

Design and Synthesis of Hosts and Emitters - From Photophysical Studies to Device Applications in Organic Light-Emitting Diodes

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Doctoral Dissertation

**Design and Synthesis of Hosts and Emitters - From
Photophysical Studies to Device Applications in Organic
Light-Emitting Diodes**

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Chapter 1

Introduction

1.1. Organic Light Emitting Diodes (OLEDs)

Display technology has undergone remarkable evolution over the past several decades, paralleling the progress of modern electronics and information science.

The earliest generation of display devices was based on cathode ray tubes (CRTs), in which high-energy electron beams were directed toward a phosphorescent screen to generate visible light. Although CRTs offered bright images and accurate color reproduction, the use of high-voltage vacuum tubes resulted in bulky structures and inefficient energy utilization. These intrinsic limitations hindered further miniaturization and restricted their deployment in compact or portable systems.

The advent of liquid-crystal displays (LCDs) marked a decisive transition to flat and lightweight architectures. LCDs rely on the electric-field-induced reorientation of liquid-crystal molecules, which modulates the transmission of polarized light. This mechanism enabled thin, low-power displays that soon dominated the market. Nevertheless, LCDs require an external backlight, resulting in optical losses, a limited contrast ratio and viewing angles. Furthermore, their rigid substrates are incompatible with flexibility and curvature, constraining future applications.

Organic light-emitting diode (OLED) technology has emerged as a transformative alternative. OLEDs utilize the electroluminescence of organic semiconductors, in which injected charge carriers recombine to form excitons that release photons through radiative decay. The self-emissive nature of OLEDs eliminates the need for a backlight, enhancing optical contrast and power efficiency. With their lightweight structure, broad viewing angle, fast response, and high flexibility, OLEDs have become the technological foundation for next-generation high-definition and flexible display systems which are widely adopted in smartphones, wearables, and advanced visualization devices.¹⁻⁴ (Figure 1-1)

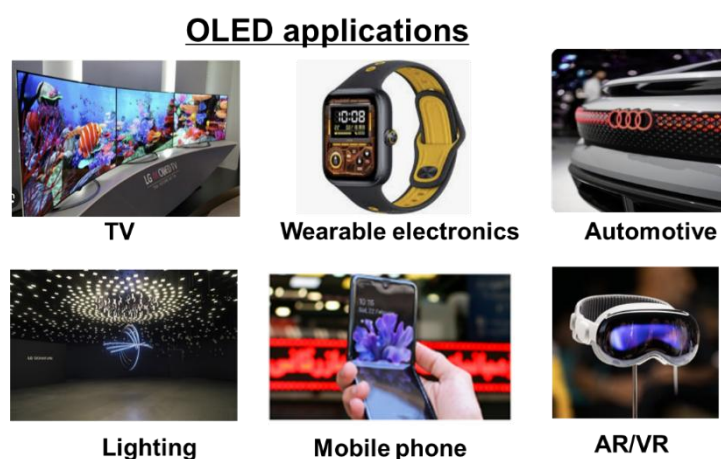


Figure 1-1: OLED applications.

The origin of the development of OLED technology dates back to the 1960s, when researchers observed visible fluorescence from anthracene single crystals under a direct current voltage of about 400 V applied through a silver–mercury electrode.⁵ Although this finding demonstrated the potential electroluminescence of organic materials, the extremely high driving voltage made such devices impractical for real applications. A significant breakthrough was made in 1987, when Tang and Van Slyke at Eastman Kodak developed the first multilayer OLED that operated efficiently at relatively low voltages.⁶ Although the maximum external quantum efficiency (EQE_{max}) being around 1%, this device marked a crucial step toward practical organic electroluminescent systems. Since then, OLED research has rapidly advanced, leading to remarkable improvements in device efficiency, lifetime, and color purity, and ultimately establishing OLEDs as a core technology for modern displays and lighting.⁷⁻⁸ An OLED typically possesses multiple organic layers that are sandwiched between two metal electrodes. The general device configuration starts with a transparent anode, and indium tin oxide (ITO) is the most common one, followed by several organic functional layers in the order of hole injection layer (HIL), hole transport layer (HTL), emissive layer (EML), electron transport layer (ETL), and electron injection layer (EIL). Finally, the device is capped with a low-work function metal cathode, e.g., aluminum, magnesium, or calcium. Careful selection of materials of each layer is crucial for the control of photophysical and electrochemical properties, which eventually determines the efficiency of charge injection, carrier transport, exciton recombination, and light generation. When an external voltage is applied, holes and electrons are injected from the anode and cathode, respectively, and subsequently transported toward the emissive layer. Then, holes and electrons recombine in the emissive layer to form excitons, which consequently decay radiatively to produce light.⁹⁻¹² The OLED structure and its working mechanism are shown in **Figure 1-2**.

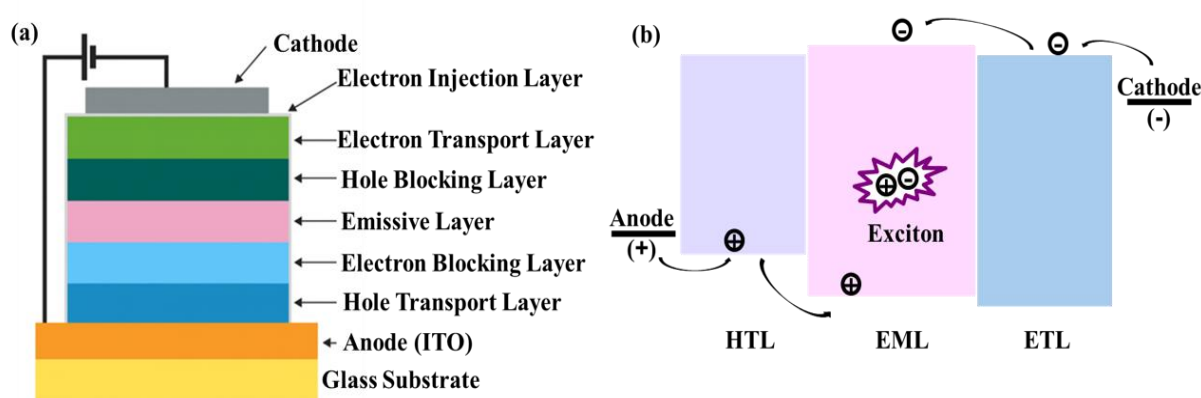


Figure 1-2: Structure and basic mechanism of OLEDs.

1.2. The Development of Emitting Materials

The development of emitters is always a decisive factor in enhancing the efficiency and color purity of OLEDs. During electroluminescence, injected charge carriers from the electrodes recombine within the emissive layer to form excitons. According to spin statistics, the ratio of generated singlet (S_1) and triplet (T_1) excitons is approximately 1:3. For simple organic molecules, only singlet excitons can undergo spin-allowed radiative decay, and triplet excitons are lost through non-radiative processes, making the design of efficient emitters a central challenge in OLED development.¹³⁻¹⁴ Over the past decades, significant advances in molecular design and photophysical understanding has resulted in a progressive development for emitters, which are broadly categorized into three generations based on their emission mechanisms and exciton utilization strategies.

The 1st-generation OLED utilized fluorescent emitters, in which light originates from radiative relaxation of excitons from the lowest singlet excited state (S_1) to the ground state (S_0). Because the transition from singlet to triplet states via intersystem crossing (ISC) is spin-restricted, only 25% of singlet excitons can participate in radiative decay. As a result, the internal and external quantum efficiencies are theoretically limited to around 25% and 5%, respectively. Representative examples of 1st-generation fluorescent emitters include Alq_3 for green emission, and anthracene-based fluorophores for blue devices.¹⁵⁻¹⁷

To harvest both singlet and triplet excitons, phosphorescent transition-metal complexes are used as 2nd-generation OLED materials, particularly iridium(III) and platinum(II) derivatives.¹⁸⁻²¹ Owing to strong spin-orbit coupling from the heavy metal, an efficient ISC from S_1 to T_1 and radiative decay from T_1 to S_0 become spin-allowed. Consequently, phosphorescent OLEDs (PhOLEDs) can achieve a theoretical internal quantum efficiency of 100%. However, the use of phosphorescent emitters involves noble transition metals, which increase fabrication costs, thereby limiting their feasibility for large-scale production. As a result, novel emission mechanisms are required to address both efficiency and cost challenges.

To address these limitations, thermally activated delayed fluorescence (TADF) emerged as the 3rd-generation OLED emitter. In contrast to noble-metal-based PhOLED, TADF materials are purely organic and can utilize both singlet and triplet excitons to achieve 100% internal quantum efficiency (IQE) (**Figure 1-3**).

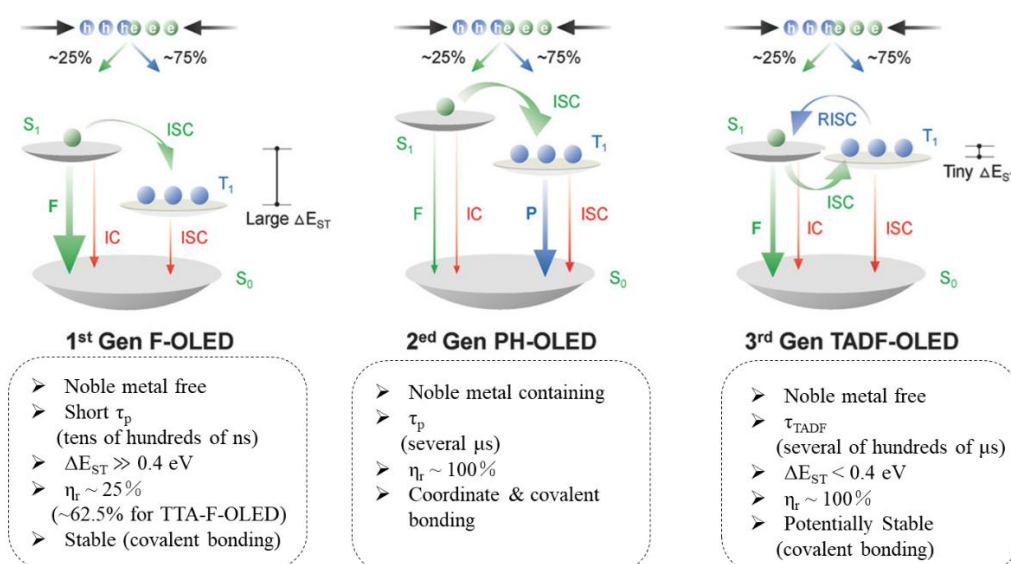


Figure 1-3. Generation of emitters in OLEDs.²²

τ_F , τ_P , and τ_{TADF} refer to the excited state lifetime of fluorescence, phosphorescence, and thermally activated delayed fluorescence, respectively; η_r refers to the exciton utilization ratio under electrical operation.

In 2012, efficient TADF emitters were first reported by Adachi and co-workers, consisting of a donor–acceptor (D–A) structure, in which electron-donating and electron-accepting moieties are connected in a twisted molecular conformation.¹⁴ This twisted molecular conformation spatially separates the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), thereby leading to a small singlet–triplet energy gap (ΔE_{ST}). Such a small ΔE_{ST} facilitates an efficient RISC from T_1 to S_1 , and then delayed fluorescence occurs. With this molecular design, both singlet and triplet excitons can be harvested, which eventually contribute to light emission, enabling efficient OLED performance. However, the spatial separation of HOMO and LUMO in D-A type TADF always induces strong long-range charge-transfer (CT) character, thereby leading to a large geometrical reorganization between the ground state and excited state. Consequently, D-A type TADF emitters exhibit broad and featureless emission bands with a full-width at half-maximum (FWHM) of over 80 nm.²³ The large FWHM of the TADF emitter significantly deteriorates color purity, and particularly, which is particularly problematic for deep-blue OLED applications. Several examples of D-A type TADF emitters are illustrated in **Figure 1-4**.²⁴

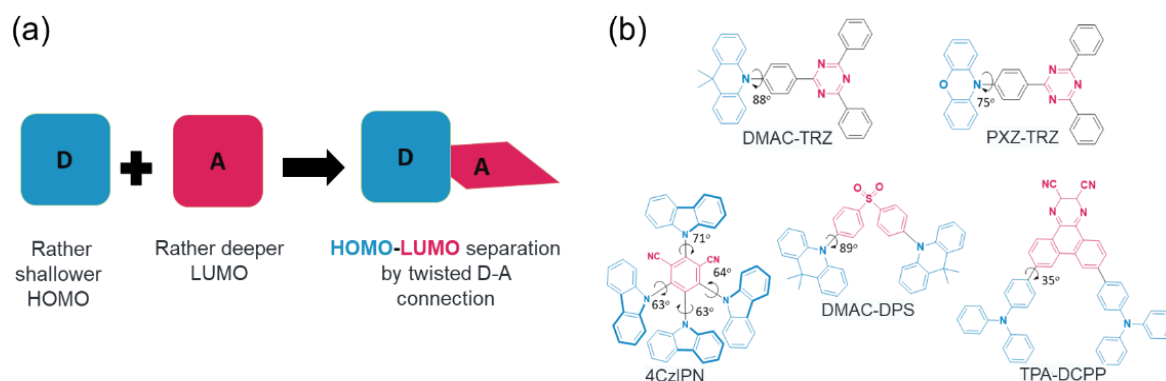


Figure 1-4. (a) Schematic of HOMO-LUMO separation by D-A connection and (b) examples for D-A type TADF emitters.

To overcome this limitation, Hatakeyama and co-workers introduced a new class of TADF emitters, namely multi-resonance (MR) emitters that contain electron-rich nitrogen and electron-deficient boron atoms.²⁵ Both nitrogen atom and boron atom are embedded in a planar and rigid polycyclic π -system. In contrast to the D-A type TADF emitter, the HOMO and LUMO of the MR emitter are separated by the multiple-resonance effect (**Figure 1-5**). The good separation of HOMO and LUMO also gives a small orbital overlap, hence a small ΔE_{ST} . This design effectively suppresses long-range CT character that results in a low reorganization energy between ground state and excited state. As a result, the MR emitter displays unique narrowband emission with FWHM $\approx$ 20–30 nm, which is comparable to those of luminescent quantum dots. Given a narrowband emission of an MR emitter, it can satisfy the harsh requirement of the blue color gamut in the BT.2020 standard, i.e., CIEy $<$ 0.05. Additionally, the well-separated HOMO-LUMO in the MR emitter always results in TADF behavior that secures high efficiency in OLEDs. Despite these advantages, MR-TADF emitters often exhibit relatively long delayed lifetimes and moderate RISC rates (k_{RISC}) of $< 10^5$ s $^{-1}$. This is because a limited spin–orbit coupling and rigid molecular skeleton of MR-TADF emitters. The low k_{RISC} leads to the accumulation of triplet excitons, which eventually results in severe efficiency roll-off at high current densities, thereby lowering device stability. Current strategies for molecular design of MR-TADF emitters involve incorporating heteroatoms (e.g., O, S, and Si) or adopting a helical configuration to enhance spin-orbital coupling (SOC) between S_1 and T_1 without sacrificing narrowband emission.²⁶

Through the continuous development of D-A type TADF emitters and MR-TADF emitters, we have come to understand the importance of molecular design of organic materials for tuning the intrinsic photophysical properties, which greatly affects the corresponding device performance of OLEDs in terms of efficiency, color purity, and, of course, operation lifetime.

In order to achieve efficient and stable TADF OLED, a TADF emitter having a small ΔE_{ST} is not only the key, but a good oscillator strength or suppressed non-radiative decay rate is also important.

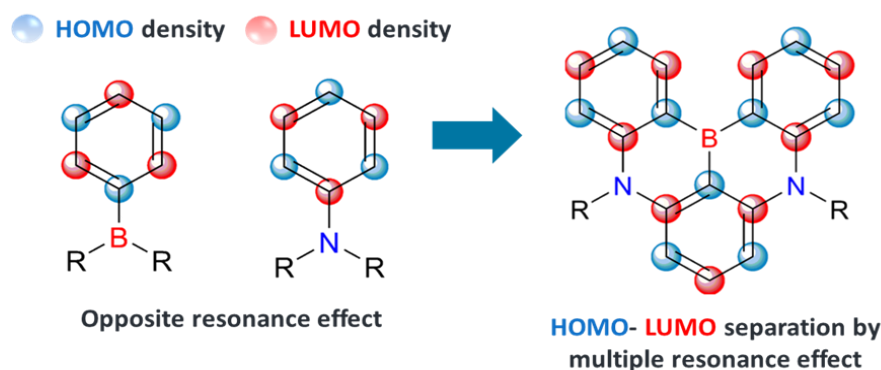


Figure 1-5. The concept of HOMO-LUMO separation by MR effect.

1.3. OLED Performances

The three basic parameters to evaluate the performance of OLEDs are (1) efficiency, (2) emission color, and (3) device lifetime. Efficiency reflects the effectiveness of electricity-to-light conversion; emission color controls the color purity; device lifetime tells the robustness of the operating device. In the following sections, each of these aspects will be discussed in detail.

1.3.1. Efficiency

To evaluate the conversion efficiency of electricity to light of OLEDs, external quantum efficiency (EQE, η_{EQE}) is the crucial indicator to describe the efficiency of OLEDs. It can be calculated by the following equation²⁷:

$$\eta_{EQE} = \eta_{IQE} \cdot \eta_{OC}$$

$$\eta_{EQE} = \gamma \cdot \phi \cdot \eta_{ex} \cdot \eta_{OC}$$

where η_{IQE} is internal quantum efficiency

η_{OC} is out-coupling efficiency

γ is ratio of electron to hole (≤ 1)

ϕ is the photoluminescent quantum yield (PLQY) of emitter

η_{ex} is fraction of luminescent excitation

In general, η_{OC} of OLED ranges from 20 to 30%; γ is related to the electrons and holes reaching the emitter; PLQY is the intrinsic and extrinsic properties of the emitter. For η_{ex} , only 25% of excitons in fluorescent emitters contribute to light emission, whereas phosphorescent and TADF emitters can utilize all singlet and triplet excitons ($\eta_{ex}=1$). Consequently, without

improving the η_{OC} of OLED, the maximum theoretical EQE of TADF OLED is ranged from 20 to 30%; however, if an emitter exists a preferential horizontal orientation, then η_{OC} will be higher than 30%, allowing EQE to reach up to 40%.²⁸

Furthermore, achieving balanced carrier transport is essential to maximize $\gamma=1$, ensuring efficient exciton formation. The PLQY is not only determined by the intrinsic molecular properties of the emitter but also strongly influenced by the host–emitter interactions. Therefore, rational molecular design of host materials is crucial for maximizing overall device efficiency.^{29–32}

1.3.2. Emission Color

For commercial displays, red, green, and blue pixels are necessary. To describe the emission color of OLEDs, the emission wavelength is the primary guide for designing molecules; however, the same wavelength with different full width at half maximum (FWHM) yields dissimilar color purity. To report the color gamut of the OLED with respect to human vision, the Commission Internationale de l'Éclairage (CIE) coordinates are used to illustrate the color points (**Figure 1-6**). For full high-definition (FHD) displays, the color gamut standard is Rec 709, in which red, green, and blue (RGB) colors require (CIEx-coordinate, CIEy-coordinate) of (0.64, 0.33), (0.30, 0.60), and (0.15, 0.06), respectively. Nowadays, FHD displays are advancing toward ultra-high definition (UHD), which require a higher color standard, i.e., BT.2020. To meet the BT.2020 requirements, the emission spectra of RGB OLEDs should be narrow enough to achieve the CIE coordinates (0.71, 0.29) for red, (0.17, 0.80) for green, and (0.13, 0.05) for blue.^{33–34}

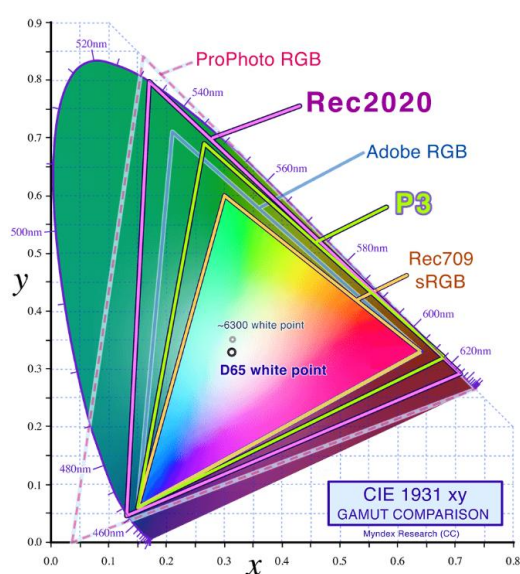


Figure 1-6. CIE coordinates showing different standards. Reproduced from <https://qox.jp/blog/css-color-space-lv4/>, accessed on 24 November 2025.

1.3.3. Device Lifetime

Apart from efficiency and emission color, the most crucial factor to evaluate the OLED performance is device lifetime. Without sufficient device stability, the commercialization of OLED displays would be impractical. The simplest way to have a long device lifetime is to design OLED materials with high chemical stability, i.e., high bond dissociation energy (BDE).³⁵ During the electrical operation of OLED, molecules with a higher BDE value are more resistant to chemical degradation, hence resulting in a longer device lifetime. Aiming for molecules with high BDEs, the molecule should avoid the presence of carbon-heteroatom bonds, i.e., C–X (X = N, P, S, etc.) (**Figure 1-7**). Especially in blue OLED, the energy of the lowest singlet excited state approaches 3 eV that can easily break the C–X bonds.

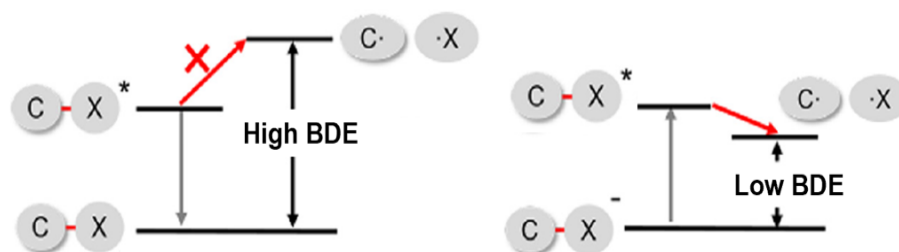


Figure 1-7. Schematic diagram of molecules having high BDE to resist bond cleavage.

In addition to intrinsic molecular stability, the overall device lifetime is also correlated with the exciton dynamics. Devices with higher EQEs can operate at lower current densities for the same brightness, reducing heat generation and degradation. Therefore, phosphorescent (Ph) and TADF emitters, which can harvest 100 % of singlet and triplet excitons, are the promising candidates for extending the device lifetime. Unfortunately, this is not true for blue Ph-/TADF-OLEDs. The long-lived and high-energy triplet excitons are detrimental to the device stability. The long-lived triplet excitons can lead to the formation of hot triplet excitons with higher energy, which will cause faster material degradation. Hot triplet excitons can be formed via the processes of triplet-polaron annihilation or triplet-triplet annihilation (**Figure 1-8**). Accordingly, apart from the design of molecules having high BDEs, the rational molecular design of OLED materials to eliminate the triplet exciton intensity within the OLEDs is equally important for the enhancement of device lifetime.³⁶⁻³⁷

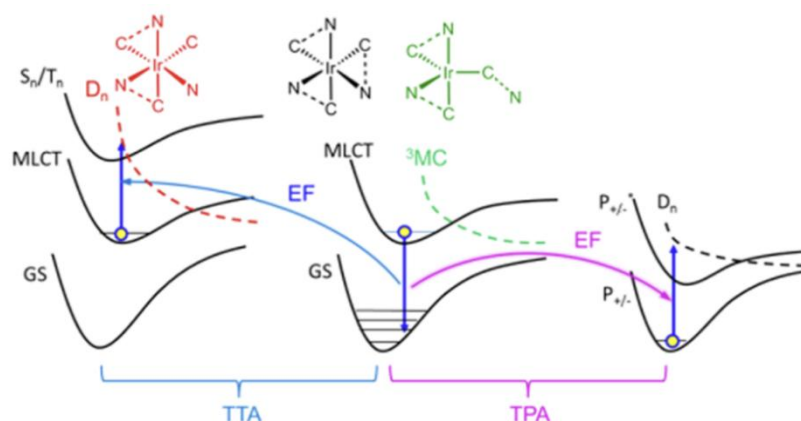


Figure 1-8. Schematic diagram of TPA and TTA processes in Iridium-based phosphorescent OLEDs. (MLCT = metal-to-ligand charge transfer; MC = metal center; D_n = ligand dissociation and EF = exciton formation)³⁷

For the TADF emitter, accelerating the RISC process efficiently converts triplet excitons into singlets, thereby suppressing triplet accumulation and extending device lifetime. On the other hand, good carrier-transporting properties are also crucial for facilitating exciton formation. An efficient exciton recombination not only enhances the efficiency and brightness of the OLED but also lowers the possibility of the TTA and TPA processes, thereby lengthening the device lifetime. Therefore, the judicious molecular design of host materials is essential for achieving both high efficiency and long operational stability.

1.4. Host-guest System in OLEDs

As aforementioned, in OLEDs, holes and electrons are injected from the anode and cathode, respectively, and then recombine within the emissive layer to form excitons, which subsequently emit light. In host-free OLEDs, strong intermolecular interactions and π - π stacking among emitter molecules are prone to red-shifted emission due to aggregation effects. In the host-guest system, the emitter is dispersed with different concentrations into a suitable host material, where intermolecular interactions can be effectively suppressed. The resulting spatial separation of emitters preserves color purity and maintains high photoluminescence efficiency.³⁸⁻⁴²

Furthermore, the host material plays a vital role in controlling carrier transport and exciton formation. Since most emitters possess low charge mobility, both holes and electrons predominantly migrate in the host matrix. By using host materials with different carrier transporting properties, the position of the recombination zone in the emissive layer can be effectively controlled. A well-balanced host ensures that holes and electrons recombine in the center of the emitting layer rather than being confined near interfaces, which in turn suppresses

exciton–exciton and exciton–polaron annihilation. Annihilation processes are the major causes of efficiency roll-off and device degradation under high-current density operation. In general, the host plays a significant role in both suppressing aggregation-induced spectral shifts and controlling charge dynamics in OLED devices.

1.4.1. Requirement of Hosts

Since host materials are so essential to govern the device performance, in order to achieve high efficiency, low efficiency roll-off and longer device lifetime, host material should meet several key requirements: high T_1 energy, suitable HOMO/LUMO energy level, and high thermal/chemical stability. Apart from intrinsic properties, the extrinsic properties of host materials, e.g., host-guest interaction that affects efficient energy transfer, are not negligible. The details will be discussed in the following section.

1.4.1.1. High T_1 Energy- Better Exciton Confinement

Both phosphorescence and TADF processes involve triplet excitons in their emissive pathways, and there are two energy transfer pathways, i.e., Förster and Dexter energy transfer, between host and guest. Excitons generated on the host can migrate to the emitter via these two mechanisms, where radiative decay or reverse intersystem crossing (RISC) efficiently emit light. To ensure energy can be transferred efficiently, the hosts must possess a sufficiently high T_1 . If the T_1 of the host is lower than that of the emitter, triplet excitons on the emitter can be transferred back to the host through the back energy transfer (BET) process (**Figure 1-9**). The excitons on the hosts cannot emit light efficiently but instead lose their energy through nonradiative decay, resulting in low external quantum efficiency (EQE).

A host with a higher triplet energy provides an energetic barrier that prevents BET, thereby confining triplet excitons to the emitter. This exciton confinement enhances internal quantum efficiency and suppresses exciton leakage to adjacent organic layers, which prevents unwanted chemical reactions. Therefore, designing host materials with high T_1 is a fundamental requirement for efficient exciton confinement and stable devices.

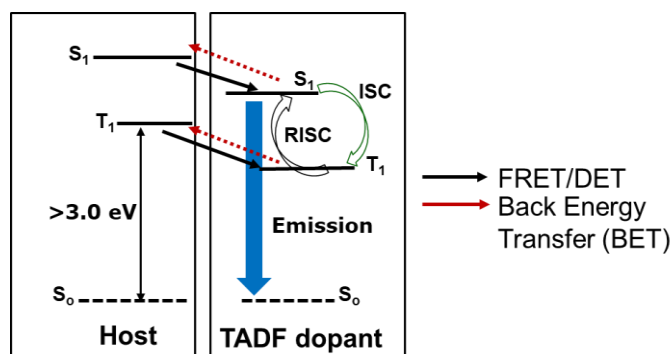


Figure 1-9. Energy confinement in host-guest system.

