A New Class of Bipolar Chemical Hybrids as Prospective Hosts for Phosphorescent Organic Light-Emitting Diodes

by

Thomas Yung-Hsin Lee

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Supervised by

Professor Shaw H. Chen

Department of Chemical Engineering Arts, Sciences and Engineering Edmund A. Hajim School of Engineering and Applied Sciences

University of Rochester

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To My Beloved Wife and My Parents
BIOGRAPHICAL SKETCH

Thomas Yung-Hsin Lee was born in 1980 in Tainan, Taiwan. In 2002, he received a Bachelors of Science degree in Chemical Engineering from the National Taiwan University, Taipei, Taiwan. He continued on at the National Taiwan University receiving a Master of Science degree in 2004. He then moved to the University of Rochester in September 2005 to pursue his doctorate in Chemical Engineering under the supervision of Professor Shaw H. Chen. His field of specialization was in organic opto-electronic materials and organic light-emitting diode devices. He has accepted a position with Applied Materials in Sunnyvale, CA to begin his professional career in September 2012.
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I am deeply grateful to Professors Lewis J. Rothberg and Ching W. Tang for having served on my thesis committee, gotten me started on the principle and measurement of charge-carrier mobility in organic materials, and granted me access to PhOLED and photocurrent TOF device fabrication and characterization facilities. In addition, I have benefited a great deal from my interactions over the years with Professor Jason U. Wallace of the D’Youville College, Professor Chung-Chih Wu of the National Taiwan University, Professor Steve D. Jacobs of the Institute of Optics, Mr. Kenneth L. Marshall of the Laboratory of Laser Energetics, Dr. David S. Weiss, Dr. Paul B. Merkel, and Dr. Jane J. Ou of the University of Rochester. I want to thank Mr. Joseph Madathil and Mr. Mike Culver of the University of Rochester, and Mr. Richard Fellows of the Laboratory of Laser Energetics for the help in the device fabrication and measurement systems, Mr. Brian L. McIntyre of the Institute of Optics and Mr. Christopher Willoughby of TA Instrument for the training for transmission electron microscopy and thermogravimetric analysis, respectively.

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My gratitude is due to my fellow postdoctoral and graduate students throughout my graduate career here at the University of Rochester: Drs. Jason U. Wallace, Sean W. Culligan, Anita Trajkovska, Andrew Chien-An Chen, Zhijian Chen, Chunki Kim, Lichang Zeng, Simon Ku-Hsien Wei, and Qiang Wang. I also would like to thank many friends after hours: Hank McLeod, Shiela McLeod, Eric H.-F. Peng, Yung-Li Wang, Kelly Lin, Chung-Yu Chen, Pin-Yi Wang, Poya Kan, Hank Lin, Tuan-Hsiu Hsieh, Chi-Sheng Chang, Shirley Liu, Tim Huang, Becky Lee, Ting-Hao Phan, Helen Wei, Yi-Ming Lai, Karl Ni, and Hui-Jung Yang for having enriched my personal life in Rochester.

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ABSTRACT

Phosphorescent organic light emitting diodes are making major impacts on consumer electronics and solid state lighting. The emitting layer comprising a guest-host system plays an important role in device efficiency and lifetime, the two critical issues to which this thesis is devoted through exploration of an emerging class of bipolar hybrid hosts. Major accomplishments are recapitulated as follows.

Two non-conjugated bipolar hybrid compounds and their parent unipolar compounds were synthesized for the characterization of their charge transport properties in vacuum-sublimed films by the photocurrent time-of-flight technique. It is demonstrated that charge-carrier mobility can be modulated over three decades without affecting HOMO and LUMO levels or triplet energies by varying the ratio of the electron-transport to hole-transport moiety, and the molecular conformation dictated by spacer length through computation. The ability to balance the electron and hole fluxes through EML will be beneficial to maximizing device efficiency and lifetime.

Three representative bipolar hybrids, \( t\text{Bu-TPA-}p\text{-TRZ} \), \( t\text{Bu-TPA-}m\text{-TRZ} \), and \( t\text{Bu-TPA-}L\text{-TRZ} \), were synthesized and characterized for a comprehensive evaluation of their potentials for PhOLEDs. External quantum efficiency is diminished by the formation of charge transfer complexes (CTC) and the deviation from charge balance through EML. The \( L\)-hybrid is the least prone to CTC formation while suffering inferior charge balance to afford an EQE intermediate between those of the \( m\)- and \( p\)-hybrids. Nevertheless, the \( L\)-hybrid offers the most stable EML against crystallization from the
desired glassy film, thus holding promise for the fabrication of superior PhOLEDs.

A mixture of mCP and SiPh4 and its chemical hybrid counterpart, mCP-L-PhSiPh3, have been employed to elucidate how thermal annealing of EMLs affects the temporal stability of blue-emitting PhOLEDs. Annealing mCP:SiPh4:F1rpic induced crystallization in 1 h, while mCP-L-PhSiPh3:F1rpic consistently resisted crystallization under all conditions. Without incurring pinhole formation in the absence of a free surface presented by EML, annealing mCP:SiPh4:F1rpic at 60 °C for 1 h led to about 50 % loss in EQE. In contrast, the pristine device’s EQE persisted with mCP-L-PhSiPh3:F1rpic annealed at 60 °C for up to 24 h. The concept of bipolar hybrids holds promise for mitigating morphological instability as one of the challenges to PhOLED lifetime.
CONTRIBUTORS AND FUNDING SOURCE

This thesis summarizes my PhD research under the guidance of my advisor, Professor Shaw H. Chen, and executed in collaboration primarily with Drs. Qiang Wang and Lichang Zeng. My thesis research was supervised by a dissertation committee consisting of Professors Shaw H. Chen and Ching W. Tang of the Department of Chemical Engineering, and Professor Lewis J. Rothberg of the Department of Chemistry, all at the University of Rochester. The contributions to the contents of my thesis are outlined as follows.

Chapter 2: I synthesized all the compounds shown in Chart 2.1 except TRZ-1Cz(MP)2 and TRZ-3Cz(MP)2 that Dr. Lichang Zeng and I collaborated in synthesis. I produced all the experimental results and collected relevant literature data presented in Figures 2.1 to 2.7 and Table 2.1. Dr. Jane J. Ou provided the computed molecular structures in Figure 2.8 for interpretation of data presented in Figures 2.6, 2.9, and 2.10. For Figure 2.11 and Table 2.2, Dr. Lichang Zeng did cyclic voltammetry measurements of Cz(MP)2, TRZ, TRZ-1Cz(MP)2, and TRZ-3Cz(MP)2, and I did the measurements of C3-2Cz(MP)2 and C2-2TRZ(2tBu). Professors Shaw H. Chen and Jason U. Wallace, Drs. Jane J. Ou, Lichang Zeng, and Qiang Wang provided the intellectual foundations for data interpretation.

Chapter 3: Dr. Qiang Wang and I synthesized the compounds shown in Chart 3.1. We collaborated to produce most of the results presented in Figures 3.1 to 3.11 except Figure 3.4 on phosphorescence, which was contributed by Professor Chung-Chih Wu and Yu-
Tang Tsai. Table 3.1 was contributed in part by Professor Chung-Chih Wu and Yu-Tang Tsai for triplet energies, and in part by Dr. Qiang Wang and me for energy levels. Professors Shaw H. Chen, Chung-Chih Wu, Jason U. Wallace, and Dr. Qiang Wang provided the foundations for data interpretation.

Chapter 4: mCP and mCP-L-PhSiPh3 in Chart 4.1 were synthesized by Dr. Lichang Zeng and me, respectively. The phosphorescent spectrum in Figure 4.1 was provided by Mr. Millard Wyman in the Chemistry department. Dr. Qiang Wang and I worked together to produce the results presented in Figures 4.2 to 4.12. Professor Shaw H. Chen offered experimental procedures for producing results reported in Figures 4.5, 4.8, and 4.12, while Dr. Qiang Wang contributed handsomely to data interpretation.

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# TABLE OF CONTENTS

**BIOGRAPHICAL SKETCH** iii  
**ACKNOWLEDGEMENTS** iv  
**ABSTRACT** vi  
**CONTRIBUTORS AND FUNDING SOURCE** viii  
**TABLE OF CONTENTS** x  
**LIST OF CHARTS** xiii  
**LIST OF REACTION SCHEMES** xiv  
**LIST OF FIGURES** xv  
**LIST OF TABLES** xxiv

## CHAPTER 1 BACKGROUND AND INTRODUCTION 1

1.1. Organic Light-Emitting Diodes 1  
1.2. Host Materials for Phosphorescent OLEDs 5  
1.3. Charge Transport 8  
1.4. Charge Transfer Complexes 12  
1.5. OLED Stability 13  
1.6. Formal Statement of Research Objectives 16  
References 19
CHAPTER 2  ELECTRON AND HOLE MOBILITY IN TRIAZINE- AND CARBAZOLE-CONTAINING COMPOUNDS  

2.1. Introduction 34  
2.2. Experimental Section 36  
2.3. Results and Discussion 45  
2.4. Summary 60  
References 62  

CHAPTER 3  CHARGE TRANSFER COMPLEX FORMATION IN THREE DISTINCT HYBRID HOSTS FOR RED-EMITTING PHOSPHORESCENT ORGANIC LIGHT-EMITTING DIODES  

3.1. Introduction 65  
3.2. Experimental Section 67  
3.3. Results and Discussion 76  
3.4. Summary 89  
References 91  

CHAPTER 4  STABILITY OF BLUE-EMITTING PHOSPHORESCENT ORGANIC LIGHT-EMITTING DIODES IN HYBRID RELATIVE TO MIXED HOST  

4.1. Introduction 95  
4.2. Experimental Section 97  
4.3. Results and Discussion 104
4.4. Summary
References

CHAPTER 5 CONCLUSIONS AND FUTURE RESEARCH

5.1. Conclusions
5.2. Future Research

Appendix 1 $^1$H NMR, MALDI-TOF and LC Mass Spectra for Chapter 2
Appendix 2 $^1$H NMR and LDI-TOF Mass Spectra for Chapter 3
Appendix 3 $^1$H NMR and LDI-TOF Mass Spectra for Chapter 4
LIST OF CHARTS

Chart 2.1  Molecular structures with their thermal transition temperatures determined by DSC second heating scans of samples preheated to beyond their crystalline melting points. Symbols: $G$, glassy; $K$, crystalline; $I$, isotropic. 46

Chart 3.1  Molecular structures with their thermal transition temperatures determined by DSC second heating scans of samples preheated to beyond their crystalline melting points. Symbols: $G$, glassy; $K$, crystalline; $I$, isotropic. 77

Chart 4.1  Molecular structures with their thermal transition temperatures determined by DSC second heating scans of samples preheated to beyond their crystalline melting points. Symbols: $G$, glassy; $K$, crystalline; $I$, isotropic. 104
LIST OF REACTION SCHEMES

Scheme 2.1  Synthesis of C3-2Cz(MP)2, C2-2TRZ(2tBu), TRZ-3Me, C3-2TRZ, Ben-3TRZ, and Ben-2TRZ. 37
Scheme 3.1  Synthesis of tBu-TPA-p-TRZ, tBu-TPA-m-TRZ, and tBu-TPA-L-TRZ. 68
Scheme 4.1  Synthesis of mCP and mCP-L-PhSiPh3. 98
LIST OF FIGURES

Figure 2.1  (a) Absorption spectra of C3-2Cz(MP)2, C2-2TRZ(2tBu), TRZ-1Cz(MP)2, and TRZ-3Cz(MP)2 films via vacuum sublimation on fused silica substrates. (b) Schematic diagram of the TOF apparatus. Nitrogen laser (337 nm) and fourth harmonic generation of Nd:YAG laser (266 nm) were used as excitation source.

Figure 2.2  Polarizing optical micrographs of vacuum-sublimed films of (a) TRZ-3Me, (b) Ben-2TRZ, (c) C3-2TRZ, (d) C2-2TRZ(2tBu), C3-2Cz(MP)2, TRZ-1Cz(MP)2, and TRZ-3Cz(MP)2.

Figure 2.3  DSC heating and cooling scans at ±20 °C/min of (a) C2-2TRZ(2tBu), (b) C3-2Cz(MP)2, (c) TRZ-1Cz(MP)2, (d) TRZ-3Cz(MP)2, (e) TRZ-3Me, (f) C3-2TRZ, (g) Ben-3TRZ, and (h) Ben-2TRZ, preheated to above their melting points followed by cooling down to −30 °C at −100 °C/min. The melting points were determined from the first heating scans of pristine samples of C2-2TRZ(2tBu), C3-2Cz(MP)2, TRZ-1Cz(MP)2, TRZ-3Cz(MP)2, TRZ-3Me, C3-2TRZ, Ben-3TRZ, and Ben-2TRZ at 361, 129, 106, 169, 159, 265, 246, and 174 °C, respectively. Symbols: G, glassy; K, crystalline; I, isotropic.

Figure 2.4  (a) Polarizing optical micrographs of vacuum-sublimed glassy C2-2TRZ(2tBu), C3-2Cz(MP)2, TRZ-1Cz(MP)2, and TRZ-3Cz(MP)2 films in TOF devices before and after mobility measurements. (b) Electron diffraction pattern of vacuum-sublimed C2-2TRZ(2tBu) film after eight 266 nm laser exposures, each for 10 s with a 20 s interval, the same
treatments as through TOF measurement.

Figure 2.5 Representative TOF transients of TRZ-3Cz(MP)2 for (a) hole carriers at an electric field of $4.4 \times 10^5$ V/cm and (b) electron carriers at an electric field of $4.1 \times 10^5$ V/cm. Insets: log-log plots to determine transit times.

Figure 2.6 (a) Hole and (b) electron mobilities as functions of electric field ($E^{1/2}$) for TRZ-1Cz(MP)2, TRZ-3Cz(MP)2, C3-2Cz(MP)2, and C2-2TRZ(2tBu) in ITO/organic layer/Al or ITO/organic layer/Ag devices. Vanishing hole and electron mobility in (a) and (b), respectively, was noted for C2-2TRZ(2tBu) and C3-2Cz(MP)2. The data points are accompanied by an average error of ±8%.

Figure 2.7 Energy diagram of PhOLED device with energy levels in neat solid films calculated from two correlations, HOMO = $-(1.4\pm0.1)qE_{1/2}$(oxd) − (4.6±0.08) eV and LUMO = $-(1.19\pm0.08)qE_{1/2}$(red) − (4.78±0.17) eV, with literature-reported energy levels in solutions. Hosts in EML: TRZ-1Cz(MP)2 (LUMO = −2.2 eV; HOMO = −5.2 eV), TRZ-3Cz(MP)2 (LUMO = −2.1 eV; HOMO = −5.1 eV).

Figure 2.8 Optimized molecular structures of (a) C2-2TRZ(2tBu) and (b) C3-2Cz(MP)2 computed with Gaussian 09 using B3LYP functional with the 6-31G(d) basis set. The same optimized structures were obtained without peripheral aliphatics.

Figure 2.9 (a) Molecular structures of unipolar TRZ-based compounds for which electron mobility values have been reported and (b) comparison of electron mobility values with C2-2TRZ(2tBu).

Figure 2.10 (a) Molecular structures of unipolar Cz-based compounds
for which hole mobility values have been reported and (b) comparison of hole mobility values with C3-2Cz(MP)2.

Figure 2.11 Cyclic voltammograms of (a) Cz(MP)2, (b) TRZ, (c) C3-2Cz(MP)2, (d) C2-2TRZ(2tBu), (e) TRZ-1Cz(MP)2, and (f) TRZ-3Cz(MP)2 in acetonitrile:toluene at 1:1 by volume.

Figure 3.1 Cyclic voltammetric scans of compounds in acetonitrile:toluene (1:1 by volume) at 10⁻³ M with 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte. Both oxidation and reduction scans are reversible for all the three hybrids. The reduction potential of tBu-TPA and the oxidation potential of TRZ are beyond the CV measurement range.

Figure 3.2 Absorption spectra at 20 °C of (a) tBu-TPA, TRZ, tBu-TPA-p-TRZ, tBu-TPA-m-TRZ, and tBu-TPA-L-TRZ in chloroform at 8.3×10⁻⁶ M. Nearly identical absorption spectra were obtained for neat solid films of the three hybrids. Fluorescence spectra at 20 °C of (b) tBu-TPA-p-TRZ, tBu-TPA-m-TRZ, and tBu-TPA-L-TRZ in toluene, chloroform and N,N-dimethylformamide at 8.3×10⁻⁶ M with photoexcitation at 277 nm, and (c) tBu-TPA-p-TRZ (95 nm), tBu-TPA-m-TRZ (97 nm), and tBu-TPA-L-TRZ (94 nm) films vacuum-sublimed on fused silica substrates receiving the same incident excitation at 281 nm with normalization by 1-10⁻¹, where A is the absorbance of photoexcitation at 281 nm.

Figure 3.3 Fluorescence spectra collected at 20 °C for (a) tBu-TPA-m-TRZ and (b) tBu-TPA-L-TRZ in toluene, chloroform, and N,N-dimethylformamide at 8.3×10⁻⁶ M with photo-
excitation at 277 nm.

Figure 3.4 CTC emission (20 °C, no time delay) and phosphorescence (77 K, 10 ms delay) spectra for (a) tBu-TPA-p-TRZ, (b) tBu-TPA-m-TRZ, and (c) tBu-TPA-L-TRZ in dichloromethane at 10⁻⁵ M. Triplet energies were estimated from the highest-energy vibronic sub-bands as indicated.

Figure 3.5 Energy diagram of PhOLED device with literature-reported energy levels in neat solid films. Hosts in EML: tBu-TPA-p-TRZ (HOMO = −2.3 eV; LUMO = −5.3 eV), tBu-TPA-m-TRZ (HOMO = −2.3 eV; LUMO = −5.3 eV), tBu-TPA-L-TRZ (HOMO = −2.2 eV; LUMO = −5.2 eV).

Figure 3.6 (a) EQE and (b) driving voltage as functions of current density for PhOLEDs with emitting layers comprising tBu-TPA-p-TRZ, tBu-TPA-m-TRZ, and tBu-TPA-L-TRZ doped with Ir(piq)₃ at a 8 wt%.

Figure 3.7 Electroluminescence spectra of PhOLEDs with (a) tBu-TPA-p-TRZ, (b) tBu-TPA-m-TRZ, and (c) tBu-TPA-L-TRZ as the hosts all doped at 8 wt% of Ir(piq)₃ as functions of current densities. The CIE coordinates are (0.654, 0.333), (0.660, 0.330), and (0.670, 0.327) for the emission spectra shown in (a), (b), and (c), respectively. Insets: expanded views of emission spectra from 425 to 475 nm.

Figure 3.8 Current as a function of driving voltage for (a) hole-only and (b) electron-only devices.

Figure 3.9 Devices incorporating a sensing layer located at (a) HTL/EML interface and (b) EML/ETL interface, and (c) EQE as a function of current density for the devices containing a sensing layer.
Figure 3.10  DSC heating and cooling scans at ±20 °C/min of samples preheated to above their melting points followed by cooling down to –30 °C at –100 °C/min for (a) pure hybrids, and (b) hybrids doped with Ir(piq)$_3$ at 8 wt%. Symbols: G, glassy; K, crystalline; I, isotropic.

Figure 3.11  Polarizing optical micrographs of 20-nm-thick vacuum-sublimed, glassy films of hybrids doped with Ir(piq)$_3$ at a 8 wt% sandwiched between ITO and Al under thermal annealing at 75 °C: (a) $t$Bu-TPA-$p$-TRZ:Ir(piq)$_3$ for 3 h, (b) $t$Bu-TPA-$m$-TRZ:Ir(piq)$_3$ for 7 h, and (c) $t$Bu-TPA-$L$-TRZ:Ir(piq)$_3$ for 33 h.

Figure 4.1  Phosphorescence spectrum at 20 K of vacuum-sublimed mCP-$L$-PhSiPh$_3$ film with excitation at 355 nm. The triplet energy was estimated from the highest energy band.

Figure 4.2  TGA thermograms of FIrpic, mCP and mCP-$L$-PhSiPh$_3$ recorded at a heating rate of 10 °C/min under nitrogen atmosphere.

Figure 4.3  DSC heating and cooling scans at ±20 °C/min of (a) mCP, (b) SiPh$_4$, (c) mCP:SiPh$_4$ and mCP:SiPh$_4$:FIrpic, and (d) mCP-$L$-PhSiPh$_3$ and mCP-$L$-PhSiPh$_3$: FIrpic preheated to above their melting points followed by cooling down to –30 °C at –100 °C/min. The melting points were determined from the first heating scans of mCP, SiPh$_4$, mCP:SiPh$_4$, mCP:SiPh$_4$:FIrpic, mCP-$L$-PhSiPh$_3$ and mCP-$L$-PhSiPh$_3$: FIrpic at 176, 252, 170, 166, 115 and 120 °C, respectively. Symbols: G, glassy; K, crystalline; I, isotropic.

Figure 4.4  Energy diagram of PhOLED device with literature-reported energy levels in neat solid films.
Figure 4.5  Current as a function of driving voltage for hole-only devices upon thermal annealing of TAPC layers with a free surface at (a) 20 °C for 0 and 72 h, 100 °C for 1 h, and 60 °C for 96 h before completing the device, ITO/MoO$_3$(3 nm)/TAPC(30 nm)/MoO$_3$(3 nm)/Al(100 nm) and (b) 100 °C for 1 h before completing the device, ITO/MoO$_3$(3 nm)/TAPC(30 nm)/MoO$_3$(3 nm)/Al(100 nm) and ITO/MoO$_3$(3 nm)/TAPC(30 nm)/Al(100 nm). Inset in (a): electron diffraction image of the two-layer film, MoO$_3$(3 nm)/TAPC(30 nm), annealed with a free surface at 20 °C for 72 h and at 100 °C for 1 h in a glove box filled with nitrogen.

Figure 4.6  Freshly deposited TmPyPB(10 nm)/BPhen(30 nm)/LiF(1 nm): (a) polarizing optical micrograph and (b) electron diffraction image.

Figure 4.7  Polarizing optical micrographs of ITO/MoO$_3$/TAPC/mCP:SiPh$_4$:FIrpic annealed at 20 °C for (a) 0 h, (b) 24 h, (c) 48 h, (d) 72 h, and (e) 80 and 100 °C for 1 h. Inset in (a): electron diffraction image of MoO$_3$/TAPC/mCP:SiPh$_4$:FIrpic prior to thermal annealing; inset in (d): electron diffraction image of MoO$_3$/TAPC/mCP:SiPh$_4$:FIrpic annealed at 20 °C for 72 h with calculated $d$-spacings ranging from 0.14 to 0.47 nm; (a) with inset also serves to represent the amorphous character of MoO$_3$/TAPC/mCP-$\mathcal{L}$-PhSiPh$_3$:FIrpic annealed with a free surface at 20 °C for up to 72 h, and at 80 and 100 °C for 1 h each in a glove box filled with nitrogen.

