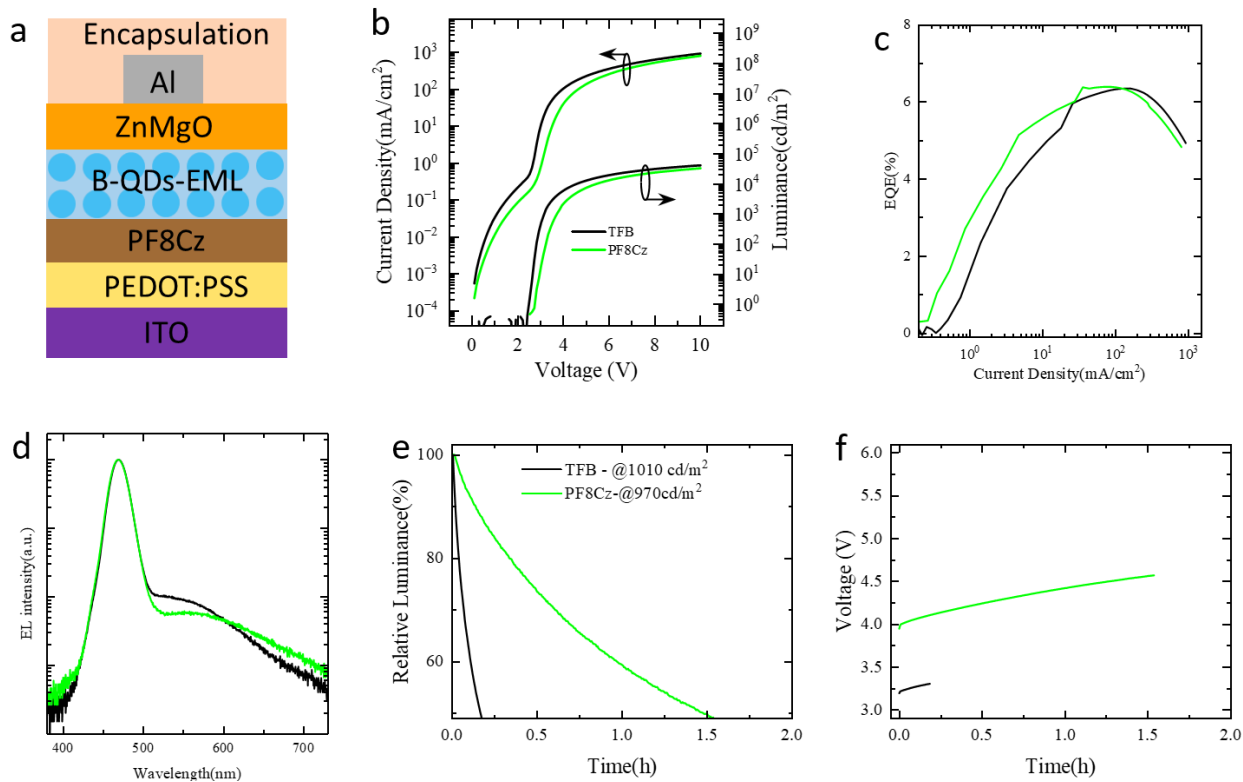


Figure 7-13 (a) Schematic diagram of the B-QLEDs structure with PF8Cz HTL. A comparison of (b) J-V-L, (c) EQE-J, (d) EL spectra, (e) relative luminance vs time, and (f) V-time of the B-QLEDs with PEI in the ETL and control device. The B-QLED lifetime is measured under a constant current density of 20 mA/cm².

7-2-3 Conclusion

In summary, modifying the ETL and HTL is performed to limit electron supply and improve hole supply in upright B-QLEDs. A thin PEI layer is added in the middle of ETL to reduce electron supply, resulting in 12X improvement in the device lifetime. Also, replacing TFB with PF8Cz in the HTL reduced electron leakage, resulting in 8X increase in lifetime. Overall, these strategies demonstrated the importance of controlling electron supply and enhancing electron-blocking properties to improve device stability, though further research is needed for performance optimization.

Chapter 8 Summary and Future Work

8.1 Summary of main conclusions

This section summarizes the main findings of this work. The fundamental objective of this research was to investigate and optimize charge balance and its effect on the efficiency and lifetime of QLEDs. The research was categorized into four main routes: (i) identifying the causes of low efficiency in inverted QLEDs with polymeric HTL, (ii) investigating the degree of charge balance in inverted R, G, and B-QLEDs and its influence on EL performance, (iii) exploring new ETL and HTL designs for optimizing charge injection and improving EL performance in inverted QLEDs, and (iv) investigating charge balance and EL loss mechanisms in upright B-QLEDs and exploring new materials for improving EL performance.

Chapter 4: Identifying the Causes of Low Efficiency in Inverted QLEDs with Polymeric HTL:

- Identified that the cause of low efficiency was the poor interface between the QDs-EML and HTL, rather than damage to the QDs-EML.
- A new architecture enabling the use of polymeric HTLs in inverted QLEDs was developed, leading to record-breaking efficiency and stability.
- A correlation between the QDs-EML bandgap and the electron and hole supply efficiencies for each color was found.