The effects of the host's T_1 on the photophysical properties and device performance of TADF-OLEDs were systematically investigated by Li et al.⁴³ In this work, the authors explored a series of polymeric host materials, namely, FI-PCzP, Ph-PCzP, Me-PCzP, and PEM-PCzP, with T_1 ranging from 2.30 to 2.80 eV. Blue TADF emitter SpiroAC-TRZ was doped in these polymeric host materials to fabricate the corresponding device. It was found that the EQEs based on these hosts showed huge dependence on T_1 energy levels. The EQE was increasing from 1.0% for **FI-PCzP** to 15.8% for **PEM-PCzP**. The low EQE was due to the relatively lower T_1 energy level of **FI-PCzP** compared with the **SpiroAC-TRZ** emitter, leading to exciton quenching. A shorter delayed lifetime was also observed from the corresponding doped film PL decay curve of **FI-PCzP** (**Figure 1-10**). This systematic comparison provided direct experimental evidence that the triplet energy alignment between host and emitter is a decisive factor governing TADF efficiency and exciton dynamics.

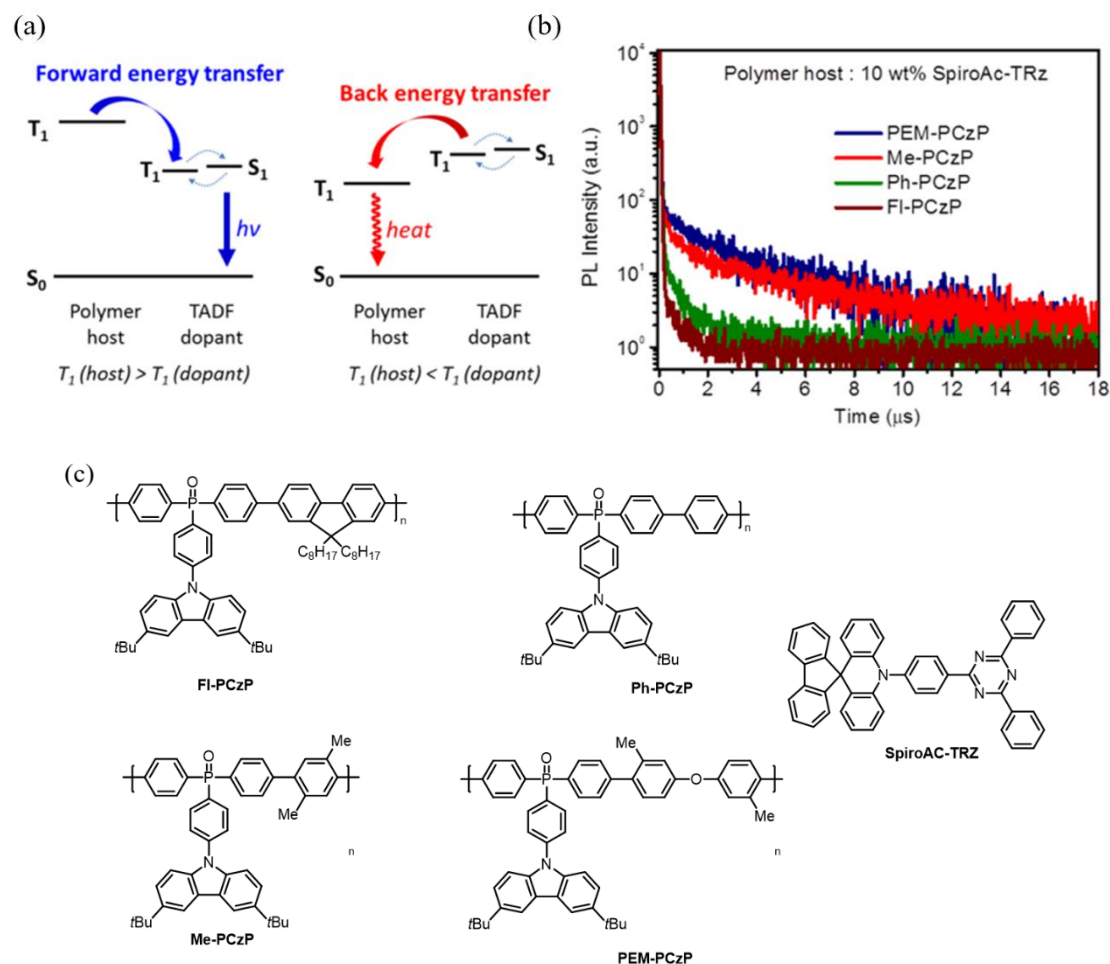


Figure 1-10. (a) Mechanism of back energy transfer from dopant to host; (b) transient PL decay curves for the polymer hosts: 10 wt% **SpiroAc-TRZ** films; (c) chemical structure.⁴³

1.4.1.2. Suitable HOMO/LUMO Energy Level-Recombination Zone

In addition to a high T_1 value, host materials having suitable HOMO/LUMO energy levels are necessary for efficient charge injection and balanced carrier transport. The HOMO level of the host should be aligned closely with that of the HTL, while its LUMO should be matched to that of the ETL, thereby minimizing injection barriers and lowering the driving voltage. At the same time, to confine exciton formation within the emitter, the host's HOMO should be deeper, whereas its LUMO should be shallower than that of the emitter (**Figure 1-11**). Such energy alignment not only enables smooth carrier transport but also broadens the exciton recombination zone, suppressing localized charge accumulation and minimizing exciton–polaron interactions. In contrast, mismatched energy levels can induce charge trapping, exciton leakage, or severe exciton–polaron annihilation, leading to decreased PLQY, lower EQE, and accelerated device degradation.

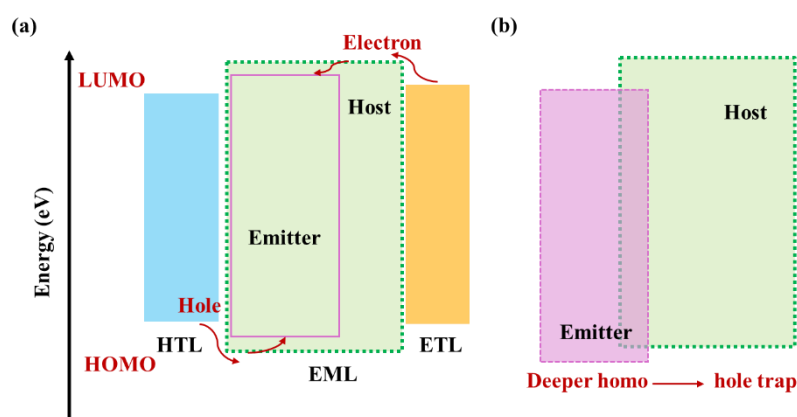


Figure 1-11. (a) Mechanism of energy transfer and HOMO/LUMO energy requirements; (b) mismatched energy level.

The significance of such energy-level alignment has been demonstrated by Yadav et al.⁴⁴ Using drift–diffusion simulations based on the following device structure: TAPC/CBP/ETL (ETL = **TPBi** or **BPhen**), they analyzed the influence of different HOMO/LUMO offsets between adjacent layers. The recombination profiles for devices employing **TPBi** and **BPhen** as ETLs clearly demonstrate the influence of energy-level alignment on charge balance. The device with **BPhen**, which possesses a lower LUMO level and higher electron mobility, exhibits a broader and more intense recombination zone that is approximately six orders of magnitude higher than the device based on **TPBi** (**Figure1-12**). This finding highlighted the dominant role of LUMO alignment in determining exciton formation efficiency and overall

device performance. Consistently, the broader and stronger recombination zone observed in the **BPhen**-based device indicates superior charge balance and enhanced operational stability when compared with the **TPBi**-based system.

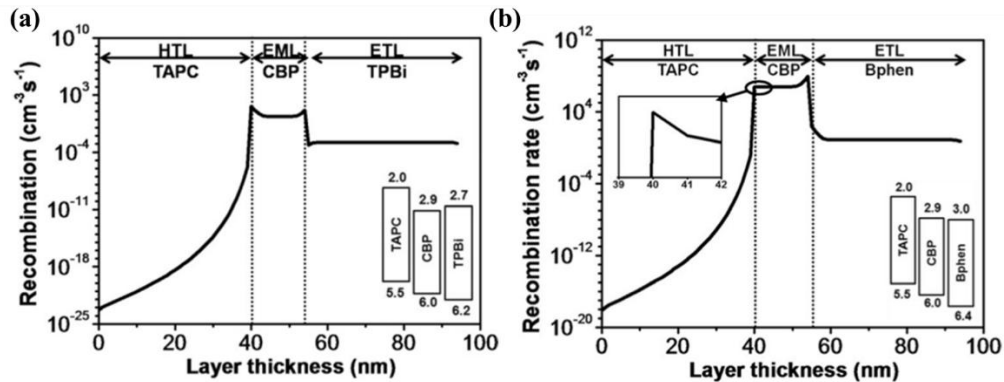


Figure1-12: (a) Recombination profile across the layers of the (a) TPBi-ETL and (b) Bphen-ETL based control device.⁴⁴

1.4.1.3. Charge Mobility and Carrier Balance in OLEDs

In addition to the HOMO/LUMO energy alignment, the ability of host materials to transport holes/electrons play a decisive role in determining carrier balance in OLEDs. Under OLED operation, devices are subject to strong internal electric fields on the order of 10^5 - 10^6 V cm^{-1} , such that charge transport is dominated by field-driven drift motion superimposed on the hopping nature of organic semiconductors. In this regime, the current density J is fundamentally governed by the following equation⁴⁵:

$$J = qn\mu E$$

where q is the elementary charge

n is the carrier density

μ is the charge carrier mobility

E is the electric field

This relation indicates that charge mobility directly determines the carrier flux through the organic layers and thus controls how efficiently injected carriers contribute to the operating current density, rather than merely influencing transport qualitatively.

In OLED devices, electron and hole mobilities differ intrinsically due to asymmetries in molecular orbital characteristics, electronic coupling, and energetic disorder. Consequently, even when electron and hole injection is energetically favorable, imbalanced mobilities inevitably result in unequal electron and hole current densities. Under such conditions, the carrier with lower mobility becomes the rate-limiting species for charge transport, leading to

carrier accumulation within the device. This accumulation is not a purely local transport phenomenon but a direct consequence of the steady-state continuity requirement, which enforces compensation through spatial redistribution of carrier densities.

As a result, carrier balance in OLEDs is strongly governed by the interplay between electron and hole mobilities. When mobilities are poorly matched, carrier accumulation occurs near interfaces where transport becomes limited, confining recombination to a narrow region with a high local exciton density. In contrast, host materials that support more balanced electron and hole transport enable comparable carrier fluxes, suppress excessive accumulation, and promote a broader recombination zone with a more uniform carrier distribution across the emissive layer. This effect is particularly pronounced under constant current operation, where insufficient mobility necessitates higher local carrier densities to sustain the same current density, thereby intensifying carrier accumulation and exciton–polaron interactions. This behavior has been experimentally demonstrated by Culligan et al., who showed that increased hole mobility in the emissive layer leads to a spatially broader recombination zone and reduced carrier accumulation, thereby contributing to improved operational stability in OLEDs. This effect is particularly pronounced under constant-current operation, where insufficient mobility necessitates higher local carrier densities to sustain the same current density, thereby intensifying carrier accumulation and exciton–polaron interactions.⁴⁶

From a materials design perspective, charge mobility should therefore be regarded as an intrinsic requirement of host materials rather than a secondary or purely kinetic parameter. Hosts that provide suitable, balanced charge-transport characteristics not only facilitate efficient current flow but also mitigate excessive carrier accumulation, which is closely linked to efficiency roll-off and operational degradation. Consequently, optimizing charge mobility constitutes a critical strategy for achieving stable carrier balance and robust device performance, complementing the roles of energy level alignment and exciton confinement discussed in the preceding section.

1.4.1.4. Thermal and Chemical Stability of Hosts

The thermal and chemical stability of the host material are vital to the operational lifetime of OLEDs, particularly for blue devices that involve high-energy triplet excitons (~ 3 eV). As reported by Tankelevičiūtė et al., host materials with higher glass transition temperatures and greater molecular rigidity exhibit improved morphological stability during electrical operation.⁴⁷ The stable thin film morphology effectively suppresses exciton-induced degradation, hence lengthening the device lifetime. In contrast, hosts with lower T_g tend to undergo phase separation or interfacial roughening, creating non-radiative recombination

centers that accelerate device degradation and efficiency loss. It is well known that when host materials have a higher molecular weight, they will have higher T_g ; however, higher molecular weight is usually accompanied by an extended conjugation, which results in low T_1 . Therefore, it is necessary to have a good molecular design to balance both T_g and T_1 .

From a chemical perspective, exciton- and polaron-induced bond cleavage represents a dominant degradation pathway in organic hosts. Bonds with low dissociation energies, such as C–N or C–S, are particularly susceptible to scission under high exciton density, generating radical species that trigger chain degradation reactions. Enhancing bond dissociation energy (BDE) and delocalizing frontier orbitals over rigid frameworks can effectively mitigate such damage. Lin and co-workers systematically compared host materials with varying bond dissociation energies (BDEs).⁴⁸ Hosts containing weak C–N or C–S bonds (BDE $\approx$ 3.0 eV) underwent rapid exciton-induced degradation, resulting in shortened device lifetimes ($LT_{50} \sim$ 2 h), whereas **mCBP** with higher C–C BDE ($\sim$ 4.4 eV) maintained its chemical integrity and achieved a prolonged operational lifetime of $\sim$ 18 h. Consequently, hosts possessing both high thermal and chemical robustness provide a stable matrix for exciton recombination, leading to improved efficiency retention and extended operational lifetime of OLED devices.

1.4.1.5. Host–Guest Interactions and Molecular Orientation

The photophysical behavior and device performance of OLEDs are not only determined by the intrinsic properties of emitters but are also profoundly affected by host–guest interactions and molecular orientation in the emissive layer. The polarity, rigidity, and molecular arrangement of the host matrix can alter the electronic environment of the dopant, influencing exciton formation, energy transfer, and charge balance. Excessive host polarity or strong dipole–dipole interactions often cause spectral shifts, exciton quenching, or nonradiative decay, whereas a well-balanced host environment enables stable exciton recombination and improved efficiency.

Reineke et al. systematically investigated the effects of host polarity and dipolar interactions on the excited-state dynamics of a blue TADF polymer (P1).⁴⁹ When P1 was doped into hosts of increasing dipole moments (**mCP**: 1.4 D, **CzSi**: 2.7 D, and **PO-T2T**: 4.2 D), the delayed fluorescence quantum yield (Φ_{DF}) decreased drastically from 16.9% in **mCP** to 0.003% in **PO-T2T**, along with a reduction of PLQY from 49.8% to 23.9%. Consequently, the OLED fabricated with **PO-T2T** exhibited a marked drop in external quantum efficiency (EQE) from 12.6% to below 3%, and its operational lifetime (LT_{50}) shortened by more than one order of magnitude. This efficiency loss was attributed to strong dipolar fields and solid-state solvation

effects that accelerated exciton–dipole interactions and promoted nonradiative decay. In contrast, hosts with moderate polarity and rigid backbones effectively preserved ΔE_{ST} and delayed fluorescence efficiency, maintaining both higher EQE (>10%) and longer operational stability.

In addition to polarity effects, the molecular orientation of the emissive layer plays a crucial role in determining device efficiency. Adachi et al. demonstrated that employing a rigid host such as **6CzPh** induced almost complete horizontal orientation of TADF emitters such as **4CzIPN**.²⁸ The fraction of horizontally oriented dipoles (Θ_h) increased from 72% ($S = -0.15$) in **mCBP** to 100% ($S = -0.50$) in **6CzPh**, leading to a significant enhancement of light outcoupling efficiency ($\eta_{out} > 30\%$). As a result, the device EQE improved from 18.5% to 27.3%, while the operational lifetime (LT_{50} at 1000 cd m^{-2}) increased from 40 to over 120 hours. The improved performance was attributed to the suppression of exciton quenching and polaron–exciton annihilation due to the stable, horizontally oriented emissive dipoles.

These studies reveal that both host–guest interactions and molecular orientation critically determine the exciton recombination efficiency, energy transfer dynamics, and operational stability of OLEDs. Rational host design should therefore aim to achieve balanced dipolar environments and controlled molecular orientation to realize highly efficient and stable devices.

1.4.2. Classification of Host Materials

Host materials are typically composed of electron-donating (D) and/or electron-accepting (A) units, which can tune their charge-transporting properties or energy levels. Rigid aromatic or heteroaromatic cores, such as carbazole, triphenylamine, phenoxazine, triazine, or phosphine oxide moieties, which provide both high triplet energy and good morphological stability, were largely used for constructing efficient host materials. According to the charge-transporting characteristics, host materials can be simply categorized into unipolar and ambipolar hosts.

Unipolar host materials refer to hosts that can transport only one type of charge carrier and can be further classified into hole-transporting (*p*-type) and electron-transporting (*n*-type) hosts. *P*-type hosts, which consist of electron-donating groups such as carbazole, triphenylamine (**TPA**), and diphenylamine (**DPA**), have a high-lying HOMO level (≈ -5.2 to -5.8 eV) and possess relatively poor electron mobility. Commonly used *p*-type hosts include **mCBP** (*N,N'*-dicarbazolylbiphenyl), **mCP** (*1,3-bis*(*N*-carbazolyl)benzene), and **TCTA** (*tris*(4-carbazoyl-9-ylphenyl)amine). The chemical structures are illustrated in **Figure1-13**. The π -

extended carbazole or triarylamine units form a rigid conjugated system that ensures a high triplet energy ($T_1 \approx 2.8\text{--}3.0\text{ eV}$), which is suitable for blue phosphorescent and TADF emitters.

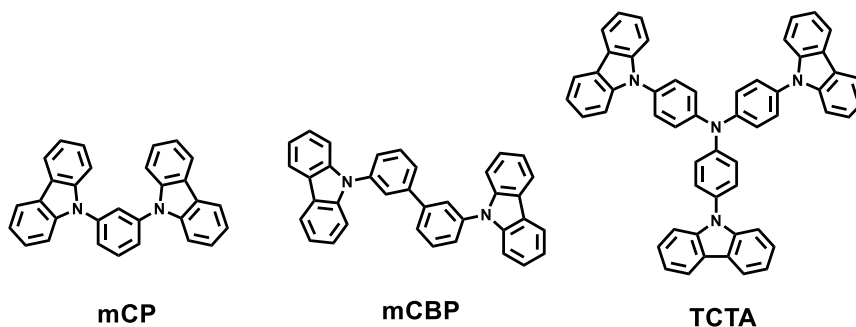


Figure1-13: Representative *p*-type host materials.

N-type hosts that contain electron-withdrawing groups, such as triazine, oxadiazole, or phosphine oxide units, exhibit relatively low LUMO levels (≈ -2.5 to -3.0 eV) and display relatively low hole mobility. Commonly used *n*-type hosts include **T2T** (2,4,6-*tris*(1,3,5-triazinyl)benzene), **TPBi** (2,2',2''-(1,3,5-benzinetriyl)-*tris*(1-phenyl-1-*H*-benzimidazole)), and **DPEPO** (*bis*[2-(diphenylphosphino)phenyl]ether oxide). The chemical structures are depicted in **Figure1-14**. These hosts efficiently confine triplet excitons due to their high T_1 s. However, their poor hole injection often results in a higher turn-on voltage.

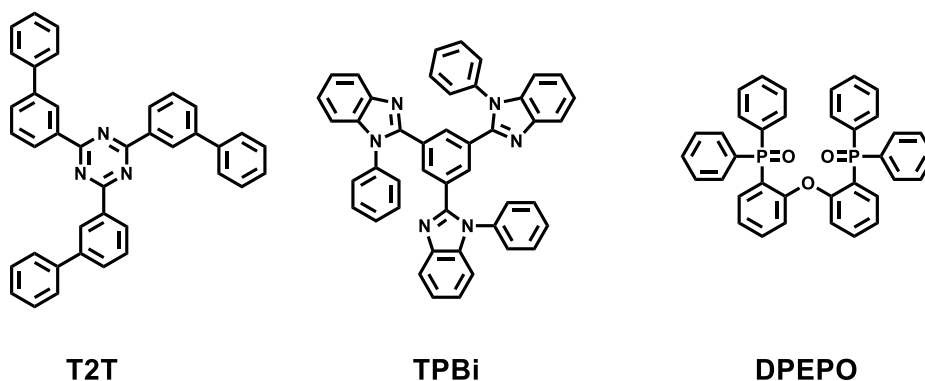


Figure1-14: Representative *n*-type host materials.

Although both *p*-type and *n*-type hosts exhibit good efficiency, they generally suffer from poor device stability. This can be attributed to the unbalanced charge carriers, resulting in the accumulation of charges or traps at the EML/ETL and EML/HTL interface, respectively. The imbalanced carrier transport properties gradually shift the recombination zone and increase exciton leakage. The leaked excitons further penetrate the adjacent layers, leading to chemical degradation and a decrease in the device stability. Therefore, unipolar hosts are usually co-

doped with other host materials, i.e., a mixed host system, to achieve the balance between device efficiency and lifetime.

In contrast to a mixed host system, an ambipolar host consists of both donor and acceptor units, which transport a hole and an electron effectively. It is expected that an ambipolar host gives balanced charge transport, hence leading to an effective exciton confinement when compared to a device based on unipolar hosts. The D-A structure enables the separation of HOMO and LUMO distributions with tunable T_1 and charge mobility. Commonly used ambipolar hosts, e.g., **PYD2**, **TRZ2**, and **PYD2**, have demonstrated the characteristics of ambipolar hosts in achieving both high efficiency and long device stability in TADF OLEDs (**Figure1-15**). However, D-A-type ambipolar hosts also suffer from intrinsic limitations caused by strong intramolecular donor-acceptor coupling, which results in CT character. The polar CT character will interact with the host, leading to a shift in the emission spectrum. Besides, asymmetric structures often lead to poor morphological and thermal stability. To mitigate these issues, recent strategies employ rigid or non-conjugated linkers, such as silicon, oxygen bridges, or meta-linked π -spacers to weaken the coupling of D and A units while retaining charge balance and high T_1 .

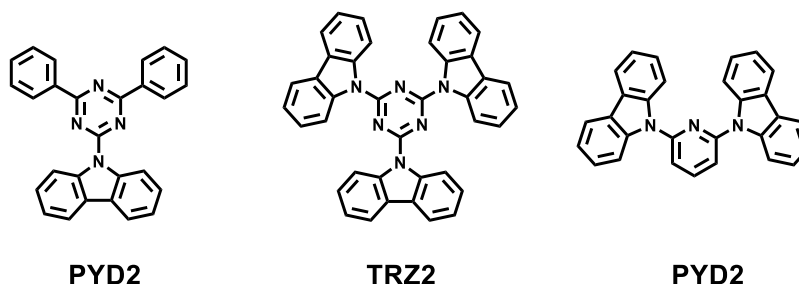


Figure1-15: Representative examples of ambipolar host materials.

In addition to conventional D-A ambipolar hosts, several symmetrical D-A type ambipolar hosts have been developed to overcome the drawbacks associated with strong coupling of D and A units. Typically, symmetrical D-A ambipolar hosts are constructed by integrating multiple hole-transporting moieties and electron-transporting units into a single, rigid, and highly symmetric molecular scaffold. Because the donor and acceptor segments are electronically decoupled, this gives a zero net dipole moment. The non-polar ambipolar host can still retain high triplet energy ($T_1 > 2.8$ eV) and maintain balanced carrier transport.

In all, the selection of an appropriate host type is crucial for having balanced charge transport, efficient exciton confinement, and high device stability in OLEDs.

1.5. Motivation for This Study

In commercial OLEDs, red and green devices have been dominated by phosphorescent emitters, while blue devices rely on blue fluorescent emitters that offer only limited efficiency and reasonable stability. Many efforts have been made to develop new blue TADF emitters, e.g., with high k_{RISC} , to achieve better device performance.⁵⁰ At present, deep-blue OLEDs can achieve EQE_{max} of approximately 41% with an emission peak near 462 nm, while green and red OLEDs reach approximately 39% (≈ 520 nm) and 35% (≈ 620 nm), respectively.⁵¹⁻⁵³ Despite their high efficiency, most blue devices still suffer from limited operational lifetimes. One of the primary reasons is that stable host materials with high T_1 energies are still limited, impeding further development. In fact, TADF emitters usually possess deeper HOMO energy levels than those of phosphorescent emitters, in which their hole- and electron-transporting properties are completely different. Although numerous high-performance host materials have been reported in the literature, most are structurally tailored for phosphorescent emitters with suitable HOMO/LUMO energy levels.⁵⁴ Thus, there is a need for rational molecular design of new host materials towards efficient and stable TADF-OLEDs.

As a result, we focus on the design and synthesis of new host materials with high T_1 energies in this study. By gradually modifying the molecular structure and examining the intrinsic and extrinsic properties of hosts, efficient OLEDs with high efficiency, high stability, and low driving voltage were achieved. All newly synthesized host materials are well-characterized, and their photophysical, electrochemical and thermal properties are also studied in detail.

In Chapter 2, two azasiline-based host materials, **2SiPh** and **2SiPy**, have been designed by employing phenyl and pyridine bridges to azasiline. And both hosts showed high T_1 more than 3.0 eV in both solution and film states. The green device based on **2SiPh** showed an EQE_{max} of 16.6%, but its LT_{95} device stability was limited to 2 hours. Further study found that the strong hole-transporting property of azasiline led to unbalanced carrier transport, thus resulting in severe roll-offs and poor device stability. But the introduction of the pyridine unit significantly improved the electron-transporting ability.

In Chapter 3, based on these findings, the commonly used p-type host material **mCBP** was chemically modified with pyridine to yield three pyridine-based hosts, **mCBP-1N**, **CzPyPhCz**, and **CzPyBF**, to improve carrier-transporting properties. Among them, **mCBP-1N** showed improved thermal stability and longer device lifetime compared with **mCBP**, while **CzPyPhCz** showed the shallowest HOMO energy, resulting in the lowest turn-on voltage with the shortest device lifetime in TADF-OLED. Surprisingly, **CzPyBF**, containing a dibenzofuran

substituent, showed the best overall device performance with an EQE_{max} of 20.3% and LT₉₅ of 26 hours, which is 1.8 times longer than the **mCBP**-based device. The improved performance was attributed to more balanced carrier transport properties and better electrochemical stability, making **CzPyBF** the champion device. However, the lifetime remains unsatisfactory, and further improvement is necessary.

In Chapter 4, building on the best performance of **CzPyBF**, we further improved device stability through structural modifications of carbazole-dibenzofuran-based host materials. Three regio-isomer hosts, **1-BF**, **2-BF**, and **4-BF**, displayed similar photophysics but markedly different device behaviors. **4-BF** exhibited the best electrochemical stability but the shortest LT₉₅ device lifetime of 8 hours, whereas **1-BF** and **2-BF** showed LT₉₅ lifetimes of 67 and 56 hours, respectively, despite slightly lower electrochemical stability. These results indicate that while the hosts' intrinsic properties affect device stability, the balance of carrier transport plays a more decisive role.

In Chapter 5, we extend our interest from host materials to host-free OLEDs. A sky-blue emitter, **36Me-HDT1**, was designed by structural modification of **HDT1**. The introduction of bulky 3,6-dimethylcarbazole in **36Me-HDT1** enhanced donor strength, suppressed aggregation, and accelerated reverse intersystem crossing ($k_{RISC} = 1.4 \times 10^6 \text{ s}^{-1}$). Consequently, **36Me-HDT1** exhibited a PLQY of 80% in neat film and achieved an EQE_{max} of 21.3% at 517 nm in the non-doped OLED, outperforming its parent emitter **HDT1** (16.5%, 507 nm). This result offers a promising pathway toward simplified and stable host-free TADF OLEDs.

Chapter 2

Azasiline-based Host Materials for Thermally Activated Delayed Fluorescence Organic Light-Emitting Diodes

2.1. Introduction

TADF-OLEDs have attracted tremendous attention as 3rd generation display and lighting technologies. Despite numerous successful demonstrations of efficient red, green, and blue (RGB) TADF-OLEDs, most of the works found in the literature focus on the design and synthesis of an RGB TADF dopant, while less attention has been given to the design of host materials for their use in TADF-OLEDs.⁵⁵⁻⁵⁷ Indeed, a good host material can largely improve the efficiency, device stability⁵⁸, or driving voltage⁵⁹ in TADF-OLEDs. The development of host materials is of great importance. In particular, hosts with a high T_1 are indispensable for blue and green OLEDs, as they prevent reverse energy transfer from the emitter and secure efficient exciton confinement. However, hosts with high- T_1 energies remain limited. Conventional high T_1 building units (**Figure 2-1**), such as carbazole and phosphine oxide analogues, have been widely employed, but each suffers from intrinsic drawbacks: carbazole derivatives often lack sufficient morphological stability, while phosphine oxide units, although providing very high T_1 energies, are chemically unstable.⁶⁰ These limitations underscore the urgent need for alternative motifs that can combine high triplet energy with improved stability.