Figure 4.8  (a) EQE and (b) driving voltage as functions of current density for PhOLED devices containing mCP-$\mathcal{L}$-
PhSiPh3:FIrpic, and (c) EQE and (d) driving voltage as functions of current density for PhOLED devices containing mCP:SiPh4:FIrpic with half-devices, ITO/MoO3/TAPC/EML, annealed at 20 °C for up to 72 h and at 80 and 100 °C for 1 h. Typical experimental errors for EQE and driving voltage are ±10 and ±8%, respectively, of the mean from three separate devices. Pristine PhOLED devices were characterized at 10 and 50 mA/cm² with pristine EMLs (×), and at 50 mA/cm² with half-devices up to EML annealed at 100 °C for 1 h (+).

Figure 4.9 Electroluminescence spectra of PhOLEDs, ITO/MoO3/TAPC/EML/TmPyPB/BPhen/LiF/Al, where EML consists of (a) mCP-PhSiPh3:FIrpic, and (b) mCP:SiPh4:FIrpic with ITO/MoO3/TAPC/EML, annealed at 20 °C for 0, 72 h and at 80 and 100 °C for 1 h before subsequent depositions of TmPyPB/BPhen/LiF/Al.

Figure 4.10 Polarizing optical micrographs of (a) TmPyPB annealed at 60 °C for up to 14 days, (b) ITO/MoO3/TAPC/mCP-PhSiPh3:FIrpic/TmPyPB annealed at 60 °C for up to 198 h, and ITO/MoO3/TAPC/mCP:SiPh4:FIrpic/TmPyPB annealed at 60 °C for (c) 1 h, (d) 2 h, (e) 3 h, and (f) 9 h. Insets in (a) and (b): electron diffraction images of TmPyPB and MoO3/TAPC/mCP-PhSiPh3:FIrpic/TmPyPB annealed at 60 °C for up to 14 days and 198 h, respectively.

Figure 4.11 Electroluminescence spectra of PhOLED devices, ITO/MoO3/TAPC/EML/TmPyPB/BPhen/LiF/Al, where EML consists of (a) mCP-PhSiPh3:FIrpic, and (b) mCP:SiPh4:FIrpic with ITO/MoO3/TAPC/EML/TmPyPB
annealed at 60 °C for varying time periods before subsequent depositions of BPhen/LiF/Al.

Figure 4.12 (a) EQE and (b) driving voltage as functions of current density for PhOLED devices containing mCP-PhSiPh3:F1rpic, and (c) EQE and (d) driving voltage as functions of current density for PhOLED devices containing mCP:SiPh4:F1rpic with half-devices, ITO/MoO3/TAPC/EML/TmPyPB, annealed at 60 °C for various periods of time. Typical experimental errors for EQE and driving voltage are ±8 and ±6%, respectively. Pristine mCP-PhSiPh3:F1rpic and mCP:SiPh4:F1rpic PhOLED devices were characterized at 50 mA/cm² half-devices, ITO/MoO3/TAPC/EML/TmPyPB, annealed at 60 °C for 198 h and 9 h indicated as × and +, respectively.

Figure A1.1 1H NMR (400 MHz) spectrum of TRZ-3Me in CDCl3 at 298 K.

Figure A1.2 1H NMR (400 MHz) spectrum of C3-2TRZ in CDCl3 at 298 K.

Figure A1.3 1H NMR (400 MHz) spectrum of Ben-3TRZ in CDCl3 at 298 K.

Figure A1.4 1H NMR (400 MHz) spectrum of Ben-2TRZ in CDCl3 at 298 K.

Figure A1.5 1H NMR (400 MHz) spectrum of C3-2Cz(MP)2 in CDCl3 at 298 K.

Figure A1.6 1H NMR (400 MHz) spectrum of C2-2TRZ(2tBu) in CDCl3 at 298 K.

Figure A1.7 LC MS spectrum of TRZ-3Me using methanol as mobile phase.

Figure A1.8 MALDI-TOF MS spectrum of C3-2TRZ using IAA as the
matrix.

Figure A1.9  MALDI-TOF MS spectrum of **Ben-3TRZ** using IAA as the matrix.

Figure A1.10 MALDI-TOF MS spectrum of **Ben-2TRZ** using IAA as the matrix.

Figure A1.11 MALDI-TOF MS spectrum of **C3-2Cz(MP)2** using IAA as the matrix.

Figure A1.12 MALDI-TOF MS spectrum of **C2-2TRZ(2tBu)** using IAA as the matrix.

Figure A2.1  $^1$H NMR (400 MHz) spectrum of **tBu-TPA-p-TRZ** in CDCl$_3$ at 298 K.

Figure A2.2  $^1$H NMR (400 MHz) spectrum of **tBu-TPA-m-TRZ** in CDCl$_3$ at 298 K.

Figure A2.3  $^1$H NMR (400 MHz) spectrum of **tBu-TPA-L-TRZ** in CDCl$_3$ at 298 K.

Figure A2.4  LDI-TOF MS spectrum of **tBu-TPA-p-TRZ**.

Figure A2.5  LDI-TOF MS spectrum of **tBu-TPA-m-TRZ**.

Figure A2.6  LDI-TOF MS spectrum of **tBu-TPA-L-TRZ**.

Figure A3.1  $^1$H NMR (400 MHz) spectrum of **mCP** in CDCl$_3$ at 298 K.

Figure A3.2  $^1$H NMR (400 MHz) spectrum of **mCP-L-PhSiPh3** in CDCl$_3$ at 298 K.

Figure A3.3  LDI-TOF MS spectrum of **mCP**.

Figure A3.4  LDI-TOF MS spectrum of **mCP-L-PhSiPh3**.
LIST OF TABLES

Table 2.1  Film thicknesses and electron and hole mobility data compiled in Figures 2.9 and 2.10 with vacuum-sublimed films of compounds A through I, C2-2TRZ(2tBu), and C3-2Cz(MP)2. 56

Table 2.2  Energy levels for TRZ, Cz(MP)2, and the chemical hybrids. 60

Table 3.1  Energy levels in neat solid films characterized at 20 °C and triplet energies measured in dichloromethane at 77 K. 81
CHAPTER 1

BACKGROUND AND INTRODUCTION

1.1. ORGANIC LIGHT-EMITTING DIODES

Since the discovery of conducting polymers in 1977 by Heeger et al.[1] organic materials have been broadly investigated. The landmark reports of relatively efficient fluorescence from small molecules by Tang et al.[2] and from polymers by Friend et al.[3] have motivated intensive research and development in the pursuit of superior materials and device structures, paving the way for commercially viable organic light emitting diodes (OLEDs).[4-7]

Since the first commercial organic light-emitting diode (OLED) display launched by the Tohoku Pioneer Company in 1997, OLEDs have been regarded as the next generation flat panel displays. This is due to their being thinner, lighter, and more flexible, while consuming less power than other displays, such as liquid crystal displays (LCDs) and plasma display panels. In addition, their rapid response time, about 1000 times faster than LCD, makes OLEDs a promising candidate for 3D displays. Nowadays, many international corporations, such as AUO, Sony, Samsung SMD, and LG Display, are devoted to the technical contest of OLED development. In 2007, Sony launched the first commercial 11” OLED television, and recently LG Display announced the availability of
55” OLED televisions in May, 2012. Another potential application of OLED is solid-state lighting. Since the first white OLED (WOLED) was developed by Kido et al.,[8,9] WOLEDs have attracted a lot of attention because they are flexible, lightweight, capable of providing surface emission without UV excitation, and environmentally friendly in comparison to fluorescent lamps, which use mercury. The Lumiotec Company began selling the first lighting systems incorporating a mass-produced OLED lighting panel (145 cm × 145 cm) in 2011. These commercial OLED products have greatly promoted research and development in the OLED field as well as widespread use of OLED technology to improve the global environment.

The early work of OLEDs focused on fluorescent emission. However, it is widely accepted that fluorescent OLEDs can only utilize singlet excitons, and thus the internal quantum efficiency is constrained by the theoretical limit of 25%, because singlet excitons represent only one-fourth of the total excited-state population, where the remaining three-fourth are triplet excitons.[10,11] Recently, fluorescent OLEDs with high external quantum efficiencies (EQE) over 5% have been achieved owing to the contribution of triplet-triplet annihilation to fluorescent emission.[12-14] A pivotal breakthrough in the enhancement of electroluminescence efficiency reported by Forrest et al. in 1998 is the implementation of phosphorescent emitters in OLEDs,[15] offering a means of achieving internal quantum efficiency (IQE) of 100% by harvesting both singlet and triplet excitons for emission. Today, several papers[16-20] have reported EQEs exceeding 20% by using phosphorescent OLEDs (PhOLEDs). Triplet emitters are usually organometallic compounds containing chelating chromophores and heavy metal atoms,
where efficient spin-orbit coupling facilitates intersystem crossing, resulting in improved triplet exciton formation and emission.\textsuperscript{[21-23]} Consequently, the emissive decay from the excited triplet state to the singlet ground state occurs with a highly efficient quantum yield. Because of the relatively long excited-state lifetime of triplet excitons, PhOLEDs usually suffer from concentration quenching,\textsuperscript{[24-26]} which can be relieved by using triplet emitters with short triplet lifetimes\textsuperscript{[25,27]} or doping triplet emitters into host materials.

A typical PhOLED consists of a transparent anode, an emitting layer (EML) comprising a triplet emitter doped into a host material, and a reflective metal cathode. Charge-injection, -transport, and -blocking layers are usually incorporated between the electrodes and the EML. Holes and electrons are injected into the organic layers from the anode and cathode, respectively, and subsequently migrate in opposite directions to recombine in the EML, leading to the generation of excitons that emit light, which is then out-coupled through the transparent electrode. The EQE is defined as the ratio of the collected photons from outside of the device to the electrons injected into the device, and is given by the product of the efficiency of radiative decay, the fraction of excited states (singlet and/or triplet) that are emissive, the charge recombination efficiency, and the fraction of photons out-coupled from the device. Highly efficient PhOLEDs can be achieved by the adoption of a multilayer device structure\textsuperscript{[28-37]} due to balance of charge fluxes, confinement of excitons inside the EML, and prevention of charge leakage. However, there are still some challenges that need to be overcome, including improvement of blue PhOLED stability and the development of economical manufacturing processes with high pixel yields.
Charge transport plays a crucial role in device efficiency because fast charge transport can reduce the operating voltage and enhance power efficiency.\textsuperscript{38-41} Due to the requirement of effective hole and electron transport in the EML to reach charge balance, the host materials need to be capable of transporting holes and electrons, \textit{viz.} bipolar, with a mobility ratio close to unity.\textsuperscript{38,42,43} Charge transport between the emitter molecules may also be important at high doping levels.\textsuperscript{33,44,45} For example, \textit{fac}-tris(2-phenylpyridine)iridium(III) is found to be capable of transporting hole carriers, further improving hole mobility in the quest for charge balance.\textsuperscript{46,47} The recombination zone should preferably be located away from the interface of the organic layers to avoid exciton quenching.\textsuperscript{48} Efficiency roll-off at high current density is also a potential limiting factor for PhOLEDs in practical applications. This problem is caused mainly by the long lifetime of the triplet state of organometallic complexes, leading to triplet-triplet annihilation and/or triplet-polaron quenching.\textsuperscript{25,26,49} It has been shown that efficiency roll-off can be mitigated by shortening the phosphorescent emitter’s triplet lifetime,\textsuperscript{50} or by decreasing triplet emitter aggregation and triplet exciton density in host materials.\textsuperscript{51,52} Uniform exciton distribution as a result of charge balance has been demonstrated\textsuperscript{53} to improve efficiency due to suppression of triplet-triplet annihilation. In addition, charge-blocking\textsuperscript{28} and exciton-confinement layers\textsuperscript{28,37,51,53} are usually applied to prevent charge leakage and exciton quenching, respectively.

Highly stable WOLEDs have been developed using the tandem device approach. Compared to a conventional non-stacked WOLED, a WOLED with tandem structure exhibits the same luminance with much lower current density, resulting in a vast
improvement of device lifetime. Today, the half-life defined as the operational time elapsed before the emission luminance decreases to 50% of its initial level has exceeded 100,000 h at an initial luminance of 1000 cd/m$^2$ in WOLEDs.$^{[54]}$ However, because blue fluorescence is often used instead of phosphorescence in the WOLEDs,$^{[54]}$ there is a potential gain in efficiency if device instability in blue PhOLEDs can be addressed.

1.2. HOST MATERIALS FOR PHOSPHORESCENT OLEDs

Since triplet emitters are usually dispersed homogeneously into a host, the selection of host materials is particularly important for highly efficient PhOLEDs. The host materials should possess sufficiently high triplet energy ($E_T$) to ensure energy transfer from the host to the guest and confine excitons on the latter. Typically, the hosts should bear minimum $E_T$ values of 2.7, 2.5, and 2.0 eV to accommodate blue,$^{[55]}$ green$^{[56]}$ and red$^{[57]}$ emitters, respectively. Such a requirement for the host materials in blue-emitting PhOLEDs becomes particularly challenging because of their high $E_T$s. In addition, the host materials should be completely miscible with the triplet emitters to avoid possible phase separation, which would limit the device operational lifetime. Appropriate energy levels of the host materials are also required to facilitate charge injection from adjacent layers into the EML, resulting in a reduction of the driving voltage and enhancement of the power efficiency. The host materials are expected to possess decent hole- and electron-transport capabilities to achieve charge balance in the EML, which is a prerequisite for high-performance PhOLEDs. Finally, host materials
should exhibit high thermal and morphological stability against thermally activated crystallization. It is challenging to satisfy all the criteria, and there is an inherent trade-off between high $E_T$ and high charge carrier mobility because constraining $\pi$-conjugation to maintain high $E_T$ inevitably impedes charge-transport capability as $\pi$ overlap is lessened.

A unipolar host usually contains a hole-transport moiety (HTM)\cite{58-60} or an electron-transport moiety (ETM)\cite{61-63} in its molecular structure with a dominant hole or electron transport. Most of the existing host materials are unipolar, capable of preferentially transporting holes or electrons, leading to a narrow recombination zone close to one of the interfaces between the EML and its adjacent layer, which is detrimental to device efficiency and lifetime.\cite{53,64} In addition, charge and exciton accumulations at interfaces may cause efficiency roll-off and device degradation due to triplet-triplet annihilation\cite{25,26} and/or triplet-polaron annihilation.\cite{26} It is an important to evenly and broadly distribute excitons in the EML to reduce the exciton density and prevent exciton accumulation, thus improving device efficiency and stability.

In past decades, extensive research has focused on the development of host materials having both hole- and electron-transport capabilities. Mixed hosts\cite{53,65-71} formed by simple physical blending of hole- and electron-transport materials have been incorporated in the EMLs of PhOLEDs with improvements in device performance and reduction of efficiency roll-off with balanced charge fluxes and a broad recombination zone. The energy levels of the EML can be matched with the adjacent layers to reduce injection barriers and hence lower the driving voltage. The hole- and electron-transport
capabilities can be independently modulated by varying the composition of the mixed host without affecting the energy levels\textsuperscript{[67-71]} The main problem with this approach is the possible phase separation over time\textsuperscript{[72,73]} to adversely affect device stability.

An alternative approach is to prepare bipolar hosts\textsuperscript{[74-77]} by chemically bonding hole- and electron-transport moieties to form a donor-acceptor type molecule to minimize phase separation. However, because of possible charge delocalization between the hole- and electron-transport moieties, this type of material usually exhibits a relatively small energy band gap and low $E_{T}$, severely limiting its application in blue PhOLEDs. Therefore, it is imperative that the bipolar host materials possess weak donor-acceptor interaction to retain high $E_{T}$, preventing energy transfer from guest to host. To this effect, the linkage between the HTM and ETM plays an important role. The general strategy to realize high $E_{T}$ is to lessen the electronic coupling between the two moieties by meta- and/or ortho-linkages\textsuperscript{[19,78,79]} or by introducing a π-conjugated spacer with a greatly twisted conformation\textsuperscript{[80-82]} More efficiently, incorporating a flexible, non-conjugated σ-spacer can completely block the electronic interactions between HTM and ETM\textsuperscript{[18,73,83,84]}

There are several building blocks which have been utilized in tailoring the molecular structures of host materials. Because of their high $E_{T}$ and adequate hole-transport ability, carbazoles\textsuperscript{[27,59,85,86]} and triphenylamines\textsuperscript{[81,87,88]} have been intensively employed as hole-transport building blocks for host materials. Arylsilane derivatives possessing ultra-high singlet and triplet bandgaps are usually adopted as hosts in blue PhOLEDs\textsuperscript{[89-91]} Triazine\textsuperscript{[92-94]} is also a common electron-transport building block in host
materials due to its high $E_T$ and high electron-transport ability. Other building blocks with high $E_T$, such as fluorenes,[95-97] pyridines,[19,34,35,98,99] arylphosphine oxides,[17,100,101] oxadiazoles,[79,88,98] benzimidazoles[42,77,81,102] and triazoles[98] have also been used in the construction of host materials of PhOLEDs. By incorporation of these HTMs and ETMs, a great number of high-$E_T$ bipolar host materials have been generated. Additional sterically-hindering groups have also been introduced in the host molecule to improve its thermal and morphological stability.[103]

1.3. CHARGE TRANSPORT

When an electric field is applied to an organic semiconductor sandwiched between anode and cathode, charge carriers will migrate from one electrode to the other across the sample. The charge carrier mobility, $\mu$, is the proportionality constant between the drift velocity of charge carriers, $v$, and the applied electric field, $E$, as expressed in equation (1.1)

$$v = \mu \times E$$  \hspace{1cm} (1.1)

Therefore, charge carrier mobility is defined as the distance over which charge carriers are transported per unit time under unit electric field.

From a macroscopic point of view, the current density, $J$, is the product of the number density of charge carriers, $n$, with the drift velocity, $v$. ($J = e \times n \times v$, where $e$ is the elementary charge, $1.602176565 \times 10^{-19}$ Coulomb) Therefore, according to this
equation and equation (1.1), the current density is proportional to charge carrier mobility, underscoring the fact that the migration of charge carriers is exactly the electric current. In addition, the current density is equal to the product of the electrical conductivity, $\sigma$, and the applied field, $E$. The relationship between the electrical conductivity and charge carrier mobility can be described as $\sigma = e \times n \times \mu$. Thus, the electrical conductivity describes how fast net charge will flow, while the charge carrier mobility describes how fast a single charge carrier can migrate.

Charge transport has been a subject of interest in organic materials. Since charge transport in oligoacenes was first explored and investigated by Pope et al.\textsuperscript{[104,105]} in 1960, the number of publications on mobility studies in organic materials has gradually increased over several decades. Early studies of charge transport focused on crystalline materials. Although they are inherently very pure, the presence of a trace amount of impurities can detrimentally affect the measured mobility.\textsuperscript{[106]} Karl investigated methods of purifying and growing crystals, and the results claimed to demonstrate intrinsic charge transport without impurity interference.\textsuperscript{[107]} In addition to crystalline materials, polymers and molecularly doped polymers, where small molecules are doped homogeneously in a polymer matrix, have also been used extensively to investigate the mechanism of charge-transport.\textsuperscript{[108-110]} Recently, significant efforts have been invested in the study of small organic molecules which readily form amorphous glasses because of their potential use in organic electronics.\textsuperscript{[111,112]}
Nowadays, organic charge-transport materials with various morphologies have been used in different kinds of devices. In general, crystalline materials exhibit superior charge-transport ability over amorphous materials. Organic devices containing single-crystalline materials have been reported,\[^{113,114}\] but the difficulty of large-area fabrication limits their practical applications. Polycrystalline materials have been widely used in organic field-effect transistors (OFETs)\[^{113,115}\] and organic photovoltaic cells (OPVs),\[^{116}\] where grain size, grain boundaries, and molecular orientation are key parameters affecting the device performance. However, due to their relative ease of processing, transparency, and homogeneity without grain boundaries, amorphous materials have been intensively investigated and developed in the fields of organic electronics.\[^{64,111,112,117,118}\]

It has been widely accepted that charge transport in an organic amorphous system is carried out by a hopping process, essentially a sequential oxidation-reduction process between molecules.\[^{64,119}\] Holes or electrons are sequentially transferred from cation or anion radicals of molecules to neutral molecules through the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively. Two postulated factors, the electronic coupling and the reorganization energy, have been utilized to describe charge transport.\[^{120}\] The electronic coupling, also called the transfer integral, is basically the spatial overlap of the energy levels, \textit{i.e.} HOMO level for hole transport and LUMO level for electron transport, while the reorganization energy arises from the change in molecular geometry during oxidation, reduction, and neutralization. Large electronic coupling and low reorganization energy produce fast hopping rates, resulting in high charge carrier mobility.
Several models have been proposed to describe the charge-transport mechanism in disordered, organic systems. The Poole-Frenkel formalism\textsuperscript{[121,122]} is an empirical equation presenting the dependence of the mobility on the electric field and temperature. The small-polaron model\textsuperscript{[123-125]} is based on the theory of hopping of small polarons, which are charge carriers with their accompanying lattice deformation, to transport charge carriers in organic materials. The most prominent model is Bässler’s disorder formalism,\textsuperscript{[126,127]} in which charge transport takes place by hopping between localized states in accordance with fluctuations in hopping site energies and molecular separation distances, which are considered to have Gaussian distributions.