Chapter 5: Investigating the Degree of Charge Balance in Inverted R, G, and B-QLEDs and Its Influence on EL Performance:

- It was found that in inverted R-QLEDs, the e/h ratio in the QDs-EML is greater than 1, whereas in G- and B-QLEDs, the e/h ratio is less than 1, with the charge balance being significantly worse in B-QLEDs.
- It was verified that, compared to electrons, holes lead to a stronger Auger quenching effect.
- Injecting electrons into the QDs-EML first, rather than holes, was shown to be more favorable for enhancing efficiency in QLEDs

Chapter 6: Exploring New ETL and HTL Designs for Optimizing Charge Injection and Improving EL Performance in Inverted QLEDs:

- A strong positive aging effect was observed in unencapsulated inverted G-QLEDs.
- A double ETL design that resulted in EQEs >23% in G, and R-QLEDs was developed.
- Controlled doping of the ETL with graphene QDs was found to enhance electron supply, resulting in improved charge balance in inverted G-QLEDs.

Chapter 7: Investigating the Charge Balance and EL Loss Mechanisms in Upright B-QLEDs and Exploring New Materials for Improving EL Stability

- It was found that electron supply was stronger than hole supply in upright B-QLEDs.
- It was revealed that electron leakage damaged the hole supply by the deterioration of HIL.
- The EL stability of upright B-QLEDs was improved 30X by limiting electron supply through cathode replacement.
- It was shown that EL stability could be improved by either limiting electron supply or enhancing hole supply efficiencies.

8.2 Future Work

This section presents recommendations for future research, drawn from the conclusions and significant findings of this study.

First, this study revealed that utilizing wide band gap QDs at the QDs/polymeric HTL interface in inverted R-QLEDs significantly enhances device performance. Such wide bandgap QDs act as non-invasive interlayers that do not disrupt the QDs-EML, preventing solvent-induced damage to the QDs and facilitating efficient charge injection. Due to their non-invasive nature and their bandgap adjustability, wide band gap QDs can be applied to both the HTL and ETL sides to improve the efficiency of hole and electron supply, respectively. Future work should explore this approach in both inverted and upright QLED architectures, as it may further optimize charge balance.

This work demonstrated that the enhancement in electron supply through the use of a double ETL, combined with reduced electron leakage by utilizing TCTA as the HTL, resulted in EQEs exceeding 23% in both inverted R- and G-QLEDs, but not in B-QLEDs. Future work should focus on identifying the key factors limiting their efficiency. Potential avenues include further

enhancing electron supply and exploring HTL materials with shallower LUMO levels, which may improve charge injection and overall device performance.

The findings in this work showed that the positive aging effect can occur in QLEDs even without encapsulation and in the absence of curable resin, which had previously been identified as the primary cause of this effect. This unexpected result highlights the need for further investigation to fully understand the underlying mechanisms of positive aging in QLEDs. Future research should aim to examine these contributing factors in more detail, with the goal of modifying device structures based on the findings. This could enable the development of devices that achieve high efficiencies and stability immediately after fabrication, eliminating the need for positive aging processes.

The results of this work indicated that electron overflow is the primary cause of EL loss in upright B-QLEDs. While some EL lifetime improvements were achieved through device engineering in this work, the EL lifetime of upright B-QLEDs still lags significantly behind that of their red and green counterparts. Therefore, further efforts are needed to enhance the EL stability of B-QLEDs. Future research should focus on developing more effective strategies to control electron overflow and improve hole supply. In addition to reducing electron supply, it is essential to find an HTL with optimized hole supply and electron-blocking properties to achieve better charge balance and improve overall device stability.

The findings in this work showed that electron leakage significantly limits the EL efficiency of upright B-QLEDs. While some EL and PL measurements were performed, the transport paths of leaked electrons are not well traced and need to be systematically explored. To address this, simultaneous EL and PL measurements using a single photon counting technique are required to accurately verify the emission contribution from each layer and to compare the charge balance factor and exciton radiative efficiency. This will provide a precise understanding of how electron leakage impacts overall emission and charge balance in upright B-QLEDs.

The results further indicated that the causes of EL loss in CdSe-based B-QLEDs are more complex than those in other colors, despite their similar chemical compositions. Additionally, it was observed that the charge injection efficiency into B-QDs changes over time when under bias. Given that B-QDs have different organic ligands compared to R- and G-QDs, the role of ligands in charge injection and their electrochemical stability becomes crucial and may contribute to the

EL stability of B-QLEDs. Future research should focus on investigating the impact of various ligands, including those with different functional groups and carbon chain lengths, to determine how these factors influence the shelf life and electrical stability of QLEDs.

The findings also showed that the EL of B-QLEDs decreases within a few minutes, suggesting that significant damage to the device's functional layers is unlikely during this time. Most of the EL loss is likely due to changes in the device's charge supply efficiencies. One possible reason for this is the charging of the functional layers. During electrical stress, carriers may accumulate in the functional layers, particularly in the QDs-EML and its interfaces with adjacent layers, negatively impacting charge supply. This effect could be more pronounced in B-QDs compared to R- and G-QDs due to their larger surface-to-bulk ratio. Therefore, it is essential to thoroughly investigate this phenomenon in future work. To achieve this, analyzing C-V characteristics, measuring static PL and TrPL under bias, and comparing them before and after electrical stress could provide precise insights into the charging effect.

Although inorganic ETLs exhibit better thermal and chemical stability compared to organic HTLs, they undergo some changes over time and under electrical stress, which can affect their properties as well as those of adjacent materials, significantly impacting the performance of QLEDs. Therefore, future studies could focus on identifying suitable organic ETLs to replace the inorganic ones. Candidate organic ETLs should have energy levels and electron mobilities comparable to ZnO and its derivatives. By using organic ETLs, it may be possible to eliminate the positive aging effect and fabricate devices that demonstrate high efficiency just after fabrication.

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