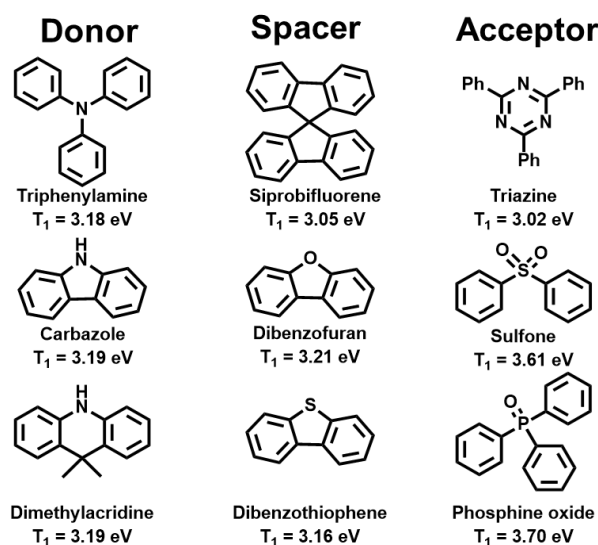


Figure 2-1: Organic chromophores possessing high T_1 energy levels.

To address this challenge, the azasiline unit is introduced for host design. Incorporating silicon into the conjugated framework is expected to provide high triplet energy. Besides, pyridine is also introduced to enhance electron-transport ability through its unique electronic characteristics. Based on this concept, two azasiline-based host materials, **2SiPh** and **2SiPy**, were designed and synthesized, aiming to provide a new molecular design principle for high-

T₁, stable, silicon-containing hosts. The structures are shown in **Figure 2-2**.

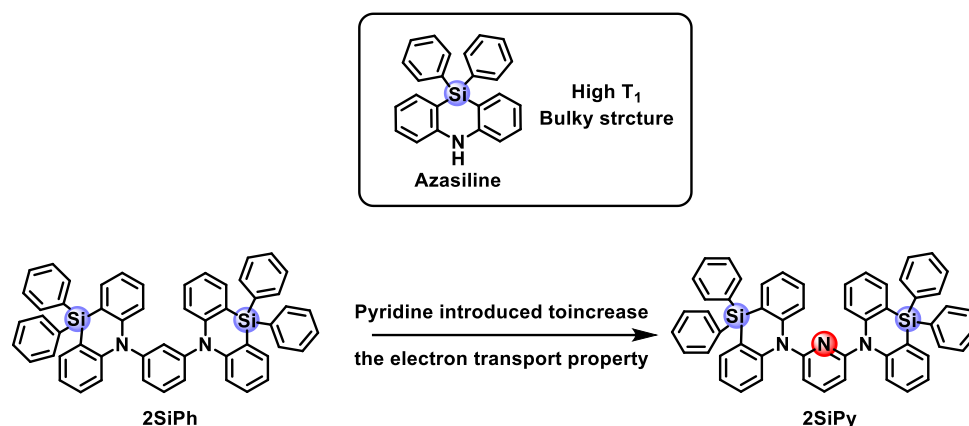


Figure 2-2: Target molecules designed in this study.

2.2. Experimental

2.2.1. Material

All reagents were purchased from commercial sources and used without further purification. **2SiPh** and **2SiPy** were characterized by nuclear magnetic resonance (NMR) and ¹H and ¹³C. ¹H NMR and ¹³C NMR spectra were obtained in CDCl₃ with a Bruker Biospin Avance-III 500 NMR spectrometer at ambient temperature. Chemical shifts (δ) are given in parts per million (ppm) relative to tetramethylsilane (TMS; δ = 0) as the internal reference.

2.2.2. Photophysical and Thermal Measurements

Ultraviolet–visible (UV–vis) absorption was recorded by a PerkinElmer Lambda 950 KPA spectrophotometer. Photoluminescence (PL) spectra and phosphorescence spectra at 77 K were both obtained using a JASCO FP-8600 spectrofluorometer. Absolute PL quantum yields were measured under a nitrogen atmosphere with a Quantaurus-QY system (C11347-11, Hamamatsu Photonics) with an excitation wavelength of 360 nm. Transient PL decay profiles of both solution and doped-film samples at room temperature were acquired on a Quantaurus-Tau fluorescence lifetime spectrometer (C11367-03, Hamamatsu Photonics). The angular dependence of PL intensity was simulated using SETFOS 5.1 (Fluxim) software to estimate the dipole orientation of the doped films and, consequently, their light-outcoupling efficiency. Thermal stability was evaluated through thermogravimetric analysis (TGA) performed on a Bruker TG-DTA 2400SA instrument at a heating rate of 10 °C min⁻¹ under nitrogen flow. Differential scanning calorimetry (DSC) measurements were carried out on a Netzsch DSC204 Phoenix calorimeter at a scan rate of 5 °C min⁻¹ in a nitrogen atmosphere. Electrochemical properties were investigated at room temperature by cyclic voltammetry (CV) and differential

pulse voltammetry (DPV) using an ALS Co., Ltd. electrochemical analyzer (Model 608D). Measurements employed a standard three-electrode configuration consisting of a glassy-carbon working electrode, a platinum-wire counter electrode, and an Ag/Ag⁺ reference electrode. Ferrocene was used as the internal standard, and all potentials were calibrated against the Fc/Fc⁺ redox couple. The measurements were performed in argon-purged dichloromethane containing 0.10 mol L⁻¹ tetrabutylammonium hexafluorophosphate (n-Bu₄PF₆) as the supporting electrolyte. The HOMO and LUMO energy levels were determined using the equations: $E_{\text{HOMO}} = - (E_{\text{ox}} - E_{1/2, \text{ferrocene}}) - 4.8 \text{ eV}$, and $E_{\text{LUMO}} = - (E_{\text{red}} - E_{1/2, \text{ferrocene}}) - 4.8 \text{ eV}$. The scan rate for CV was set at 0.10 V s⁻¹, whereas DPV was performed using a step potential of 4.0 mV and a pulse amplitude of 50 mV. The ionization potentials, corresponding to the HOMO energy levels of thin-film samples, were determined at low photon energy via the RIKEN KEIKI AC-3E photoelectron yield spectrometer.

2.2.3. Device Fabrication and Evaluation

OLED devices were constructed on glass substrates coated with a 100 nm patterned indium tin oxide (ITO) layer. All the ITO substrates were successively cleaned in an ultrasonic bath for 10 min each with detergent, deionized water, acetone, and isopropanol, followed by drying under boiled isopropanol. After that, the substrates were treated with ultraviolet–ozone for 15 min immediately before vacuum deposition.

All functional layers were deposited by thermal evaporation under a high vacuum of approximately 1.0×10^{-5} Pa. After deposition, the devices were encapsulated inside a nitrogen-filled glovebox (O₂ < 0.1 ppm, H₂O < 0.1 ppm) using glass lids and epoxy adhesive. Current density–voltage–luminance (J–V–L) characteristics were measured at room temperature under DC bias using a source meter (Keysight B2911A, Keysight Technologies, USA) coupled with a luminance meter (CS-2000, Konica Minolta, Japan). Device lifetimes were evaluated at a constant current density of 3.3 mA cm⁻² using a luminance meter (SR-3AR, TOPCON, Japan).

2.3. Results and Discussion

2.3.1. Synthesis

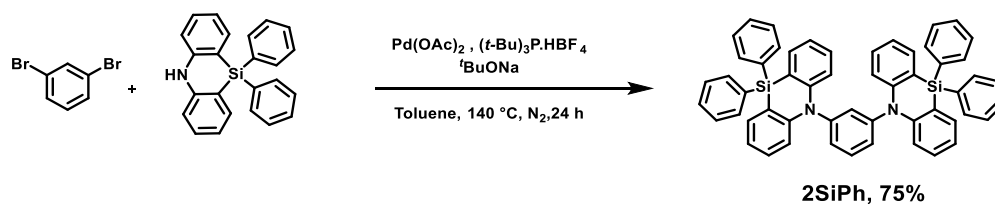


Figure 2-3. Synthesis route of **2SiPh**.

The azasiline was prepared according to the synthetic procedure reported in the literature.⁶¹ **2SiPh** was synthesized by the reaction of 1,3-dibromobenzene and azasiline via the Buchwald reaction (**Figure 2-3**). The details were as follows. 1,3-dibromobenzene (471.8 mg, 2.00 mmol, 1.0 eq), azasiline (1.745g, 5.00 mmol, 2.5 eq), *t*-BuONa (1.745g, 5.00 mmol, 2.5 eq), HBF₄·(t-Bu)₃P (58.0 mg, 0.2 mmol, 0.1 eq) and Pd(OAc)₂ (0.224 g, 0.100 mmol, 0.05 eq) were dissolved in degassed toluene (20 ml) under nitrogen atmosphere. The mixture was heated to reflux for 24 hours. After cooling to room temperature, the solution was filtered and washed with dichloromethane. The filtrate was evaporated under reduced pressure, and the residue was purified by column chromatography to give the product as a white solid with 75% yield. ¹H NMR (500 MHz, CD₂Cl₂) δ 7.92 (t, *J* = 7.9 Hz, 1H), 7.57 (ddd, *J* = 15.3, 7.7, 1.8 Hz, 12H), 7.50 (dd, *J* = 7.9, 2.1 Hz, 2H), 7.43 – 7.30 (m, 12H), 7.25 (ddd, *J* = 8.8, 5.3, 1.8 Hz, 5H), 6.94 (t, *J* = 7.2 Hz, 4H), 6.63 (d, *J* = 8.7 Hz, 4H). ¹³C NMR (500 MHz, CD₂Cl₂) δ 150.15, 146.84, 136.34, 136.31, 135.63, 134.57, 133.76, 131.77, 130.86, 130.06, 128.36, 120.57, 117.76, 116.15. (**Figure 2-4** and **2-5**)

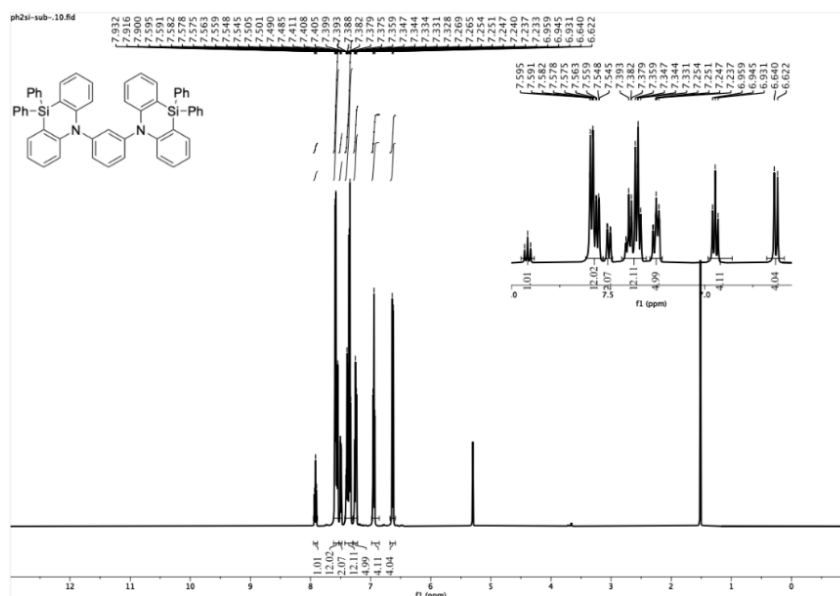


Figure 2-4. ¹H NMR of **2SiPh**.

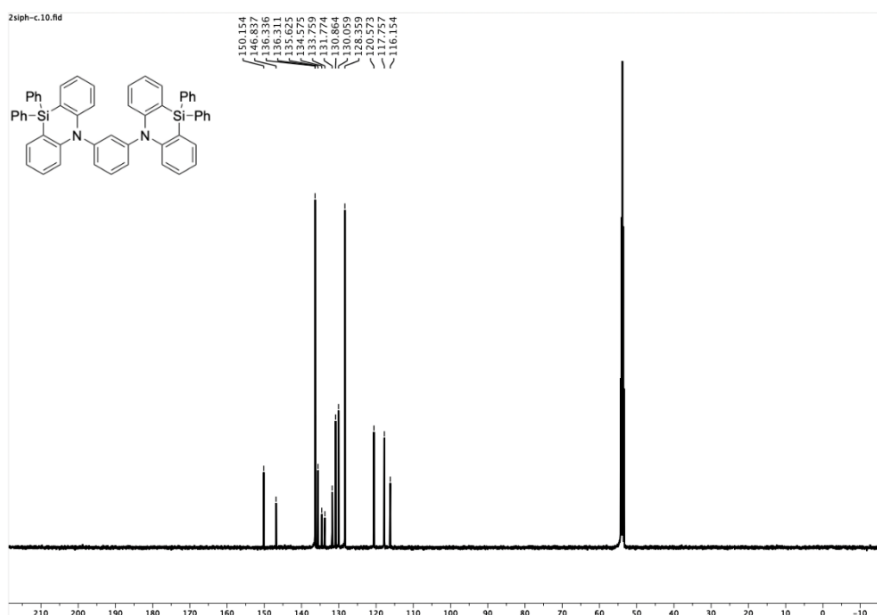


Figure 2-5. ¹³C NMR of 2SiPh.

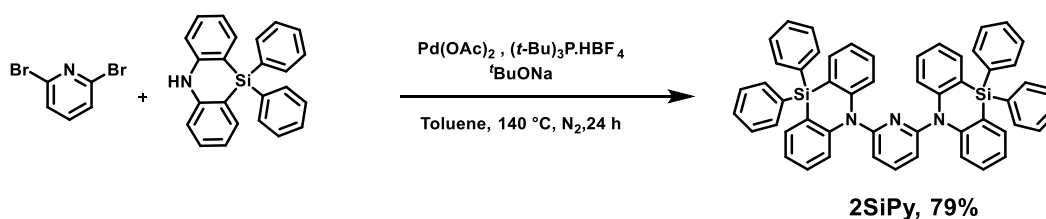


Figure 2-6. Synthesis route of 2SiPh.

2SiPy was synthesized with a procedure similar to that used for 2SiPh, but with 2,6-dibromopyridine (473.8 mg, 2.0 mmol) instead of 1,3-dibromobenzene as a white solid in 79% yield (1.22 g, 1.58 mmol) (Figure 2-6). ¹H NMR (500 MHz, CD_2Cl_2): δ =7.60 – 7.56 (m, 8H), 7.53 (dd, J = 7.4, 1.8 Hz, 4H), 7.47 – 7.42 (m, 4H), 7.41 – 7.32 (m, 13H), 7.17 – 7.11 (m, 8H), 6.52 (d, J = 7.8 Hz, 2H). ¹³C NMR (500 MHz, CD_2Cl_2) δ 156.91, 149.78, 141.04, 136.48, 135.55, 133.77, 130.46, 130.21, 128.31, 125.03, 123.22, 123.14, 112.57. (Figure 2-67 and 2-8)

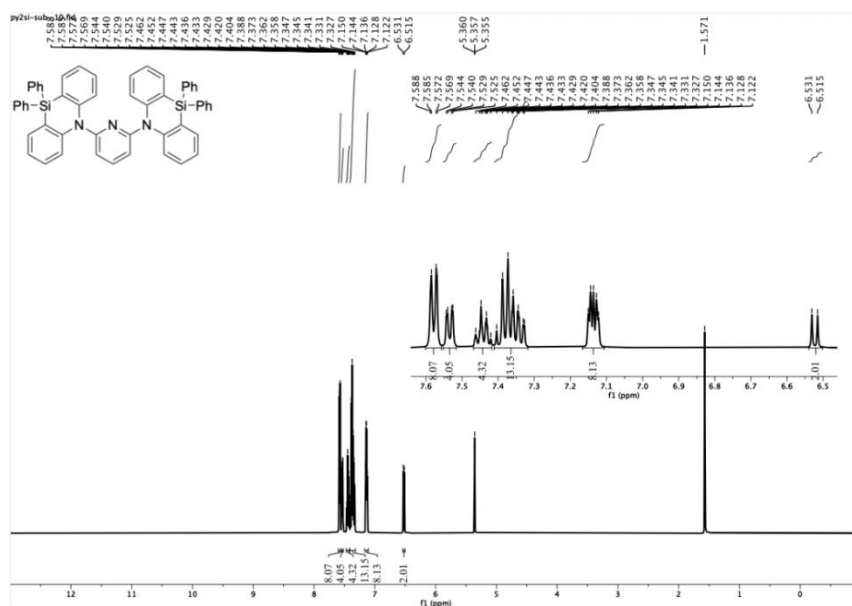


Figure 2-7 ¹H NMR of 2SiPy.

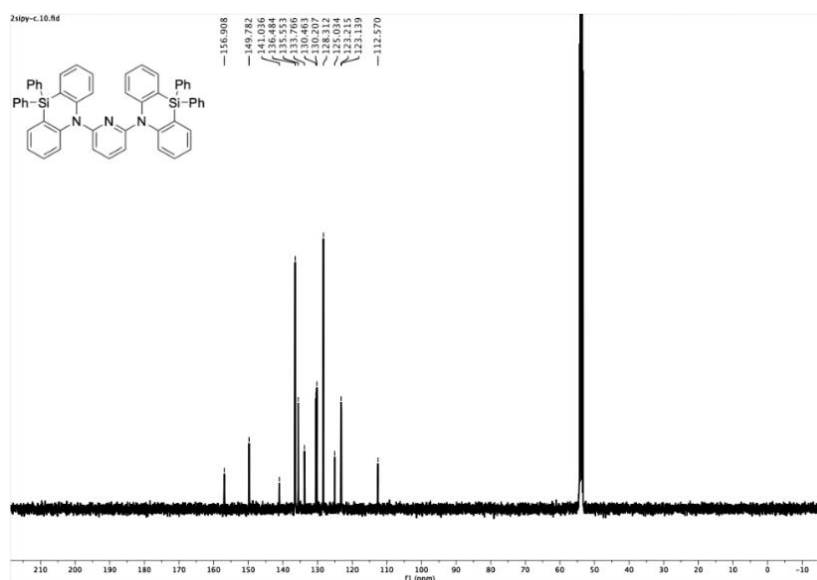


Figure 2-8 ¹³C NMR of 2SiPy.

2.3.2. Theoretical Calculations

Time-dependent density functional theory (TD-DFT) calculations at the B3LYP/6-31G level were conducted to predict the S_1 and T_1 energy levels of two hosts and their corresponding HOMO and LUMO distributions. The HOMO and LUMO energy levels of **2SiPh** were calculated to be -5.42 and -1.21 eV, respectively, while the HOMO was mainly localized on the two azasiline units and the LUMO localized over the central phenyl ring. After introducing the pyridine, the HOMO level of **2SiPy** became shallower to -5.32 eV. This can be attributed to the polar nature of **2SiPy**, which gives rise to a charge-transfer (CT) character and leads to

a narrower energy gap. The S_1 energies were calculated to be 3.48 eV for **2SiPh** and 3.43 eV for **2SiPy**. As expected, both hosts showed high T_1 energies of 3.24 eV for **2SiPh** and 3.25 eV for **2SiPy**. It is expected that the high T_1 energies of both hosts are enough to confine the excitons of blue and green dopants. (**Figure 2-9**)

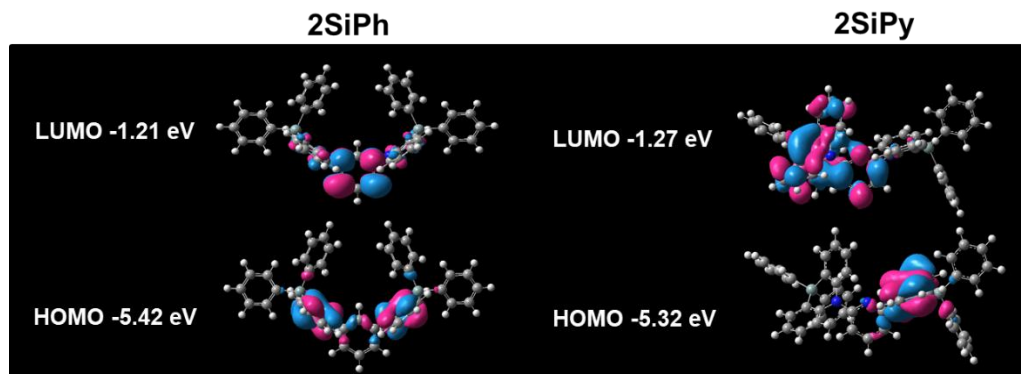


Figure 2-9. Molecular orbitals of **2SiPh** and **2SiPy**.

2.3.3. Photophysical Study

The photophysical properties of the **2SiPh** and **2SiPy** were first studied by ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) spectrometry in toluene solutions (**Figure 2-10**). Both hosts exhibited absorption bands below 400 nm, which originate from localized π - π^* transitions. Owing to its donor-acceptor character, **2SiPy** exhibits a slightly red-shifted emission together with a weak absorption tail extending beyond 350 nm, when compared to that of **2SiPh**. Interestingly, the absorption and emission spectra of **2SiPh** showed a sharp cutoff. Thus, the excitation spectrum was measured to confirm the mirroring of the cutoff region of both excitation and emission spectra (**Figure 2-11**). From the excitation and emission spectra, it was confirmed that the mirroring of the cutoff region of both spectra; the peak of 338 nm on the excitation spectra is related to the excitation band corresponding to the emission ($\lambda_{em} = 350$ nm). The S_1 energies were measured from the onset of fluorescent spectra, which were 3.7, and 3.5 eV for **2SiPh** and **2SiPy**, respectively. The T_1 energies, obtained from the onset of phosphorescence spectra, were found to be 3.2 eV for **2SiPh** and **2SiPy**, which are in agreement with the calculated values. Photophysical properties of neat films were also evaluated (**Figure 2-12**). Surprisingly, the T_1 energies were both very high, which measured to be 3.1, and 3.0 eV for **2SiPh** and **2SiPy**, respectively. The high T_1 energies can be attributed to the bulky and twisted molecular structures, which reduce the conjugation between each fragment. Such high T_1 energies highlight their potential as promising host candidates for OLEDs.

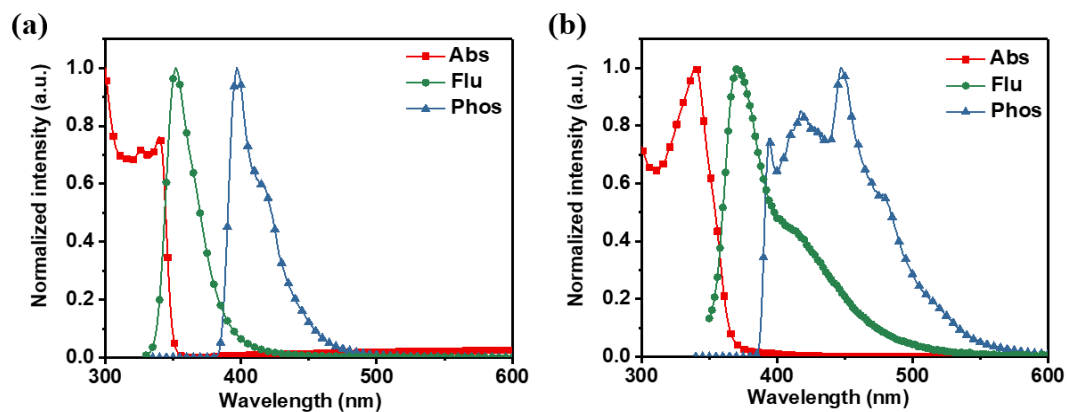


Figure 2-10. (a) Absorption and photoluminescence spectra of (a) **2SiPh** and (b) **2SiPy** in toluene at 298 K and at 77 K (1.0×10^{-5} mol dm $^{-3}$).

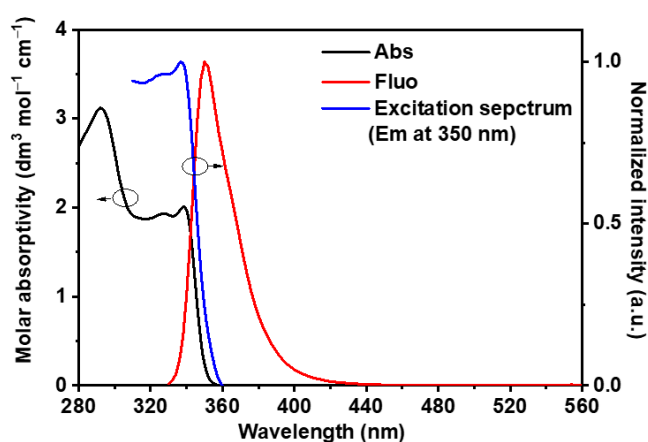


Figure 2-11. Absorption, emission, and excitation spectra of **2SiPh** in toluene solution at a concentration of 1.0×10^{-5} mol dm $^{-3}$.

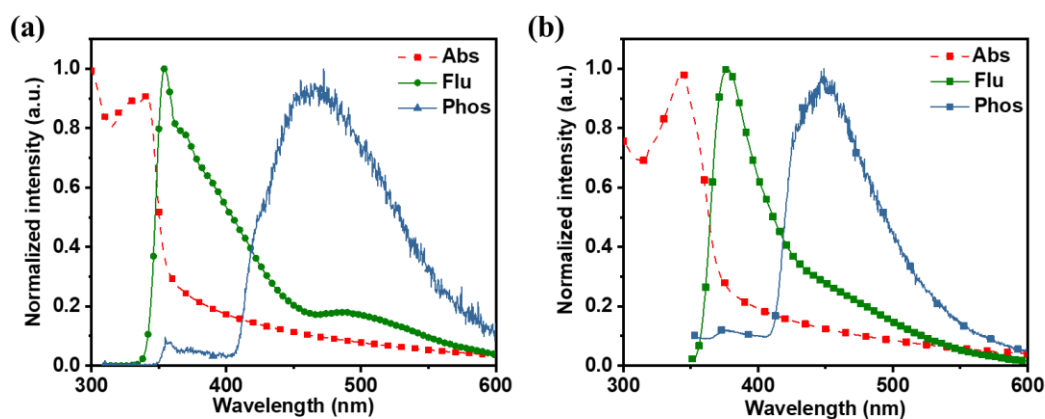


Figure 2-12. (a) Absorption and photoluminescence spectra of (a) **2SiPh** and (b) **2SiPy** in neat film at 298 K and at 77 K.

The HOMOs of both hosts were measured by cyclic voltammetry (solution) and photo-

electron spectroscopy (thin film) (**Figures 2-13** and **2-14**). It was found that **2SiPh** and **2SiPy** displayed similar HOMO levels of -5.5 and -5.4 eV, respectively, in the solution state.

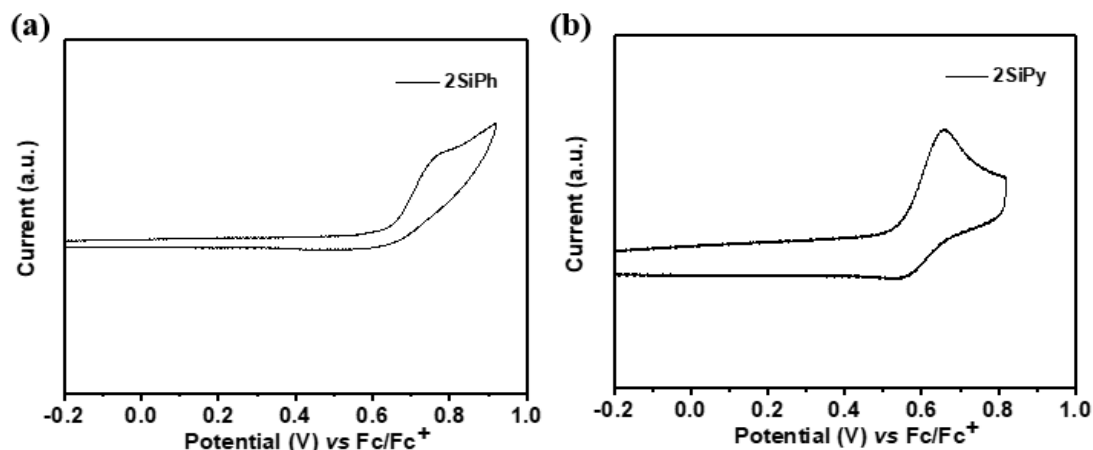


Figure 2-13. Cyclic voltammogram of the oxidative scan of **2SiPh** and **2SiPy** in *N,N*-dimethylformamide.

However, in the neat films, **2SiPy** showed a slightly shallower HOMO level of -5.7 eV when compared to that of **2SiPh** (-5.9 eV), which is consistent with the calculations. Since the shallower HOMO energy, we expect a better hole transporting property of **2SiPy**.