There are a number of experimental methodologies yielding mobility values either indirectly or in a straightforward manner. Steady-state space-charge limited current\textsuperscript{[128,129]} and analysis of the OFET performance\textsuperscript{[113,115,130]} are common indirect methods involving sustained steady-state current. Mobility can also be extracted from frequency change in pulse-radiolysis time-resolved microwave conductivity\textsuperscript{[27,131,132]} and admittance spectroscopy\textsuperscript{[133-135]} Charge carrier mobility can be measured directly by determination of the time for charges to be transported across the sample. These methods include transient space-charge limited current,\textsuperscript{[48,136,137]} xerographic discharge,\textsuperscript{[107]} photocurrent time-of-flight (TOF),\textsuperscript{[64,138]} and transient electroluminescence.\textsuperscript{[48,139]}
1.4. CHARGE TRANSFER COMPLEXES

A charge transfer complex (CTC) consists of a donor and an acceptor stabilized by electron transfer between the two.[140] Typically, the formation of an CTC requires that (i) one of the two moieties is excited, (ii) the two moieties are in close contact with the appropriate configurations, and (iii) the donor has a relatively low ionization potential and the acceptor bears a relatively high electron affinity. In general, the formation is favored by a significant difference between the HOMO level of the donor and the LUMO level of the acceptor.[141] The distance and configuration requirements between the donor and the acceptor are determined by the electron-transfer process involving molecular orbital overlap.[142]

In OLEDs, the emission from CTCs mostly occurs in the heterojunction interface between the charge-transport layer and the EML[143-151] or in the bulk of mixed EMLs.[152-154] In general, CTC formation is detrimental to OLED performance because of their potentially low quantum efficiency and the adverse effects on the spectral purity of the additional long-wavelength band. Therefore, many studies have been made to prevent the formation of CTCs for the improvement of OLED performance by selecting the appropriate energy levels of the relevant organic layers.[141,155-157] For example, the formation of CTCs between the common acceptor, Alq3, and donors with various HOMO levels has been investigated by Adachi et al.[141,157] Their results suggested that no CTC is formed when the difference between the HOMO levels of the donor and the acceptor is small (< 0.4 eV). However, there is no paper reporting the quantitative correlation
between CTC formation and the difference between LUMO levels. As result, the CTC formation in OLEDs has remained unpredictable. Highly efficient charge trapping on the emitters in a guest-host system may alleviate CTC emission in OLEDs if charge recombination mostly occurs on the emitters, possibly preventing CTC formation on the host. The efficiency of charge trapping is strongly dependent on the doping level of the emitter in the EML and the energy level offsets between the host and the emitter.

Attempts have been made to fabricate WOLEDs by taking advantage of the broad emission band of CTCs. In addition, CTCs can also provide potential means to modulate the color of electroluminescence in OLEDs by choosing molecules with proper energy levels. However, their often low device efficiencies may severely limit their practical application.

1.5. OLED STABILITY

A prerequisite for the practical application of any electronic device is adequate device stability. As far as OLEDs are concerned, instability generally means a loss of device luminance efficiency over time. Tremendous efforts have been devoted to developing stable OLEDs for information display and solid-state lighting applications. In the 1990s, many scientists focused on the study of dark-spot growth in OLEDs because dark spots usually grow very fast and become readily visible. As the name implies, dark spots refer to non-emissive defects which cause a decrease in device luminance. Without sufficient protection to avoid exposure to ambient conditions,
moisture may penetrate into devices through pinholes at defect sites. Consequently, gas is evolved in an electrochemical process at the cathode/organic layer interface by decomposition of the organic layer. This results in local delamination of the cathode and dark-spot formation. Morphological instability induced by the ambient moisture sometimes can give rise to the cathode delamination.[166,167] Dark spots may also be produced at the anode/organic layer interface because of pre-existing absorbed moisture on the anode.[168,169] Dark-spot degradation is the result of poor adhesion between the electrodes and the adjacent organic layers, causing interruption of charge injection, and the non-emissive region may grow under continuous operation. By proper encapsulation and careful control of device fabrication, the potential for dark-spot degradation can be effectively suppressed. Encapsulation to protect devices from ambient conditions has been common practice in many applications of organic electronics.

In 1999, Lee et al. first proposed that indium species released from the most common anode material, indium tin oxide (ITO), into the organic layers causes luminescence quenching.[170] The charged indium ions, possibly assisted by the applied potential, may penetrate very deeply into the organic layers, and subsequently lead to OLED degradation. The release of indium can be suppressed by stabilizing the ITO surface with exposure to UV-ozone or oxygen plasma.[170] On the other hand, oxygen effusion from ITO might be harsher than that of indium with respect to the adverse effects on the OLED stability.[171] The device lifetime can be improved by coating a hole-injection layer, typically the PEDOT:PSS layer, on top of ITO which can facilitate hole injection and also serves as a barrier to prevent oxygen diffusion into the EML.[172-175]
To explain the appreciable decrease in OLED efficiency associated with trapped positive charges, Kondakov et al. proposed that OLED degradation can be caused by trap formation. The trapped charges can serve as nonradiative recombination sites, leading to a continuous decrease in OLED efficiency during operation. In addition, the traps could also reduce charge carrier mobility, hence resulting in a high driving voltage. In addition, degradation at the interfaces inside OLEDs is a complicated problem because charge injection and charge/exciton accumulation are involved. Interface degradation, especially in the multilayer OLEDs, has received considerable attention. It is widely believed that charge/exciton accumulation at the interface between the EML and the charge transport layer is detrimental to device efficiency and stability. Especially in the case of PhOLEDs, triplet-triplet annihilation and triplet-polaron quenching would cause severe efficiency roll-off under high current density due to just such accumulation at interfaces.

Morphological instability has been considered to be one of the origins of OLED degradation. The idea was initiated from the well-known hole-transport material, TPD. The TPD layer in OLEDs tends to crystallize, resulting in interlayer delamination, which may interrupt charge injection. Crystallization may also produce nonradiative recombination sites at the grain boundaries of the crystalline domains. Joule heating during device operation may facilitate the growth of crystallites. Many studies have focused on the design and synthesis of organic materials with high glass transition temperatures \( T_{gs} \) in order to improve morphological stability. However, detailed investigations have revealed no correlation between \( T_{gs} \) and device stability. Organic
materials forming a stable amorphous glass\cite{111,112} are promising candidates for OLEDs due to their homogeneous and isotropic properties without presence of the grain boundaries. In general, nonplanar molecular structures hinder close-packed molecular geometry and thus suppress crystallization. Various molecular design approaches have been reported regarding nonplanar molecular structures, such as incorporation of bulky groups,\cite{97,189-191} flexible σ-spacers,\cite{18,73,83,84} and twisted geometry.\cite{81,192}

As has been discussed in the preceding paragraphs, degradation of OLEDs involves many intricate factors. It has taken researchers several decades to uncover some of the issues. Full-color PhOLEDs with high efficiency are very promising for commercialization, but blue PhOLEDs still lack adequate device lifetime. For the flat panel display application, power efficiency of 60-80 lm/W and lifetime, LT70 (time to decay to 70% of the initial emission luminance), of at least 15,000 h at an initial luminance of 2000 cd/m² are needed.\cite{193}

1.6. FORMAL STATEMENT OF RESEARCH OBJECTIVES

Organic light-emitting diodes have been commercialized in various types of consumer electronic products, such as flat panel displays and solid-state lighting applications. Host materials are of particular importance with respect to the efficiency and stability of PhOLEDs because they are responsible for not only charge transport and injection to achieve the balance of charge fluxes, but also the homogeneous dispersion of phosphorescent emitters to avoid concentration quenching.
For the purpose of charge balance, not only hole- and electron-transport capability but also the charge injection barriers into host materials should be taken into account. Although the charge transport characteristics are generally considered to have a significant impact on device performance, there are a few reports of hole and/or electron mobilities in bipolar host materials.\textsuperscript{[42,45,77,194]} The optimization of PhOLEDs often involves modulation of the charge transport properties in the bipolar host materials through chemical modification, but their energy levels are often altered as well. Thus, studies involving systematic modulation of charge transport properties in bipolar hybrid hosts with unaltered energy levels would provide valuable insight into achieving charge balance in PhOLEDs.

Most bipolar host materials bear a donor-acceptor structure, in which CTC formation can occur to the detriment of device performance. Charge trapping on the emitters may reduce the adverse effect from the CTC, but this requires high doping levels in the EML at the risk of immiscibility and concentration quenching. One approach to effectively suppress CTC formation is through the interruption of conjugation between the HTM and ETM moieties. Although many papers have discussed CTC formation at the interface between organic layers\textsuperscript{[143-151]} and in EML containing mixed\textsuperscript{[152-154]} and hybrid\textsuperscript{[16,77-79,102,195]} hosts, the effects of the CTC in bipolar host materials on the device performance have been reported.

Although highly efficient blue PhOLEDs have been developed using novel materials and sophisticated device architectures, their relatively short device lifetime is
still a bottleneck for practical applications. Despite the fact that extrinsic factors such as moisture and oxygen can be effectively controlled by means of proper device encapsulation, device degradation has remained major challenges. Morphological instability is one of the most deleterious factors influencing device performance for organic materials tend to crystallize. Because triplet emitters have to be uniformly distributed in host materials to prevent concentration quenching, morphologically stable host materials are particularly important for the development of long-lived PhOLEDs. It is imperative to ensure morphological stability against crystallization in the organic layers to arrive at sufficiently long-lived PhOLEDs.

Therefore, this thesis was motivated by the following objectives.

(1) To explore a chemical approach to modulating charge transport while achieving morphological stability and retaining sufficiently high $E_T$s without affecting energy levels.

(2) To unravel CTC formation in bipolar hybrid compounds with various linkages between HTMs and ETMs, and to characterize the effects of CTC on PhOLED performance.

(3) To investigate the effects of morphological stability against crystallization on blue PhOLED performance in terms of device efficiency and driving voltage by annealing EMLs with a mixed host and its equivalent bipolar hybrid.
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CHAPTER 2

ELECTRON AND HOLE MOBILITY IN TRIAZINE- AND CARBAZOLE-CONTAINING COMPOUNDS

2.1. INTRODUCTION

Organic semiconductors have been actively explored for potential applications to full-color displays, solid-state lighting, and solar cells to take advantage of their light weight, large-area fabrication, low processing cost, and mechanical flexibility. Charge transport through semiconducting films is one of the critical parameters affecting device performance. Effective charge transport entails hopping from one molecule to another without being trapped or scattered. Charge traps resulting from impurities or defects may act as localized low-energy sites that can immobilize charge carriers, thus depressing mobility. Favorable molecular packing is known to facilitate charge transport through improved overlap of electronic wavefunctions. Single crystalline materials possess superior charge carrier mobility, but their practical applications is hampered by inherent difficulty with large-area fabrication. Mobility in polycrystalline materials increases with domain size because of fewer grain boundaries to trap charge carriers. While not as effective charge transport media as crystalline materials, amorphous materials offer isotropic and homogeneous properties without grain
boundaries across sizable glassy films. Balanced hole and electron fluxes through the emitting layer in an OLED are known to yield superior device efficiency and lifetime.\cite{8} Charge carrier mobility can be tuned in principle to reach charge balance by mixing hole- and electron-transport components,\cite{9} but potential phase separation with simultaneous crystallization may adversely affect long-term device stability. Charge transport capability could be modulated by coupling HTMs directly with ETMs at the expense of modifying their HOMO and LUMO levels while depressing $E_T$.\cite{10,11}

As an alternative approach, chemical hybrids comprising HTMs and ETMs linked through a non-conjugated spacer, \textit{viz.} a series of $\text{C–C } \sigma$-bonds, would retain the HOMO and LUMO levels and $E_T$ values inherent to the independent moieties. The insertion of such a spacer should also prevent phase separation with enhanced stability of glassy films against undesired crystallization. During thermal vacuum sublimation, molecules departing from a high temperature source possess conformational multiplicity tend to form a glassy film upon arriving at a substrate at ambient temperature. Thereafter, molecular dynamics tending toward crystallization takes over across a widely varying time scale contingent upon the specific molecular system. To illustrate this idea, a series of bipolar hybrids, including $\text{TRZ-1Cz(MP)2}$ and $\text{TRZ-3Cz(MP)2}$ depicted in Chart 2.1 to follow, were synthesized and characterized for implementation in phosphorescent OLEDs.\cite{12} The selection of TRZ and Cz(MP)2 was motivated by the facts that unipolar carbazole\cite{1,13} and triphenyltriazine\cite{14,15} derivatives have practically useful hole and electron mobility values from $10^{-7}$ to $10^{-2}$ and $10^{-5}$ to $10^{-3}$ cm$^2$/V-s, respectively, with HOMO and LUMO levels suitable for charge injection in OLEDs. In the present study,
both unipolar and bipolar compounds with non-conjugated spacers have been synthesized for a systematic investigation of charge transport properties in relation to chemical composition via synthesis and intermolecular packing through computation.

2.2. EXPERIMENTAL SECTION

Material Synthesis and Characterization

All chemicals, reagents, solvents, and polyvinylpyrrolidone (PVP, weight-average molecular weight of 360,000) were used as received from commercial sources without further purification except toluene and tetrahydrofuran (THF), which were distilled over sodium and benzophenone. Two intermediates 3-allyl-6-(9-(2-methylpropyl)carbazol-3-yl)-9-(2-methylpropyl)-carbazole (1) and 3-bromo-6-(9-(2-methylpropyl)-carbazol-3-yl)-9-(2-methylpropyl)-carbazole (2), and the two bipolar hybrids, 2-(4-(3-(6-(9-(2-methylpropyl)carbazol-3-yl)-9-(2-methylpropyl)-carbazol-3-yl)propyl)-phenyl)-4,6-diphenyl-1,3,5-triazine (TRZ-1Cz(MP)2) and 2,4,6-tris(4-(3-(6-(9-(2-methyl-propyl)carbazol-3-yl)-9-(2-methylpropyl)carbazol-3-yl)propyl)-phenyl)-1,3,5-triazine (TRZ-3Cz(MP)2), were synthesized following previously reported procedures.[12] Another intermediate, 1,2-bis(4-bromo-phenyl)ethane (3), was synthesized following a literature report.[16] All reactions were carried out under argon and anhydrous conditions unless noted otherwise. $^1$H NMR spectra were acquired in CDCl$_3$ with an Avance-400 spectrometer (400 MHz) at 298 K using tetramethylsilane as an internal standard. Elemental analysis was carried out
at the Elemental Analysis Facility, University of Rochester. Molecular weights were measured with a MALDI-TOF mass spectrometer (Brüker Autoflex III) with trans-3-indoleacrylic acid (IAA) as the matrix or LC mass spectrometer (Thermo LTQ Velos Ion Trap LC/MS) with methanol as mobile phase. Six new unipolar compounds were synthesized according to Scheme 2.1, followed by purification and characterization to validate their molecular structures.

Scheme 2.1 Synthesis of C3-2Cz(MP)2, C2-2TRZ(2tBu), TRZ-3Me, C3-2TRZ, Ben-3TRZ, and Ben-2TRZ.
1,2-Bis(4-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)phenyl)ethane, 4: n-BuLi (2.5 M in hexanes, 5.75 ml, 14.36 mmol) was added dropwise into a solution of 3 (1.63 g, 4.79 mmol) in THF (24 ml) at –78 °C, where the mixture was stirred for 3 h before adding 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (4.08 g, 20.00 mmol) in one portion. The reaction mixture was allowed to warm up to room temperature over a period of 12 h, quenched with water, and then extracted with ether. The organic extracts were combined, washed with water, and dried over MgSO₄. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexanes/ethyl acetate 9:1 (v/v) as the eluent to yield 4 (1.10 g, 53%) as a white powder. 

¹H NMR (400 MHz, CDCl₃, 298 K): δ (ppm) 7.73-7.71 (d, J = 8.0 Hz, 4H), 7.19-7.17 (d, J = 8.0 Hz, 4H), 2.92 (s, 4H), 1.35-1.34 (m, 24H).

2-Chloro-4,6-bis(4-(1,1-dimethylethyl)phenyl)-1,3,5-triazine, 7: A Grignard reagent (6) prepared by reacting 1-bromo-4-(1,1-dimethylethyl)-benzene (5.00 g, 23.46 mmol) with Mg (0.87 g, 35.90 mmol) and small amount of iodine in THF (25 mL) was added dropwise into a solution of 5 (0.96 g, 5.21 mmol) in THF (55 mL) at 0 °C. After the addition was completed, the reaction mixture was stirred under reflux overnight, quenched with 0.2 M HCl, and extracted with methylene chloride. The organic extracts were combined, washed with water, and dried over MgSO₄. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexanes/chloroform 5:1 (v/v) as the eluent to yield 7 (0.89 g, 45%) as a white powder. 

¹H NMR (400 MHz, CDCl₃, 298 K): δ (ppm) 8.55-8.53 (d, J = 8.0 Hz, 4H), 7.57-7.55 (d, J = 8.0 Hz, 4H), 1.39 (m, 18H).
2-(4-Allylphenyl)-4,6-diphenyl-1,3,5-triazine, 9: THF (24 ml) was added into a mixture of 8 (0.41 g, 1.04 mmol), allyltributylin (0.69 g, 2.09 mmol), Pd(PPh₃)₄ (0.060 g, 0.052 mmol), and LiCl (0.089 g, 2.09 mmol). The reaction mixture was stirred at 90 °C for 24 h. After evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexanes/chloroform 6:1 (v/v) as the eluent to yield 9 (0.35 g, 96 %) as a white powder. ¹H NMR (400 MHz, CDCl₃, 298 K): δ (ppm) 8.79-8.76 (m, 4H), 8.72-8.70 (d, J = 8.0 Hz, 2H), 7.63-7.55 (m, 6H), 7.41-7.39 (d, J = 8.0 Hz, 2H), 6.07-6.00 (m, 1H), 5.17-5.13 (m, 2H), 3.53-3.51 (d, J = 8.0 Hz, 2H).

1,3-Bis(6-(9-(2-methylpropyl)carbazol-3-yl)-9-(2-methylpropyl)carbazol-3-yl)-propane, C₃-2Cz(MP)₂: 9-BBN (0.5 M in THF, 2.4 ml, 1.2 mmol) was added dropwise into a solution of 1 (0.29 g, 0.60 mmol) in THF (5 ml) at 0 °C. The mixture was stirred at room temperature for 15 min and then at 35 °C for 18 h before transferring into a mixture of 2 (0.35 g, 0.66 mmol), Pd(PPh₃)₄ (0.014 g, 0.012 mmol), Na₂CO₃ (3.82 g, 36 mmol), water (18 ml) and toluene (30 ml). The reaction mixture was stirred at 90 °C for 24 h, cooled down to room temperature, and extracted with chloroform. The organic extracts were combined, washed with water, and dried over MgSO₄. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexanes/chloroform 3:2 (v/v) as the eluent to yield C₃-2Cz(MP)₂ (0.30 g, 54%) as a white powder. ¹H NMR (400 MHz, CDCl₃, 298 K): δ (ppm) 8.39-8.38 (t, J = 2.2 Hz, 4H), 8.18-8.16 (d, J = 8.0 Hz, 2H), 8.03 (s, 2H), 7.82-7.77 (m, 4H), 7.47-7.40 (m, 8H), 7.34 (s, 4H), 7.24-7.20 (m, 2H), 4.13-4.10 (m, 8H), 2.96-2.93 (t, J = 7.6 Hz, 4H), 2.44-2.40 (m, 4H), 2.26-2.19 (m, 2H), 1.02-1.00 (m, 24H). MALDI-TOF MS (IAA) m/z
([M]⁺): 929.2. Anal. calcd. for C₆₇H₆₈N₄: C, 86.60%; H, 7.38%; N, 6.03%. Found: C, 86.05%; H, 7.43%; N, 5.91%.

1,2-Bis(4-(4,6-bis(1,1-dimethylethyl)phenyl-1,3,5-triazin-2-yl)phenyl)ethane, C₂-2TRZ(2tBu): Toluene (12 ml) and water (7 ml) were added into a mixture of 7 (0.43 g, 1.13 mmol), 4 (0.25 g, 0.56 mmol), Pd(PPh₃)₄ (0.023 g, 0.020 mmol), and Na₂CO₃ (1.50 g, 14.15 mmol). The reaction mixture was stirred at 95 °C for 40 h, cooled to room temperature, and then extracted with methylene chloride. The organic extracts were combined, washed with water, and dried over MgSO₄. Upon evaporating the solvent, the crude product was purified by column chromatography on silica gel with hexanes/chloroform 2:1 (v/v) to yield C₂-2TRZ(2tBu) (0.27 g, 55%) as a white powder.

¹H NMR (400 MHz, CDCl₃, 298 K): δ (ppm) 8.70-8.67 (m, 12H), 7.60-7.58 (d, J = 8.0 Hz, 8H), 7.38-7.36 (d, J = 8.0 Hz, 4H), 3.13 (s, 4H), 1.40 (s, 36H). MALDI-TOF MS (IAA) m/z ([M]⁺): 870.1. Anal. calcd. for C₆₀H₆₄N₆: C, 82.91%; H, 7.42%; N, 9.67%. Found: C, 82.53%; H, 7.31%; N, 9.62%.

2,4,6-Tri(3-methylphenyl)-1,3,5-triazine, TRZ-3Me: The procedure for the synthesis of 7 was followed to prepare TRZ-3Me from 5 and m-bromotoluene as a white powder in 58 % yield. ¹H NMR (400 MHz, CDCl₃, 298 K): δ (ppm) 8.60-8.57 (m, 6H), 7.50-7.42 (m, 6H), 2.54 (s, 9H). LC MS (methanol) m/z ([M]⁺): 352.2. Anal. calcd. for C₆₀H₆₄N₆: C, 82.02%; H, 6.02%; N, 11.96%. Found: C, 81.76%; H, 5.96%; N, 12.16%.

1,3-Bis(4-(4,6-biphenyl-1,3,5-triazin-2-yl)phenyl)propane, C₃-2TRZ: The procedure for the synthesis of C₃-2Cz(MP)₂ was followed to prepare C₃-2TRZ from 8 and 9 as a
white powder in 80 % yield. $^1$H NMR (400 MHz, CDCl$_3$, 298 K): $\delta$ (ppm) 8.80-8.77 (m, 8H), 8.72-8.70 (d, $J = 8.0$ Hz, 4H), 7.63-7.55 (m, 12H), 7.42-7.40 (d, $J = 8.0$ Hz, 4H), 2.85-2.81 (m, 4H), 2.16-2.10 (m, 2H). MALDI-TOF MS (IAA) m/z ([M]$^+$): 659.6. Anal. calcd. for C$_{60}$H$_{64}$N$_6$: C, 84.01%; H, 5.20%; N, 12.76%. Found: C, 81.88%; H, 4.88%; N, 13.13%.

1,3,5-Tri(3-(4-(4,6-biphenyl-1,3,5-triazin-2-yl)phenyl)propyl)benzene, **Ben-3TRZ**: Following the procedure for C$_3$-2Cz(MP)$_2$, Ben-3TRZ was synthesized from 9 and 1,3,5-tribromobenzene as a white powder in 58 % yield. $^1$H NMR (400 MHz, CDCl$_3$, 298 K): $\delta$ (ppm) 8.75-8.68 (m, 18H), 7.60-7.52 (m, 18H), 7.41-7.39 (d, $J = 8.0$ Hz, 6H), 6.90 (s, 3H), 2.82-2.78 (m, 6H), 2.70-2.66 (m, 6H), 2.10-2.02 (m, 6H). MALDI-TOF MS (IAA) m/z ([M]$^+$): 1127.5. Anal. calcd. for C$_{60}$H$_{64}$N$_6$: C, 83.17%; H, 5.64%; N, 11.19%. Found: C, 83.01%; H, 5.43%; N, 11.11%.

1,3-Bis(3-(4-(4,6-biphenyl-1,3,5-triazin-2-yl)phenyl)propyl)benzene, **Ben-2TRZ**: The procedure for the synthesis of C$_3$-2Cz(MP)$_2$ was followed to prepare Ben-2TRZ from 9 and m-dibromobenzene as a white powder in 78 % yield. $^1$H NMR (400 MHz, CDCl$_3$, 298 K): $\delta$ (ppm) 8.77-8.75 (m, 8H), 8.70-8.68 (d, $J = 8.0$ Hz, 4H), 7.61-7.53 (m, 12H), 7.40-7.38 (d, $J = 8.0$ Hz, 4H), 7.25-7.22 (m, 1H), 7.07-7.05 (m, 3H), 2.81-2.77 (m, 4H), 2.71-2.67 (m, 4H), 2.09-2.01 (m, 4H). MALDI-TOF MS (IAA) m/z ([M]$^+$): 778.0. Anal. calcd. for C$_{60}$H$_{64}$N$_6$: C, 83.48%; H, 5.71%; N, 10.82%. Found: C, 83.13%; H, 5.54%; N, 10.61%.
Morphology and Phase Transition Temperatures

Phase transition temperatures were determined by differential scanning calorimetry (DSC, Perkin-Elmer DSC-7) with a continuous nitrogen purge at 20 ml/min. Samples were preheated to above their melting temperatures and then cooled down to –30 °C at –100 °C/min before the reported second heating and cooling scans were recorded at ±20 °C/min. The nature of the phase transitions was characterized by hot-stage polarizing optical microscopy (POM, DMLM, Leica, FP90 central processor and FP82 hot stage, Mettler Toledo).

Electrochemical Characterization

Cyclic voltammetry (CV) was conducted in an EC-Epsilon potentiostat (Bioanalytical Systems Inc.) A silver/silver chloride (Ag/AgCl) wire, a platinum wire, and a glassy carbon disk with a diameter of 3 mm were used as the reference, counter, and working electrodes, respectively. Samples were dissolved at a concentration of 10^{-3} M in acetonitrile:toluene at 1:1 by volume containing 0.1 M tetaethylammonium tetrafluoroborate as the supporting electrolyte, which had been purified as described previously.[17] Acetonitrile and toluene were freshly distilled over calcium hydride and sodium with benzophenone, respectively. The dilute sample solutions exhibit reduction and oxidation scans against the Ag/AgCl reference electrode. The reduction and oxidation potentials were adjusted to ferrocene as an internal standard with an oxidation potential of 0.51 ± 0.02 V over Ag/AgCl. The resultant reduction and oxidation potentials, \( E_{1/2}(\text{red}) \) and \( E_{1/2}(\text{oxd}) \), relative to ferrocence/ferrocenium (Fc/Fc^+) were used
to calculate the LUMO and HOMO levels in solution and neat film as presented in Table 2.1.

**Thin Film Preparation and Characterization**

Thin films for the characterization of absorption and morphology were prepared by thermal vacuum deposition on fused silica substrates (International Crystal Laboratories) at 1 nm/s under $5 \times 10^{-6}$ torr. Films thicknesses were determined by a stylus-type profilometer (XP-200, Ambios technology). Absorption spectra of films were acquired with a UV-vis-NIR spectrophotometer (Lambda 900, Perkin-Elmer). The optical micrographs of organic films were produced with a digital camera (MicroPix C-1024) mounted on a polarizing optical microscope (Leitz Orthoplan-Pol). Films for electron diffraction were prepared by thermal vacuum deposition on sodium chloride substrates (International Crystal Laboratories) at 1 nm/s under $5 \times 10^{-6}$ tor. The films were floated off in deionized water, caught with copper grids, and characterized with a transmission electron microscope (FEI Tecnai F20). The same thermal vacuum deposition procedure was followed to prepare another set of films covered with an amorphous PVP film spin-cast from a 0.5 wt% methanol solution at 4000 rpm on top of the prior vacuum-sublimed organic layer on a NaCl substrate. An absorbance of 0.005 optical density unit, equivalent to 99% transmittance, was found for the 40-nm-thick PVP film at 266 nm using the aforementioned spectrophotometer. The PVP layer serves to suppress transformation of an initially amorphous organic layer into a polycrystalline film that may scatter photoexcitation laser beam. To simulate the condition of TOF measurement, a freshly
prepared stack of PVP/C2-2TRZ-(2tBu)/NaCl was subjected to eight pulses of 266 nm laser (after passing through a fused silica substrate coated with a Ag layer), each for 10 s with a 20 s interval.

**TOF Device Fabrication and Characterization**

The absorption spectra of the four compounds are shown in Figure 2.1a. Glass substrates coated with patterned ITO were thoroughly cleaned and treated with oxygen plasma prior to use. Two device structures were employed: Al/organic layer/ITO for C3-2Cz(MP)2, TRZ-1Cz(MP)2 and TRZ-3Cz(MP)2, and Ag/organic layer/ITO for C2-2TRZ(2tBu) for characterization by the photocurrent TOF system described in Figure 2.1b.[18] The organic layers were prepared by thermal vacuum deposition onto ITO-coated substrates at 1 nm/s to yield a film thickness of 7 to 12 µm as determined by a stylus-type profilometer (XP-200, Ambios technology), greater than the penetration depth by more than one order of magnitude as commonly practiced.[19] The devices were completed by thermal vacuum deposition of 30-nm-thick silver for C2-2TRZ(2tBu) or 100-nm thick aluminum for C3-2Cz(MP)2, TRZ-1Cz(MP)2 and TRZ-3Cz(MP)2 at 1 nm/s through a shadow mask to define an active area of 0.1 cm². All vacuum deposition processes were carried out at a base pressure less than 5×10⁻⁶ torr. A power supply (Hewlett Packard 6110A, DC) was connected to the device’s semi-transparent electrode, through which a nitrogen laser (Photochemical Research Associates, λ = 337 nm, pulse duration = 800 ps FWHM) for C3-2Cz(MP)2, TRZ-1Cz(MP)2 and TRZ-3Cz(MP)2 or the fourth harmonic generation of a Nd:YAG laser (GCR-100, Quanta-Ray Spectra-Physics, λ =
266 nm, pulse duration = 4-5 ns FWHM) for C2-2TRZ(2tBu) was used as photoexcitation. A load resistor was connected to the other electrode and an oscilloscope (Tektronix TDS 2024B, 200 MHz) measured the voltage drop, yielding the photocurrent transient. Measurements were carried out in a vacuum chamber with an appropriate window (LTS-22-1CH) under high vacuum provided by a turbo pump. The measurement of mobility in organic semiconductors was reported to carry a typical error of 20%.[20]

![Figure 2.1](image)

**Figure 2.1** (a) Absorption spectra of C3-2Cz(MP)2, C2-2TRZ(2tBu), TRZ-1Cz(MP)2, and TRZ-3Cz(MP)2 films via vacuum sublimation on fused silica substrates. (b) Schematic diagram of the TOF apparatus. Nitrogen laser (337 nm) and fourth harmonic generation of Nd:YAG laser (266 nm) were used as excitation source.

### 2.3. RESULTS AND DISCUSSION

Motivated by practically relevant transport properties of their derivatives, Cz and TRZ were employed as building blocks for the construction of bipolar hybrids in the
present study. The ethylene and propylene linkages are intended to improve morphological stability against crystallization from a glassy film, and to decouple the two \( \pi \)-systems to retain their independent HOMO and LUMO levels. Thus, hole and electron transport capabilities can be modulated without affecting energy levels. Depicted in Chart 2.1 are the compounds intended for preferential hole or electron transport as well as bipolar charge transport. The compounds with propylene spacers were synthesized by treating Cz(MP)2 or TRZ carrying an allyl group with 9-BBN for the subsequent Suzuki coupling reaction. The compound with an ethylene spacer, \textit{i.e.} C2-2TRZ(2tBu), was synthesized following a divergent route starting with 1,2-bis(4-bromo-phenyl)ethane.

![Molecular structures](image)

**Chart 2.1** Molecular structures with their thermal transition temperatures determined by DSC second heating scans of samples preheated to beyond their crystalline melting points. Symbols: \( G \), glassy; \( K \), crystalline; \( I \), isotropic.
Polycrystallinity was visible under POM of the vacuum-sublimed films of TRZ-3Me, C3-2TRZ, and Ben-2TRZ (Figures 2.2a through c), while Ben-3TRZ was not vacuum-sublimable. In contrast, unipolar C2-2TRZ(2tBu) and C3-2Cz(MP)2 and bipolar TRZ-3Cz(MP)2 and TRZ-1Cz(MP)2, with varying TRZ:Cz(MP)2 ratios, all form amorphous films. According to the second DSC heating scans (Figure 2.3), TRZ-3Cz(MP)2, TRZ-1Cz(MP)2, and C3-2Cz(MP)2 exhibit amorphous character with glass transition at 144, 98 and 119 °C, respectively, while C2-2TRZ(2tBu) is crystalline with a glass transition and two crystalline melting temperatures at 148, 185 and 361 °C, respectively, upon heating as identified under hot-stage POM. The characterized solid morphologies are consistent between the DSC thermograms of bulk samples and POM micrographs of vacuum-sublimed thin films with the exception of Ben-2TRZ as Figure 2.2b is compared with Figure 2.3h. The issues of bulk phase vs. thin film and thermal scanning vs. static observation aside, the ability to form a stable glassy film generally improves with an increasing molecular size, conformational flexibility, and the presence of peripheral aliphatics.
Figure 2.2 Polarizing optical micrographs of vacuum-sublimed films of (a) TRZ-3Me, (b) Ben-2TRZ, (c) C3-2TRZ, (d) C2-2TRZ(2tBu), C3-2Cz(MP)2, TRZ-1Cz(MP)2, and TRZ-3Cz(MP)2.
Figure 2.3 DSC heating and cooling scans at ±20 °C/min of (a) C2-2TRZ(2tBu), (b) C3-2Cz(MP)2, (c) TRZ-1Cz(MP)2, (d) TRZ-3Cz(MP)2, (e) TRZ-3Me, (f) C3-2TRZ, (g) Ben-3TRZ, and (h) Ben-2TRZ, preheated to above their melting points followed by cooling down to –30 °C at –100 °C/min. The melting points were determined from the first heating scans of pristine samples of C2-2TRZ(2tBu), C3-2Cz(MP)2, TRZ-1Cz(MP)2, TRZ-3Cz(MP)2, TRZ-3Me, C3-2TRZ, Ben-3TRZ, and Ben-2TRZ at 361, 129, 106, 169, 159, 265, 246, and 174 °C, respectively. Symbols: G, glassy; K, crystalline; I, isotropic.
Thin-film morphologies of all the compounds in TOF devices were verified as amorphous in Figure 2.4a under POM before and after mobility measurements. Electron diffraction was further used to validate the amorphous character of the C2-2TRZ(2tBu) film as it tends to crystallize based on its DSC thermograms (Figure 2.3b). A freshly prepared stack of PVP/C2-2TRZ(2tBu)/NaCl was subjected to incident 266 nm laser pulses as conducted in a TOF measurement. Upon dissolving the PVP layer and NaCl in deionized water, the isolated C2-2TRZ(2tBu) film was characterized by electron diffraction (Figure 2.4b), showing a typical amorphous electron diffraction pattern. The TOF transients are illustrated for TRZ-3Cz(MP)2 in Figure 2.5, where the transit time can be determined by the point at which the photocurrent starts to drop from a plateau on a linear plot with time. It is difficult, however, to extract transit time from dispersive hole and electron photocurrents in the linear plot; the rest of compounds exhibit a similar behavior. In practice, a log-log plot of photocurrent with time enables the transit time to be readily determined by the two intersecting dashed straight lines (insets in Figure 2.5) to obtain unambiguous data in call cases. The accessible range of electric field is limited by electric ringing, thus preventing measurements on time scales shorter than 100 ns. In addition, a high applied voltage may cause shorting in TOF devices.
Figure 2.4 (a) Polarizing optical micrographs of vacuum-sublimed glassy C2-2TRZ(2tBu), C3-2Cz(MP)2, TRZ-1Cz(MP)2, and TRZ-3Cz(MP)2 films in TOF devices before and after mobility measurements. (b) Electron diffraction pattern of a vacuum-sublimed C2-2TRZ(2tBu) film after eight 266 nm laser exposures, each for 10 s with a 20 s interval, the same treatments as through a TOF measurement.

Figure 2.5 Representative TOF transients of TRZ-3Cz(MP)2 for (a) hole carriers at an electric field of 4.4×10^5 V/cm and (b) electron carriers at an electric field of 4.1×10^5 V/cm. Insets: log-log plots to determine transit times.

As shown in Figure 2.6, the Poole-Frenkel relationship[^21] is obeyed by TRZ-1Cz(MP)2, TRZ-3Cz(MP)2, C3-2Cz(MP)2, and C2-2TRZ(2tBu). The hole mobility values of C3-2Cz(MP)2, TRZ-3Cz(MP)2, and TRZ-1Cz(MP)2 decrease with a
decreasing Cz content, and so do the electron mobility values of C2-2TRZ(2tBu), TRZ-1Cz(MP)2, and TRZ-3Cz(MP)2 with a decreasing TRZ content. No hole and electron mobility were detectable for C2-2TRZ(2tBu) and C3-2Cz(MP)2, respectively, across the same range of applied field. Phosphorescent OLEDs, ITO/MoO3(10nm)/emitting layer(40–50 nm)/1,3,5-tris(N-phenylbenz-imidazol-2-yl)-benzene (30 nm)/CsF(1 nm)/Al(100 nm) with an EML consisting of TRZ-1Cz(MP)2 and TRZ-3Cz(MP)2 doped with 10 wt% Ir(mppy)3, were also fabricated and characterized in our previous study.[12] The energy diagram of the PhOLED device is shown in Figure 2.7. The relatively low current efficiency of 18 cd/A at 10 mA/cm² with TRZ-1Cz(MP)2 was attributed to the recombination zone being close to the anode as a result of the slightly greater electron mobility than hole and the electron-transport capability of Ir(mppy)3 as the dopant. At the same doping level and the same charge injection barriers into the EMLs comprising the two distinct hybrids (Table 2.1), the higher hole mobility and the lower electron mobility of TRZ-3Cz(MP)2 than those of TRZ-1Cz(MP)2 should shift the recombination zone away from the anode, thereby improving the current efficiency to 28 cd/A at 10 mA/cm² as observed.
Figure 2.6 (a) Hole and (b) electron mobilities as functions of electric field ($E^{1/2}$) for TRZ-1Cz(MP)$_2$, TRZ-3Cz(MP)$_2$, C3-2Cz(MP)$_2$, and C2-2TRZ(2tBu) in ITO/organic layer/Al or ITO/organic layer/Ag devices. Vanishing values of hole and electron mobility are not shown in (a) and (b) for C2-2TRZ(2tBu) and C3-2Cz(MP)$_2$, respectively. The data points are accompanied by an average error of ±8%.

Figure 2.7 Energy diagram of PhOLED device with energy levels in neat solid films calculated from two correlations, HOMO = −(1.4±0.1)$\times qE_{1/2}$(oxd)−(4.6±0.08) eV and LUMO = −(1.19±0.08)$\times qE_{1/2}$(red)−(4.78±0.17) eV,\textsuperscript{[22,23]} with literature-reported energy levels in solutions.\textsuperscript{[24-27]} Hosts in EML: TRZ-1Cz(MP)$_2$ (LUMO = −2.2 eV; HOMO = −5.2 eV), TRZ-3Cz(MP)$_2$ (LUMO = −2.1 eV; HOMO = −5.1 eV).
It is further noted that unipolar C3-2Cz(MP)2 possesses a hole mobility about an order of magnitude higher than the two bipolar hybrids, all with propylene spacers. In sharp contrast, unipolar C2-2TRZ(2tBu) with an ethylene spacer exhibits an electron mobility more than three orders of magnitude higher than the two hybrids with propylene spacers. In addition to the concentration effect in transition from bipolar to unipolar compounds expected of the same spacers, the striking difference in mobility values can be rationalized by intermolecular packing. Gaussian 09 was used to optimize the geometries of C2-2TRZ(2tBu) and C3-2Cz(MP)2 using B3LYP functional with the 6-31G(d) basis set. As shown in Figure 2.8a, the energetically favored anti-conformation in the Newman projection across the ethylene spacer and the co-planarity of the two TRZ groups in C2-2TRZ(2tBu) ensure effective intermolecular packing in favor of charge transport despite the peripheral t-butyl groups. In contrast, the computed twisted and angular structure for C3-2Cz(MP)2 shown in Figure 2.8b does not allow effective intermolecular packing of the Cz(MP)2 moieties. These results exemplify how molecular conformation can vary significantly from the ethylene to propylene spacer to permit tunability of charge-carrier mobility over more than three decades, although mobility limitations in organics could be extrinsic.
Figure 2.8 Optimized molecular structures of (a) C2-2TRZ(2tBu) and (b) C3-2Cz(MP)2 computed with Gaussian 09 using B3LYP functional with the 6-31G(d) basis set; a torsion angle of 38° found between the two carbazole groups within Cz(MP)2. The same optimized structures were obtained without peripheral aliphatics.

The argument for the role played by molecular conformation is strengthened by comparing the reported mobility data for unipolar s-triazine- and carbazole-based compounds capable of forming glassy films in similar TOF device structures to those employed in the present study (Table 2.1). As demonstrated in Figures 2.9 and 2.10, the optimized structures depicted in Figure 2.8 represent the upper and lower bounds on electron and hole mobility presented by C2-2TRZ(2tBu) and C3-2Cz(MP)2, respectively, for all the unipolar compounds meeting the selection criteria for a valid comparison. The general idea that the ethylene spacer improves intermolecular packing and hence elevates charge-carrier mobility over the propylene spacer is likely to apply to bipolar hybrids, TRZ-1Cz(MP)2 and TRZ-3Cz(MP)2, but perhaps with less dramatic effects because of the twist between the two carbazole rings within the Cz(MP)2 group. Whereas the optimized molecular structures shown in Figure 2.8 represent the lowest-
energy conformers, thermal vapor sublimation might have introduced a plethora of additional conformers into the deposited films, which cannot be experimentally quantified for validation at this time. Nevertheless, the energetically favored anti-conformation of \( \text{C2-2TRZ(2tBu)} \) in addition to the co-planarity of the two TRZ(2tBu) moieties and the twisted and angular conformation of \( \text{TRZ-3Cz(MP)2} \), are reassuring of the computational results in support of the mobility data compared to those of unipolar counterparts and between the two bipolar hybrids.

**Table 2.1** Film thicknesses and electron and hole mobility data compiled in Figures 2.9 and 2.10 with vacuum-sublimed films of compounds A through I, \( \text{C2-2TRZ(2tBu)} \), and \( \text{C3-2Cz(MP)2} \).

<table>
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<td>I</td>
<td>0.3</td>
<td>ITO/organic[^c]/CuPc(50nm)/Al(30nm)</td>
<td><em>Synth. Met.</em> 2004, 145, 229.</td>
</tr>
<tr>
<td><strong>C3-2Cz(MP)2</strong></td>
<td>10</td>
<td>ITO/organic[^a]/Al(100nm)</td>
<td>present work</td>
</tr>
</tbody>
</table>

Deposition rates at \[^a\] 1.0 nm/sec, \[^b\] 0.1 nm/sec, and \[^c\] 0.2 nm/sec.
Figure 2.9 (a) Molecular structures of unipolar TRZ-based compounds for which electron mobility values have been reported and (b) comparison of electron mobility values with C2-2TRZ(2tBu).

Figure 2.10 (a) Molecular structures of unipolar Cz-based compounds for which hole mobility values have been reported and (b) comparison of hole mobility values with C3-2Cz(MP)2.
The characterization of HOMO and LUMO levels of the bipolar and unipolar compounds as follows is intended to demonstrate the modulation of charge-carrier mobility by varying the TRZ:Cz(MP)2 ratio without altering their HOMO and LUMO levels. The oxidation and reduction potentials were characterized by CV, as displayed in Figure 2.11, and the results are presented in Table 2.2 for energy levels in both solution and neat solid film using equations based on various solvents including dichloromethane, acetonitrile, and N,N-dimethylformamide.[22,23] Protected or not at the 3-, 6-, and/or 9- (i.e. N-) positions, carbazole has been reported to suffer oxidative instability.[28,29] This problem, however, was considerably alleviated here to allow for the characterization of oxidation potentials of Cz(MP)2, C3-2Cz(MP)2, TRZ-1Cz(MP)2, and TRZ-3Cz(MP)2. Because of the absence of π–conjugation across the two moieties, the HOMO and LUMO levels of TRZ-1Cz(MP)2 and TRZ-3Cz(MP)2 are essentially imported from those of Cz(MP)2 and TRZ, respectively. It is evident that both energy levels are not affected within typical errors. It is worth noting that HOMO and LUMO levels are relatively close to those of commonly used hole- and electron-transport materials in OLEDs, such as NPB at –5.4 eV[30] and Alq3 at –2.3 eV,[23] respectively.
Figure 2.11 Cyclic voltammograms of (a) Cz(MP)2, (b) TRZ, (c) C3-2Cz(MP)2, (d) C2-2TRZ(2tBu), (e) TRZ-1Cz(MP)2, and (f) TRZ-3Cz(MP)2 in acetonitrile:toluene at 1:1 by volume.
Table 2.2 Energy levels for TRZ, Cz(MP)2, and the chemical hybrids.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}$(oxid) [a] vs. Fc/Fc$^+$ (V)</th>
<th>$E_{1/2}$(reduced) [a] vs. Fc/Fc$^+$ (V)</th>
<th>HOMO [d] (eV)</th>
<th>LUMO [e] (eV)</th>
<th>HOMO [f] (eV)</th>
<th>LUMO [g] (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2-2TRZ(2tBu)</td>
<td>N.A. [b]</td>
<td>–2.23</td>
<td>N.A.</td>
<td>–2.57</td>
<td>N.A.</td>
<td>–2.1</td>
</tr>
<tr>
<td>C3-2Cz(MP)2</td>
<td>0.35</td>
<td>N.A. [b]</td>
<td>–5.15</td>
<td>N.A.</td>
<td>–5.1</td>
<td>N.A.</td>
</tr>
<tr>
<td>TRZ-1Cz(MP)2</td>
<td>0.41[c]</td>
<td>–2.20[c]</td>
<td>–5.21</td>
<td>–2.60</td>
<td>–5.2</td>
<td>–2.2</td>
</tr>
<tr>
<td>TRZ-3Cz(MP)2</td>
<td>0.38[c]</td>
<td>–2.23[c]</td>
<td>–5.18</td>
<td>–2.57</td>
<td>–5.1</td>
<td>–2.1</td>
</tr>
<tr>
<td>Cz(MP)2</td>
<td>0.41[c]</td>
<td>N.A. [b]</td>
<td>–5.21</td>
<td>N.A.</td>
<td>–5.2</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

[a] Half-wave potentials, $E_{1/2}$, relative to Fc/Fc$^+$ with an oxidation potential at 0.51 V vs. Ag/AgCl, determined as the average of forward and reverse oxidation or reduction peaks
[b] Oxidation or reduction potential beyond the CV measurement range
[c] Data from Ref. 10.
[d] HOMO level = $-4.80 - qE_{1/2}$(oxid) eV with a typical error of ±0.04 eV, where $q$ is the electron charge
[e] LUMO level = $-4.80 - qE_{1/2}$(reduced) eV with a typical error of ±0.04 eV
[f] HOMO = $-1.4\pm0.1\times qE_{1/2}$(oxid)–$4.6\pm0.08$ eV for neat solid films$^{[22]}$ with a typical error of ±0.1 eV
[g] LUMO = $-1.19\pm0.08\times qE_{1/2}$(reduced)–$4.78\pm0.17$ eV for neat solid films$^{[23]}$ with a typical error of ±0.2 eV.