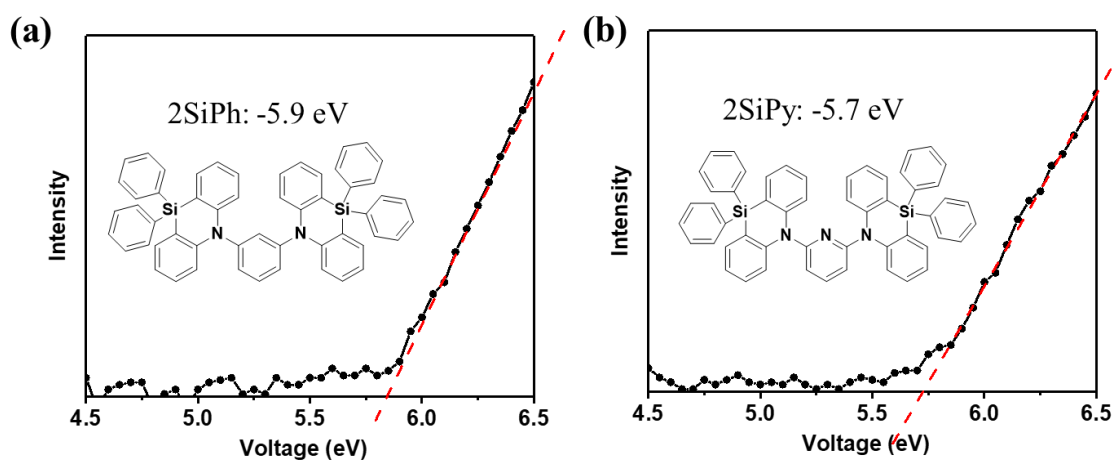


Figure 2-14. Photoelectron spectral measurements of (a) **2SiPh**, (b) **2SiPy** neat films under nitrogen atmosphere.

The thermal stability was another critical parameter. Thus, the thermal stability of both host materials was measured by thermogravimetric analysis (TGA). Both hosts exhibited high thermal stability with decomposition temperatures exceeding 400°C (**Figure 2-15**), which can meet the requirements for device fabrication.

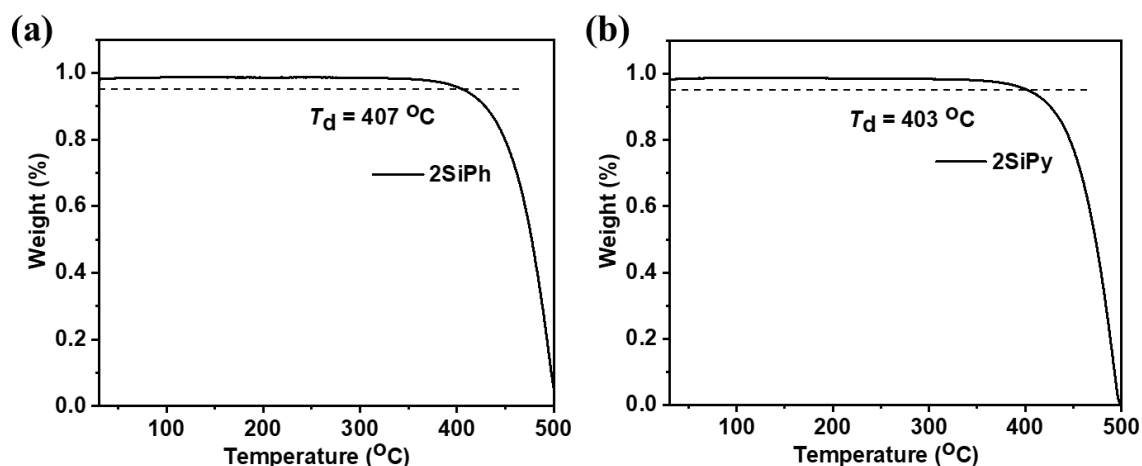


Figure 2-15. TGA measurement of **2SiPh** and **2SiPy**.

4CzIPN has drawn a lot of attention and has been widely reported as a stable green TADF-OLED, so it is worth studying green TADF-OLED with **4CzIPN** and newly synthesized host materials so that device performance can be further improved.⁶² The PLQY measurement has been examined with the use of thermally deposited doped films by doping 6, and 15 wt% of **4CzIPN** in the various hosts (Figure 2-16, 2-18, and Table 2-1). The PLQY of all the **2SiPh**-doped films exhibited reasonable PLQYs of 63.5% with emission maxima of 529 nm for the 15 wt% doped film and 62.9% with emission maxima of 523 nm for the 6 wt% doped film. In contrast, the PLQY of the **2SiPy**-doped film was unexpectedly low, which was only 23.6%, and 35.1% for 15 wt% and 6 wt%. Moreover, in the 15 wt% doped film, the emission spectra of **2SiPy** were redshifted to 535 nm and broadened compared with **2SiPh**. From the transient PL decay profiles, a decay tail was found in **2SiPy**, indicating a different origin from the **2SiPh**-doped film. We suspect that the polar nature of **2SiPy** leads to stronger molecular interactions in the doped film. Such interactions redshift the emission and increase the nonradiative decay pathways, ultimately giving rise to the markedly low PLQY. And the calculated k_{nr} increases from $3.07 \times 10^6 \text{ s}^{-1}$ in **2SiPh** doped film to $9.82 \times 10^6 \text{ s}^{-1}$ in **2SiPy** doped film.

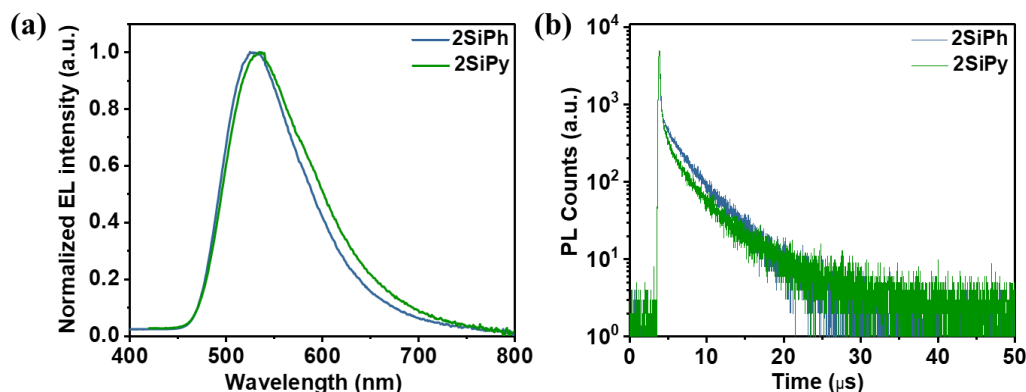


Figure 2-16. (a) PL spectra and (b) transient emission decay profiles of 15 wt% of **4CzIPN** doped in various hosts.

Moreover, we also monitored the decay profiles at 530 and 600 nm for both doped films, in which the decay profiles of the **4CzIPN:2SiPh** doped film were almost identical (2.2 and 2.3 μs) (**Figure 2-17a**); however, the decay profiles of the **4CzIPN:2SiPy** doped film showed slightly different decay lifetimes (1.6 and 2.1 μs) (**Figure 2-17b**).

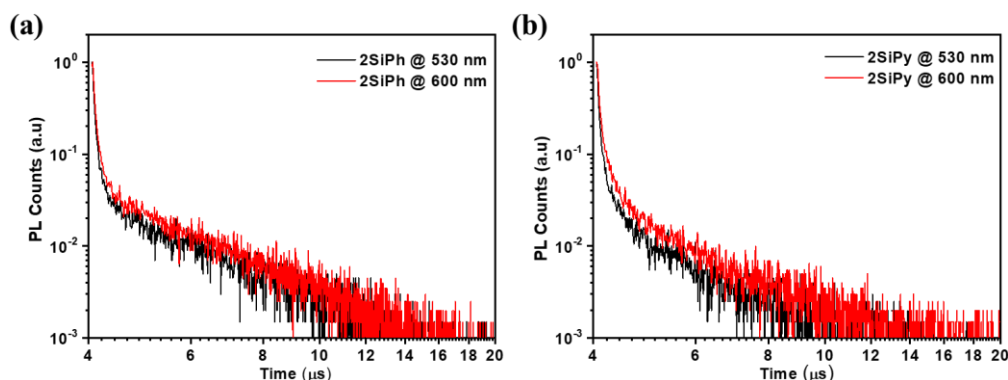


Figure 2-17. Transient emission decay profiles of 15 wt% **4CzIPN** doped in various hosts.

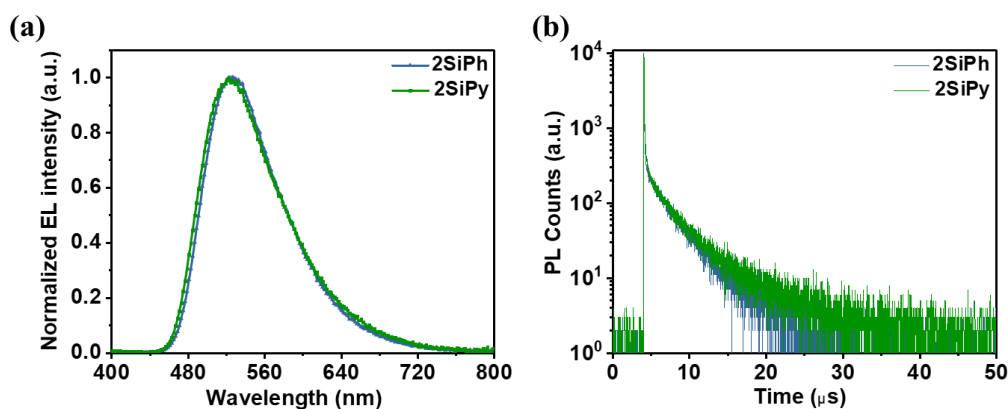


Figure 2-18. (a) PL spectra and (b) transient emission decay profiles of 6 wt% of **4CzIPN** doped in various hosts.

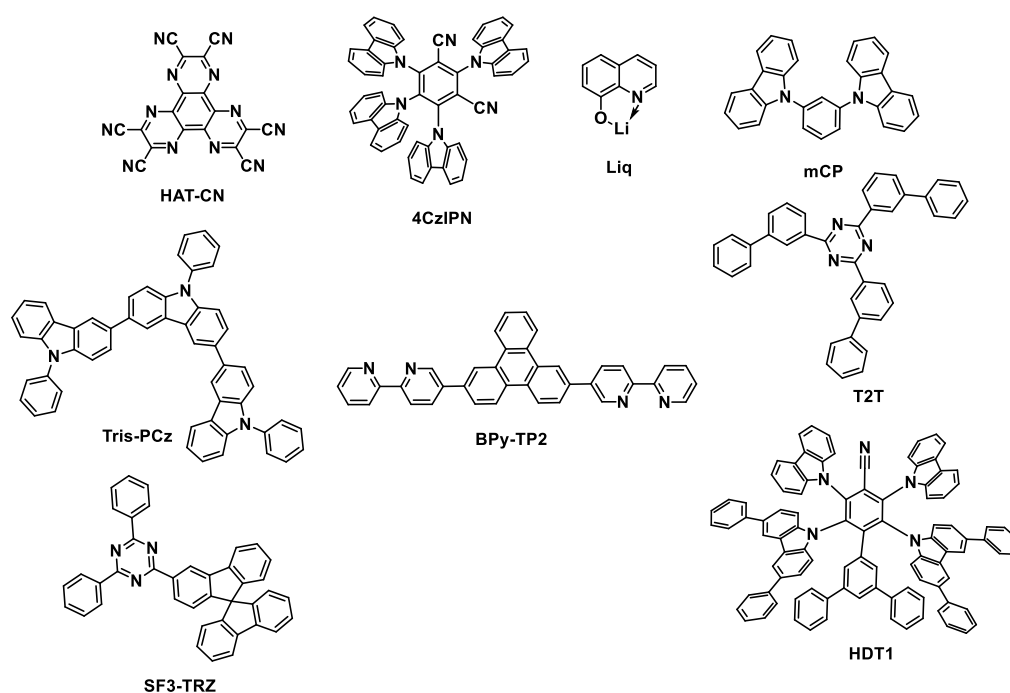
Table 2-1. Physical properties of four host materials.

Doped-film	λ_{em} (nm) ^a	PLQY (%)	τ_p (ns) ^b	τ_d (μ s) ^c	k_{RISC} (10^5 s ⁻¹)	k_{nr}^S (10^6 s ⁻¹)	k_{ISC} (10^7 s ⁻¹)
15 wt% 4CzIPN:2SiPh	529	63.5	32.6	3.15	10.8	3.07	2.34
15 wt% 4CzIPN:2SiPy	535	23.6	34.3	3.17	10.6	9.82	2.10
6 wt% 4CzIPN:2SiPh	523	62.9	27.6	1.79	10.2	4.21	2.65
6 wt% 4CzIPN:2SiPy	522	35.1	38.5	2.10	9.71	5.06	2.03

^aEmission maximum; ^bprompt lifetime; ^cdelayed lifetime.

2.3.4. OLED Performance

The host properties of **2SiPh** and **2SiPy** were evaluated in green-OLEDs using **4CzIPN** as the emitter. The TADF-OLEDs were fabricated using the following architecture: ITO/HAT-CN(10 nm)/Tris-PCz(30 nm)/15 wt%-**4CzIPN: 2SiPh** or **2SiPy**/T2T(10 nm)/BPy-TP2(40 nm)/Liq(2 nm)/Al(70 nm). In the device, HAT-CN, Tris-PCz, T2T, BPy-TP2, and Liq serve as the hole-injection layer (HIL), hole-transport layer (HTL), electron-blocking layer (EBL), electron-transporting layer (ETL), and electron-injection layer (EIL), respectively. Al is the cathode layer. All the chemical structures used for device fabrication are illustrated in **Figure 2-19**.

**Figure 2-19.** Molecular structures used for OLEDs.

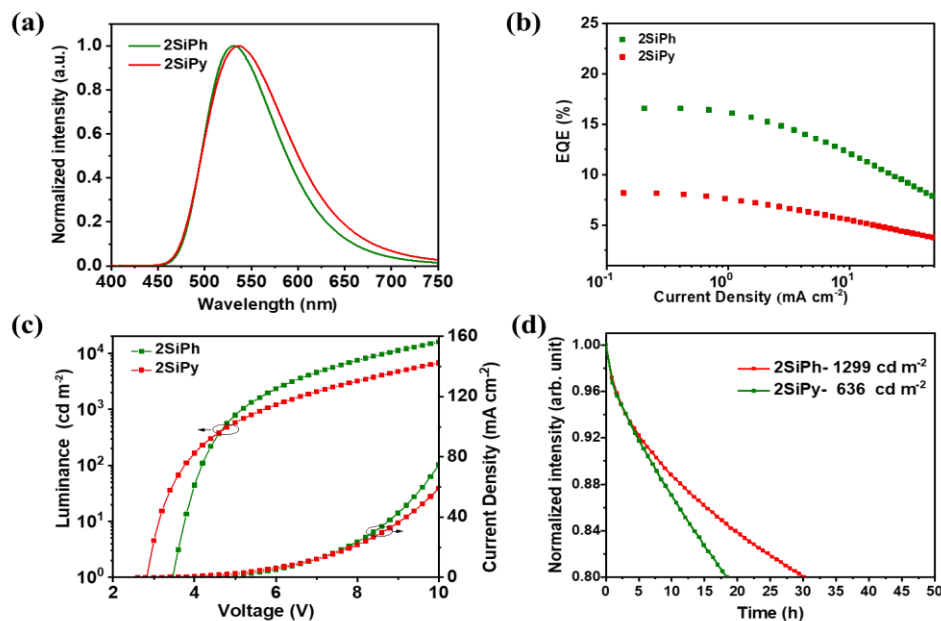


Figure 2-20. Device performance of green TADF-OLEDs using **4CzIPN** with different hosts: **2SiPh** and **2SiPy**. (a) EL spectra; (b) current density and luminescence versus voltage curves; (c) external quantum efficiency versus current density; (d) device lifetime at constant current density of 3.3 mA cm^{-2} .

The device performances of **2SiPh** and **2SiPy** are depicted in **Figure 2-20** and **Table 2-2**. The OLED device based on **2SiPh** showed a higher EQE_{max} of 16.6% and maintained a high EQE of 15.3% at 10^3 cd cm^{-2} , outperforming the **2SiPy**-based device. In comparison, the EQE_{max} of the **2SiPy**-based device was limited to 8.2%, which is consistent with the markedly lower PLQY of its doped film. Such a low EQE was attributed to the exciton quenching by the strong intermolecular interaction between **2SiPy** and **4CzIPN**.

Given that the internal quantum efficiencies are equal to the PLQYs, we noticed that the outcoupling efficiency of **2SiPy** was estimated to be 0.35, which is much higher than that of **2SiPh** (0.26) and respectively. To determine whether this enhancement originates from the transition dipole moment (TDM) of the emitter, angular-dependent PL measurements were conducted (**Figure 2-21**). The resulting TDM was analyzed with the help of SETFOS, to obtain the horizontal-dipole ratios (Θ), where Θ values of 0, 0.33, and 1, represent perfectly horizontal, isotropic, and vertical orientations, respectively. For the 15 wt%-**4CzIPN:2SiPh** doped film, a Θ value of 0.28 was obtained, indicating a slightly horizontal orientation rather than a random orientation. In the case of **4CzIPN:2SiPy** doped film, Θ was 0.21, which means the TDM of **4CzIPN** is horizontally oriented rather than that in **2SiPh**. By applying Θ to the green device structure in SETFOS, the outcoupling efficiencies of **2SiPh**- and **2SiPy**-based devices were

simulated to be 0.21 and 0.24, respectively. The **2SiPy** devices showed higher outcoupling efficiency than expected based on molecular orientation and require further investigation.

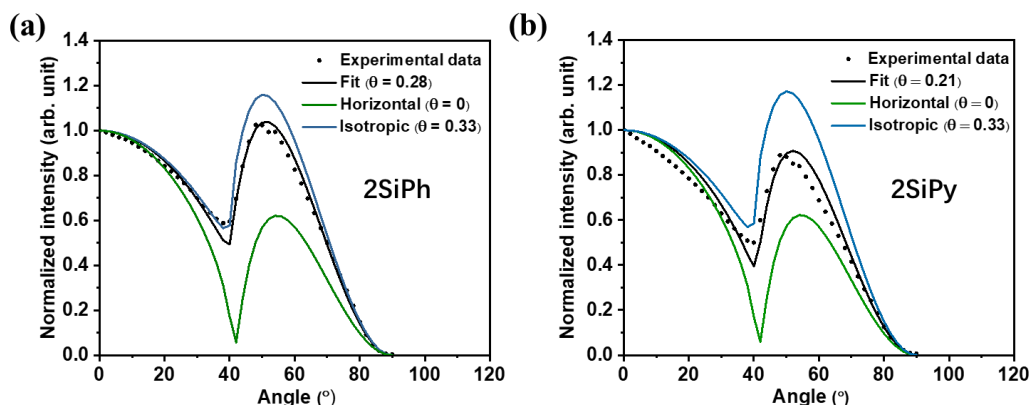


Figure 2-21. Angular-dependent PL profiles of 15 wt% **4CzIPN** doped in various hosts.

The EL spectra of these two hosts also showed a significant difference. The **2SiPy**-containing device exhibited a red-shifted emission peak at 537 nm, whereas the emission of the **2SiPh** device appeared at 531 nm. The redshifted behavior would be due to the higher polarity of the **2SiPy** host, which strengthens host-guest interactions and enhances charge-transfer character in the excited states. Further, the **2SiPh**-based device showed a turn-on voltage (V_{on}) of 3.6 V; in contrast, the **2SiPy**-based device showed a noticeably lower V_{on} s of 2.8 V. This was attributed to the shallower HOMO energy of **2SiPy**, which facilitates hole injection. Finally, we also measured the device lifetime at a constant current density of 3.3 mA m^{-2} . Unfortunately, despite the huge difference in EQE, their operational lifetimes were comparable. The device stabilities of LT_{95} (95% of the initial luminance) for **2SiPh** and **2SiPy** were found to be 2.3 and 2.2 h, respectively.

Table 2-2. Device performance of green TADF-OLEDs based on **2SiPh** and **2SiPy** hosts.

Host	Voltage (V) ^a	L_{max} (cd/m ²) ^b	CE (cd/A) ^c	PE (lm/W) ^d	$EQE_{max/1000/roll-off}$ (%) ^e	λ_{EL} (nm) ^f	LT_{95} (h) ^h
2SiPh	3.6	15983	53.9	41.4	16.6/15.3/7.8 ^g	531	2.3
2SiPy	2.8	6731	25.9	24.4	8.2/6.2/24.4 ^g	537	2.2

^a) Turn-on voltage at 1 cd m^{-2} ; ^b) maximum luminance at 10 V; ^c) maximum current efficiency; ^d) maximum power efficiency; ^e) values at 1 and 10³ cd m^{-2} ; ^f) electroluminescence maximum at 1000 cd m^{-2} ; ^g) roll-off percentage; ^h) at a constant current density of 3.3 mA cm^{-2} .

We suspect the poor device lifetime may be caused by the unbalanced carrier transport. Therefore, the hole-only and electron-only devices, i.e., HODs and EODs of **2SiPh** and **2SiPy** were firstly fabricated based on the **4CzIPN**-doped films of **2SiPh** and **2SiPy**, respectively (**Figure 2-22**). In the EODs curves, it shows that the current density at 12V of **2SiPh** and **2SiPy** were below 0.01 mA cm^{-2} , while in the HODs, the current density were 2.0 and 0.5 mA cm^{-2} for **2SiPh** and **2SiPy**, respectively. This clearly shows that the electron transporting abilities of both hosts were much lower than the hole transporting abilities, indicating the imbalanced carrier transporting properties. By calculating the ratio of hole transportation (HT) to electron transportation (ET) at 12V, both **2SiPh** and **2SiPy** showed a large ratio of 194:1 and 260:1, respectively, which eventually shifted the recombination site close to ETL, hence resulting in the shorter device lifetimes in both devices. Moreover, the huge HOD/EOD ratio of **2SiPy** gave rise to a severe efficiency rolloff in the device.

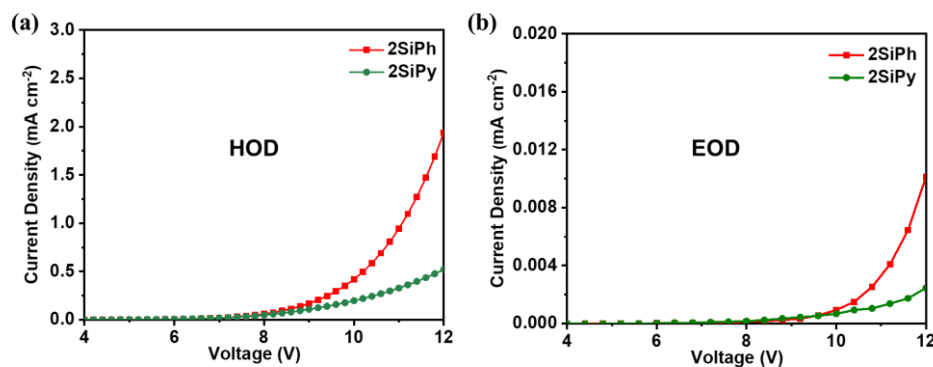


Figure 2-22. Current density – Voltage (J-V) characteristics of HOD and EOD for different hosts in 15 wt% **4CzIPN** doped films. Device structure of HOD: HATCN (10 nm)/Tris-PCz (30 nm)/15 wt% **4CzIPN: Host** (30 nm) /Tris-PCz (50 nm)/Al (100 nm). EOD: T2T (30 nm)/15 wt% **4CzIPN: Host** (30 nm)/T2T (10 nm)/Bpy-TP2 (80 nm)/LiQ (2 nm)/Al (100 nm).

In addition, the HODs and EODs based on the neat films of **2SiPh** and **2SiPy** were also fabricated to understand the hole/electron transport properties. (**Figure 2-23**). From the EODs, we can see that **2SiPy** displayed a better electron transport ability than that of **2SiPh**, indicating that the introduction of the pyridine unit did improve the electron transport property.

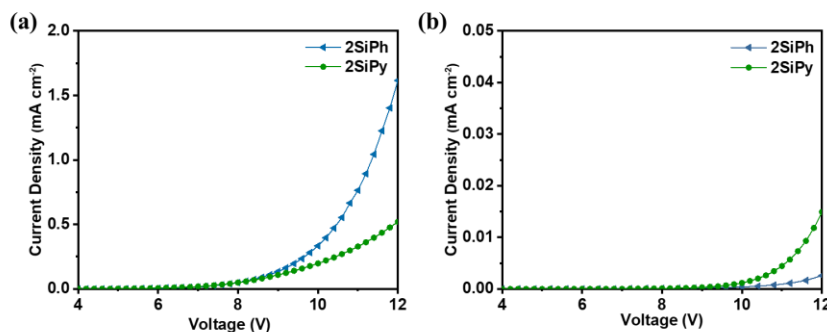


Figure 2-23. Current density – Voltage (J-V) characteristics of HOD and EOD for different hosts in neat films. Device structure of HOD: HATCN (10 nm)/Tris-PCz (30 nm)/mCBP (5 nm)/Host (30 nm)/Tris-PCz (50 nm)/Al (100 nm); EOD: T2T (30 nm)/Host (30 nm)/T2T (10 nm)/Bpy-TP2 (80 nm)/LiQ (2 nm)/Al (100 nm).

Since the T_{1S} of **2SiPh** and **2SiPy** were more than 3 eV, indicating them as good candidates as hosts for blue OLEDs. A sky-blue emitter **HDT-1** was used for OLED fabrication. Since **mCP** has a similar chemical structure to **2SiPh** and **2SiPy**, an **mCP**-based blue OLED was also fabricated for comparison. The structure was as follows: ITO/HAT-CN(10 nm)/Tris-PCz(30 nm)/mCBP(5 nm)/15 wt%-**HDT-1**: **mCP** (reference) or **2SiPh** (device A) or **2SiPy** (device B)/T2T(30 nm)/BPy-TP2(40 nm)/LiQ(2 nm)/Al(100 nm). Details were depicted in **Figure 2-24** and **Table 2-3**.

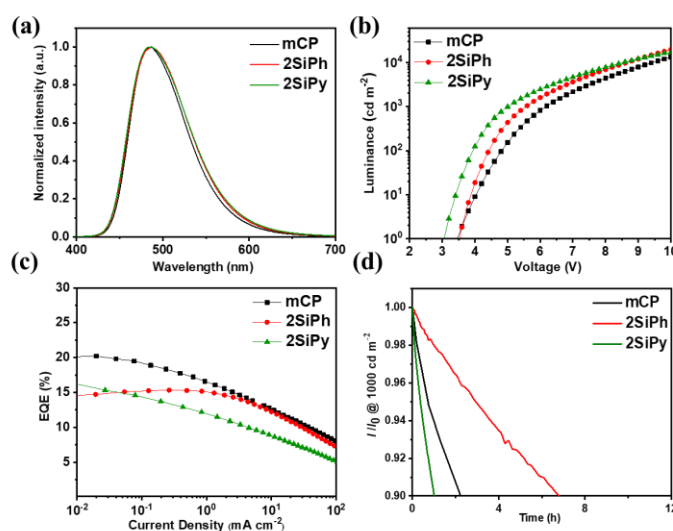


Figure 2-24. Device performance of blue TADF-OLEDs using HDT-1 with the different hosts: mCP (reference), 2SiPh (device A), and 2SiPy (device B). (a) EL spectra of all blue devices; (b) current density and luminescence versus voltage; (c) external quantum efficiency versus current density; (d) device stability.

Table 2-3. Summary of device performance.

Device	Host	Voltage (V) ^a	L _{max} (cd/m ²) ^b	CE (cd/A) ^c	PE (lm/W) ^d	EQE _{max} /1000/roll- off (%) ^e	λ _{EL} (nm) ^f
Ref.	mCP	3.5	24197	45.1	37.8	20.2/14.6/ 27.7 ^g	486
A	2SiPh	3.6	28866	34.9	29.5	15.3/ 14.0/ 8.3 ^g	487
B	2SiPy	3.2	18173	37.9	37.2	17.5/ 9.9/ 43.3 ^g	487

a) Turn-on voltage at 1 cd m⁻²; b) maximum luminance at 10 V; c) maximum current efficiency; d) maximum power efficiency; e) values at 1 and 103 cd m⁻²; f) electroluminescence maximum at 1000 cd m⁻²; g) roll-off percentage.