2.4. SUMMARY

Non-conjugated bipolar hybrid compounds, TRZ-1Cz(MP)2 and TRZ-3Cz(MP)2, with variable TRZ:Cz(MP)2 ratios and unipolar compounds, C3-2Cz(MP)2 and C2-2TRZ(2tBu), were characterized for their charge transport properties by the photocurrent TOF technique. Ethylene and propylene spacers were incorporated in these compounds to improve morphological stability against crystallization and to
electronically decouple the two \( \pi \)-systems with an aim of retaining independent energy levels. The film morphologies of these compounds in TOF devices were characterized as amorphous by polarizing optical microscopy, while electron diffraction was used to further verify the amorphous character of the \textbf{C2-2TRZ(2tBu)} film, the most prone to crystallization of all four compounds. Hole mobility increases from \textbf{TRZ-1Cz(MP)2}, \textbf{TRZ-3Cz(MP)2} to \textbf{C3-2Cz(MP)2} over a factor of about 10, while electron mobility increases from \textbf{TRZ-3Cz(MP)2}, \textbf{TRZ-1Cz(MP)2} to \textbf{C2-2TRZ(2tBu)} over a factor of more than \( 10^3 \). The remarkable difference in the ranges of mobility between these two series can be understood in terms of intermolecular packing beyond the TRZ:Cz(MP)2 ratio. Based on the optimized molecular structures acquired by Gaussian 09, the \textit{anti-} conformation across the ethylene spacer and the co-planarity between the two TRZ groups result in effective intermolecular packing in \textbf{C2-2TRZ(2tBu)}, while the twisted and angular structure of \textbf{C3-2Cz(MP)2} does not allow effective intermolecular packing of the Cz(MP)2 moieties. Moreover, the distinct molecular conformations rendered by the ethylene and propylene spacers are responsible for \textbf{C2-2TRZ(2tBu)} and \textbf{C3-2Cz(MP)2} defining the upper and lower bounds, respectively, for the electron and hole mobilities in a diversity of unipolar compounds. The HOMO and LUMO levels of the two bipolar hybrids remain unaltered from those of Cz(MP)2 and TRZ, respectively. In a nutshell, the concept of non-conjugated spacer has proven to be a powerful tool for designing potentially useful charge transport media with predictable morphological and electronic properties and highly tunable charge transport capability.
REFERENCES


CHAPTER 3

CHARGE TRANSFER COMPLEX FORMATION IN
THREE DISTINCT HYBRID HOSTS FOR RED-EMITTING
PHOSPHORESCENT ORGANIC LIGHT-EMITTING
DIODES

3.1. INTRODUCTION

Phosphorescent organic light-emitting diodes have been intensively investigated because of their promise for solid-state lighting and flat panel displays. The triplet emitter is preferably dispersed into a host at the molecular level to prevent concentration quenching. Host materials used to prepare EML play a crucial role in device performance. To substantially improve device efficiency and lifetime, it is imperative that excitons be evenly distributed through EML, and that the accumulation of charges and excitons at interfaces be prevented. Mixtures of electron- and hole-transport components have been widely employed to accomplish bipolar charge transport. Alternatively, chemical hybrids offer tunable charge injection and transport with superior morphological properties while avoiding phase separation and crystallization. To achieve sufficiently high $E_T$, $\pi$-conjugation between the electron- and hole-transport moieties can be minimized or prevented altogether through a large torsion angle.
substitution,$^{[6]}$ or insertion of an sp$^3$-hybridized C or Si atoms.$^{[7,8]}$ The coexistence of electron- and hole-transport moieties, however, may lead to intra- or intermolecular electron transfer as widely reported in bipolar hosts.$^{[6,9]}$ The formation of CTCs requires an appreciable difference in HOMO and/or LUMO levels between the two transport moieties.$^{[10]}$ Adachi $et$ $al.$$^{[11]}$ reported CTC formation with a HOMO level difference greater than or equal to 0.4 eV in mixtures of Alq$_3$ with various hole-transport materials, but no quantitative correlation with the difference between LUMO levels has been reported. Although a number of bipolar hosts have been shown to afford high external quantum efficiency,$^{[4]}$ EQE, CTC formation is a potential culprit for diminished device efficiency and spectral impurity.$^{[12]}$ It is important that CTC formation be probed in bipolar hosts to figure out how to avoid it through molecular design. In the present study, tBu-TPA-$p$-TRZ, tBu-TPA-$m$-TRZ, and tBu-TPA-$L$-TRZ representing a broad spectrum of prospective materials were synthesized by linking triazine$^{[13,14]}$ to triphenylamine$^{[15,16]}$ as typical charge-transport moieties in three distinct modes. The HOMO/LUMO levels, $E_T$s, propensity to CTC formation, and morphological stability against crystallization of EML containing Ir(piq)$_3$ are characterized to appraise their potentials as hosts without engineering chemical composition or device architecture for maximum efficiencies.
3.2. EXPERIMENTAL SECTION

Material synthesis and characterization

N,N'-diphenyl-N,N'-bis(1-napthyl)-1,1'-biphenyl-4,4'-diamine (NPB, >99%, Kodak), 4,7-diphenyl-[1,10]phenanthroline (BPhen, >99%, Nichem, Taiwan), and tris(1-phenylisoquinolinolato-C2,N)iridium(III) (Ir(piq), >99%, Kodak) were used as received without further purification. Synthesis, purification, and characterization data are described as follows for 2-(4-(4-(N,N-bis(4-(1,1-dimethyl-ethyl)phenyl)amino)phenyl)phenyl)-4,6-diphenyl-1,3,5-triazine, tBu-TPA-p-TRZ, 2-(3-(3-(N,N-bis(4-(1,1-dimethyl-ethyl)phenyl)amino)phenyl)-phenyl)-4,6-diphenyl-1,3,5-triazine, tBu-TPA-m-TRZ, and 2-(4-(3-(4-(N,N-bis(4-(1,1-dimethyl-ethyl)-phenyl)amino)phenyl)propyl)-phenyl)-4,6-diphenyl-1,3,5-triazine, tBu-TPA-L-TRZ. Synthesized according to Scheme 3.1, bipolar hybrids were purified following the procedures described below. All starting chemicals, reagents, and solvents were used as received from commercial sources without further purification except toluene and THF that had been distilled over sodium and benzophenone. Intermediates, 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (4) and 2-chloro-4,6-biphenyl-1,3,5-triazine (10) were synthesized following literature procedures. All reactions were carried out under argon and anhydrous conditions unless noted otherwise. 1H NMR spectra were acquired in CDCl3 with an Avance-400 spectrometer (400 MHz). Elemental analysis was carried out at the Elemental Analysis Facility, University of Rochester. Molecular weights were measured with a MALDI-TOF mass spectrometer (Brüker Autoflex III).
Scheme 3.1 Synthesis of tBu-TPA-p-TRZ, tBu-TPA-m-TRZ, and tBu-TPA-L-TRZ.

4-Bromo-N,N-bis(4-(1,1-dimethylethyl)phenyl)aniline, 2. To a solution of Pd$_2$(dba)$_3$ (0.25 g, 0.27 mmol) and dppf (0.23 g, 0.41 mmol) in toluene (50 ml) was added NaOtBu (2.36 g, 24.50 mmol) at 25 °C. The mixture was stirred for 15 min before adding 1,4-dibromobenzene (16.76 g, 71.06 mmol), and stirred for another 15 min. Bis(4-tert-butylphenyl)amine (1) (5.00 g, 17.77 mmol) was added and the reaction mixture was heated to 90 °C for 15 h. The reaction mixture was subsequently cooled to 25 °C and then poured into a large amount of water for extraction with toluene. The organic extracts were combined, washed with water, and dried over MgSO$_4$. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with
hexanes/chloroform 9:1 (v/v) as the eluent to yield 2 (3.50 g, 45%) as a white powder. \(^1\)H NMR (400 MHz, CDCl\(_3\), 298K):  \(\delta\) (ppm) 7.30-7.23 (m, 6H), 7.01-6.96 (m, 4H), 6.95-6.89 (m, 2H), 1.30 (s, 18H).

4-(N,N-bis(4-(1,1-dimethylethyl)phenyl)amino)phenyl-boronic acid, 3. To a solution of 2 (1.00 g, 2.30 mmol) in anhydrous THF (20 ml) was added n-BuLi (2.5 M in hexanes, 1.19 ml, 3.00 mmol) at \(-78\) °C. The reaction mixture was stirred for 3 h before tri-iso-propyl borate (1.05 ml, 4.60 mmol) was added in one portion. The mixture was warmed to room temperature, stirred overnight, and poured into a large amount of water for extraction with ether. The organic extracts were combined, washed with water, and dried over MgSO\(_4\). Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexanes/ethyl acetate 2:1 (v/v) as the eluent to yield 3 (0.62 g, 67%) as a white powder. \(^1\)H NMR (400 MHz, CDCl\(_3\), 298K): \(\delta\) (ppm) 7.98-7.96 (d, 8.0 Hz, 2H), 7.38-7.26 (m, 4H), 7.14-6.98 (m, 6H), 1.32 (s, 18H).

4-Allyl-N,N-bis(4-(1,1-dimethylethyl)phenyl)aniline, 5. THF (50 ml) was added into a mixture of 2 (0.74 g, 1.70 mmol), allyltributyltin (3.37 g, 10.17 mmol), Pd(PPh\(_3\))\(_4\) (0.098 g, 0.085 mmol), and LiCl (0.14 g, 3.39 mmol). The reaction mixture was stirred at 90 °C for 24 h, cooled down to room temperature, and extracted with chloroform. The organic extracts were combined, washed with water, and dried over MgSO\(_4\). After evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexanes/chloroform 8:1 (v/v) as the eluent to yield 5 (0.30g, 45%) as a white powder. \(^1\)H NMR (400 MHz, CDCl\(_3\), 298K): \(\delta\) (ppm) 7.25-7.22 (m, 2H), 7.22-7.20 (m,
2-H), 7.08-6.96 (m, 8H), 6.08-5.90 (m, 1H), 5.15-5.00 (m, 2H), 3.34-3.32 (d, \( J = 8.0 \) Hz, 2H), 1.30 (s, 18H).

3-Bromo-N,N-bis(4-(1,1-dimethylethyl)phenyl)aniline, 6. To a solution of \( \text{Pd}_2(\text{dba})_3 \) (0.25 g, 0.27 mmol) and \( \text{dppf} \) (0.23 g, 0.41 mmol) in toluene (50 ml) was added NaO\( \text{tBu} \) (2.36 g, 24.50 mmol) at 25 °C. The mixture was stirred for 15 min followed by addition of 1,3-dibromobenzene (16.76 g, 71.06 mmol), and stirred for another 15 min. Bis(4-tert-butylphenyl)amine (1) (5.00 g, 17.77 mmol) was added and the reaction mixture was heated to 90 °C for 15 h. The reaction mixture was subsequently cooled to 25 °C and poured into a large amount of water for extraction with toluene. The organic extracts were combined, washed with water, and dried over MgSO\(_4\). Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexanes/chloroform 8:1 (v/v) as the eluent to yield 6 (5.56 g, 72%) as a white powder. \(^1\)H NMR (400 MHz, CDCl\(_3\), 298K): \( \delta \) (ppm) 7.32-7.27 (m, 3H), 7.18-7.15 (m, 1H), 7.07-6.98 (m, 7H), 6.95-6.90 (m, 1H), 1.31 (s, 18H).

2-(3-(N,N-bis(4-(1,1-dimethylethyl)phenyl)amino)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane, 7. \( n\)-BuLi (2.5 M in hexanes, 5.50 ml, 13.75 mmol) was added dropwise into a solution of 6 (4.0 g, 9.17 mmol) in THF (70 ml) at −78 °C, where the mixture was stirred for 3 h before adding 2-isoproxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (3.92 g, 21.08 mmol) in one portion. The reaction mixture was allowed to warm up to room temperature over a period of 12 h, quenched with water, and then extracted with ether. The organic extracts were combined, washed with water, and dried over MgSO\(_4\).
Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexanes/ethyl acetate 20:1 (v/v) as the eluent to yield 7 (3.15 g, 71%) as a white powder. $^1$H NMR (400 MHz, CDCl$_3$, 298K): $\delta$ (ppm) 7.61-7.58 (m, 1H), 7.47-7.45 (d, $J = 8.0$ Hz 1H), 7.26-7.19 (m, 5H), 7.18-7.14 (m, 1H), 7.00-6.94 (m, 4H), 1.37-1.27 (m, 30H).

3-(3-Bromophenyl)-N,N-bis(4-(1,1-dimethylethyl)phenyl)aniline, 8. Toluene (50 ml) and water (30 ml) were added into a mixture of 7 (2.55 g, 5.27 mmol), 1,3-dibromobenzene (3.73 g, 15.82 mmol), Pd(PPh$_3$)$_4$ (0.22 g, 0.11 mmol), and Na$_2$CO$_3$ (6.36 g, 60 mmol). The reaction mixture was stirred at 90 °C for 12 h, cooled to room temperature, and extracted with methylene chloride. The organic extracts were combined, washed with water, and dried over MgSO$_4$. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexanes/chloroform 7:1 (v/v) to yield 8 (2.20 g, 81%) as a white powder. $^1$H NMR (400 MHz, CDCl$_3$, 298K): $\delta$ (ppm) 7.66-7.62 (m, 1H), 7.45-7.39 (m, 2H), 7.32-7.21 (m, 7H), 7.15-7.10 (m, 1H), 7.08-7.01 (m, 5H), 1.31 (s, 18H).

2-(3-(3-(N,N-bis(4-(1,1-dimethylethyl)phenyl)amino)phenyl)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane, 9. n-BuLi (2.5 M in hexanes, 2.46 ml, 6.15 mmol) was added dropwise into a solution of 8 (2.10 g, 4.10 mmol) in THF (40 ml) at $-78$ °C, where the mixture was stirred for 3 h before adding 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (1.75 g, 9.42 mmol) in one portion. The reaction mixture was allowed to warm up to room temperature over a period of 12 h, quenched with water, and then
extracted with ether. The organic extracts were combined, washed with water, and dried over MgSO₄. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexanes/ethyl acetate 20:1 (v/v) as the eluent to yield 9 (1.70 g, 74%) as a white powder. ¹H NMR (400 MHz, CDCl₃, 298K): δ (ppm) 7.95 (s, 1H), 7.76-7.74 (d, J = 8.0 Hz, 1H), 7.62-7.57 (m, 1H), 7.43-7.33 (m, 2H), 7.32-7.18 (m, 6H), 7.09-6.98 (m, 5H), 1.37-1.27 (m, 30H).

2-(4-(4-(N,N-bis(4-(1,1-dimethylethyl)phenyl)amino)phenyl)phenyl)-4,6-diphenyl-1,3,5-triazine, tBu-TPA-p-TRZ. Toluene (15 ml) and water (6 ml) were added into a mixture of 3 (0.48 g, 1.20 mmol), 4 (0.42 g, 1.08 mmol), Pd(PPh₃)₄ (0.028 g, 0.024 mmol), and Na₂CO₃ (1.27 g, 12.00 mmol). The reaction mixture was stirred at 90 °C for 12 h, cooled to room temperature, and extracted with methylene chloride. The organic extracts were combined, washed with water, and dried over MgSO₄. Upon evaporating off the solvent, the crude product was purified by gradient column chromatography on silica gel with hexanes/chloroform 3:1 to 2:1 (v/v) to yield tBu-TPA-p-TRZ (0.51 g, 71%) as a yellow powder. ¹H NMR (400 MHz, CDCl₃, 298K): δ (ppm) 8.83-8.78 (m, 6H), 7.79-7.77 (d, J = 8.0 Hz, 2H), 7.62-7.56 (m, 8H), 7.31-7.29 (m, 4H), 7.17-7.15 (d, J = 8.0 Hz, 2H), 7.10-7.08 (m, 4H), 1.33 (s, 18H). LDI-TOF MS m/z ([M]⁺): 664.3. Anal. calcd. for C₄₇H₄₄N₄ (%): C 84.90, H 6.67, N 8.43; found: C 84.64, H 6.56, N 8.33.

2-(3-(3-(N,N-bis(4-(1,1-dimethylethyl)phenyl)amino)phenyl)phenyl)-4,6-diphenyl-1,3,5-triazine, tBu-TPA-m-TRZ. Toluene (20 ml) and water (12 ml) were added into a mixture of 9 (1.00 g, 1.79 mmol), 10 (0.48 g, 1.79 mmol), Pd(PPh₃)₄ (0.041 g, 0.036 mmol), and
Na₂CO₃ (2.54 g, 24.00 mmol). The reaction mixture was stirred at 90 °C for 40 h, cooled to room temperature, and then extracted with methylene chloride. The organic extracts were combined, washed with water, and dried over MgSO₄. Upon evaporating off the solvent, the crude product was purified by gradient column chromatography on silica gel with hexanes/chloroform 3:1 to 2:1 (v/v) as the eluent to yield tBu-TPA-m-TRZ (1.07 g, 90%) as a white powder. ¹H NMR (400 MHz, CDCl₃, 298K): δ (ppm) 8.92 (s, 1 H), 8.79-8.77 (d, J = 8.0 Hz, 4H), 8.73-8.71 (d, J = 8.0 Hz, 1H), 7.73-7.71 (m, 1H), 7.66-7.56 (m, 7H), 7.43-7.28 (m, 7H), 7.13-7.08 (m, 5H), 1.29 (s, 18H). LDI-TOF MS m/z ([M]⁺): 664.0. Anal. calcd. for C₄₇H₄₄N₄ (%): C 84.90, H 6.67, N 8.43; found: C 84.83, H 6.71, N 8.43.

2-(4-(4-(3-(4-(N,N-bis(4-(1,1-dimethylethyl)phenyl)amino)phenyl)propyl)phenyl)-4,6-diphenyl-1,3,5-triazine, tBu-TPA-L-TRZ. 9-BBN (0.5 M in THF, 4.2 ml, 2.1 mmol) was added dropwise into a solution of 5 (0.28 g, 0.70 mmol) in THF (8 ml) at 0 °C. The mixture was stirred at room temperature for 15 min and then at 35 °C for 3 h before transferring into a mixture of 4 (0.38 g, 0.99 mmol), Pd(PPh₃)₄ (0.016 g, 0.014 mmol), Na₂CO₃ (3.18 g, 30 mmol), water (15 ml) and toluene (25 ml). The reaction mixture was stirred at 90 °C for 24 h, cooled down to room temperature, and extracted with chloroform. The organic extracts were combined, washed with water, and dried over MgSO₄. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexanes/chloroform 3:1 (v/v) as the eluent to yield tBu-TPA-L-TRZ (0.25 g, 50%) as a pale yellow powder. ¹H NMR (400 MHz, CDCl₃, 298K): δ (ppm) 8.79-8.77 (d, J = 8.0 Hz, 4H), 8.71-8.69 (d, J = 8.0 Hz, 2H), 7.64-7.56
(m, 6H), 7.41-7.39 (d, $J = 8.0$ Hz, 2H), 7.26-7.21 (m, 4H), 7.08-6.98 (m, 8H), 2.84-2.76 (m, 2H), 2.69-2.61 (m, 2H), 2.08-2.00 (m, 2H), 1.30 (s, 18H). LDI-TOF MS m/z ([M]$^+$): 706.1. Anal. calcd. for C$_{50}$H$_{50}$N$_4$ (%): C 84.95, H 7.13, N 7.93; found: C 84.68, H 7.10, N 7.78.

**Morphology and Phase Transition Temperatures**

Thermal transition temperatures were acquired on a DSC (Perkin-Elmer DSC-7) with nitrogen flow at 20 ml/min. Samples were preheated to above their melting points, and then cooled down to $-30$ °C at $-100$°C/min before the second heating and cooling scans were recorded at 20 °C/min. All three hybrids doped with Ir(piq)$_3$ at 8 wt% were prepared by co-dissolution in chloroform. The nature of phase transition was characterized by hot-stage POM (DMLM, Leica, FP90 central processor and FP82 hot-stage, Mettler Toledo). Film morphology was characterized by polarizing optical microscopy (Leitz Orthoplan-Pol) and recorded with a digital camera (MicroPix C-1024).

**Photophysical Properties**

Thin films were prepared by thermal vacuum evaporation on fused silica substrates at 4 Å/sec under $5\times10^{-6}$ torr. The thickness was measured by a stylus-type profilometer (D-100, KLA Tencor). Absorption and photoluminescence of the resulting thin films and dilute solutions in chloroform were characterized by UV-vis-NIR spectrophotometer (Lambda-900, Perkin-Elmer) and spectrofluorimeter (Quanta Master C-60SE, Photon Technology International), respectively. Phosphorescence measurements were conducted for hybrids in dichloromethane at 77 K (the liquid nitrogen temperature) by a
A spectrofluorometer (FluoroMax-P, Horiba Jobin Yvon Inc.) equipped with a microsecond flash lamp as the pulsed excitation source. A 10-ms delay time was inserted between the pulsed excitation and the collection of the emission spectrum. The $E_T$s of the compounds were determined by the highest-energy vibronic sub-bands of the phosphorescence spectra.