In **2SiPh**-based blue OLEDs (device A), a high maximum external quantum efficiency (EQE_{max}) of 15.3 % was achieved and an EQE of 14.0 % at 10³ cd cm⁻². In contrast to device A, **2SiPy**-based device B obtained a higher EQE_{max} of 17.5 % with a severe roll-off, leading to an EQE of only 9.9% at 10³ cd cm⁻². Such a severe roll-off may be due to the imbalanced carrier transporting properties. The turn-on voltages of devices A and B were found to be 3.6 and 3.2 V, respectively, with the same EL maximum of 487 nm. Although the **mCP**-based reference device displayed a higher EQE of 20.2 %, its device stability of LT₉₀ was around 1 hour, which was much worse than that of the **2SiPh**-based device (7 hours). We believe that with device optimization, **2SiPh** can achieve a higher EQE with improved device lifetime than **mCP**.

2.4. Conclusion

Two azasiline-based host materials, **2SiPh** and **2SiPy**, have been successfully designed and synthesized. The triplet energy levels of **2SiPh** and **2SiPy** are as high as 3.0 eV in both solution and film states, indicating them as a candidate for OLEDs. The PLQY of 15 wt% **4CzIN-2SiPy** doped film is as low as 23.6% due to the strong intermolecular interaction between **2SiPy** and **4CzIPN**. The Green TADF-OLEDs with **4CzIPN** as the emitter have been fabricated based on **2SiPh** and **2SiPy**, leading to an EQE_{max} of 16.6% and 8.2%, respectively. Unfortunately, both **2SiPh**- and **2SiPy**-based devices showed poor device lifetimes of LT₉₅ around 2 hours, which originated from the extremely imbalanced carrier transporting property. Moreover, the electron transport property was greatly improved in the pyridine-containing host **2SiPy**. In the following study, we are going to focus on the pyridine unit to achieve balanced carrier transporting properties.

Chapter 3

Judicious Design of Pyridine-based Hosts for Stable, Efficient, and Low-Driving Thermally Activated Delayed Fluorescence Organic Light-Emitting Diodes

3.1. Introduction

In Chapter 2, we successfully developed two host materials featuring high triplet energies. Although the operational lifetime of the green OLEDs was not yet satisfactory, the devices revealed a clear improvement in electron-transporting characteristics upon the introduction of pyridine units into the molecular framework. This suggests that incorporating pyridine motifs might be an effective strategy to enhance electron transport and to achieve more balanced carrier transport properties.

Pyridine-based electron-transporting materials have been well-reported to exhibit excellent electron-transporting properties. Yokoyama and co-workers systematically investigated a series of pyridine-containing electron-transport materials and showed that the pyridyl nitrogen atoms participate in weak intermolecular C–H···N hydrogen bonding, inducing short-range molecular stacking and horizontal orientation in vacuum-deposited films.⁶³ This hydrogen-bond-driven packing order significantly reduces energetic and positional disorders, resulting in higher electron mobility compared to non-pyridyl analogues. (Figure 3-1)

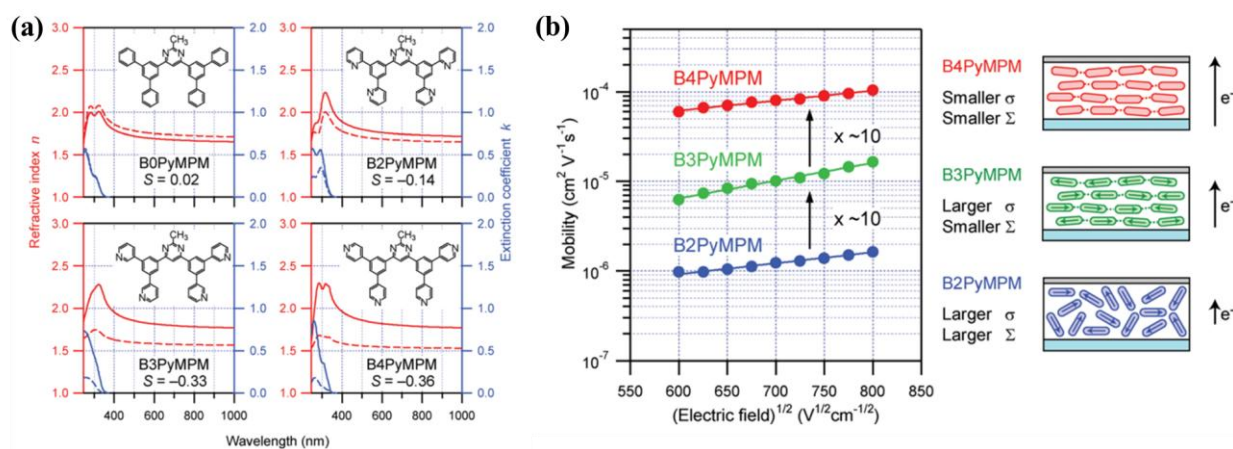


Figure 3-1. (a) Molecular orientation of regio-isomeric pyridine-based electron-transporting materials; (b) horizontal orientation enhancing electron-transporting properties.⁶³

Although **mCBP** has been widely used as a host material in OLEDs, its fairly high T1 and chemical stability render it less suitable for commercialization. Moreover, the electron-transporting properties of **mCBP** are comparably weak, which, in turn, leads to imbalanced carrier-transporting properties, resulting in a shift in the recombination zone. Taking advantage of the good electron-transporting properties of pyridine units, three new pyridine-based hosts, namely **mCBP-1N**, **CzPyPhCz**, and **CzPyBF** (Figure 3-2), were designed and synthesized.

Regarding the common *p*-type host, **mCBP**, a pyridine ring was first introduced in **mCBP-1N** to enhance electron-transporting properties. Then, we also synthesized the structural isomer (**CzPyPhCz**) to compare the isomeric effect. Finally, we replaced the phenylcarbazole with a chemically stable dibenzofuran moiety (**CzPyBF**).

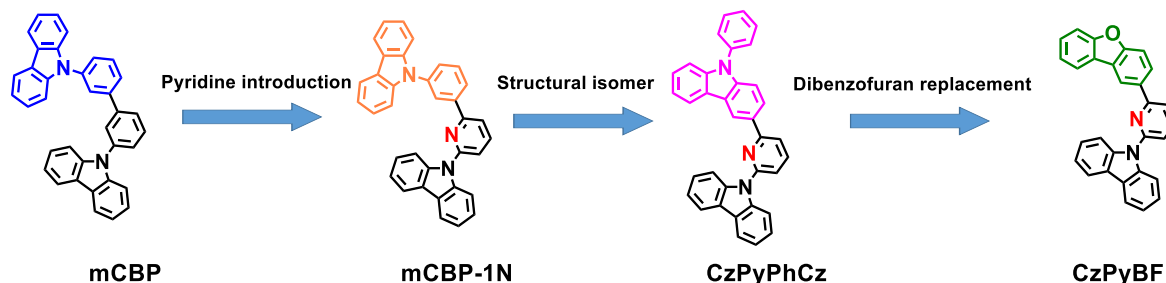


Figure 3-2. Design strategy of pyridine-based host materials.

3.2. Synthesis

mCBP-1N, **CzPyPhCz**, and **CzPyBF** were synthesized according to **Figure 3-3**. 9*H*-Carbazole was first deprotonated by sodium hydride and reacted with 2-bromo-5-fluoropyridine via nucleophilic substitution to result in **CzPyBr**. After that, various boronic acids were reacted with **CzPyBr** to give the corresponding host materials with high yields. All the materials were characterized by NMR.

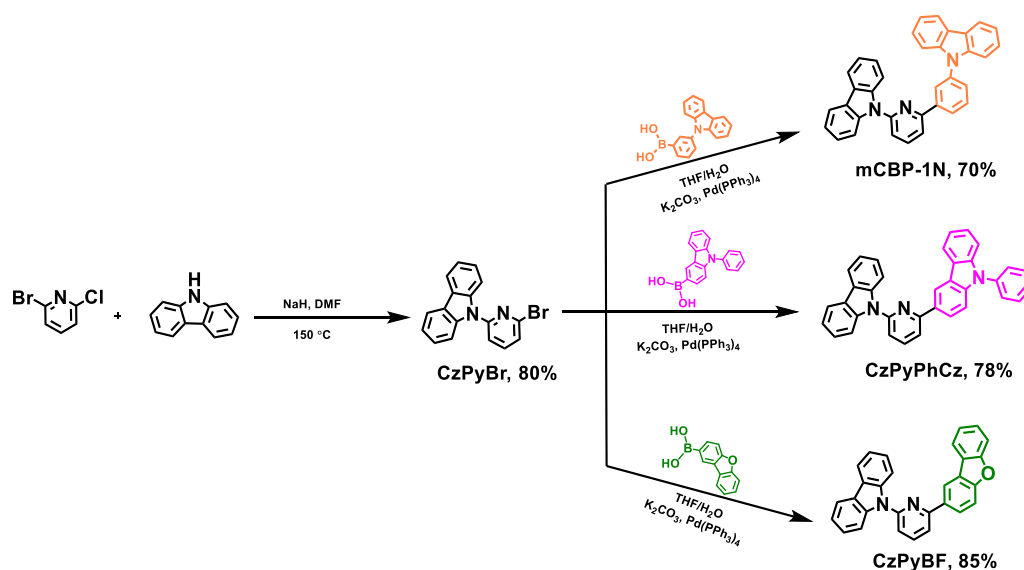


Figure 3-3. Target pyridine-based host materials and their synthetic routes.

The synthesis details of **CzPyBr** were as follows. Under a nitrogen atmosphere, 9*H*-carbazole (1.1 mmol) was dissolved in dry *N,N*-dimethylformamide (30 mL) in a two-neck round-bottom flask equipped with a condenser. The reaction mixture was cooled to 0 °C, and then NaH (1.1 mmol) was added. The reaction mixture was slowly warmed to room temperature and stirred for half an hour. After that, 2-bromo-6-fluoropyridine (1 mmol) was

added and the reaction was heated to 150 °C for 16 hours. The reaction was quenched with water and the precipitate was filtered off. The crude product was purified by column chromatography. Yield: 258 mg (80%). ^1H NMR (500 MHz, acetone- d_6 , 298 K, relative to Me_4Si): δ = 8.21 (d, 2H, 7.5Hz), 8.07 (t, 1H, 7.5Hz), 7.95 (d, 2H, 8Hz), 7.86 (d, 1H, 8 Hz), 7.67 (d, 1H, 8Hz), 7.50 (t, 2H, 8Hz), 7.36 (t, 2H, 8Hz) (**Figure 3-4**).

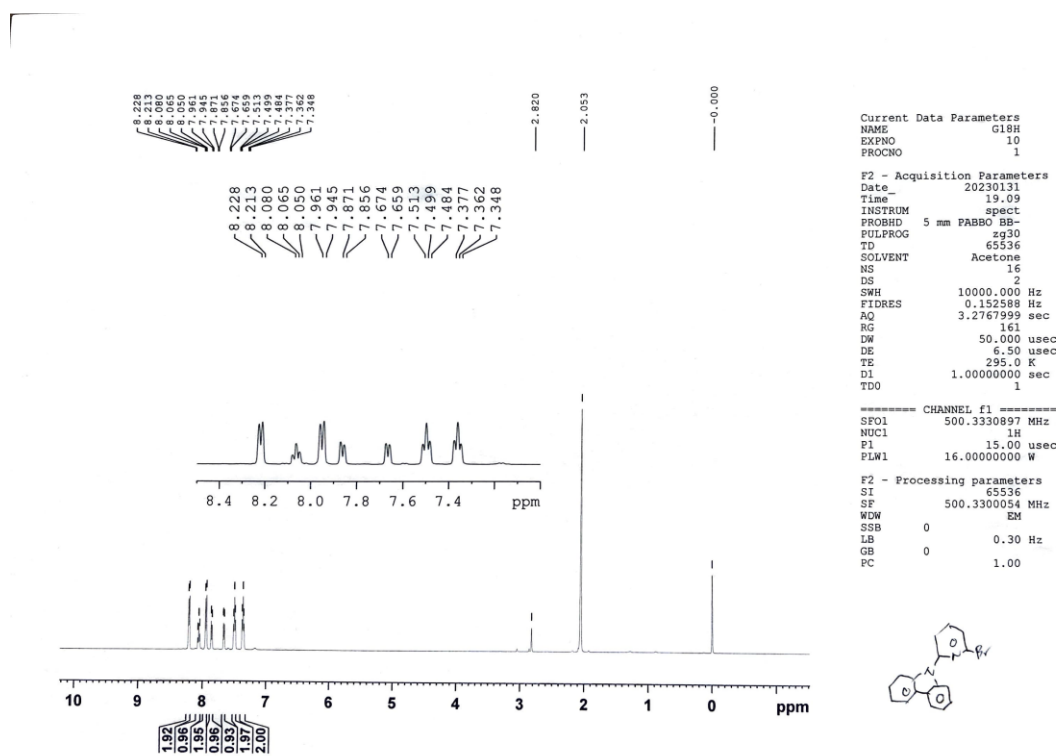
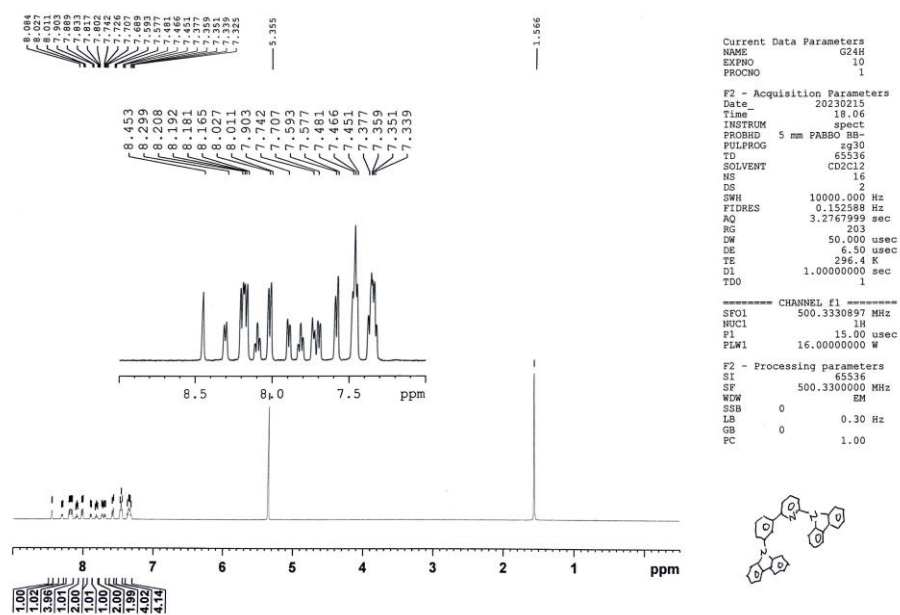
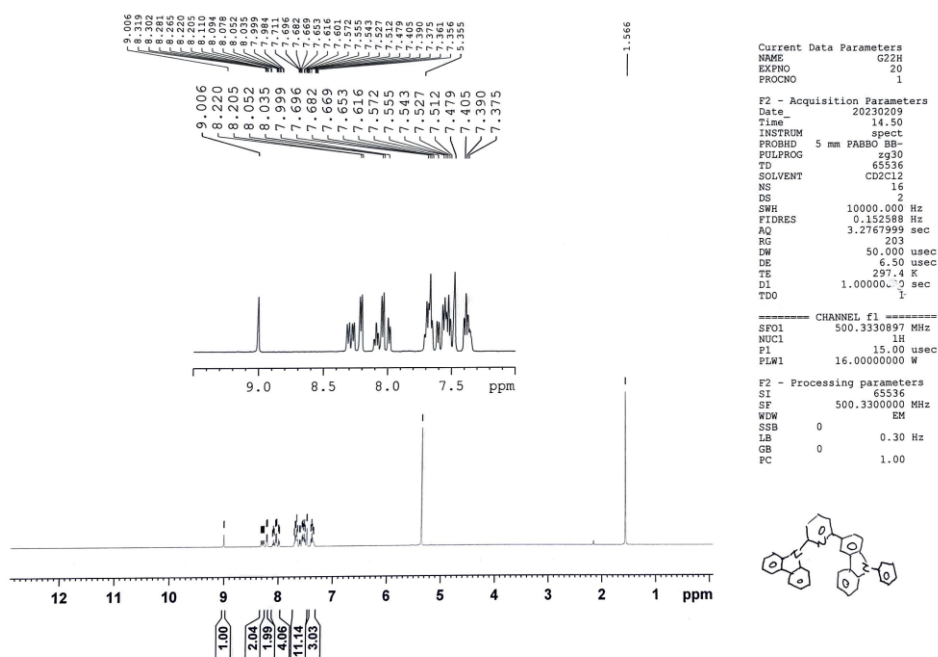


Figure 3-4. ^1H NMR of CzPyBr.

The synthetic procedure for **mCBP-1N** was conducted as follows. **CzPyBr** (386 mg, 1.2 mmol), (3-(9*H*-carbazol-9-yl)phenyl)boronic acid (287 mg, 1 mmol), K_2CO_3 (414 mg, 3 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (58 mg, 0.05 mmol) were dissolved in degassed THF/water (30 ml/10 ml) mixture and heated to reflux overnight. The crude reaction mixture was extracted with dichloromethane and purified by column chromatography. Yield: 340 mg (70%). ^1H NMR (500 MHz, CD_2Cl_2 , 298 K, relative to Me_4Si): δ = 8.45 (s, 1H), 8.31 (d, 1H, 8 Hz), 8.21-8.16 (m, 4H), 8.10 (t, 1H, 8 Hz), 8.02 (d, 2H, 8 Hz), 7.89 (d, 1H, 8 Hz), 7.82 (t, 1H, 8 Hz), 7.74-7.69 (m, 2H), 7.58 (d, 2H, 8 Hz), 7.48-7.45 (m, 4H), 7.38-7.32 (m, 4H) (**Figure 3-5**).

Figure 3-5. ^1H NMR of mCBP-1N.

CzPyPhCz was synthesized with the same procedure as **mCBP-1N**, except (3-(9H-carbazol-9-yl)phenyl)boronic acid was replaced by (9-phenyl-9H-carbazol-3-yl)boronic acid (287 mg, 1 mmol). Yield: 378 mg (78%). ^1H NMR (500 MHz, CD_2Cl_2 , 298 K, relative to Me_4Si): δ = 9.00 (s, 1H), 8.31 (d, 2H, 8 Hz), 8.27 (d, 2H, 8 Hz), 8.22-7.98 (m, 4H), 7.71-7.48 (m, 11H), 7.41-7.36 (m, 3H) (Figure 3-6).

Figure 3-6. ^1H NMR of CzPyPhCz.

CzPyBF was prepared following the same methods used for **mCBP-1N**, except (3-(9H-carbazol-9-yl)phenyl)boronic acid was replaced by dibenzo[*b,d*]furan-2-ylboronic acid (212 mg, 1 mmol). Yield: 349 mg (85%). ^1H NMR (500 MHz, CD_2Cl_2 , 298 K, relative to Me_4Si): δ = 8.82 (s, 1H), 8.34 (d, 1H, 8 Hz), 8.21 (d, 2H, 8 Hz), 8.11 (t, 2H, 6 Hz), 8.02 (t, 2H, 8 Hz), 7.96 (d, 1H, 8 Hz), 7.74 (d, 1H, 8 Hz), 7.65 (d, 2H, 8 Hz) 7.55-7.52 (m, 3H), 7.43-7.38 (m, 3H) (Figure 3-7).

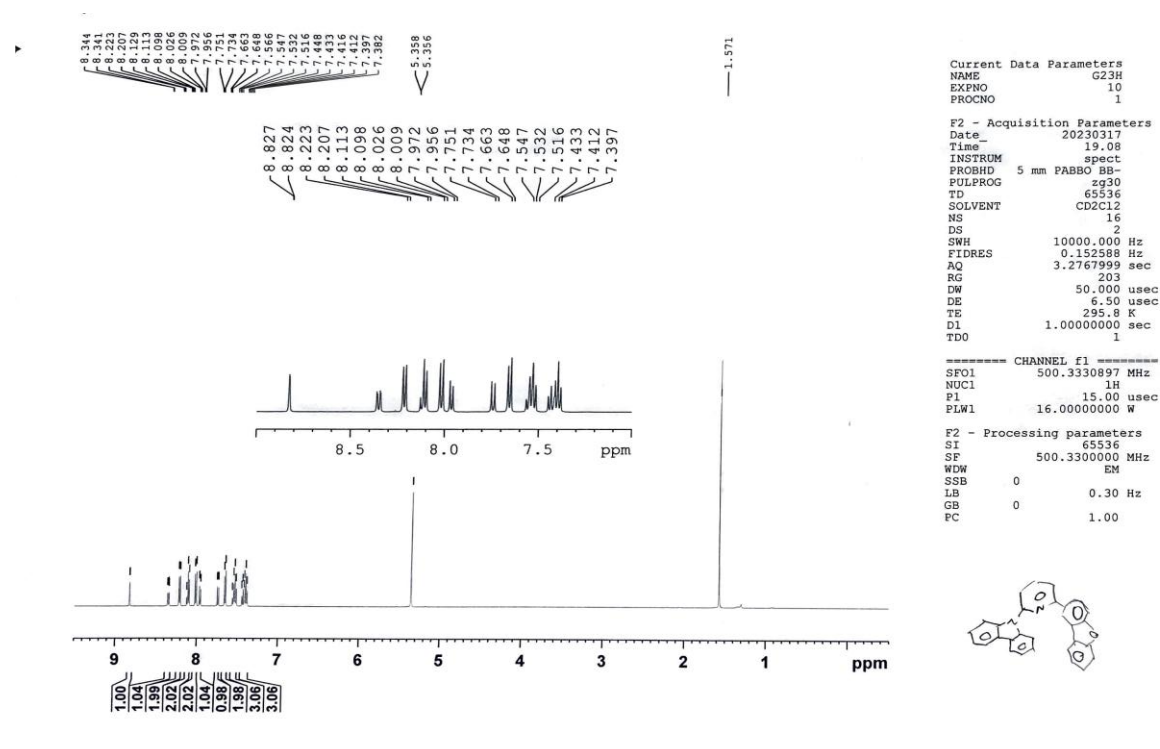


Figure 3-7. ^1H NMR of **CzPyBF**.

3.3. Results and Discussion

3.3.1. Theoretical Calculations

To predict the photophysical and electrochemical properties of **mCBP-1N**, **CzPyPhCz**, and **CzPyBF**, time-dependent density functional theory (TD-DFT) calculations were performed at the B3LYP/6-31G level to evaluate both their ground- and excited-state properties. The calculated HOMOs and LUMOs are shown in **Figure 3-8**. In all three hosts, the LUMOs are localized on the pyridine unit, whereas the HOMO of **CzPyBF** is localized on the carbazole attached to the pyridine ring. When comparing **CzPyPhCz** and **CzPyBF**, **CzPyPhCz** exhibits a shallower calculated HOMO energy than that of **CzPyBF**. This is because of the stronger electron-donating property of 9H-phenylcarbazole than that of dibenzofuran. Furthermore, when comparing two hosts with isomeric structures, **mCBP-1N** and **CzPyPhCz**, the more

delocalized HOMO distribution of **CzPyPhCz** leads to a shallower calculated HOMO energy. The calculated T_1 energies of **mCBP-1N**, **CzPyPhCz**, and **CzPyBF** were also determined to be 2.93, 2.87, and 2.96 eV, respectively, which are high enough to confine excitons in blue or green TADF-OLEDs (~ 2.7 eV).

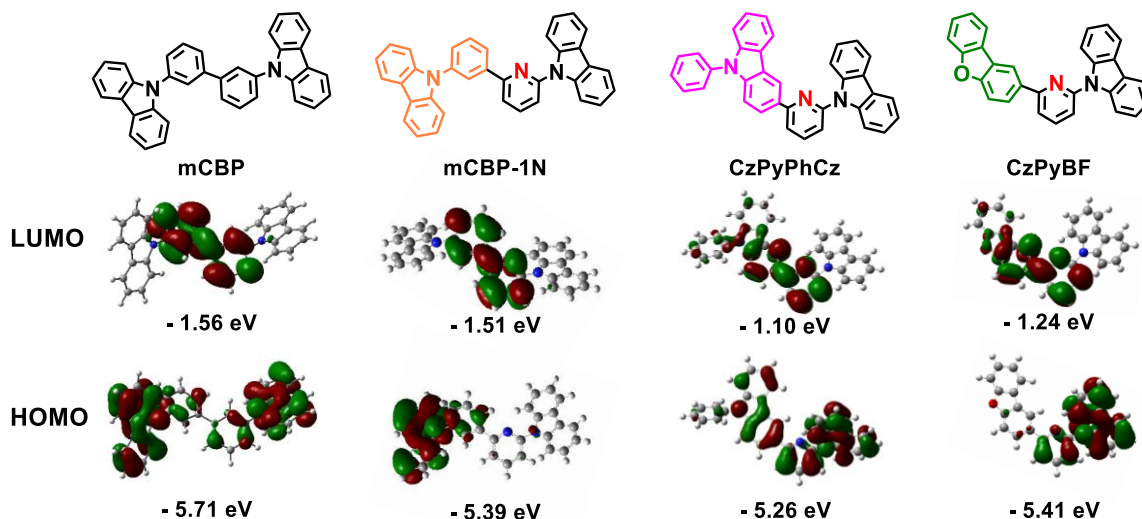


Figure 3-8. Molecular orbitals of hosts.

3.3.2. Photophysical Study

In order to understand the photophysical properties of the newly synthesized hosts, ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) spectra of **mCBP-1N**, **CzPyPhCz**, and **CzPyBF** were measured in toluene (**Figure 3-9a**). All three host materials exhibit absorption bands below 350 nm, which can be attributed to their $n-\pi^*$ transition of the carbazole moieties. Since all the hosts emitted within the UV region, it is expected that energy can be effectively transferred from the hosts to red, green, and blue (RGB) dopants. Estimating from the onset of the fluorescent spectra, the S_1 of **mCBP-1N**, **CzPyPhCz**, and **CzPyBF** were found to be 3.4, 3.5, and 3.6 eV, respectively, which are similar to that of **mCBP** (3.5 eV).⁶⁴ **mCBP-1N** displayed the most redshifted emission and lowest S_1 , which may be due to a high charge-transfer (CT) character as shown in the DFT calculation, while both **CzPyPhCz** and **CzPyBF** showed a moderate mixing of localized excited state and CT state. T_1 energies of **mCBP-1N**, **CzPyPhCz**, and **CzPyBF** were found to be 2.84, 2.87, and 2.87 eV, respectively, which were calculated from the onset of phosphorescence spectra measured at low temperature (77K) in a frozen toluene matrix (**Figure 3-9b**). Although the experimental T_1 energies were lower than the calculated values, the T_1 energies of all new hosts were high enough to confine triplet excitons of a green TADF emitter **4CzIPN** ($T_1 = 2.5$ eV).

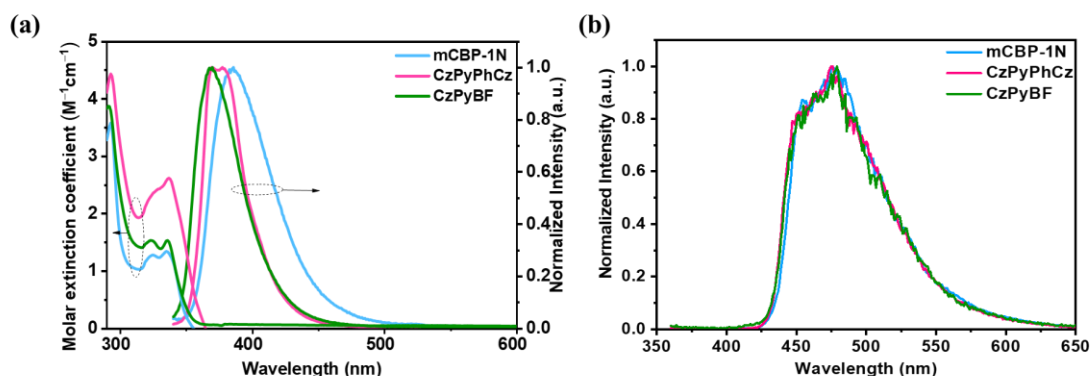


Figure 3-9. (a) Absorption and photoluminescence spectra of **mCBP-1N**, **CzPyPhCz**, and **CzPyBF** in toluene at 298 K (1.0×10^{-5} mol dm $^{-3}$); (b) phosphorescent spectra of **mCBP-1N**, **CzPyPhCz**, and **CzPyBF** in frozen toluene matrix at 77 K.

The HOMO level of each host was measured with the help of a photoelectron spectrometer (**Figure 3-10**). The HOMO of **mCBP** was found to be -6.1 eV, which is consistent with the literature value. The calculated HOMOs of **mCBP-1N**, **CzPyPhCz**, and **CzPyBF** were found to be -5.39 , -5.26 , and -5.41 eV, respectively. The experimental HOMOs were consistent with the calculated values, in which **CzPyPhCz** showed the shallowest value of -5.7 eV. Therefore, we expect a good hole transport property from **CzPyPhCz**. And the HOMOs of **mCBP-1N** and **CzPyBF** were found to be -5.9 and -6.0 eV, respectively.

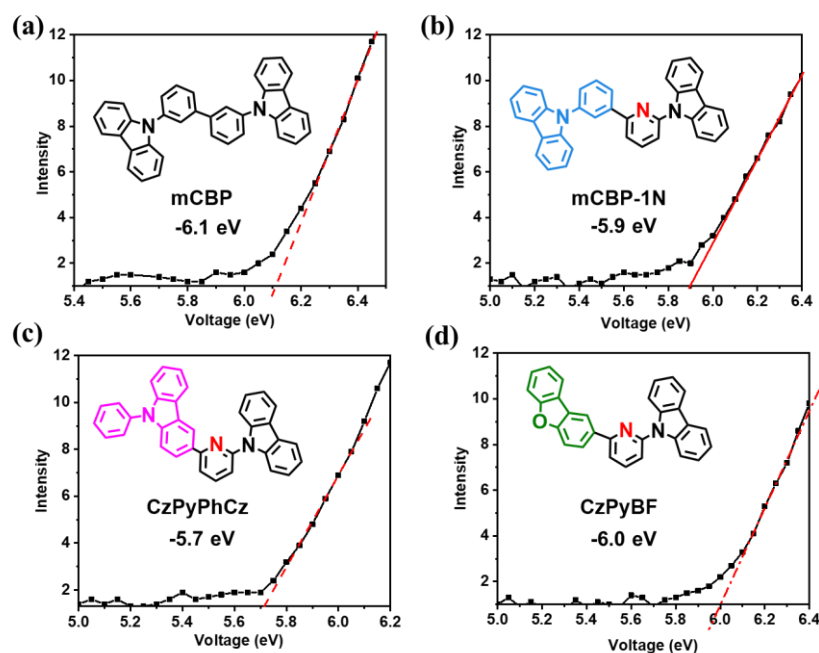


Figure 3-10. Photoelectron spectral measurements of (a) **mCBP**, (b) **mCBP-1N**, (c) **CzPyPhCz**, and (d) **CzPyBF** neat films under nitrogen atmosphere.

The thermal properties of host materials were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in **Figures 3-11** and **Figure 3-12**, respectively. In TGA, **CzPyBF** showed the lowest decomposition temperature (T_d : 5% weight loss) of 397 °C, while other host materials displayed high T_d s of over 400 °C. In DSC, the glass transition temperature (T_g) of **CzPyBF** was only 69 °C, whereas T_g s of **mCBP**, **mCBP-1N**, and **CzPyPhCz** were found to be 90, 97, and 102 °C, respectively. The lower T_d and T_g of **CzPyBF** may be due to the lower molecular weight and intermolecular interactions. All photophysical, electrochemical, and thermal data are summarized in **Table 3-1**.

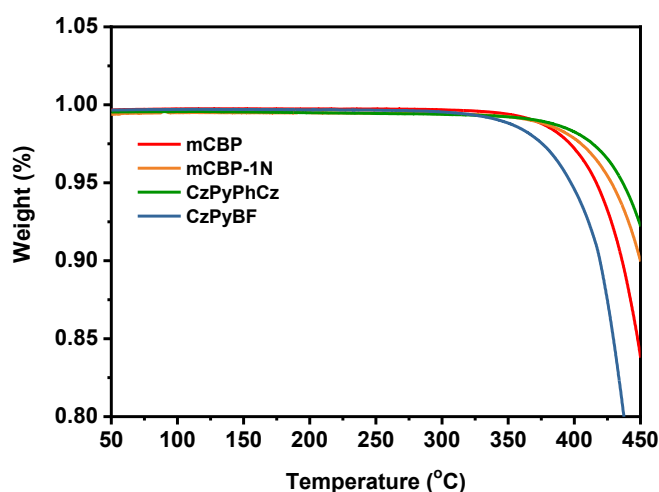


Figure 3-11. Thermogravimetric analysis (TGA) of different host materials.

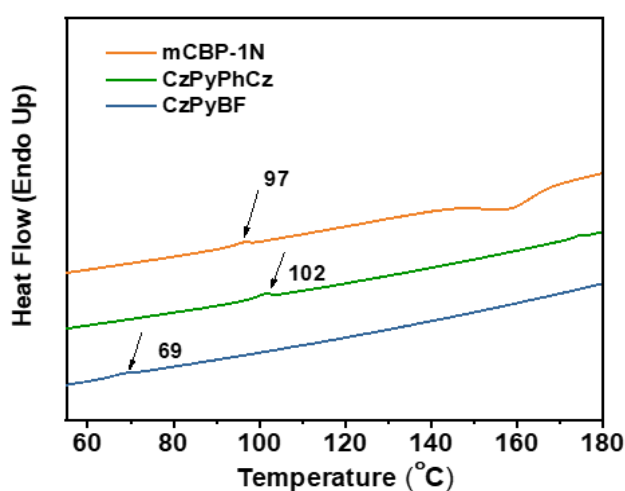


Figure 3-12. Differential scanning calorimetry (DSC) of different host materials.

Although **CzPyBF** displayed a lower thermal stability than **mCBP**, we found that it shows a better photostability by testing the PL intensities of **mCBP** and **CzPyBF** neat films under continuous UV irradiation in a nitrogen atmosphere. It was found that the LT_{50} of a **CzPyBF** film was 12.4 h, which is more stable than an **mCBP** film (6.9 h). (Figure 3-13) With all the improved photophysical properties, we expect better performance of the devices.

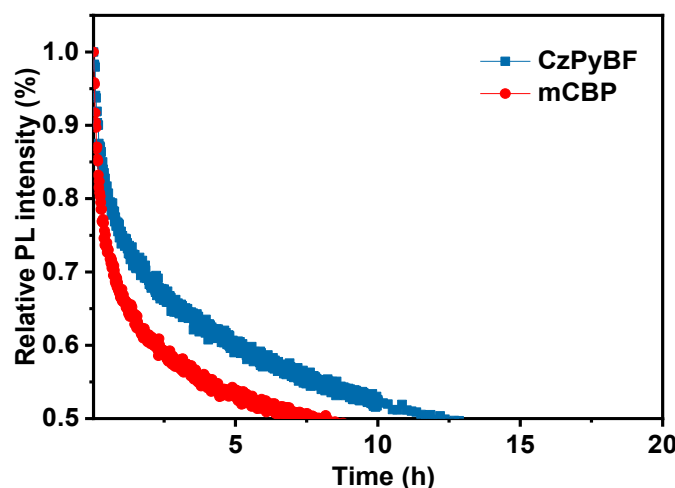


Figure 3-13. PL stability study of **CzPyBF** and **mCBP** neat films.

Table 3-1. Physical properties of four host materials.

Host	λ_{FL}^b (nm)	PLQY ^b (%)	S_1^c (eV)	T_1^d (eV)	HOMO ^e (eV)	LUMO ^f (eV)	T_g^g (°C)	T_d^h (°C)
mCBP	527	74	3.6	2.80 ⁱ	−6.1	−2.5	90 ^j	417
mCBP-1N	536	78	3.4	2.84	−5.9	−2.4	97	428
CzPyPhCz	536	69	3.5	2.87	−5.7	−2.2	102	436
CzPyBF	537	78	3.6	2.87	−6.0	−2.4	69	397

^aEmission peak measured in 15 wt% **4CzIPN**-doped film; ^bmeasured in 15 wt% **4CzIPN**-doped film; ^cestimated from the onset of fluorescent spectrum in solution; ^dmeasured in solution at 77K; ^emeasured on film samples using photo-electron yield spectroscopy; ^festimated from the HOMO values and optical band gap; ^gglass transition temperature; ^hdecomposition temperature at 5% weight loss; ⁱfrom ref. 65; ^jfrom ref. 66.

Photophysical properties were also examined with the use of thermally deposited doped films by doping 15 wt% of **4CzIPN** in the various hosts. The PLQYs of **4CzIPN** with the excitation wavelength of 340 nm were 74, 78, 69, and 78% for **mCBP**, **mCBP-1N**, **CzPyPhCz**, and **CzPyBF**, respectively. The emission spectra of all doped films displayed the emission

from **4CzIPN** without any emission from host materials, which means the successful energy transfer from each host to the green TADF emitter (**Figure 3-14**). Transient decay profiles were also studied at room temperature, in which prompt and delayed fluorescence originating from **4CzIPN** were found in all doped films; however, there was no difference among them (**Figure 3-14**).

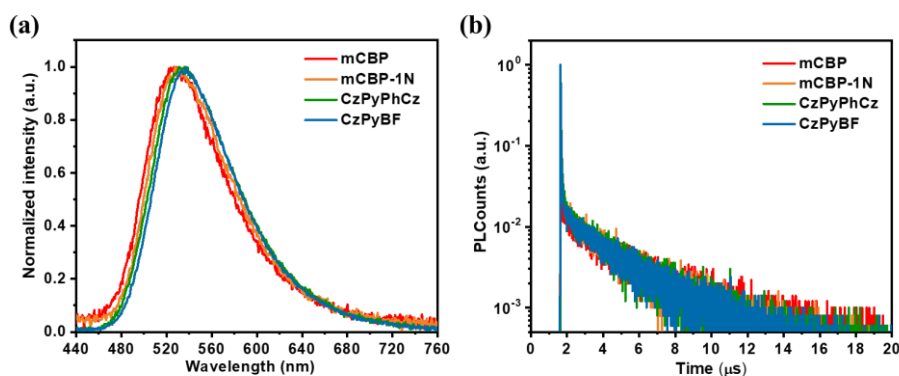


Figure 3-14. (a) Emission spectra of 15 wt% **4CzIPN** doped in various hosts; (b) transient emission decay profiles of 15 wt% of **4CzIPN** doped in various hosts.

3.3.3. OLED Performance

Same as last chapter, green TADF-OLEDs were fabricated with these three hosts with the device structure as follows: ITO/HAT-CN(10 nm)/Tris-PCz(30 nm)/15 wt%-**4CzIPN**: **mCBP** or **mCBP-1N** or **CzPyPhCz** or **CzPyBF**/T2T(10 nm)/BPy-TP2(40 nm)/LiF(0.8 nm)/Al(70 nm), and the details were depicted in **Figure 3-15** and **Table 3-2**.

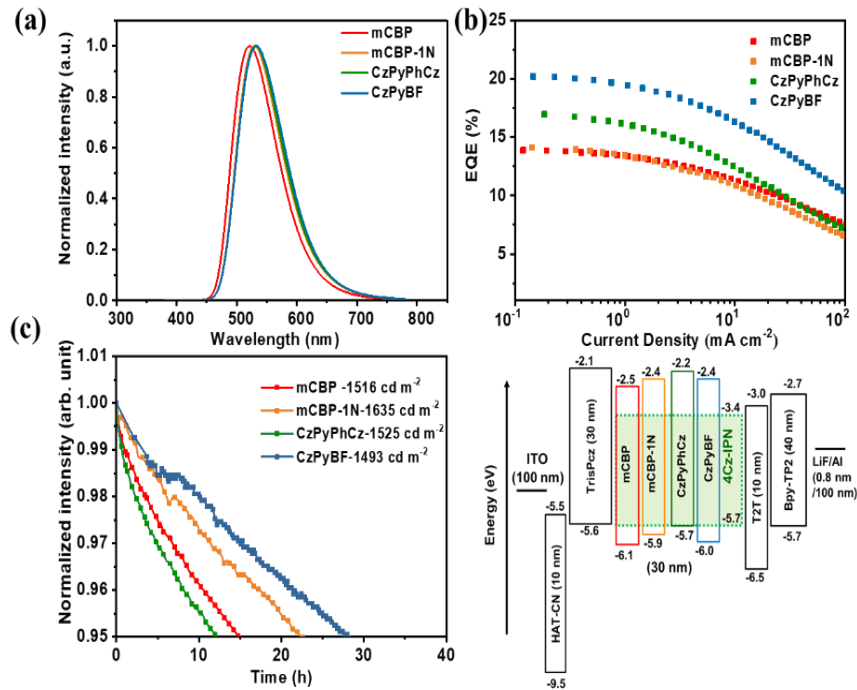


Figure 3-15. Device performance of green TADF-OLEDs based on various hosts: **mCBP**, **mCBP-1N**, **CzPyPhCz**, and **CzPyBF**. (a) Emission spectra of all devices; (b) external quantum efficiency versus current density; (c) normalized luminance versus time (at constant current density of 3.3 mA m^{-2}); (d) device structure.

Table 3-2. Device performance of green TADF-OLEDs based on **mCBP** and three new hosts.

Host	V_{on}^a (V)	L_{max}^b (cd m^{-2})	CE^c (cd A^{-1})	PE^d (lm W^{-1})	EQE^e (%)	λ_{EL}^f (nm)	CIE (x, y) ^g	LT_{95}^h (h)
mCBP	3.6/6.8	27659	45.4	38.9	14.0/12.9	522	0.31, 0.58	15
mCBP-1N	3.8/6.6	27996	47.8	37.9	14.0/12.5	529	0.34, 0.59	22
CzPyPhCz	2.8/4.8	56900	58.1	63.4	17.2/15.5	533	0.34, 0.59	12
CzPyBF	3.2/5.8	56383	67.8	57.2	20.3/19.2	533	0.35, 0.58	26

^a Voltage at 1 cd m^{-2} and 10^3 cd m^{-2} ; ^b maximum luminance at 12 V; ^c maximum current efficiency; ^d maximum power efficiency; ^e values at 1 and 10^3 cd m^{-2} ; ^f electroluminescence maximum at 10^3 cd m^{-2} ; ^g value at 10^3 cd m^{-2} ; ^h at a constant current density of 3.3 mA m^{-2} .

Electroluminescence (EL) of all devices was superimposable with their PL spectra,

indicating that excitons were well confined in **4CzIPN**. The EL spectra of devices based on three new hosts showed redshifted emissions of 529, 533, and 534 nm for **mCBP-1N**, **CzPyPhCz**, and **CzPyBF**, respectively, when compared with the reference device **mCBP** (522 nm). The redshifted emission would be due to the more polar nature of the three new hosts, which is confirmed by the solvatochromic emission study (**Figure 3-16**).

mCBP-1N-based device resulted in a maximum external quantum efficiency (EQE) of 14.0%, which is the same as that of **mCBP**. In contrast, devices based on **CzPyPhCz** and **CzPyBF** exhibited higher maximum EQEs of 17.2 and 20.3%, respectively, and showed small rollofts with EQEs of 15.5 and 19.2 % at 1000 cd m⁻². Given that all the PLQYs of doped films showed comparable EQEs, the higher EQEs might be caused by the better horizontal orientation in **CzPyPhCz** and **CzPyBF**-based devices, which gives a higher outcoupling efficiency. The devices based on **CzPyPhCz** and **CzPyBF** also showed high current efficiencies (CEs) of 58.2 and 67.8 cd A⁻¹ and power efficiencies (PEs) of 63.4 and 57.2 lm W⁻¹, respectively. On the other hand, the turn-on voltage (V_{on}) of **mCBP-1N**-based device is 3.8 V, which is slightly higher than that of **mCBP** (3.6 V); however, the device based on the isomer **CzPyPhCz** resulted in the lowest V_{on}s of 2.8 V. The lower turn-on voltage is ascribed to the lower HOMO energy level of **CzPyPhCz**, which in turn facilitates more efficient hole injection. It is worth mentioning that the driving voltages for devices **CzPyPhCz** and **CzPyBF** at the brightness of 1000 cd m⁻² were 4.8 and 5.8 V, respectively, which were significantly lower than that of Ref-**mCBP** (6.8 V).

The device stabilities of all the devices were also measured at a constant current density of 3.3 mA cm⁻² for a better comparison. The reference device **mCBP** displayed the LT₉₅ of 15 h. In contrast, the device based on **mCBP-1N** showed an extended operational lifetime of 22 h. However, although the structural isomer **CzPyPhCz** displayed a higher EQE than **mCBP**, its device lifetime was shorter, reaching only 12 h. Among the three new hosts, the device based on **CzPyBF** demonstrated the longest device stability, achieving an LT₉₅ of 26 h, which is 1.7 times higher than **mCBP**.

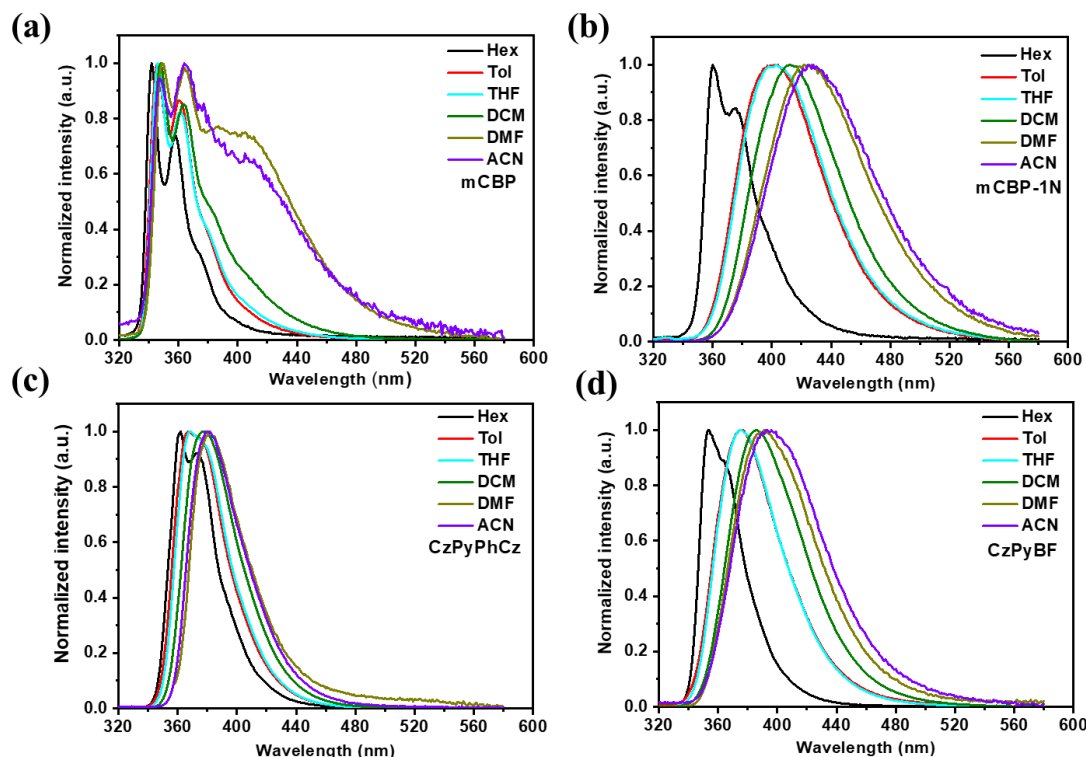


Figure 3-16. Solvatochromic emission study of different hosts in various solvents.

To get a better understanding of carrier transport properties and device lifetime in green TADF devices, hole-only and electron-only devices (HOD and EOD) were also fabricated (**Figure 3-17**). In contrast to azasilene-based hosts, it was found that the introduction of pyridine effectively balanced the carrier transporting properties. From the HODs, **CzPyPhCz** was found to exhibit superior hole-transporting behavior. Such a good hole transporting ability can be attributed to its relatively shallow HOMO energy. In addition, **mCBP**, **mCBP-1N**, and **CzPyPhCz** contained two electron-donating 9H-carbazole units (when compared to only one in **CzPyBF**), which effectively facilitated the hole hopping process. As a result, these three hosts show better hole-transporting properties than **CzPyBF**. While looking at the EODs, just like Chapter 2, we also found that the electron-transporting property of **mCBP-1N** was increased by pyridine introduction.

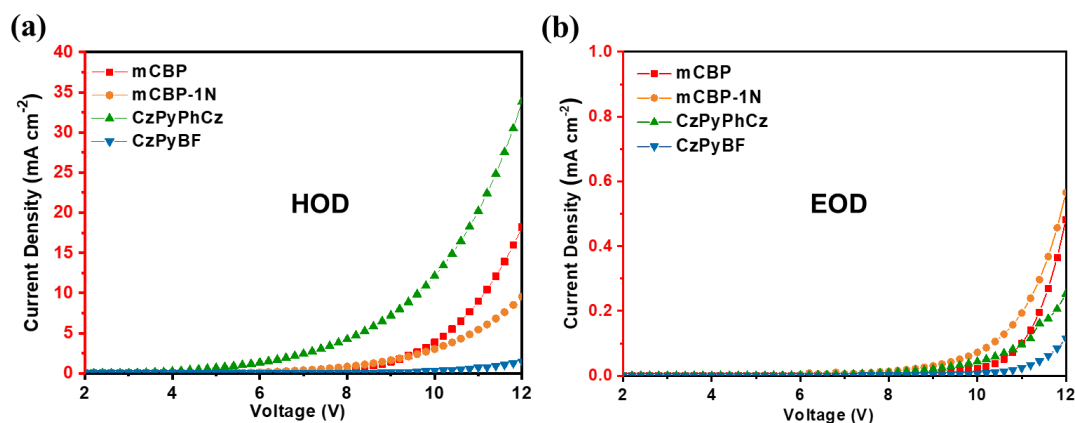


Figure 3-17. Current density – Voltage (J-V) characteristics of HOD and EOD for different hosts in 15 wt% **4CzIPN** doped films. Device structure of HOD: HATCN (10 nm)/Tris-PCz (30 nm)/15 wt% **4CzIPN:Host** (30 nm) /Tris-PCz (50 nm)/Al (100 nm). EOD: T2T (30 nm)/15 wt% **4CzIPN:Host** (30 nm)/T2T (10 nm)/Bpy-TP2 (80 nm)/Liq (2 nm)/Al (100 nm).

By calculating the ratio of hole transportation (HT) to electron transportation (ET) at 12V, it was found that although the shallow HOMO of **CzPyPhCz** gave rise to exceptionally high hole-transporting property, the resulting HOD/EOD ratio was 134:1, which was still better than those of azasilene-based hosts in Chapter 2. The improved HOD/EOD gave rise to enhanced device stability with an LT_{95} of 12 h. Interestingly, **mCBP-1N** and **CzPyBF** even led to even better HOD/EOD ratios of 17:1 and 12:1, respectively, which, in turn, extended the LT_{95} to 22 and 26 h. In addition to the more balanced carrier transporting properties of **CzPyBF**, the enhanced stability may also be due to the more stable dibenzofuran moiety than phenylcarbazole.^{37,38}

Table 3-3. Hole/Electron ratio of HODs/EODs and device lifetime based on these hosts.

Host	Hole/Electron ratio	Device Lifetime
		$LT_{95}(h)$
mCBP	39:1	15
mCBP-1N	17:1	22
CzPyPhCz	134:1	12
CzPyBF	12:1	26

3.4. Conclusion

In summary, three novel pyridine-based host materials, **mCBP-1N**, **CzPyPhCz**, and **CzPyBF**, have been successfully designed and synthesized, in which all hosts have high T_{1s} (>2.8 eV). Green TADF-OLEDs were fabricated by doping 15 wt% of **4CzIPN** in various hosts.

CzPyPhCz unexpectedly resulted in a lower driving voltage, a higher EQE, and a longer device stability than that of **mCBP**-based OLEDs. On the other hand, **CzPyBF**-based OLEDs outperformed reference **mCBP**-based OLEDs, which achieved a high EQE_{max} of 20% and long device stability of LT₉₅ = 26 h. The enhanced device performance in **CzPyBF**-based OLEDs is due to its good photostability and more balanced carrier transporting property. Most importantly, by simple molecular modification of **mCBP**, the thermal stability, chemical stability, and balanced carrier transport property were achieved at the same time. This study gives the guiding principle on the design of pyridine-based host materials for achieving high efficiency, high stability, and low driving voltage simultaneously in TADF-OLEDs. In addition, the results highlight that dibenzofuran is a promising candidate to build host materials with balanced carrier transporting properties. In the next chapter, we will demonstrate further modification of dibenzofuran host materials for achieving better device stability.

Chapter 4

Regio-isomeric Effect of Dibenzofuran-Based Host Materials on Photophysics and Device Performance in Organic Light-Emitting Diodes

4.1. Introduction

Based on the results in Chapter 3, we found that the dibenzofuran (**DBF**)-substituted host material **CzPyBF** exhibited better device lifetime compared with the commonly used host material **mCBP**. In fact, **DBF** has been demonstrated as an effective unit as a versatile building unit in organic optoelectronic materials. With a relatively high triplet energy (~ 3.2 eV) and excellent thermal and chemical stability, the **DBF** unit has been widely utilized for the construction of stable phosphorescent emitters, electron-transporting materials, and blue fluorescent emitters (**Figure 4-1**).⁶⁸⁻⁷⁰ Although a few studies have reported on **DBF**-based host materials in TADF-OLEDs, the number of reports is still limited.

Carbazole has been extensively used in OLED hosts due to its efficient hole-transporting characteristics and suitable energy levels, though carbazole-based hosts often suffer from insufficient morphological stability. To combine the strengths of both units, a series of regio-isomeric **DBF**-Carbazole-based host materials is designed to establish their structure–property relationships and to provide insights into the rational design of high-performance host materials for TADF-OLEDs in this chapter.

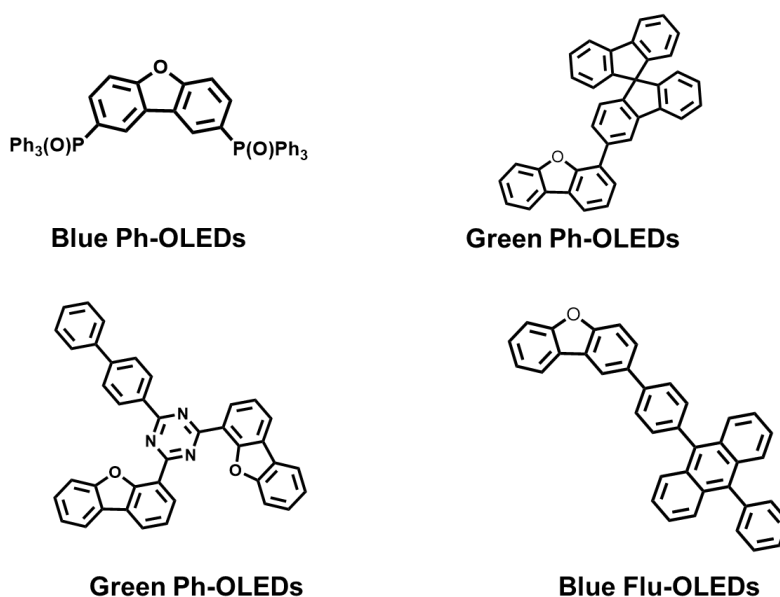


Figure 4-1. DBF-based organic functional materials.

Three new **DBF**-based host materials, **1-BF**, **2-BF**, and **4-BF**, in which the **DBF** unit is connected to a phenylcarbazole (PhCz) at different linkage positions (positions 1, 2, and 4, respectively). Since all of the hosts show twisted structures, the T_1 s are expected. In addition, we suppose that with different linkage positions, the interaction between host and emitter can be largely changed in the emitting layer, leading to different device performance.

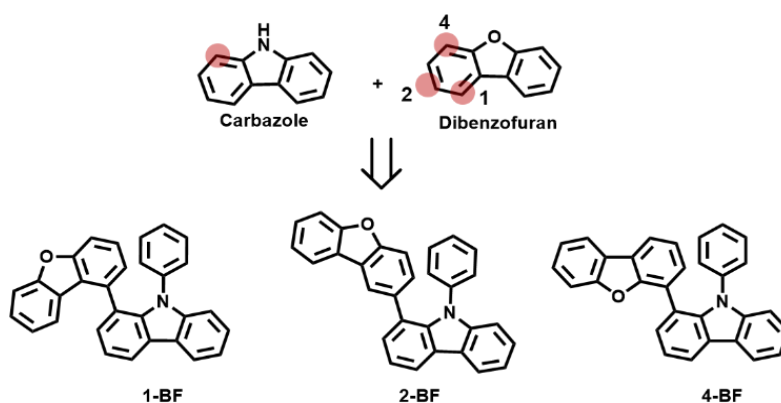


Figure 4-2: Target molecules designed in this study.