**Electrochemical Characterization**

Cyclic voltammetry was conducted on an EC-Epsilon potentiostat (Bioanalytical Systems Inc.) A silver/silver chloride wire, a platinum wire, and a glassy carbon disk with a 3-mm diameter were used as the reference, counter, and working electrodes, respectively. Tetraethylammonium tetrafluoroborate was used as the supporting electrolyte, which had been purified as described previously.\[^{19}\] Samples were dissolved at a concentration of $10^{-3}$ M in acetonitrile/toluene (1:1 by volume) containing 0.1 M supporting electrolyte. Acetonitrile and toluene were distilled with calcium hydride and sodium/benzophenone, respectively. The dilute sample solutions exhibit reduction and oxidation scans against the Ag/AgCl reference electrode. The reduction and oxidation potentials were adjusted to Fc as an internal standard with an oxidation potential of 0.51±0.02 V with respect to Ag/AgCl. The reduction and oxidation potentials, $E_{1/2}$(red) and $E_{1/2}$(oxd), relative to Fc/Fc$^+$ were used to calculate the LUMO and HOMO levels as $-4.8-\frac{1}{q}E_{1/2}$(red) eV and $-4.8-\frac{1}{q}E_{1/2}$(oxd) eV, respectively, where $q$ is electron charge.\[^{20}\]
PhOLED and Unipolar Device Fabrication and Characterization

ITO substrates were thoroughly cleaned and treated with oxygen plasma prior to depositing a 3 nm-thick MoO$_3$ layer by thermal vacuum evaporation at 0.3 Å/sec, followed by a hole-transport layer (30 nm), NPB, and an EML (20 nm) comprising Host:Ir(piq)$_3$ at a mass ratio of 8%, both at 4 Å/sec. Layers of BPhen (40 nm) and LiF (1 nm) were consecutively deposited at 4 Å/sec and 0.2 Å/sec, respectively. The devices were completed by deposition of aluminum (100 nm) at 10 Å/sec through a shadow mask to define an active area of 0.1 cm$^2$. All evaporation processes were carried out at a base pressure less than $5 \times 10^{-6}$ torr. The unipolar devices and PhOLEDs containing the sensing layer were fabricated by the same procedure. All PhOLEDs were characterized by a source-measure unit (Keithley 2400) and a spectroradiometer (PhotoResearch PR650) in the ambient environment without encapsulation. The front-view performance data were collected, and the EQE$s$ were calculated assuming the Lambertian distribution of emission intensities. The current-voltage characterizations of the unipolar devices were carried out by a source-measure unit (Keithley 2400).

3.3. RESULTS AND DISCUSSION

Depicted in Chart 3.1 are three prototypical bipolar hybrids, $t$Bu-TPA-$p$-TRZ, $t$Bu-TPA-$m$-TRZ and $t$Bu-TPA-$L$-TRZ, with para- and meta- linkages and a propylene spacer. The tert-butyl groups on the TPA moiety are intended to overcome electrochemical instability by blocking the active para-sites on phenyl rings.$^{[21]}$ It has
been reported that TRZ exhibits reversible reduction in its CV scan without protection. Indeed, the three bipolar hybrids exhibited reversible oxidation and reduction scans in dilute solution (Figure 3.1) for the measurement of energy levels.

Chart 3.1 Molecular structures with their thermal transition temperatures determined by DSC second heating scans of samples preheated to beyond their crystalline melting points. Symbols: G, glassy; K, crystalline; I, isotropic.

Figure 3.1 Cyclic voltammetric scans of compounds in acetonitrile:toluene (1:1 by volume) at 10^{-3} M with 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte. Both oxidation and reduction scans are reversible for all the three hybrids. The reduction potential of tBu-TPA and the oxidation potential of TRZ are beyond the CV measurement range.
The high-energy absorption bands from 250 to 350 nm in dilute chloroform solutions shown in Figure 3.2a for \( p \), \( m \), and \( L \)-hybrids can be represented approximately by the sum of \( \text{tBu-TPA} \)'s and \( \text{TRZ} \)'s. In addition, the \( p \)-hybrid presents a distinct absorption peak at 400 nm responsible for photo-induced intramolecular CTC formation enabled by some degree of \( \pi \)-conjugation through the biphenyl core that is substantially suppressed in the \( m \)-hybrid and absent in the \( L \)-hybrid. With excitation at 277 nm, fluorescence of both \( \text{tBu-TPA} \) and \( \text{TRZ} \) as independent chemical entities in chloroform at \( 10^{-5} \text{M} \) was beyond detection from 300 to 800 nm. Photoexciting the three hybrids at the same concentration level results in fluorescence all at 535 nm, as shown in Figures 3.2b and 3.3, which collectively place CTC formation on solid grounds based on fluorescence bathochromism at an increasing solvent polarity,\(^{[23,24]}\) from toluene to chloroform and \( N,N \)-dimethylformamide. Moreover, the relative intensities shown in Figures 3.2b and c are consistent with intermolecular electron transfer being promoted by tight molecular packing in neat solid film compared to dilute solution. The observed fluorescence enhancement in the sequence: \( L > m > p \)-hybrids reflects the relative contribution of intermolecular over intramolecular processes to CTC formation. Overall, the extent of CTC formation is by far the most prominent in the \( p \)-hybrid, and the least in the \( L \)-hybrid.
Figure 3.2 Absorption spectra at 20 °C of (a) tBu-TPA, TRZ, tBu-TPA-p-TRZ, tBu-TPA-m-TRZ, and tBu-TPA-L-TRZ in chloroform at $8.3 \times 10^{-6}$ M. Nearly identical absorption spectra were obtained for neat solid films of the three hybrids. Fluorescence spectra at 20 °C of (b) tBu-TPA-p-TRZ, tBu-TPA-m-TRZ, and tBu-TPA-L-TRZ in toluene, chloroform and N,N-dimethylformamide at $8.3 \times 10^{-6}$ M with photoexcitation at 277 nm, and (c) tBu-TPA-p-TRZ (95 nm), tBu-TPA-m-TRZ (97 nm), and tBu-TPA-L-TRZ (94 nm) films vacuum-sublimed on fused silica substrates receiving the same incident excitation at 281 nm with normalization by $1 - 10^{-A}$, where A is the absorbance of photoexcitation at 281 nm.

Figure 3.3 Fluorescence spectra collected at 20 °C for (a) tBu-TPA-m-TRZ and (b) tBu-TPA-L-TRZ in toluene, chloroform, and N,N-dimethylformamide at $8.3 \times 10^{-6}$ M with photoexcitation at 277 nm.
That the three hybrids have the same fluorescence peak wavelengths both in neat solid film and solution could be the consequence of the same HOMO–LUMO gaps in a given medium,[25] as expected of the HOMO and LUMO levels presented in Table 3.1. Characterized by phosphorescence in dichloromethane at 77 K (Figure 3.4), the $E_T$ value represents the electronic transition from the first triplet state, $T_1(v=0)$, to the ground state, $S_0(v=0)$, where $v=0$ denotes the vibrational ground state. In its $T_1(v=0)$ state, the biphenyl core has been reported to have a vanishing torsion angle[26] in contrast to ~40° in its $S_0(v=0)$ state.[27] That the difference in the extents of $\pi$-conjugation through the biphenyl core in the $T_1(v=0)$ state is more pronounced than in the $S_0(v=0)$ state is borne out by the relative $E_T$ values, $p- < m- < L$-hybrids. The absence of $\pi$-conjugation across the biphenyl core permits the $L$-hybrid to retain (i) as its $E_T$ value the lower of those of independent TPA and TRZ moieties at 3.1 and 3.0 eV,[7,28] and (ii) the HOMO and LUMO levels of those of independent $t$Bu-TPA and TRZ moieties. The oft-quoted relationship, absorption edge = HOMO – LUMO, is obeyed by the $p$-hybrid with the 400 nm absorption peak representing the electronic transition from $t$Bu-TPA’s HOMO level to TRZ’s LUMO level, which are probed in the CV measurement of all three hybrids. This electronic transition, however, is absent in the $m$- and $L$-hybrids where the two moieties absorb light independently in the 250 to 350 nm spectral region. Within typical errors, the HOMO and LUMO levels presented in Table 3.1 are not sufficiently sensitive to the finite extent of $\pi$-conjugation in the $p$-hybrid compared to the $m$- and $L$-hybrids.
Table 3.1 Energy levels in neat films characterized at 20 °C and triplet energies measured in dichloromethane at 77 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}$(oxd)$^{[a]}$ vs. Fc/Fc$^+$ (V)</th>
<th>$E_{1/2}$(red)$^{[a]}$ vs. Fc/Fc$^+$ (V)</th>
<th>HOMO$^{[c]}$ (eV)</th>
<th>LUMO$^{[d]}$ (eV)</th>
<th>$E_T$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>tBu-TPA</td>
<td>0.42±0.02</td>
<td>N.A.$^{[b]}$</td>
<td>–5.2±0.1</td>
<td>N.A.</td>
<td>3.1$^{[e]}$</td>
</tr>
<tr>
<td>TRZ</td>
<td>N.A.$^{[b]}$</td>
<td>–2.18±0.02</td>
<td>N.A.</td>
<td>–2.2±0.2</td>
<td>3.0$^{[f]}$</td>
</tr>
<tr>
<td>tBu-TPA-p-TRZ</td>
<td>0.48±0.01</td>
<td>–2.11±0.02</td>
<td>–5.3±0.1</td>
<td>–2.3±0.2</td>
<td>2.5$^{[g]}$</td>
</tr>
<tr>
<td>tBu-TPA-m-TRZ</td>
<td>0.49±0.04</td>
<td>–2.13±0.04</td>
<td>–5.3±0.1</td>
<td>–2.3±0.2</td>
<td>2.7$^{[g]}$</td>
</tr>
<tr>
<td>tBu-TPA-L-TRZ</td>
<td>0.40±0.04</td>
<td>–2.19±0.03</td>
<td>–5.2±0.1</td>
<td>–2.2±0.2</td>
<td>3.0$^{[g]}$</td>
</tr>
</tbody>
</table>

$^{[a]}$ Half-wave potentials, $E_{1/2}$, relative to Fc/Fc$^+$ with an oxidation potential at 0.51 V vs. Ag/AgCl, determined as the average of forward and reverse oxidation or reduction peaks.

$^{[b]}$ Oxidation or reduction potential beyond the CV measurement range.

$^{[c]}$ HOMO$=-(1.4±0.1)\times qE_{1/2}$(oxd)$-(4.6±0.08)$ eV for neat solid films.$^{[29]}$

$^{[d]}$ LUMO$=-(1.19±0.08)\times qE_{1/2}$(red)$-(4.78±0.17)$ eV for neat solid films.$^{[30]}$

$^{[e]}$ Phosphorescence in ethanol at 77 K.$^{[28]}$

$^{[f]}$ Phosphorescence in ethyl acetate at 77 K.$^{[7]}$

$^{[g]}$ $E_T$ measured in dichloromethane at 77 K with a typical error of ±0.1 eV.

Figure 3.4 CTC emission (20 °C, no time delay) and phosphorescence (77 K, 10 ms delay) spectra for (a) tBu-TPA-p-TRZ, (b) tBu-TPA-m-TRZ, and (c) tBu-TPA-L-TRZ in dichloromethane at $10^{-5}$ M. Triplet energies were estimated from the highest-energy vibronic sub-bands as indicated.
To evaluate PhOLED performance in relation to the extent of CTC formation, red-emitting \textbf{Ir(piq)}\textsubscript{3} with an $E_T$ of 2.1 eV\textsuperscript{[31]} was doped in the three hybrids for the fabrication of devices: ITO/MoO\textsubscript{3}(3 nm)/NPB(30 nm)/Host:Ir(piq)\textsubscript{3}(8 wt\%, 20 nm)/BPhen(40 nm)/LiF(1 nm)/Al(100 nm), which energy diagram is shown in Figure 3.5 with energy levels in neat solid film reported in literature. Note that the $E_T$ values of all three hybrids are higher than that of \textbf{Ir(piq)}\textsubscript{3} to ensure energy transfer from the former to the latter. As shown in Figure 3.6a, the highest EQE was achieved with \textbf{tBu-TPA-m-TRZ} containing device, while \textbf{tBu-TPA-p-TRZ} containing device yielded the lowest. The driving voltage, however, does not follow the same trend as EQE; see Figure 3.6b. The \textbf{tBu-TPA-ō-TRZ} containing device requires the highest driving voltage of the three hybrid hosts caused by the weakest charge transport capability as to be elaborated in what follows. With the three hybrid hosts having largely the same charge injection barriers (Table 3.1) incorporated in otherwise identical device architectures, the differences in EQE and driving voltage are accountable by the extents of CTC formation and charge imbalance across the EML.
Figure 3.5 Energy diagram of PhOLED device with reported energy levels in neat solid films$^{[29,30,32-35]}$. Hosts in EML: *t*Bu-TPA-*p*-TRZ (LUMO = −2.3 eV; HOMO = −5.3 eV), *t*Bu-TPA-*m*-TRZ (LUMO = −2.3 eV; HOMO = −5.3 eV), *t*Bu-TPA-*L*-TRZ (LUMO = −2.2 eV; HOMO = −5.2 eV).

Figure 3.6 (a) EQE and (b) driving voltage as functions of current density for PhOLEDs with emitting layers comprising *t*Bu-TPA-*p*-TRZ, *t*Bu-TPA-*m*-TRZ, and *t*Bu-TPA-*L*-TRZ doped with Ir(piq)$_3$ at a 8 wt%.
The electroluminescence spectra shown in Figure 3.7 indicate that the emission spectra of all three PhOLED devices are largely the same as typical phosphorescence spectrum of \( \text{Ir(piq)}_3 \) in dilute toluene solution.\(^{[31]} \) In addition, as shown in the insets of Figures 3.7a and b, weak peaks at about 500 nm appear in devices containing \( \text{tBu-TPA-}p\text{-TRZ} \) and \( \text{tBu-TPA-}m\text{-TRZ} \) originating from CTCs involving these two hybrids. In these hybrid hosts, CTC formation is the result of electroexcitation resulting from holes on HOMO levels recombining with electrons on LUMO levels. The intensity of CTC emission is further observed to increase at an increasing current density, a consequence of energy transfer from host to dopant being less effective while allowing excitons on the host to decay through CTCs. The inset in Figure 3.7c shows electroluminescence from \( \text{tBu-TPA-}L\text{-TRZ} \) containing devices without detectable CTC emission at current densities up to 100 mA/cm\(^2\). The relative significance of CTC emission in PhOLEDs is consistent with relative fluorescence from neat solid films of hybrid hosts shown in Figure 3.2c. In addition to causing emissive color impurity, the CTC formation from host could also reduce EQE values. Therefore, the lowest EQE of \( \text{tBu-TPA-}p\text{-TRZ} \) containing device might be a consequence of the most intensive CTC emission in its PhOLED.
Figure 3.7 Electroluminescence spectra of PhOLEDs with (a) tBu-TPA-p-TRZ, (b) tBu-TPA-m-TRZ, and (c) tBu-TPA-L-TRZ as the hosts all doped at 8 wt% of Ir(piq)$_3$ as functions of current densities. The CIE coordinates are (0.654, 0.333), (0.660, 0.330), and (0.670, 0.327) for the emission spectra shown in (a), (b), and (c), respectively. Insets: expanded views of emission spectra from 425 to 475 nm.

Relative charge transport capability and hence the deviation from charge balance through the EML will be invoked to explain why tBu-TPA-m-TRZ yields the highest EQE value followed by tBu-TPA-L-TRZ. Unipolar devices were fabricated to compare the charge transport capabilities of the three hybrids. The device structures of hole-only and electron-only devices are ITO/MoO$_3$(3 nm)/NPB(30 nm)/Host(20 nm)/MoO$_3$(3 nm)/Al(100 nm) and ITO/Al(20 nm)/Host(20 nm)/BPhen(40 nm)/LiF(1 nm)/Al(100 nm), respectively. The three hybrids sustain identical hole fluxes (Figure 3.8a), while the tBu-TPA-p-TRZ containing device allows the highest electron flux (Figure 3.8b) followed by tBu-TPA-m-TRZ and then tBu-TPA-L-TRZ under the same driving voltage. That the three hybrids conduct holes more readily than electrons is demonstrated below using sensing layers.$^{[36]}$
Figure 3.8 Current as a function of driving voltage for (a) hole-only and (b) electron-only devices.

Depicted in Figures 3.9a and b are the device structures in which NPB and BPhen are employed as the hole- and electron-transport layers, HTL and ETL, respectively, throughout this study. Additionally, a 3-nm-thick hybrid host doped with 8 wt% Ir(piq)$_3$ is inserted as a sensing layer, one each at the HTL/EML and EML/ETL interfaces in two PhOLED devices. The $t$Bu-TPA-$p$-TRZ containing device with the sensing layer located at EML/ETL interface produced the higher EQE than that at HTL/EML (see Figure 3.9c), suggesting that recombination occurs near the ETM/ETL interface and hence a higher hole flux than electron flux is encountered in this device. With the lower electron fluxes shown in Figure 3.8b, the inferior charge balance of $t$Bu-TPA-$m$-TRZ and $t$Bu-TPA-$L$-TRZ as the hosts is expected in comparison to $t$Bu-TPA-$p$-TRZ. The experimental results summarized in Figures 3.8 and 3.9 combine to conclude that $t$Bu-TPA-$p$-TRZ containing PhOLED possesses the best charge balance across EML, while $t$Bu-TPA-$L$-TRZ containing device the worst. Despite the best charge balance, the device containing $t$Bu-TPA-$p$-TRZ produced the lowest EQE value because of the most energy loss of
excitons to CTC (see Figure 3.7a). The better charge balance in \( tBu-TPA-m-TRZ \) containing device results in the higher EQE value than \( tBu-TPA-L-TRZ \) containing device despite the more pronounced CTC in the former (Figures 3.7b vs. c). Although \( tBu-TPA-L-TRZ \) containing device did not manage to produce the highest EQE of the three, the flexible linkage is an effective way to minimize loss of device efficiency and to attain high spectral purity where the conditions for CTC formation are favorable.

**Figure 3.9** Devices incorporating a sensing layer located at (a) HTL/EML interface and (b) EML/ETL interface, and (c) EQE as a function of current density for the devices containing a sensing layer.

In addition, bipolar hybrids with a flexible linkage have the potential for strengthening the morphological stability of a glassy EML against crystallization.\([7]\) The differential scanning calorimetric thermograms reveal that noncrystalline \( tBu-TPA-m-TRZ \) and \( tBu-TPA-L-TRZ \) have \( T_g \) at 99 and 85 °C, respectively, while \( tBu-TPA-p-TRZ \) exhibits \( T_g \) at 132 °C followed by crystallization at 192 °C and then crystalline melting at 282 °C (Figure 3.10a). As shown in Figure 3.11, freshly deposited amorphous EMLs containing the three distinct hybrids, ITO(100 nm)/Host:Ir(piq)_3(8 wt%, 20 nm)/Al(100 nm), were thermally annealed at 75 °C, which is below their respective \( T_g \)s at
135, 107, and 88 °C of EMLs consisting of \( p \)-, \( m \)-, and \( L \)-hybrids; see Figure 3.10b. Polycrystallinity emerged under polarizing optical microscopy with \( t\text{Bu-TPA-}p\text{-TRZ:Ir(piq)}_3 \) and \( t\text{Bu-TPA-}m\text{-TRZ:Ir(piq)}_3 \) in 3 and 7 h, respectively, while \( t\text{Bu-TPA-}L\text{-TRZ:Ir(piq)}_3 \) remained amorphous for 33 h. Therefore, the stronger morphological stability of an amorphous film does not necessarily follow from the higher \( T_g \). As noted previously,\(^{[7]}\) it is the conformational multiplicity rendered by the propylene spacer that contributes to a higher free energy barrier to crystallization from amorphous \( t\text{Bu-TPA-}L\text{-TRZ:Ir(piq)}_3 \) compared to \( t\text{Bu-TPA-}p\text{-TRZ:Ir(piq)}_3 \) and \( t\text{Bu-TPA-}m\text{-TRZ:Ir(piq)}_3 \). The relative stability of \( t\text{Bu-TPA-}L\text{-TRZ:Ir(piq)}_3 \) against crystallization should contribute at least in part to the longevity of the corresponding PhOLED.

**Figure 3.10** DSC heating and cooling scans at ±20 °C/min of samples preheated to above their melting points followed by cooling down to −30 °C at −100 °C/min for (a) pure hybrids, and (b) hybrids doped with \( \text{Ir(piq)}_3 \) at 8 wt%. Symbols: \( G \), glassy; \( K \), crystalline; \( I \), isotropic.
Figure 3.11 Polarizing optical micrographs of 20-nm-thick vacuum-sublimed, glassy films of hybrids doped with Ir(piq)₃ at a 8 wt% sandwiched between ITO and Al under thermal annealing at 75 °C: (a) tBu-TPA-p-TRZ:Ir(piq)₃ for 3 h, (b) tBu-TPA-m-TRZ:Ir(piq)₃ for 7 h, and (c) tBu-TPA-L-TRZ:Ir(piq)₃ for 33 h.