4.2. Synthesis

All of these three hosts were synthesized through two steps and acquired with high yields. After synthesis, the hosts were purified by train sublimation twice to obtain pure compounds for photophysical studies and device fabrication. The synthetic routes are depicted in **Figure 4-3**

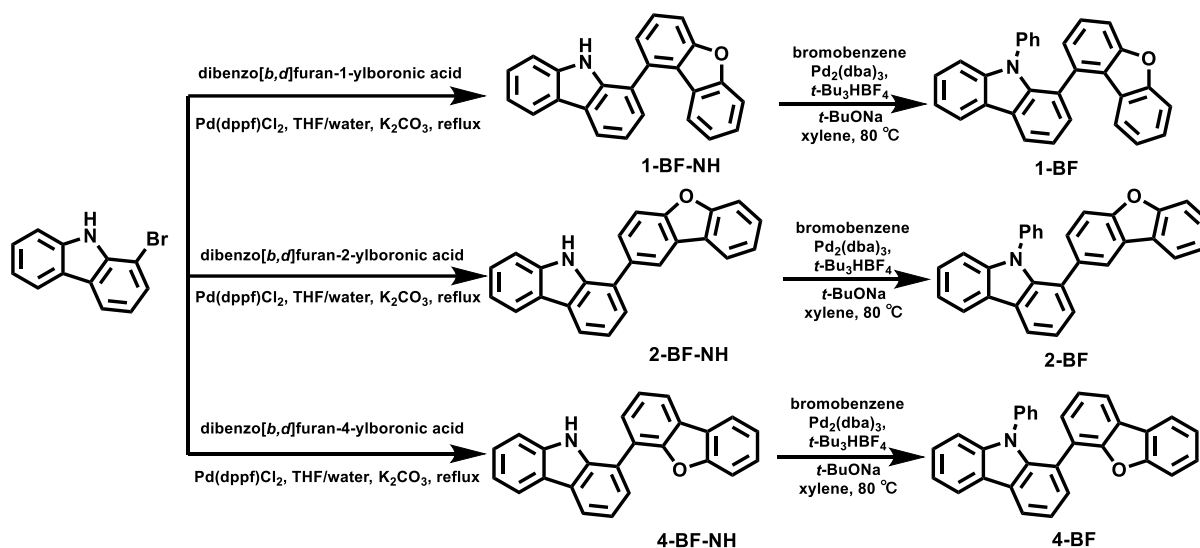
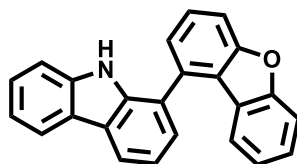
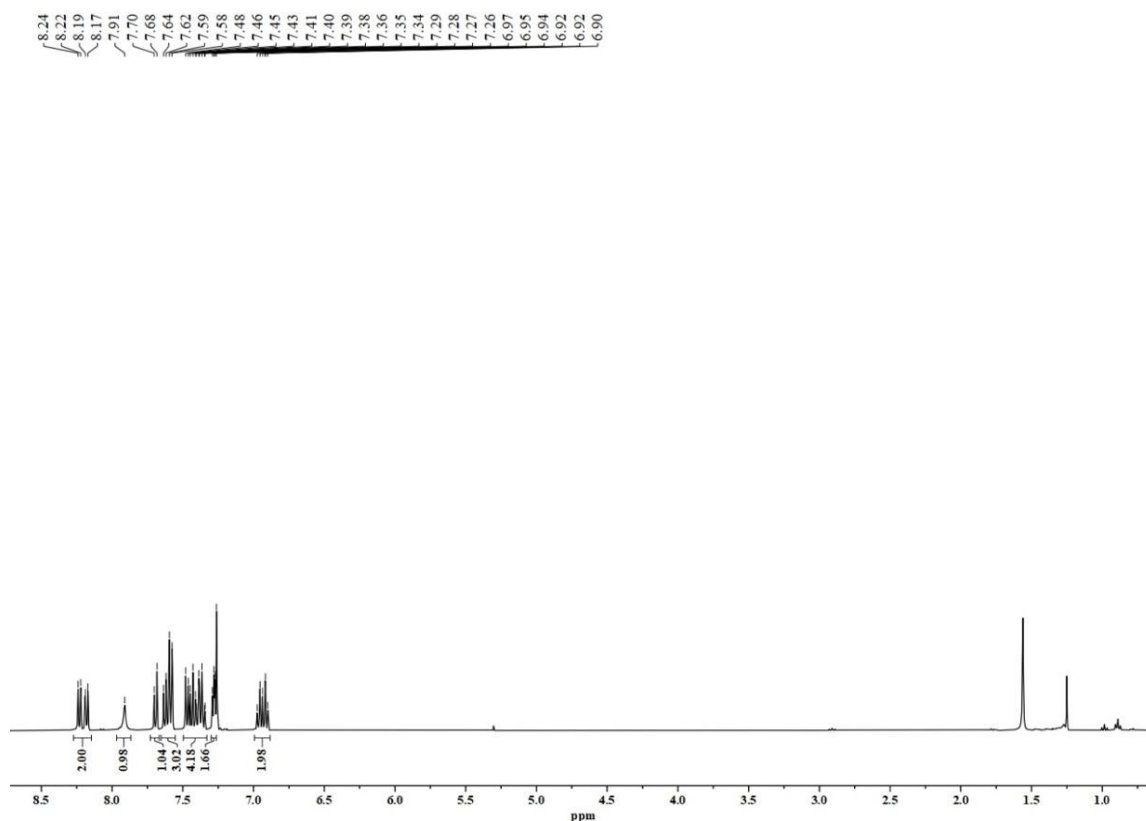


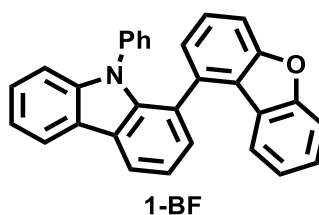
Figure 4-3. Synthetic route for three DBF-based hosts.



1-BF-NH

1-Bromo-9H-carbazole (1.50 g, 6.10 mmol, 1.0 eq), dibenzo[b,d]furan-1-ylboronic acid (1.97 g, 6.70 mmol, 1.1 eq), K_2CO_3 (2.53 g, 18.3 mmol, 3.0 eq) and $Pd(dppf)Cl_2$ (0.223 g, 0.305 mmol, 0.05 eq) were dissolved in degassed THF/water (50 ml/10 ml) mixture and heated to reflux for 12 hours. Extraction of the crude reaction mixture with dichloromethane, followed by purification by column chromatography using n-hexane:dichloromethane (25:1), gave the product as a white solid. Yield: 1.35 g, 83%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.27–8.15 (m, 2H), 7.91 (s, 1H), 7.69 (d, $J = 8.2$ Hz, 1H), 7.65–7.56 (m, 3H), 7.51–7.33 (m, 4H), 7.30–7.26 (m, 2H), 6.99–6.88 (m, 2H) (Figure 4-4).

Figure 4-4. ^1H NMR for 1-BF-NH.



To a solution of **1-BF-NH** (1.0 g, 3.00 mmol, 1.0 eq), bromobenzene (0.471 g, 3.00 mmol, 1.0 eq), and *t*-BuONa (0.576 g, 6.00 mmol, 2.0 eq) in degassed xylene (40 ml) was added *t*-Bu₃PHBF₄ (69.6 mg, 0.240 mmol, 0.08 eq), and stirred at 80 °C for 15 min. Under an N₂ atmosphere, Pd₂(dba)₃ (54.9 mg, 0.060 mmol, 0.02 eq) was added, and the reaction was stirred at 130 °C for 14 hours. Upon cooling down to room temperature, the mixture was diluted with CH₂Cl₂ and filtered through silica gel. The concentration of the crude product, followed by column chromatography using *n*-hexane:dichloromethane = 30:1, gave the product as a white solid. Yield: 1.02 g, 75%. ¹H NMR (400 MHz, CDCl₃): δ 8.35 (dd, *J* = 7.3, 1.6 Hz, 1H), 8.27 (dd, *J* = 6.2, 2.2 Hz, 1H), 7.53–7.44 (m, 3H), 7.39–7.29 (m, 3H), 7.29–7.21 (m, 2H), 7.14–7.03 (m, 2H), 6.97–6.84 (m, 3H), 6.81 (s, 1H), 6.66 (d, *J* = 8.3 Hz, 1H), 6.59–6.47 (m, 1H), 6.29 (d, *J* = 7.5 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃): δ 155.85, 155.41, 142.39, 137.88, 136.98, 134.48, 128.33, 127.79, 127.09, 126.79, 126.72, 126.48, 126.12, 124.53, 124.41, 124.32, 123.48, 123.01, 122.96, 122.46, 121.93, 120.21, 120.12, 120.09, 119.91, 111.01, 110.20, 109.87 (Figure 4-5 and 4-6).

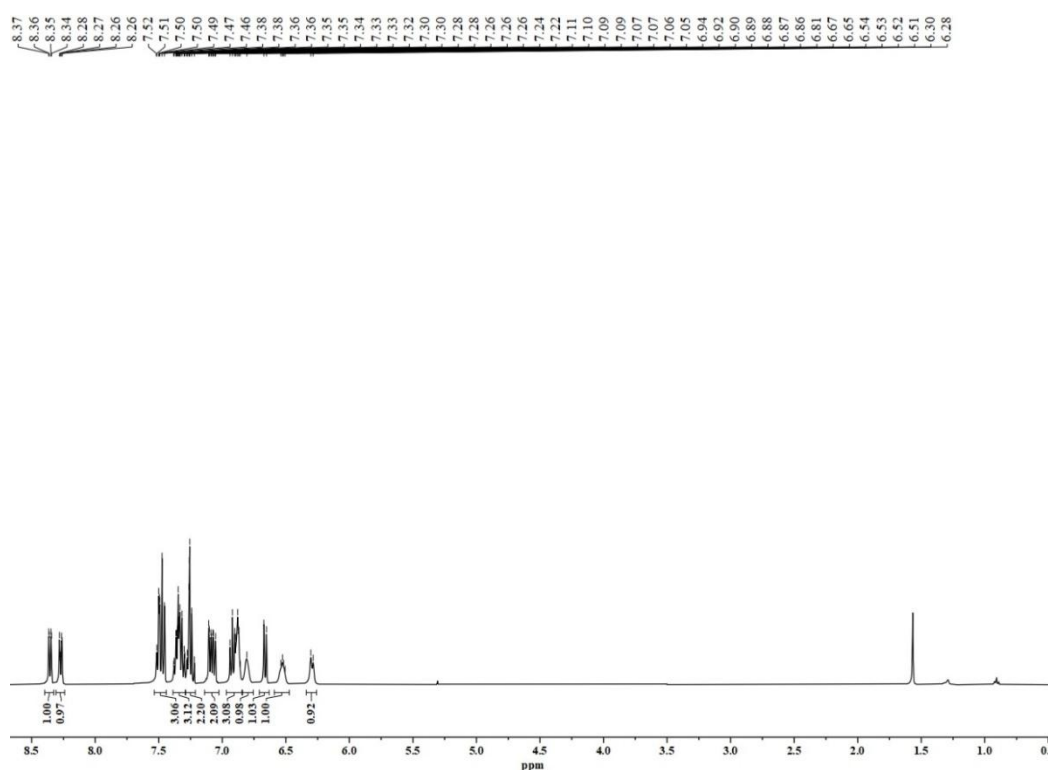


Figure 4-5. ¹H NMR for **1-BF**.

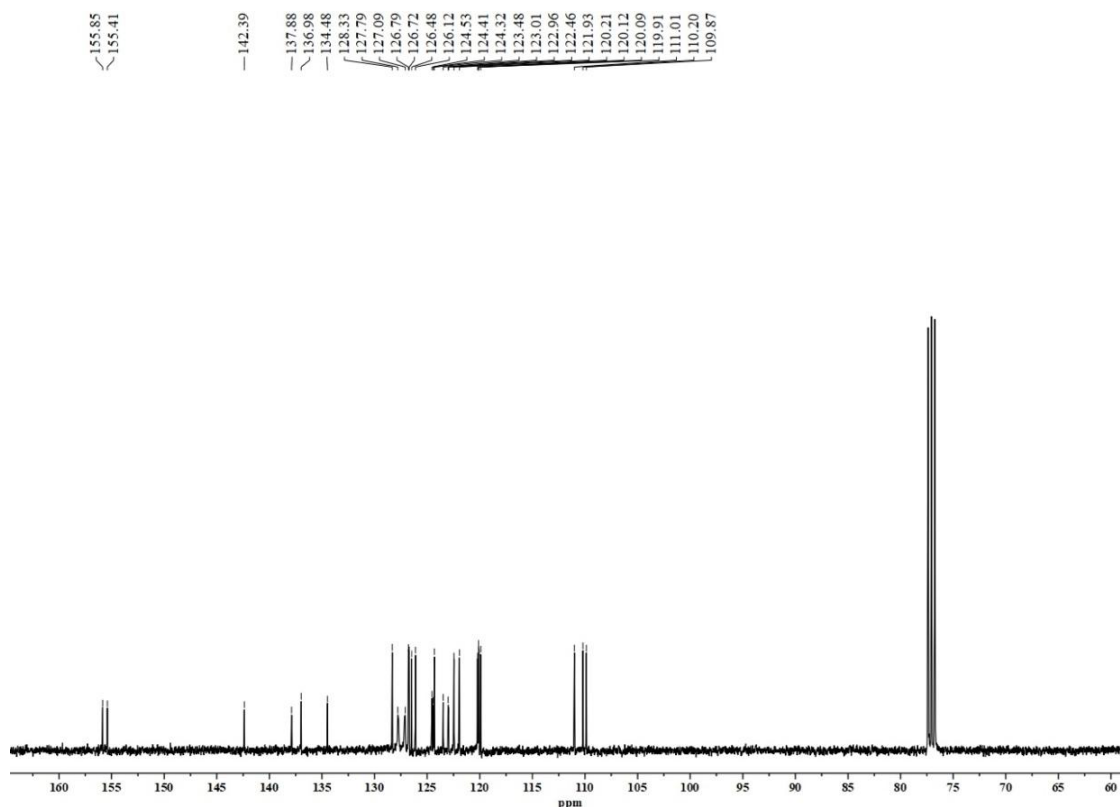
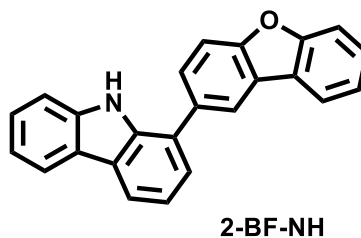


Figure 4-6. ^{13}C NMR for **1-BF**.



The procedure is similar to **1-BF-NH**, except dibenzo[b,d]furan-2-ylboronic acid is used instead of dibenzo[b,d]furan-1-ylboronic acid. Yield: 1.81 g, 89%. ^1H NMR (400 MHz, CDCl_3): δ 8.36 (s, 1H), 8.25 (d, $J = 1.4$ Hz, 1H), 8.13 (dd, $J = 12.0, 7.8$ Hz, 2H), 8.02 (d, $J = 7.2$ Hz, 1H), 7.81–7.72 (m, 2H), 7.65 (d, $J = 8.2$ Hz, 1H), 7.56–7.49 (m, 2H), 7.47–7.43 (m, 2H), 7.43–7.34 (m, 2H), 7.29 (m, 1H) (**Figure 4-7**).

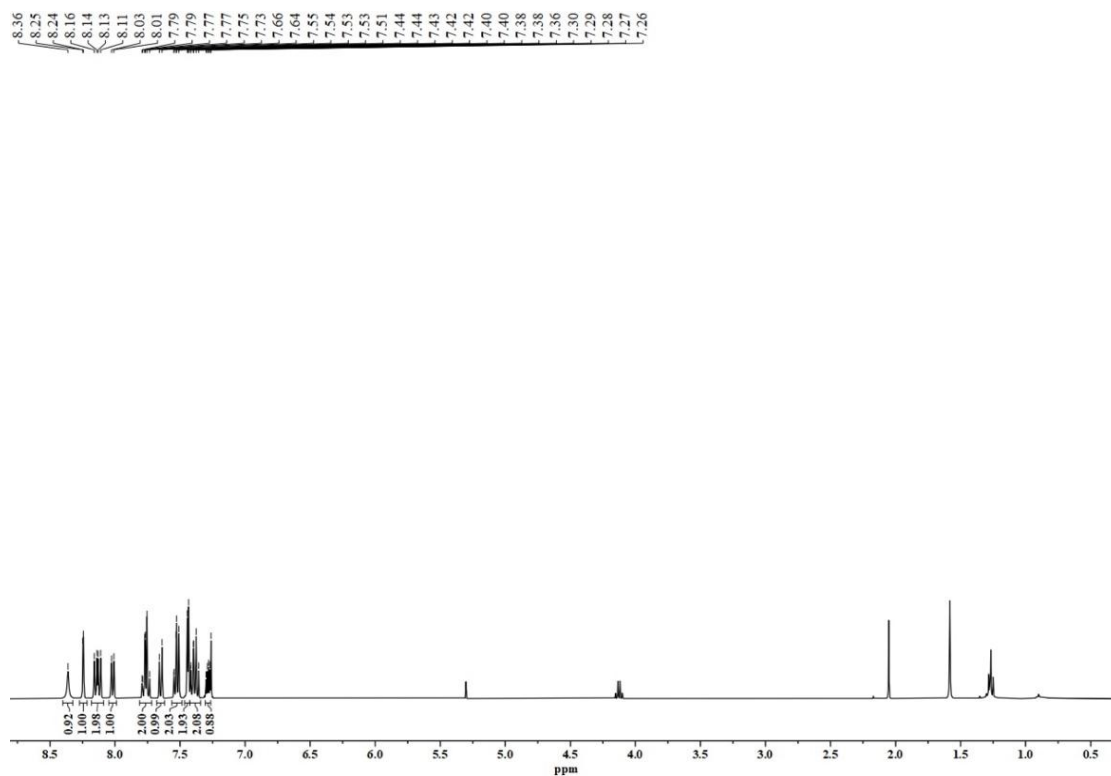
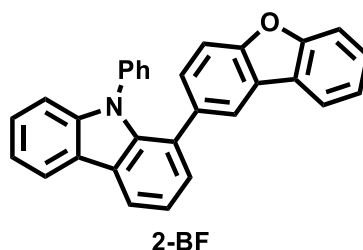


Figure 4-7. ^1H NMR for **2-BF-NH**.



The procedure is similar to **1-BF**, except **2-BF-NH** is used instead of **1-BF-NH**. Yield: 1.11 g, 90%. ^1H NMR (300 MHz, CDCl_3): δ 8.30–8.21 (m, 2H), 7.79 (d, $J = 7.0$ Hz, 1H), 7.63–7.53 (m, 2H), 7.51–7.27 (m, 7H), 7.19 (s, 2H), 7.05 (d, $J = 7.1$ Hz, 2H), 6.92 (t, $J = 7.9$ Hz, 2H), 6.76 (t, $J = 7.4$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ 156.43, 154.86, 142.35, 138.44, 138.06, 133.78, 129.05, 128.53, 128.35, 127.73, 126.98, 126.73, 126.41, 126.14, 124.84, 124.07, 123.22, 123.15, 122.61, 121.64, 120.64, 120.18, 120.13, 119.86, 119.43, 111.58, 110.25, 110.22 (**Figure 4-8** and **4-9**).

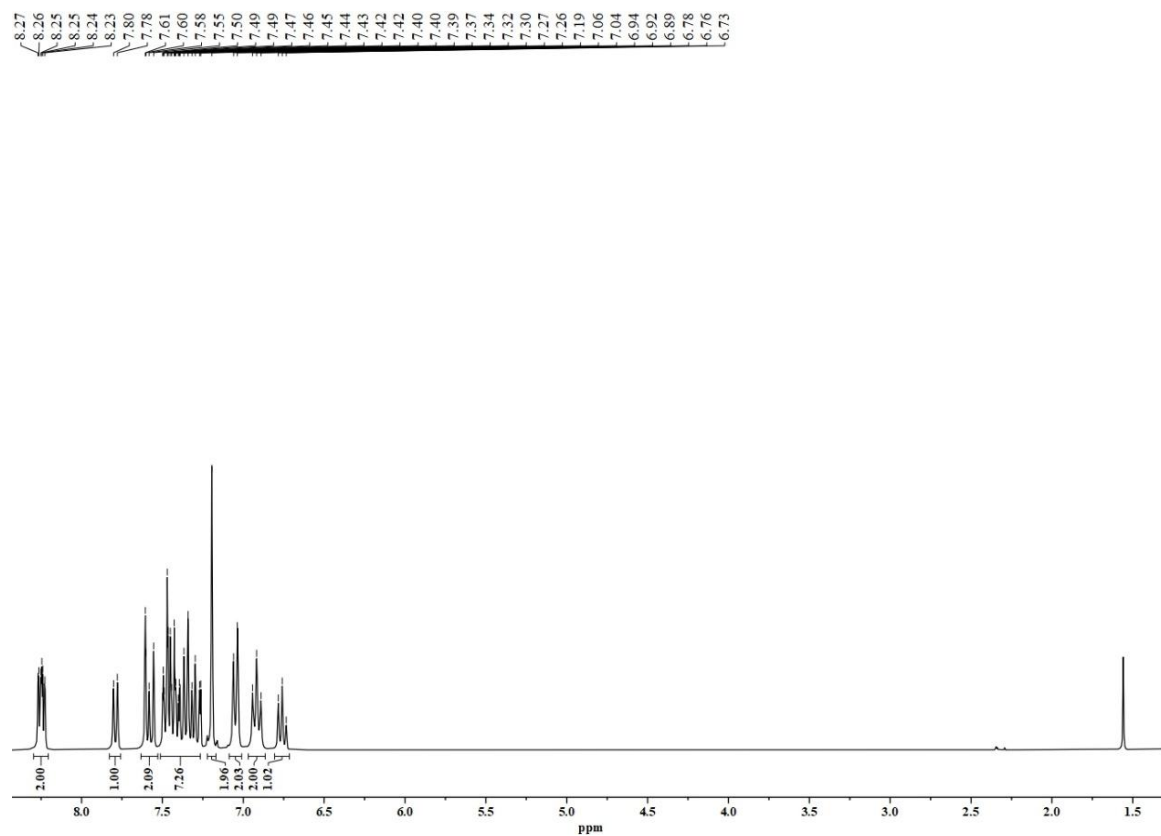


Figure 4-8. ¹H NMR for 2-BF.

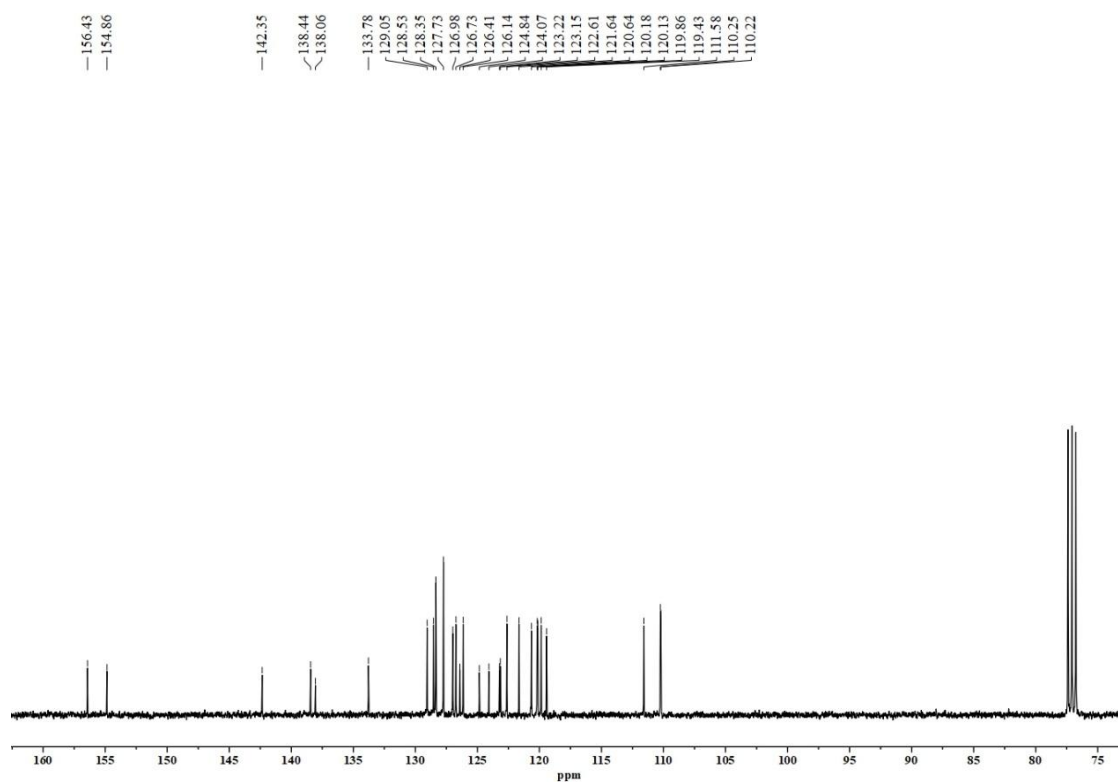
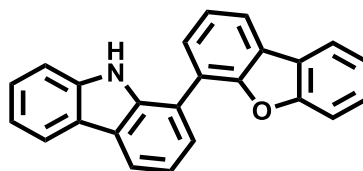
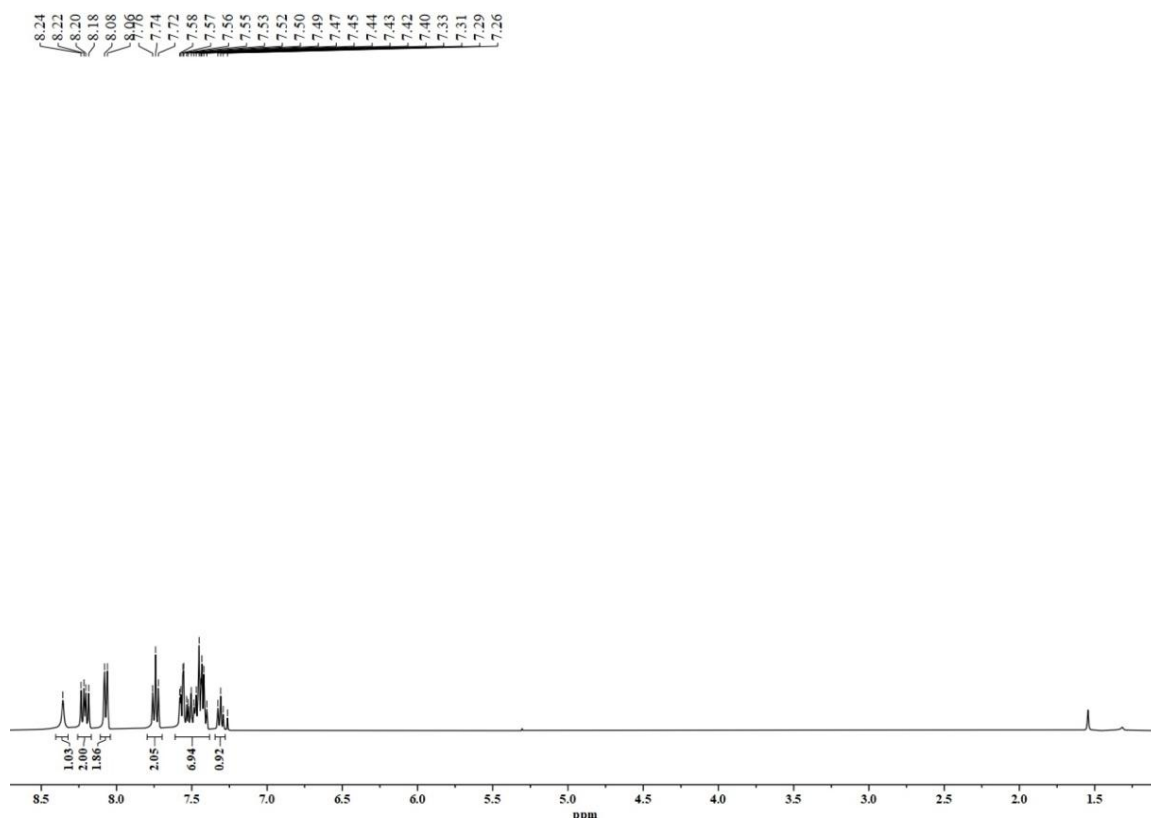
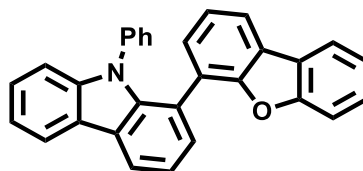


Figure 4-9. ¹³C NMR for 2-BF.