3.4. SUMMARY

Three representative bipolar hybrid compounds with distinct chemical linkages were synthesized to evaluate their potentials as hosts for PhOLEDs. The two moieties in these hybrids are tBu-TPA and TRZ linked together through two of their phenyl rings in a para- or meta- attachment or via a propylene spacer, producing tBu-TPA-p-TRZ, tBu-TPA-m-TRZ, and tBu-TPA-L-TRZ, respectively. These three hybrids showed similar absorption bands from 250 to 350 nm associated with electronic transitions in independent moieties, while tBu-TPA-p-TRZ exhibits an additional absorption peak at 400 nm associated with intramolecular electron transfer facilitated by effective π-conjugation through the central biphenyl core. Fluorescence bathochromism at an increasing solvent polarity was demonstrated in support of CTC formation by all three hybrids. Both intramolecular and intermolecular electron transfer processes are invoked
for the construction of mechanisms to explain CTC formation. The \( \mathcal{L} \)-hybrid was found to be the least prone to fluorescence from its CTC. The \( E_T \) values decreased from \( tBu-TPA-\mathcal{L}-TRZ \) (3.0 eV) to the \( m- \) (2.7 eV) and then \( p- \)hybrid (2.5 eV), all suitable for hosting the red-emitting dopant, \( \text{Ir(piq)}_3 \). The three hybrids were tested in red-emitting PhOLEDs to examine the effects of CTC formation. The lowest external quantum yield was encountered with \( tBu-TPA-p-TRZ \) because of the most extensive emission from the CTC that also caused spectral impurity from the device. Hole-only, electron-only, and sensing-layer-containing PhOLED devices were used to interpret the superior EQE and lower driving voltage of \( tBu-TPA-m-TRZ \) over \( tBu-TPA-\mathcal{L}-TRZ \). Better charge balance in the device utilizing \( tBu-TPA-m-TRZ \) as the EML host gave rise to its improved performance, despite the device utilizing \( tBu-TPA-\mathcal{L}-TRZ \) having the lesser extent of CTC formation. Additionally, the flexible linkage in \( tBu-TPA-\mathcal{L}-TRZ \) was demonstrated to be the most favorable in terms of morphological stability as well as attaining high spectral purity, showing promise for the realization of superior PhOLEDs. The modest EQEs reported herein are expected to be significantly improved through engineering of chemical composition and device architecture by exploiting the extensive knowledge base in place.
REFERENCES


CHAPTER 4

STABILITY OF BLUE-EMITTING PHOSPHORESCENT ORGANIC LIGHT-EMITTING DIODES IN HYBRID RELATIVE TO MIXED HOST

4.1. INTRODUCTION

Blue PhOLEDs are essential to full-color displays and solid-state lighting. The development of highly efficient and long-lived devices has remained a major challenge. In addition to the need for efficient and stable blue emitters,[1,2] the technological advances in blue PhOLEDs entail the understanding of intricate material and interface degradation mechanisms that are electrochemical, photochemical (i.e. bond dissociation at excited states), thermal and morphological in nature.[3-5] Since the phosphorescent dopant is preferably dispersed at the molecular level into a host to prevent concentration quenching,[6] host materials with sufficiently high $E_T$s are imperative to blue emitters for excitons to remain on dopant molecules. Most of the existing host materials are capable of preferentially transporting holes[7,8] or electrons[9-11]. In consequence, charge recombination tends to occur near the interface of the emitting layer, EML, with either the electron- or hole-transport layer, which is detrimental to device efficiency and
lifetime due to triplet-triplet annihilation\cite{12} and triplet-polaron quenching\cite{13} under high current densities pertaining to practical application.

Capable of bipolar charge transport, physically mixed hosts\cite{14-16} and hybrid hosts\cite{17,18} with chemically bonded hole- and electron-transport moieties, HTMs and ETMs, have been demonstrated for broadening the recombination zone to alleviate efficiency roll-off. Although crystallization in EML has been recognized as a factor limiting device efficiency and lifetime\cite{19,20}, there has been no definitive report using a polycrystalline EML relative to its amorphous counterpart of the same chemical composition without altering other aspects of the OLED. Demonstrated for superior morphological stability against crystallization, bipolar hybrid compounds with flexible linkages\cite{21} appear to be well suited for such an endeavor. Possessing sufficiently high $E_T$ and hole mobility values, carbazole derivatives are the most commonly used HTMs for the construction of bipolar hybrid hosts.\cite{22,23} Thanks to their ultra-high $E_T$ values, arylsilane derivatives have been utilized as ETMs in blue PhOLEDs.\cite{24,25} In the present study, mCP and SiPh4 -- the HTM and ETM, respectively -- are linked with a propylene spacer to generate a new bipolar hybrid host, mCP-L-PhSiPh3, expected to have significantly improved morphological stability against crystallization over the physically mixed counterpart at the same HTM:ETM molar ratio. Through selective annealing of the EMLs comprising these two distinct hosts doped with FIrpic, the effects of thermally activated crystallization on blue PhOLED device performance will be elucidated in terms of external quantum efficiency and driving voltage.
4.2. EXPERIMENTAL SECTION

Material Synthesis and Characterization

All chemicals, reagents, and solvents were used as received from commercial sources without further purification except toluene and THF that had been distilled over sodium and benzophenone. All reactions were carried out under argon and anhydrous conditions unless noted otherwise. The compounds, 1,1-bis[4-([N,N-di(p-tolyl)aminophenyl]-cyclohexane (TAPC, >99%, Nichem, Taiwan), 1,3,5-tri(m-pyrid-3-yl-phenyl)benzene (TmPyPB, >99%, Nichem, Taiwan), BPhen (>99%, Nichem, Taiwan), and bis(4,6-difluorophenyl)-pyridinato-N,C2'iridium(III) picolinate (Flrpic, >99%, Nichem, Taiwan) were used as received without further purification. Tetraphenylsilane (SiPh4, 95%, Alfa Aesar) was purified by sublimation before use. \(^1\)H NMR spectra were acquired in CDCl\(_3\) with an Avance-400 spectrometer (400 MHz). Elemental analysis was carried out at the Elemental Analysis Facility, University of Rochester. Molecular weights were measured with a MALDI-TOF mass spectrometer (Brüker Autoflex III). The host materials, mCP:SiPh4 and mCP-PhSiPh3, depicted in Chart 4.1 were synthesized and purified in accordance to Scheme 4.1.
Scheme 4.1 Synthesis of mCP and mCP-L-PhSiPh3.

9,9'-(5-Bromo-1,3-phenylene)bis(9H-carbazole), 4. A mixture of 1 (5.31 g, 31.77 mmol), 3 (5.00 g, 15.88 mmol), Cu (4.04 g, 63.53 mmol), K$_2$CO$_3$ (17.56 g, 127.06 mmol), and 18-crown-6 (2.29 g, 6.35 mmol) was stirred in o-dichlorobenzene (60 ml) at 190 °C for 48 h. The crude mixture was filtered, and the solvent was distilled off under reduced pressure. The mixture was extracted with chloroform and the organic extracts were combined, washed with water, and dried over MgSO$_4$. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexanes/chloroform 8:1 (v/v) as the eluent to yield 4 (1.61 g, 21%) as a white powder. $^1$H
NMR (400 MHz, CDCl₃, 298K): δ (ppm) 8.16-8.14 (d, J = 8.0 Hz, 4H), 7.87-7.86 (d, J = 4.0 Hz, 2H), 7.80-7.78 (m, 1H), 7.55-7.53 (m, 4H), 7.48-7.44 (m, 4H), 7.35-7.31 (m, 4H).

(4-Bromophenyl)triphenylsilane, 7. n-BuLi (2.5 M in hexanes, 5.09 ml, 12.72 mmol) was added dropwise to a solution of 5 (3.00 g, 12.72 mmol) in THF (45 ml) at –78 °C, where the mixture was stirred for 3 h before adding 6 (3.75 g, 12.72 mmol) slowly. The reaction mixture was allowed to warm up to room temperature, quenched with water, and then extracted with chloroform. The organic extracts were combined, washed with water, and dried over MgSO₄. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexanes/methylene chloride 4:1 (v/v) as the eluent to yield 7 (3.00 g, 56%) as a white powder. ¹H NMR (400 MHz, CDCl₃, 298K): δ (ppm) 7.56-7.55 (m, 3H), 7.54-7.52 (m, 4H), 7.51-7.50 (m, 1H), 7.47-7.42 (m, 4H), 7.41-7.36 (m, 7H).

(4-Allylphenyl)triphenylsilane, 8. THF (60 ml) was added to a mixture of 7 (1.00 g, 2.41 mmol), allyltributyltin (2.22 g, 7.22 mmol), Pd(PPh₃)₄ (0.14 g, 0.12 mmol), and LiCl (0.20 g, 4.81 mmol). The reaction mixture was stirred at 90 °C for 24 h, cooled down to room temperature, and extracted with chloroform. The organic extracts were combined, washed with water, and dried over MgSO₄. After evaporating off the solvent, the crude product was purified by gradient column chromatography on silica gel with hexanes/chloroform 49:1 to 24:1 (v/v) as the eluent to yield 8 (0.80g, 88%) as a white powder. ¹H NMR (400 MHz, CDCl₃, 298K): δ (ppm) 7.57-7.55 (m, 6H), 7.51-7.49 (m,
1,3-Bis(9-carbazolyl)benzene, mCP. A mixture of o-dichlorobenzene (120 ml) and 2 (2.56 ml, 21.20 mmol) was added to a mixture of 1 (10.62 g, 63.59 mmol), Cu (8.08 g, 127.17 mmol), K$_2$CO$_3$ (35.15 g, 254.35 mmol), and 18-crown-6 (4.58 g, 12.72 mmol). The reaction mixture was stirred at 190 °C for 36 h. The crude mixture was filtered and the solvent was distilled off under reduced pressure. The mixture was extracted with chloroform and the organic extracts were combined, washed with water, and dried over MgSO$_4$. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexanes/methylene chloride 9:1 (v/v) as the eluent to yield mCP (5.01 g, 58%) as a pale purple powder. The synthesized mCP was further purified by sublimation to give a white solid in 55% yield. $^1$H NMR (400 MHz, CDCl$_3$, 298K): $\delta$ (ppm) 8.17-8.15 (d, $J = 8.0$ Hz, 4H), 7.87-7.82 (m, 2H), 7.72-7.69 (m, 2H), 7.55-7.53 (m, 4H), 7.46-7.42 (m, 4H), 7.33-7.29 (m, 4H). LDI-TOF MS m/z ([M]$^+$): 408.5. Anal. calcd. for C$_{30}$H$_{20}$N$_2$ (%): C 88.21, H 4.93, N 6.86; found: C 87.77, H 4.80, N 6.79.

(4-(3-(3,5-Bis(9-carbazolyl)phenyl)propyl)phenyl)triphenylsilane, mCP-Ph$_2$SiPh$_3$. 9-BBN (0.5 M in THF, 9 ml, 4.5 mmol) was added dropwise to a solution of 8 (0.54 g, 1.44 mmol) in THF (8 ml) at 0 °C. The mixture was stirred at room temperature for 15 min and then at 35 °C for 3 h before transferring to a mixture of 4 (0.77 g, 1.59 mmol), Pd(PPh$_3$)$_4$ (0.033 g, 0.029 mmol), Na$_2$CO$_3$ (3.82 g, 36.04 mmol), water (18 ml), and
toluene (30 ml). The reaction mixture was stirred at 90 °C for 24 h, cooled down to room temperature, and extracted with chloroform. The organic extracts were combined, washed with water, and dried over MgSO₄. Upon evaporating off the solvent, the crude product was purified by gradient column chromatography on silica gel with hexanes/chloroform 3:1 to 2:1 (v/v) as the eluent to yield mCP-L-PhSiPh₃ (0.86 g, 76%) as a white powder. 

\[
d \text{H NMR (400 MHz, CDCl}_3, 298K): \delta (ppm) 8.16-8.14 (d, J = 8.0 Hz, 4H), 7.47-7.46 (m, 1H), 7.56-7.49 (m, 14H), 7.45-7.39 (m, 7H), 7.36-7.28 (m, 10H), 7.25-7.22 (m, 2H), 2.92-2.89 (m, 2H), 2.81-2.78 (m, 2H), 2.18-2.10 (m, 2H). LDI-TOF MS m/z ([M]⁺): 785.0. Anal. calcd. for C₅₇H₄₄N₂Si (%): C 87.20, H 5.65, N 3.57; found: C 87.06, H 5.67, N 3.55.
\]

Tetraphenylsilane, SiPh₄. \text{H NMR (400 MHz, CDCl}_3, 298K): \delta (ppm) 7.58-7.56 (d, J = 8.0 Hz, 8H), 7.46-7.34 (m, 12H). Anal. calcd. for C₂₄H₂₀Si (%): C 85.66, H 5.99; found: C 85.82, H 6.03.

**Morphology, Thermal Stability, and Phase Transition Temperatures**

Decomposition temperatures were characterized by thermogravimetric analysis (Q500, TA Instruments, TGA) at a ramping rate of 10 °C/min under a nitrogen flow of 60 ml/min. Thermal transition temperatures were acquired on a DSC (Perkin-Elmer DSC 8500) with nitrogen flow at 20 ml/min. The mixed samples, mCP:SiPh₄, mCP:SiPh₄:FIrpic and mCP-L-PhSiPh₃:FIrpic, were prepared by codissolution in dichloromethane, followed by drying thoroughly in vacuo. All samples were preheated to above their melting point, and then cooled down to –30 °C at –100 °C/min before the
second heating and cooling scans were recorded at 20 °C/min. The nature of phase transition was characterized by hot-stage POM (DMLM, Leica, FP90 central processor and FP82 hot-stage, Mettler Toledo).

**Photophysical Properties**

Absorption of thin films on the fused silica substrate was characterized by UV-Vis-NIR spectrophotometer (Lambda-900, Perkin-Elmer). For phosphorescence measurements, thin films held on a cryostat (HC-2, APD Cryogenic Inc.) at 20 K in a vacuum chamber were excited at 355 nm with a 45° incident angle using a pulsed frequency-tripled neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (GCR-100, Quanta-Ray Spectra-Physics). Phosphorescence spectra were collected using the detector of CCD camera (DH50118F-01, Andor) with a monochromatic system (260i, ORIEL).

**Thin Film Preparation and Characterization**

Thin films were prepared by thermal vacuum evaporation on fused silica substrates at 4 Å/sec under 5×10⁻⁶ torr. Thickness was measured by a stylus-type profilometer (D-100, KLA Tencor). Film morphology was characterized by polarizing optical microscopy (Leitz Orthoplan-Pol) with a digital camera (MicroPix C-1024). With a transmission electron microscope (FEI Tecnai F20), electron diffraction images were collected on films mounted onto copper grids after floating off sodium chloride substrates (International Crystal Laboratories) in deionized water.
**PhOLED Fabrication and Characterization**

ITO substrates were thoroughly cleaned and treated with oxygen plasma prior to depositing a 3 nm-thick MoO$_3$ layer by thermal vacuum evaporation at 0.3 Å/sec, followed by hole-transport layer (30 nm), TAPC, and an EML (30 nm) comprising Host:Flrpic at a mass ratio of 9:1, both at 4 Å/sec. Layers of TmPyPB (10 nm), BPhen (30 nm), LiF (1 nm) were deposited consecutively at 4 Å/sec, 4 Å/sec, and 0.2 Å/sec, respectively. The devices were completed by deposition of aluminum (100 nm) at 10 Å/sec through a shadow mask to define active areas of 0.1 cm$^2$ (0.32 cm × 0.32 cm) each. All evaporation processes were carried out at a base pressure less than 5×10$^{-6}$ torr. Thermal annealing of ITO/MoO$_3$/TAPC/EML was performed at 20 °C for varying time periods and at 80 and 100 °C for 1 h each, and of ITO/MoO$_3$/TAPC/EML/TmPyPB at 60 °C for varied time periods in a glove box filled with nitrogen. All devices were characterized by a source-measure unit (Keithley 2400) and a spectroradiometer (PhotoResearch PR650) in the ambient environment without encapsulation. Only the front-view performance data were collected.
4.3. RESULTS AND DISCUSSION

Depicted in Chart 4.1 are the molecular structures of the three compounds used in this study: mCP, SiPh4 and mCP-\(\mathcal{L}\)-PhSiPh3, accompanied by their thermal transition temperatures. The \(E_T\) values of mCP\textsuperscript{[26]} SiPh4\textsuperscript{[27]} and mCP-\(\mathcal{L}\)-PhSiPh3 are 3.0, 3.5 and 3.0 eV, respectively, all sufficiently high for hosting FIrpic\textsuperscript{[28]} (\(E_T = 2.6\) eV) as the blue phosphorescent dopant; see Figure 4.1 for the phosphorescence spectrum of a vacuum-sublimed mCP-\(\mathcal{L}\)-PhSiPh3 film. Thermogravimetric analysis was conducted to characterize the thermal stability of mCP, mCP-\(\mathcal{L}\)-PhSiPh3 and FIrpic up to 312, 383, and 378 °C, respectively (Figure 4.2), while that of SiPh4 was reported previously at 482 °C\textsuperscript{[29]}.

According to the second heating scans using DSC (Figure 4.3), \(T_g\)s were located at 92 and 53 °C for mCP-\(\mathcal{L}\)-PhSiPh3 and mCP, respectively, while SiPh4 is crystalline without detectable glass transition as observed under hot-stage polarizing optical microscopy.

![Chart 4.1](image)

**Chart 4.1** Molecular structures with their thermal transition temperatures determined by DSC second heating scans of samples preheated to beyond their crystalline melting points. Symbols: \(G\), glassy; \(K\), crystalline; \(I\), isotropic.
Figure 4.1 Phosphorescence spectrum at 20 K of vacuum-sublimed mCP-L-PhSiPh3 film with excitation at 355 nm. The triplet energy was estimated from the highest energy band.

Figure 4.2 TGA thermograms of Flrpic, mCP and mCP-L-PhSiPh3 recorded at a heating rate of 10 °C/min under nitrogen atmosphere.
Figure 4.3 DSC heating and cooling scans at ±20 °C/min of (a) mCP, (b) SiPh4, (c) mCP:SiPh4 and mCP:SiPh4:Firpic, and (d) mCP-L-PhSiPh3 and mCP-L-PhSiPh3:Firpic preheated to above their melting points followed by cooling down to –30 °C at –100 °C/min. The melting points were determined from the first heating scans of mCP, SiPh4, mCP:SiPh4, mCP:SiPh4:Firpic, mCP-L-PhSiPh3 and mCP-L-PhSiPh3:Firpic at 176, 252, 170, 166, 115 and 120 °C, respectively. Symbols: G, glassy; K, crystalline; I, isotropic.

To explore the effects of thermal annealing of EMLs on device performance, a series of PhOLEDs -- ITO/MoO3(3 nm)/TAPC(30 nm)/Host:Firpic(10 wt%, 30 nm)/TmPyPB(10 nm)/Bphen(30 nm)/LiF(1 nm)/Al(100 nm) -- were prepared comprising
initially amorphous EMLs thermally annealed for predetermined durations. The energy diagram of the PhOLED device is shown in Figure 4.4 with energy levels in neat solid films reported in literature.\textsuperscript{[24,30-36]} The layers underlying EMLs, ITO/MoO\textsubscript{3}/TAPC, were found to remain amorphous with thermal annealing at 20 °C for up to 72 h and at 100 °C for 1 h, as evidenced by electron diffraction; see the inset in Figure 4.5a. In addition, MoO\textsubscript{3} and Al layers were deposited on the annealed ITO/MoO\textsubscript{3}/TAPC layers to fabricate hole-only devices, ITO/MoO\textsubscript{3}(3 nm)/TAPC(30 nm)/MoO\textsubscript{3}(3 nm)/Al(100 nm). The MoO\textsubscript{3} layer adjacent to ITO serves as a hole injection layer, while the other MoO\textsubscript{3} layer next to Al prevents electrons from being injected into the TAPC layer. The identical I-V curves to that prior to thermal annealing, as shown in Figure 4.5, indicate that hole injection and transport from ITO through TAPC was not affected by thermal annealing under all conditions without possible adverse effects caused by material and/or interface degradation in the absence of crystallization in any layer. The absence of pinholes in the TAPC layer under 100 °C annealing for 1 h was confirmed with the consistent, marginally higher current at the same driving voltage from 0 to 8 V without the 3-nm-thick electron-blocking MoO\textsubscript{3} layer (Figure 4.5b). In view of TAPC having a crystalline melting point at 183 °C,\textsuperscript{[37]} the maximum crystallization rate from its melt is estimated at $(183 + 273) \times 0.90 - 273 = 137 °C$.\textsuperscript{[38,39]} Therefore, crystallization of the TAPC melt at 80 °C is expected to be slower than that at 100 °C since both thermal annealing temperatures are on the rising side of the bell-shaped crystallization rate profile. This observation assures that the results presented in Figure 4.5 are applicable to annealing at 80 °C.
**Figure 4.4** Energy diagram of PhOLED device with literature-reported energy levels in neat solid films.\textsuperscript{[24,30-36]}

**Figure 4.5** Current as a function of driving voltage for hole-only devices upon thermal annealing of TAPC layers with a free surface at (a) 20 °C for 0 and 72 h, 100 °C for 1 h, and 60 °C for 96 h before completing the device, ITO/MoO\textsubscript{3}(3 nm)/TAPC(30 nm)/MoO\textsubscript{3}(3 nm)/Al(100 nm) and (b) 100 °C for 1 h before completing the device, ITO/MoO\textsubscript{3}(3 nm)/TAPC(30 nm)/MoO\textsubscript{3}(3 nm)/Al(100 nm) and ITO/MoO\textsubscript{3}(3 nm)/TAPC(30 nm)/Al(100 nm). Inset in (a): electron diffraction image of the two-layer film, MoO\textsubscript{3}(3 nm)/TAPC(30 nm), annealed with a free surface at 20 °C for 72 h and at 100 °C for 1 h in a glove box filled with nitrogen.
A mixed host, \textbf{mCP:SiPh4} at a 1:1 molar ratio, and a hybrid host, \textbf{mCP-\text{\textregistered} PhSiPh3}, both doped with \textbf{F1rpic} at 10 wt\%, constitute the EMLs for a legitimate comparison, other elements of the PhOLEDs being identical. For hole and electron injection layers, MoO$_3$ and LiF were used, respectively. The TAPC layer was deposited on the MoO$_3$ layer to aid in hole transport. Inserted between EML and LiF, BPhen serves not only as an electron-transport layer but also to prevent exciton quenching by lithium ions diffusing into EML.$^{[40]}$ The hole-blocking TmPyPB ($E_T=2.8$ eV)$^{[41]}$ layer, and hole-transporting TAPC ($E_T=2.9$ eV)$^{[42]}$ layer should help to confine excitons on \textbf{F1rpic} in EML. Half-devices ITO/MoO$_3$/TAPC/EML were annealed at 20 °C for up to 72 h, and at 80 and 100 °C for 1 h under nitrogen before depositing TmPyPB/BPhen/LiF/Al sequentially to complete PhOLED devices. While the BPhen film with a free surface was found to crystallize at 20 °C overnight, the three freshly deposited layers on top of EML, TmPyPB(10 nm)/BPhen(30 nm)/LiF(1 nm), were verified to be amorphous with polarizing optical microscopy and electron diffraction (see Figure 4.6). As shown in Figure 4.7, crystallization was observed under polarizing optical microscopy in the EML comprising \textbf{mCP:SiPh4:F1rpic} annealed at 20 °C for 24 to 72 h and at 80 and 100 °C for 1 h, while the EML comprising \textbf{mCP-\text{\textregistered} PhSiPh3:F1rpic} remained amorphous under the same annealing conditions. The amorphous character of the pristine \textbf{mCP:SiPh4:F1rpic} and that of \textbf{mCP-\text{\textregistered} PhSiPh3:F1rpic} annealed at 20 °C for up to 72 h and 80 and 100 °C for 1 h were further validated by electron diffraction; see the inset in Figure 4.7a. The morphological stability of \textbf{mCP-\text{\textregistered} PhSiPh3:F1rpic} against crystallization over that of \textbf{mCP:SiPh4:F1rpic} is imparted largely by the flexible linkage in the former.$^{[21]}$
**Figure 4.6** Freshly deposited TmPyPB(10 nm)/Bphen(30 nm)/LiF(1 nm): (a) polarizing optical micrograph and (b) electron diffraction image.

**Figure 4.7** Polarizing optical micrographs of ITO/MoO$_3$/TAPC/mCP:SiPh$_4$:FIrpic kept at the ambient temperature of 20 °C for (a) 0 h, (b) 24 h, (c) 48 h, (d) 72 h, and (e) 80 and 100 °C for 1 h. Inset in (a): electron diffraction image of MoO$_3$/TAPC/mCP:SiPh$_4$:FIrpic prior to thermal annealing; inset in (d): electron diffraction image of MoO$_3$/TAPC/ mCP:SiPh$_4$:FIrpic annealed at 20 °C for 72 h with calculated $d$-spacings$^{[43]}$ ranging from 0.14 to 0.47 nm; (a) with inset also serves to represent the amorphous character of MoO$_3$/TAPC/ mCP-2-PhSiPh$_3$:FIrpic annealed with a free surface at 20 °C for up to 72 h, and at 80 and 100 °C for 1 h each in a glove box filled with nitrogen.
Degradation of materials or interfaces could be inevitable in operational devices during characterization over a range of current density up to 50 mA/cm². Potential electrochemical, morphological, photochemical, and thermal degradations must be precluded to enable the effects of crystallization in EMLs to be scrutinized. Pristine PhOLEDs referred to hereafter represent untested devices consisting of all amorphous layers except EMLs independently characterized as amorphous or polycrystalline upon thermal annealing. As indicated by symbols + and x in Figures 4.8, cumulative characterizations of devices consisting of mCP-L-PhSiPh3:FIrpic and mCP:SiPh4:FIrpic exhibit the same driving voltages and external quantum efficiencies, EQEs, as those of pristine PhOLEDs at 10 and 50 mA/cm², thus precluding potential adverse effects caused by repeated current drives incurred with device characterization. All PhOLEDs with both types of EML annealed at 20 °C for up to 72 h and with mCP-L-PhSiPh3:FIrpic at 80 °C for 1 h emit nearly the same phosphorescence spectra as FIrpic at 10⁻⁵ M in chloroform. Compared to mCP-L-PhSiPh3:FIrpic, polycrystallinity is present in mCP:SiPh4:FIrpic upon thermal annealing of ITO/MoO₃/TAPC/EML at 20 °C for 24 through 72 h and at 80 and 100 °C for 1 h (Figures 4.7b to e versus Figure 4.7a).
Figure 4.8 (a) EQE and (b) driving voltage as functions of current density for PhOLED devices containing mCP-L-PhSiPh3:FIrpic, and (c) EQE and (d) driving voltage as functions of current density for PhOLED devices containing mCP:SiPh4:FIrpic with half-devices, ITO/MoO3/TAPC/EML, annealed at 20 °C for up to 72 h and at 80 and 100 °C for 1 h. Typical experimental errors for EQE and driving voltage are ±10 and ±8%, respectively, of the mean from three separate devices. Pristine PhOLED devices were characterized at 10 and 50 mA/cm² with pristine EMLs (×), and at 50 mA/cm² with half-devices up to EML annealed at 100 °C for 1 h (+).
Annealing EMLs above the mixed and hybrid hosts’ $T_g$s at 57 and 97 °C (Figures 4.3c and d), respectively, produced satellites at about 420 and 580 nm (Figures 4.9a and b) flanking FIrpic’s emission peaks at 470 and 500 nm. These fortuitous satellites are identifiable with emission from TAPC’s singlet state and tri-$p$-tolylamine ion pairs.\cite{44,45} It is likely that pinholes filled with TAPC (during annealing of EML) and TmPyPB (subsequent deposition on EML) are present for charges to bypass the EML in operational PhOLEDs. Annealing melts may also result in interlayer mixing between TAPC, with $T_g$ at 78 °C,\cite{37} and EML for TAPC to compete favorably for excitons with the mixed and hybrid hosts by virtue of its lower $E_T$ value than those of the hybrid and mixed hosts. Annealing mCP-$\mathcal{L}$-PhSiPh3:FIrpic at 20 °C for up to 72 h and at 80 °C for 1 h did not depress the EQE profiles while causing driving voltages to vary somewhat erratically, as shown in Figures 4.8a and b. Upon thermal annealing at 100 °C for 1 h, a considerable loss in EQE accompanied by driving voltage reduction was observed, consistent with pinholes and interlayer mixing for the interpretation of satellites in the emission spectra. The sharp decline in both EQE and driving voltage shown in Figures 4.8c and d upon annealing of mCP:SiPh4:FIrpic at 80 and 100 °C well above its $T_g$ at 57 °C corroborates the proposition that pinholes and interlayer mixing are responsible for similar behaviors to the hybrid host. In addition, crystallization in mCP:SiPh4:FIrpic may also reduce driving voltage through improved charge transport capability.\cite{46}
As Figure 4.8c is contrasted with Figure 4.8a, a higher EQE value was achieved with pristine EML comprising mCP:SiPh4:F1rpic than mCP-PhSiPh3:F1rpic, an observation to be rationalized by comparing charge injection barrier and transport property. To a good approximation, mCP:SiPh4 and mCP-PhSiPh3 should possess the same HOMO and LUMO levels\cite{21} to render identical electron and hole injection barriers into the two EMLs both doped with 10 wt% F1rpic. The higher EQE value accomplished with mCP:SiPh4:F1rpic than mCP-PhSiPh3:F1rpic, both amorphous prior to thermal annealing, could be attributed to the superior charge transport ability of the mixed host to that of the hybrid host as indicated by the I-V characteristics of the PhOLEDs with pristine EMLs; Figure 4.8d versus 4.8b. Further comparison of EQE
values between the two host systems is made difficult by crystallization of EMLs with the mixed host but not the hybrid host upon thermal annealing.

With the physical integrity of EMLs in question during thermal annealing above their $T_g$s, ITO/MoO$_3$/TAPC/EML/TmPyPB stacks were fabricated for thermal annealing at 60 °C, i.e. 19 °C below TmPyPB’s $T_g$ for varying durations. Annealing at 60 °C was intended for expedited thermal evaluation while accommodating the expected temperature rise in a typical operational device.[47] An independent vacuum-sublimed TmPyPB film and all layers in the stack ITO/MoO$_3$/TAPC/mCP-$2$-PhSiPh$_3$:FIrpic/TmPyPB remained amorphous after thermal annealing at 60 °C for 14 days and 198 h, respectively based on polarizing optical microscopy and electron diffraction (Figures 4.10a and b). The polycrystalline features of EML, however, emerged upon thermal annealing at 60 °C of ITO/MoO$_3$/TAPC/mCP:SiPh$_4$:FIrpic/TmPyPB beginning in 1 h; see Figures 4.10c to e. No satellite peaks, however, were observed in the emission spectra shown in Figures 4.11a and b for amorphous and polycrystalline EMLs in hybrid and mixed hosts annealed at 60 °C, thus arguing against pinholes and interlayer mixing as with annealing at 80 or 100 °C.
Figure 4.10 Polarizing optical micrographs of (a) TmPyPB annealed at 60 °C for up to 14 days, (b) ITO/MoO$_3$/TAPC/\textit{mCP-\ell-PhSiPh3:F1rpic}/TmPyPB annealed at 60 °C for up to 198 h, and ITO/MoO$_3$/TAPC/\textit{mCP:SiPh4:F1rpic}/TmPyPB annealed at 60 °C for (c) 1 h, (d) 2 h, (e) 3 h, and (f) 9 h. Insets in (a) and (b): electron diffraction images of TmPyPB and MoO$_3$/TAPC/\textit{mCP-\ell-PhSiPh3:F1rpic}/TmPyPB annealed at 60 °C for up to 14 days and 198 h, respectively.

A PhOLED device subjected to repeated uses over the range of current density from 0.1 to 50 mA/cm$^2$ is shown in Figure 4.12 to be equivalent to a pristine PhOLED tested at 50 mA/cm$^2$ in terms of EQE and driving voltage. According to Figure 4.12a, EQE values with \textit{mCP-\ell-PhSiPh3:F1rpic} are by and large unaffected at 7 to 8% with annealing at 60 °C up to 24 h before decreasing monotonically with extended annealing time. In the absence of crystallization, pinholes and interlayer mixing, there must be other sources of device instability beyond 24 h annealing as shown in Figure 4.12a. A similar hybrid host, \textit{SimCP}$^{[48]}$, consisting of \textit{mCP} linked to SiPh4 without a flexible linkage
afforded EQE values at 9 and 14% with FIrN4 and FIrpic as blue dopants, respectively, in a different device structure than ours. Moreover, FIrN4 at 7 wt% in a SimCP thin film was found to crystallize at 70 °C,[49] evidently lacking in morphological stability. In sharp contrast to mCP-L-PhSiPh3:FIrpic, EQE values with mCP:SiPh4:FIrpic decrease by 40 to 80 % (Figure 4.12c) with about 40 % reduction in driving voltage (Figure 4.12d) upon annealing at 60 °C from 1 to 3 h as a result of crystallization. Note in addition the slightly lesser extent of voltage reduction than shown in Figure 4.8d with annealing at 80 and 100 °C for 1 h where both crystallization and pinhole formation might have come into play.

**Figure 4.11** Electroluminescence spectra of PhOLED devices, ITO/MoO3/TAPC/EML/TmPyPB/BPhen/LiF/Al, where EML consists of (a) mCP-L-PhSiPh3:FIrpic, and (b) mCP:SiPh4:FIrpic with ITO/MoO3/TAPC/EML/TmPyPB annealed at 60 °C for varying time periods before subsequent depositions of BPhen/LiF/Al.
Figure 4.12 (a) EQE and (b) driving voltage as functions of current density for PhOLED devices containing mCP-2-PhSiPh3:FIrpic, and (c) EQE and (d) driving voltage as functions of current density for PhOLED devices containing mCP:SiPh4:FIrpic with half-devices, ITO/MoO3/TAPC/EML/TmPyPB, annealed at 60 °C for various periods of time. Typical experimental errors for EQE and driving voltage are ±8 and ±6%, respectively. Pristine mCP-2-PhSiPh3:FIrpic and mCP:SiPh4:FIrpic PhOLED devices were characterized at 50 mA/cm² half-devices, ITO/MoO3/TAPC/EML/TmPyPB, annealed at 60 °C for 198 h and 9 h indicated as × and +, respectively.
With the reported $T_g$ and $T_m$ at 62 and 220 °C, respectively, polycrystallinity was found to prevail in a vacuum-sublimed, amorphous BPhen film left at 20 °C overnight, thus disabling an investigation of how thermal annealing of PhOLED device in its entirety may affect its performance, particularly with a relatively stable EML comprising mCP-$\mathcal{L}$-PhSiPh3:F1rpic. To improve the modest EQE values using mCP-$\mathcal{L}$-PhSiPh3, electron and hole fluxes through EML should be balanced by mixing chemical hybrids of mCP and SiPh4 at varying molar ratios while ensuring miscibility, elevated $T_g$, and stability against crystallization over those of equivalent physical mixtures.

4.4. SUMMARY

A mixed host, mCP:SiPh4 at a 1:1 molar ratio, and its hybrid counterpart, mCP-$\mathcal{L}$-PhSiPh3, both doped with F1rpic at 10 wt%, are used to elucidate how thermally activated morphological changes in EML may affect PhOLED performance. Annealing temperature relative to EML’s $T_g$ and whether or not EML presents a free surface during annealing are two governing parameters. Annealing mCP:SiPh4:F1rpic at 20, 60, 80, and 100 °C relative to its $T_g$ at 57 °C with and without a free surface all induced crystallization. Flanking F1rpic’s major phosphorescence peaks at 470 and 500 nm upon annealing above $T_g$ with a free surface, satellites at 420 and 580 nm are attributable to emission from TAPC’s singlet state and tri-p-tolylamine ion pairs filling the pinholes in EML and interlayer mixing. Crystallization, pinhole formation, and/or interlayer mixing are responsible for the decreased EQE and driving voltage for the most part, depending
on the involvement of a free surface. Annealing mCP:SiPh4:F1rpic at 60 °C without a free surface for 1 h led to about 50 % loss in EQE. In contrast, annealing mCP-\(\mathcal{L}\)-PhSiPh3:F1rpic at 20, 60, and 80 °C relative to its \(T_g\) at 97 °C with and without a free surface did not cause crystallization or satellite emission. In particular, a pristine device’s EQE persisted up to 24 h annealing at 60 °C without a free surface, beyond which other sources of device failure took over. Annealing mCP-\(\mathcal{L}\)-PhSiPh3:F1rpic at 100 °C with a free surface, however, resulted in considerable decline in both EQE and driving voltage accompanied by relatively minor satellite emission attributable to pinholes and interlayer mixing. Compared to physical mixing, the concept of chemical hybrid with a flexible linkage holds promise for long-lived PhOLED devices by elevating \(T_g\) while preventing crystallization of amorphous EML.
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CHAPTER 5

CONCLUSIONS AND FUTURE RESEARCH

5.1. CONCLUSIONS

Over the past couple of decades, tremendous efforts have been devoted to novel organic materials and sophisticated device structures for highly efficient and stable OLEDs. This thesis has evaluated new chemical hybrids as prospective hosts for PhOLEDs in terms of (i) charge transport, (ii) CTC formation, and (iii) morphological stability in relation to molecular structure. Non-conjugated bipolar and unipolar compounds with flexible linkages were synthesized for the measurement of electron and hole mobilities. Donor-acceptor compounds with varied linkages were synthesized to investigate how CTC formation may affect PhOLED device characteristics. Finally, a mixed host and its bipolar hybrid counterpart were employed to elucidate how thermal annealing of EMLs affects blue PhOLED performance.

In place of physical mixtures as bipolar hosts for phosphorescent OLEDs, chemical hybrids comprising non-conjugated spacers are explored to ensure miscibility and morphological stability. Bipolar TRZ-3Cz(MP)2 and TRZ-1Cz(MP)2 as well as unipolar C2-2TRZ(2rBu) and C3-2Cz(MP)2 were synthesized with ethylene or propylene spacers serving to decouple the Cz(MP)2 and TRZ moieties. Glassy films were
prepared by thermal vacuum sublimation for the characterization of transport properties using the photocurrent time-of-flight technique. The results indicate that not only the TRZ:Cz(MP)2 ratio but also the molecular conformation dictated by the spacer enable tunable charge-carrier mobilities. The significant role played by molecular conformation in charge transport is supported by analyzing literature data for s-triazine- and carbazole-based unipolar compounds capable of forming glassy films in similar device structures. A new approach has been demonstrated for modulating charge transport by varying the chemical hybrid’s composition through material synthesis and molecular conformation through computation while retaining predetermined HOMO and LUMO levels.

Three representative bipolar hybrids, \textit{tBu}-TPA-\textit{p}-TRZ, \textit{tBu}-TPA-\textit{m}-TRZ, and \textit{tBu}-TPA-\textit{L}-TRZ, were synthesized and characterized for a comprehensive evaluation of their potentials for hosting red-emitting \textit{Ir}(pipq)\textsubscript{3} in PhOLEDs. Formation of CTCs was diagnosed by fluorescence bathochromism in increasingly polar solvents. Both intra- and inter-molecular electron transfer processes are invoked for the construction of mechanisms to explain CTC formation in all three hybrids. The \textit{p}-hybrid is by far the most susceptible to CTC formation both in solution and neat solid film, resulting in a PhOLED with reduced EQE and slightly impaired spectral purity despite the best charge balance across EML, as revealed by the electron- and hole-only devices as well as PhOLEDs containing sensing layers. The highest EQE is achieved with the \textit{m}-hybrid thanks to the compromise between charge balance and CTC formation. The \textit{L}-hybrid is the least prone to CTC formation while suffering inferior charge balance in the tested device architecture to afford an EQE intermediate between those of the \textit{m}- and \textit{p}-hybrids.
Nevertheless, the  \( \mathcal{L} \)-hybrid offers the most stable EML against crystallization from the desired glassy film, thus holding promise for the fabrication of superior PhOLEDs.

Lastly, \( \text{FIrpic} \)-doped emitting layers were thermally annealed at 20 to 100 °C for varied durations without causing phase transformation in the rest of the PhOLEDs. Heating EMLs above their \( T_g \)s with a free surface created pinholes filled by the underlying TAPC melt with concurrent interlayer mixing to emit satellite peaks accompanying \( \text{FIrpic} \)'s phosphorescence. With a robust glassy TmPyPB layer on top of EML, pinholes and fortuitous fluorescence could be prevented. Annealing \( \text{mCP:SiPh4:FIrpic} \) induced crystallization in 1 h, while \( \text{mCP-\mathcal{L}-PhSiPh3:FIrpic} \) consistently resisted crystallization under all conditions. Crystallization or pinhole formation diminished EQE and driving voltage at the same time. Without incurring pinhole formation in the absence of a free surface presented by EML, annealing \( \text{mCP:SiPh4:FIrpic} \) at 60 °C for 1 h led to about 50 % loss in EQE. In contrast, the pristine device’s EQE persisted with \( \text{mCP-\mathcal{L}-PhSiPh3:FIrpic} \) annealed at 60 °C for up to 24 h, beyond which other sources of device failure took over. The concept of bipolar hybrids holds promise for mitigating morphological instability as part of the PhOLED device lifetime.
5.2.  FUTURE RESEARCH

The formation of CTCs in bipolar mixtures and hybrids is unpredictable \textit{a priori}. As a matter of fact, some CTCs could well be non-emissive. Of particular interest are to identify the conditions favorable to their formation, characterization of their triplet energies and quantum yields, and so on, all of which are indeed long-term challenges. In the relatively short term, the following projects are contemplated to help to bring blue-emitting PhOLEDs to commercial fruition as an essential component to solid-state lighting.

Based on the observations in our laboratory, glassy liquid crystalline films could stay glassy at room temperature for two decades still going strong. There are great opportunities to investigate kinetic and thermodynamic stabilities of thermal vacuum sublimation of organics into amorphous glassy films in relation to molecular structures and processing conditions. To EMLs consisting of guest-host systems, miscibility and morphological stability are critical to device stability. Additionally, it is proposed to construct binary and ternary phase diagrams involving mixed and hybrid hosts to establish the concentration and temperature ranges appropriate for device fabrication and application in the single phase regime for maximum device efficiency and lifetime. Useful techniques may include DSC, POM, XRD, AFM, TEM, NSOM, and so on.

As a follow-up to mobility measurements and data interpretation for bipolar and unipolar hybrids, it is proposed to study charge transport in the mixtures of HTMs and ETMs in the miscible regime for a comparison with their chemical hybrid counterparts,
both in glassy film, to elucidate the role of flexible spacers. Furthermore, computations can be exploited to identify optimized molecular structures of HTMs, ETMs and their chemical hybrids conducive to transport of charge carriers.

With the successful demonstration of the non-conjugated chemical hybrids as promising hosts for PhOLEDs, it is proposed to investigate their electrochemical stability in neat solid film rather than in solution by CV. Single-layer devices containing neat bipolar hybrid films could be electrically driven with a constant current for varied durations. The tested devices will then be characterized by I-V measurement coupled with chemical analysis to uncover possible origins of electrochemical instability.
APPENDIX 1

$^1$H NMR, MALDI-TOF and LC Mass Spectra for Chapter 2
Figure A1.1 $^1$H NMR (400 MHz) spectrum of TRZ-3Me in CDCl$_3$ at 298 K.
Figure A1.2 $^1$H NMR (400 MHz) spectrum of C3-2TRZ in CDCl$_3$ at 298 K.
Figure A1.3 $^1$H NMR (400 MHz) spectrum of **Ben-3TRZ** in CDCl$_3$ at 298 K.
Figure A1.4 $^1$H NMR (400 MHz) spectrum of Ben-2TRZ in CDCl$_3$ at 298 K.
Figure A1.5 $^1$H NMR (400 MHz) spectrum of C3-2Cz(MP)2 in CDCl$_3$ at 298 K.
Figure A1.6 $^1$H NMR (400 MHz) spectrum of C2-2TRZ(2tBu) in CDCl$_3$ at 298 K.
Figure A1.7 LC MS spectrum of TRZ-3Me using methanol as mobile phase.
Figure A1.8 MALDI-TOF MS spectrum of C3-2TRZ using IAA as the matrix.
**Figure A1.9** MALDI-TOF MS spectrum of **Ben-3TRZ** using IAA as the matrix.
Figure A1.10 MALDI-TOF MS spectrum of **Ben-2TRZ** using IAA as the matrix.
Figure A1.11 MALDI-TOF MS spectrum of C3-2Cz(MP)2 using IAA as the matrix.
Figure A1.12 MALDI-TOF MS spectrum of C2-2TRZ(2fBu) using IAA as the matrix.
APPENDIX 2

$^1$H NMR and LDI-TOF Mass Spectra for Chapter 3
Figure A2.1 $^1$H NMR (400 MHz) spectrum of $t$Bu-TPA-$p$-TRZ in CDCl$_3$ at 298 K.
Figure A2.2 $^1$H NMR (400 MHz) spectrum of $t$Bu-TPA-\textit{m}-TRZ in CDCl$_3$ at 298 K.
Figure A2.3 $^1$H NMR (400 MHz) spectrum of $t$Bu-TPA-$ξ$-TRZ in CDCl$_3$ at 298 K.
Figure A2.4 LDI-TOF MS spectrum of tBu-TPA-p-TRZ.
Figure A2.5 LDI-TOF MS spectrum of $t\text{Bu-TPA-}m\text{-TRZ}$. 
Figure A2.6 LDI-TOF MS spectrum of \( \tau \text{Bu-TPA-L^2TRZ} \).
APPENDIX 3

$^1$H NMR and LDI-TOF Mass Spectra for Chapter 4
Figure A3.1 $^1$H NMR (400 MHz) spectrum of mCP in CDCl$_3$ at 298 K.
Figure A3.2 $^1$H NMR (400 MHz) spectrum of mCP-$\mathcal{L}$PhSiPh3 in CDCl₃ at 298 K.
Figure A3.3 LDI-TOF MS spectrum of mCP.
Figure A3.4 LDI-TOF MS spectrum of mCP-\( \mathcal{C} \)-PhSiPh3.