**4-BF-NH**

The procedure is similar to **1-BF-NH**, except dibenzo[b,d]furan-4-ylboronic acid is used instead of dibenzo[b,d]furan-1-ylboronic acid. Yield: 1.28 g, 79%. ^1H NMR (400 MHz, CDCl_3): δ 8.36 (s, 1H), 8.26–8.17 (m, 2H), 8.07 (d, $J = 7.7$ Hz, 2H), 7.74 (t, $J = 8.0$ Hz, 2H), 7.61–7.38 (m, 7H), 7.31 (t, $J = 7.2$ Hz, 1H) (**Figure 4-10**).

**Figure 4-10.** ^1H NMR for **4-BF-NH**.**4-BF**

The procedure is similar to **1-BF**, except **4-BF-NH** is used instead of **1-BF-NH**. Yield: 1.16 g, 86%. ^1H NMR (400 MHz, CDCl_3): δ 8.33 (d, $J = 7.7$ Hz, 1H), 8.26 (d, $J = 7.9$ Hz, 1H), 7.82 (d, $J = 7.6$ Hz, 1H), 7.65 (d, $J = 7.7$ Hz, 1H), 7.54 (d, $J = 7.3$ Hz, 1H), 7.47 (t, $J = 7.5$ Hz,

1H), 7.43–7.28 (m, 6H), 7.22–7.15 (m, 2H), 7.01 (s, 1H), 6.87–6.67 (m, 3H), 6.40 (s, 1H). ¹³C NMR (101 MHz, CDCl₃): δ 155.66, 153.01, 142.38, 138.19, 136.78, 128.82, 127.90, 127.29, 126.93, 126.63, 126.07, 124.55, 124.32, 124.22, 123.51, 123.05, 122.43, 122.42, 120.54, 120.44, 120.33, 120.17, 120.04, 119.75, 119.47, 111.76, 110.06 (Figure 4-11 and 4-12).

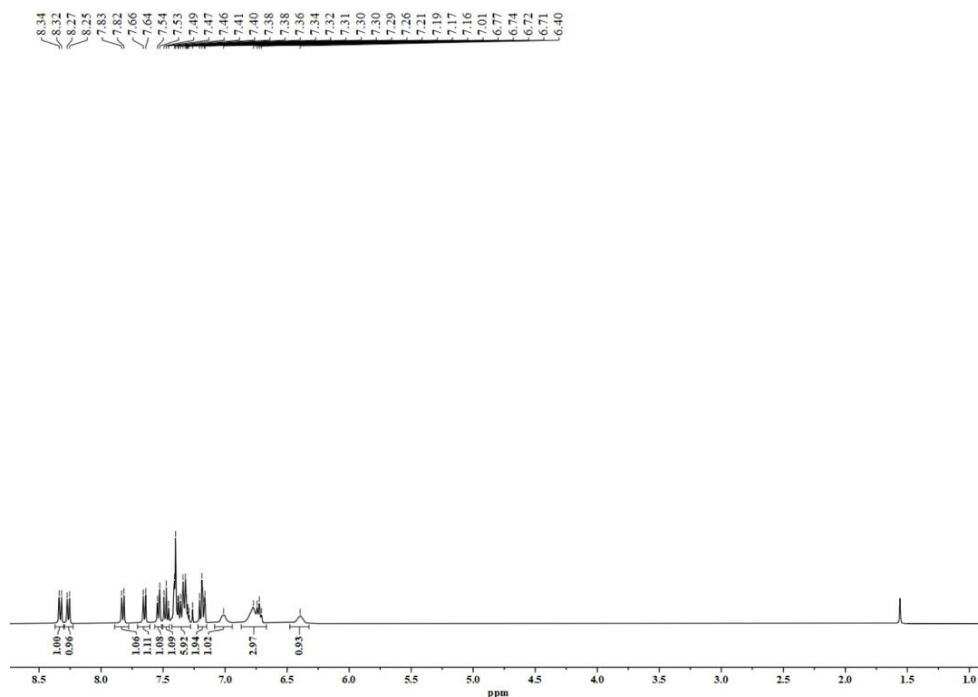


Figure 4-11. ¹H NMR for 4-BF.

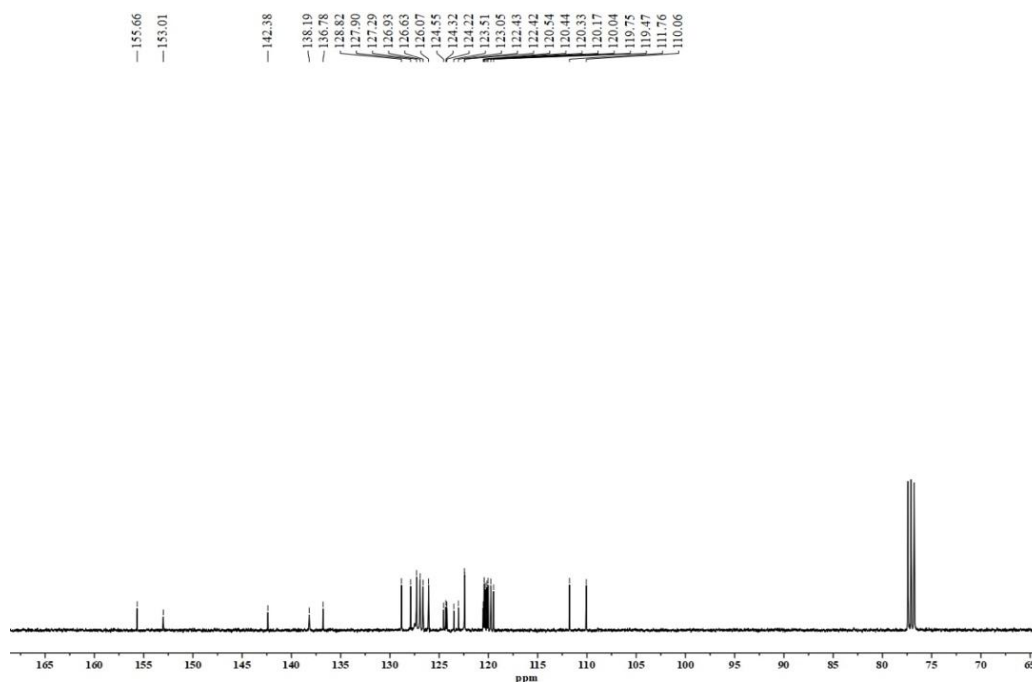


Figure 4-12. ¹³C NMR for 4-BF.

4.3. Results and Discussion

4.3.1. Theoretical Calculations

TD-DFT calculations have been performed with the B3LYP/6-31G level of theory to estimate the S_1 and T_1 energy levels of three host materials and their corresponding HOMO and LUMO (**Figure 4-13**). The calculated S_1 energies of **1-BF**, **2-BF**, and **4-BF** were found to be 3.71, 3.76, and 3.68 eV, respectively, while their corresponding T_1 energies were 3.05, 3.06, and 3.01 eV. As expected, DBF-based host materials possess high S_1 and T_1 energies that are appropriate for the confinement of blue/green excitons. The HOMOs were localized on the PhCz unit in all three materials, whereas the LUMO of **2-BF** was only localized on the DBF unit, leading to intramolecular charge-transfer (CT) character. In contrast to **2-BF**, the LUMOs of **1-BF** and **4-BF** were mainly localized on the DBF unit with a slight delocalization on the PhCz unit, leading to a hybridized local and CT character in their ground states. The HOMO levels of these three hosts showed no difference, calculated at -5.68, -5.63, and -5.63 for **1-BF**, **2-BF**, and **4-BF**, respectively. Their LUMO levels were also comparable, determined to be -1.40, -1.36, and -1.41 eV for **1-BF**, **2-BF**, and **4-BF**, respectively.

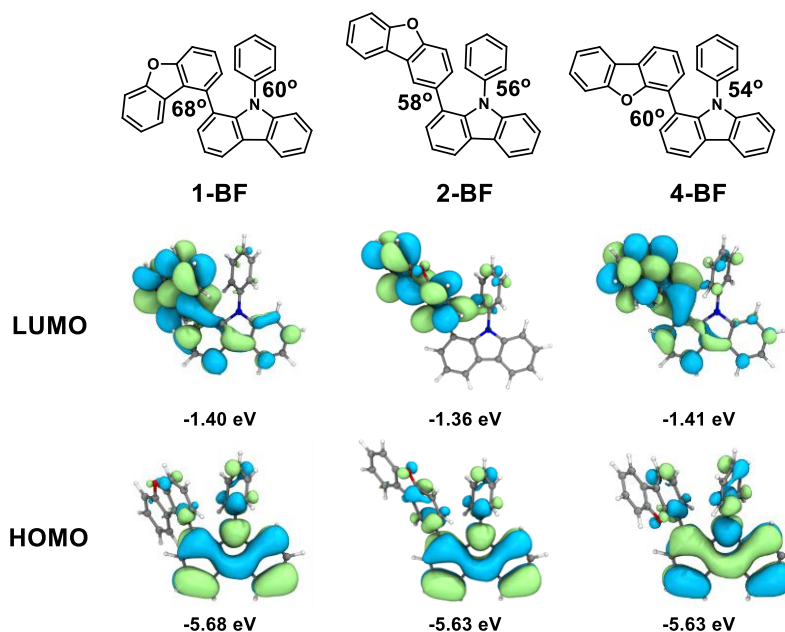


Figure 4-13. Chemical structures for **1-BF**, **2-BF**, and **4-BF** and their HOMO and LUMO distributions with excited state energies based on B3LYP/6-31G level.

Table 4-1. TD-DFT calculations.

Host	S ₁ (eV)	T ₁ (eV)	HOMO (eV)	LUMO (eV)
1-BF	3.71	3.05	-5.68	-1.40
2-BF	3.76	3.06	-5.63	-1.36
4-BF	3.68	3.01	-5.63	-1.41

4.3.2. Photophysical Study

The three hosts' photophysical properties were studied by ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) spectroscopy in toluene solutions and neat thin films (**Figures 4-14** and **4-15**). All host materials exhibited an absorption band below 400 nm. The absorption bands below 325 nm were assigned as the π - π^* transitions of the host materials, while the weak absorption bands above 325 nm were assigned intramolecular CT transitions. Interestingly, the emission characteristics depend on the linking position of the DBF units. In the case of **2-BF**, the LUMO was localized on the DBF unit, giving rise to a vibronic emission spectrum with the emission maxima at 357 and 369 nm. On the other hand, the LUMOs of **1-BF** and **4-BF** were delocalized over the DBF and PhCz units, which, in turn, showed structureless emission spectra with emission maxima at 373 and 369 nm, respectively (**Figure 14a**). The T₁ energy levels of **1-BF**, **2-BF**, and **4-BF** in toluene were determined from the spectral onset of the phosphorescence in a frozen medium at 77 K as 2.88, 2.99, and 2.93 eV, respectively, which were consistent with the calculated values (**Figure 14b**).

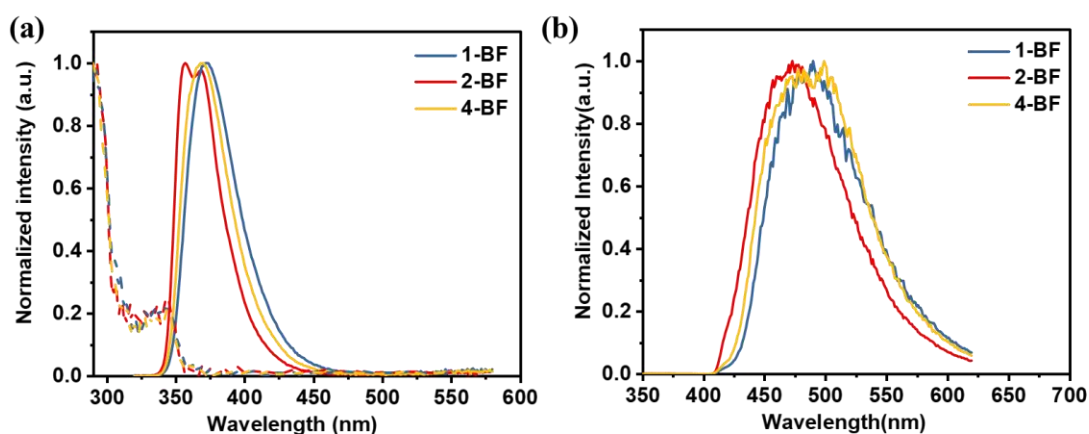


Figure 4-14. (a) Absorption and PL spectra of **1-BF**, **2-BF**, and **4-BF** in toluene at 298 K and (b) at 77 K (1.0×10^{-5} mol dm⁻³). For phosphorescence spectra, a delayed time of 106 ms and an integration time of 150 ms were used.

The S_1 and T_1 energy levels of the films were also estimated from the spectral onset of the neat films. The emission spectra of **1-BF**, **2-BF**, and **4-BF** in neat films at room temperature were all similar to those in toluene. The T_1 energy levels of **1-BF**, **2-BF**, and **4-BF** in neat films were determined to be 2.74, 2.77, and 2.74 eV, respectively, which were slightly lower in energy than those in toluene solutions (**Figure 15d**). The reason for the lower T_1 s of three host materials in neat films was due to the fact that intermolecular p-p interactions exist, resulting in an extended electron delocalization. Both phosphorescent spectra in solution and in neat films at 77 K showed structureless emission bands, indicating CT character in the T_1 states. All the photophysical data are summarized in **Table 4-2**.

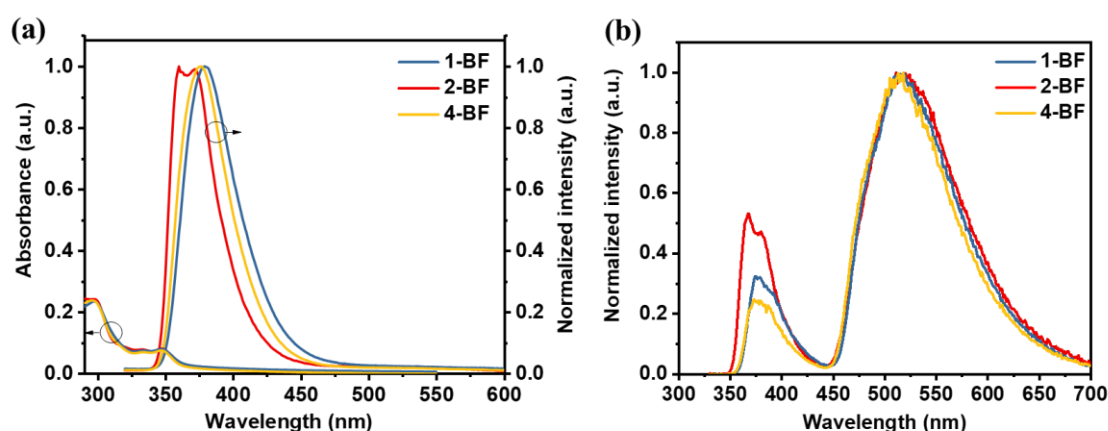


Figure 4-15. (a) Absorption and PL spectra of **1-BF**, **2-BF**, and **4-BF** in neat films at 298 K (30 nm) on quartz substrate at 298 K and (b) phosphorescence spectra at 77 K. For phosphorescence spectra, a delayed time of 106 ms and an integration time of 150 ms were used.

Table 4-2. Photophysical properties of **1-BF**, **2-BF**, and **4-BF** in toluene. Photophysical and thermal properties of **1-BF**, **2-BF**, and **4-BF** in toluene and neat films.

Host	Solution ^a λ_{PL} (nm)	Solution ^a S_1/T_1^c (eV)	Neat film ^b S_1/T_1^c (eV)	HOMO ^d (eV)	LUMO ^e (eV)	T_d^f (°C)
1-BF	373	3.58/2.88	3.54/2.74	-6.1	-2.7	281
2-BF	357, 369	3.62/2.99	3.58/2.77	-6.0	-2.6	307
4-BF	369	3.59/2.93	3.57/2.74	-5.9	-2.5	295

^a At the concentration of 10^{-5} mol dm⁻³; ^b vacuum deposited films; ^c at 77 K; ^d measured on film samples using Riken AC-3; ^e Estimated from the HOMO values and optical band gap; ^f decomposition temperature at 5% weight loss.

The HOMO levels of all host materials were estimated by electrochemical measurement (solution, **Figure 4-16**) and photo-electron yield spectroscopy in air (thin film, **Figure 4-17**). From oxidation waves of cyclic voltammograms, **1-BF**, **2-BF**, and **4-BF** exhibited similar potentials for oxidation at 0.9, 0.8, and 0.9 V, respectively, versus ferrocene/ferrocenium (Fc/Fc^+). In the neat film, the estimated HOMO levels were deeper (-6.1 eV, -6.0 , and -5.9 eV for **1-BF**, **2-BF**, and **4-BF**, respectively) than those in the solution.

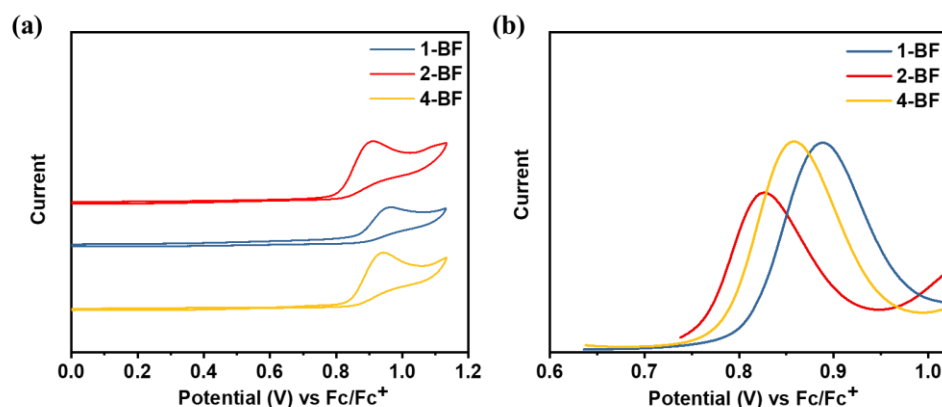


Figure 4-16. (a) Cyclic voltammogram (b) differential pulse voltammetry of the oxidative scan and of **1-BF**, **2-BF**, and **4-BF** in N,N -dimethylformamide.

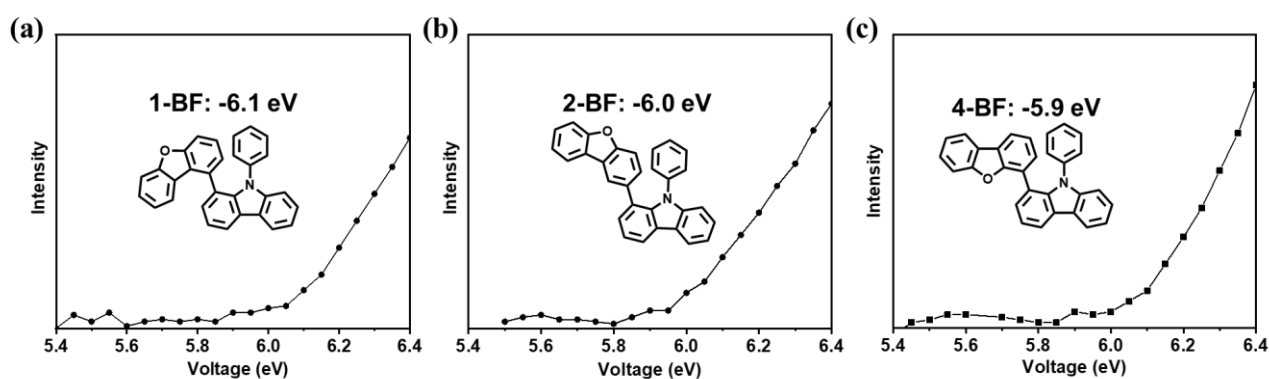


Figure 4-17. Photoelectron spectral measurements of (a) **1-BF**, (b) **2-BF**, and (c) **4-BF** neat films under nitrogen atmosphere.

All host materials exhibited high thermal stability, with the decomposition temperature at 5% weight loss (T_d) over 250 °C (**Figure 4-18**), in which **2-BF**, with a more planar structure, showed the highest T_d of 307 °C.

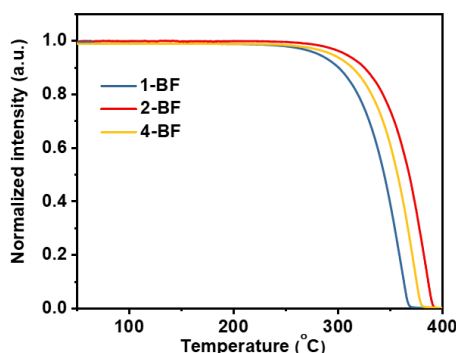


Figure 4-18. TGA measurement of **1-BF**, **2-BF**, and **4-BF**.

By doping a 15 wt%-green TADF emitter (**4CzIPN**) in three host materials, **1-BF**, **2-BF**, and **4-BF**, doped films showed comparable PL quantum yield (PLQY) of 73, 77, and 75%, respectively, together with an emission maximum of 529, 529, and 527 nm. The reverse intersystem crossing rates for 15 wt% **4CzIPN** in **1-BF**-, **2-BF**-, and **4-BF**-doped films were comparable at 8.21×10^5 , 7.72×10^5 , and $7.48 \times 10^5 \text{ s}^{-1}$, respectively (**Figure S14**).¹⁸ All the data is shown in **Figure 4-19** and summarized in **Table 4-3**.

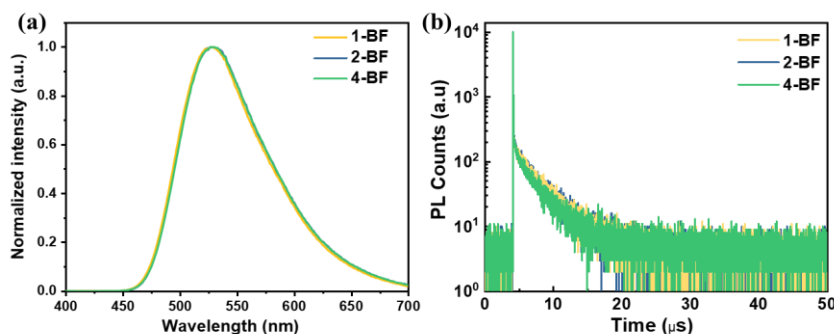


Figure 4-19. (a) PL spectra and (b) transient emission decay profiles of 15 wt% of **4CzIPN** doped in various hosts.

Table 4-3. Photophysical properties of 15 wt% of **4CzIPN** doped in various hosts.

Host	λ_{PL} (nm) ^a	PLQY (%)	τ_{p} (ns) ^b	τ_{d} (μs) ^c	k_{RISC} (10^5 s^{-1})	k_{nr}^{S} (10^6 s^{-1})	k_{ISC} (10^7 s^{-1})
1-BF	529	72.7	17.25	3.17	8.21	5.88	3.84
2-BF	529	77.3	18.91	3.40	7.72	6.56	3.58
4-BF	527	74.7	18.93	3.05	7.48	8.15	3.34

^a Emission maximum; ^b prompt lifetime; ^c delayed lifetime.

4.3.3. OLED Performance

The performance of three DBF-based hosts in green TADF-OLEDs was also studied. The configuration of the **4CzIPN**-based device is: ITO/HAT-CN (10 nm)/Tris-PCz (30 nm)/ 15 wt%-**4CzIPN**: **1-BF**, **2-BF** or **4-BF** (30 nm)/T2T (10 nm)/BPy-TP2 (40 nm)/Liq (2 nm)/Al (100 nm). The detailed device performance is shown in **Figure 4-20** and **Table 4-4**.

The reference device based on **mCBP** resulted in electroluminescence (EL) of 522 nm with a decent maximum external quantum efficiency (EQE_{max}) of 14.8 %. Devices based on **1-BF**, **2-BF**, and **4-BF** showed comparable EL with the emission maximum at 521, 522, and 527 nm, respectively. **2-BF** and **4-BF** displayed similar EQE_{max} s of 14.6 and 14.0 %, respectively, to the reference **mCBP** device (14.8%), while **1-BF** achieved a slightly lower EQE_{max} of 13.3 %. The lower EQE_{max} values may originate from the lower PLQY resulting from the **1-BF**-doped film. Despite the lower EQE, **1-BF** exhibited decent device stability with LT_{95} of 67 h at a constant current density of 3.3 mA cm^{-2} , which outperformed the **2-BF** (56 h) and reference devices (30 h).

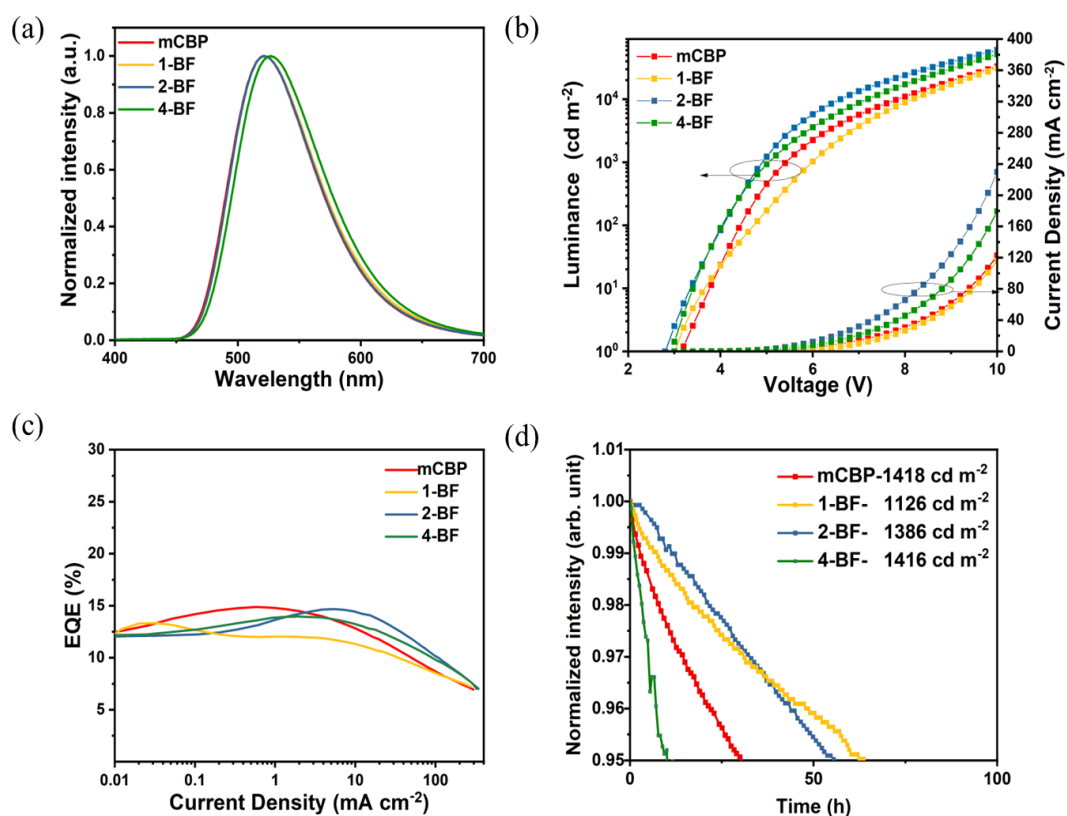


Figure 4-20. OLED performance of green TADF OLEDs based on four hosts with 15 wt% of 4CzIPN. (a) EL spectra of all devices at 1000 cd m^{-2} ; (b) current density versus voltage versus luminance; (c) external quantum efficiency versus current density; (d) normalized luminance versus time (at a constant current density of 3.3 mA cm^{-2}).

Table 4-4. Device performance of green TADF-OLEDs based on **mCBP** and DBF-based hosts.

Host	V_{on}^a (V)	L_{max}^b (cd m ⁻²)	CE^c (cd A ⁻¹)	PE^d (lm W ⁻¹)	EQE^e (%)	λ_{EL}^f (nm)	CIE (x, y) ^g	LT_{95} (h) ^h
mCBP	3.2	33045	49.5	40.6	14.8	522	0.297, 0.593	30
1-BF	3.0	30988	43.6	37.9	13.3	521	0.296, 0.590	67
2-BF	2.8	60288	48.6	40.4	14.6	522	0.298, 0.594	56
4-BF	3.0	51435	47.4	41.1	14.0	527	0.322, 0.594	8

^aTurn-on voltage at 1 cd m⁻²; ^bmaximum luminance at 12 V; ^cmaximum current efficiency; ^dmaximum power efficiency; ^evalues at 1 cd m⁻²; ^felectroluminescence maximum at 10³ cd m⁻²; ^gvalue at 10³ cd m⁻²; ^hat a constant current density of 3.3 mA cm⁻².

In Chapter 3, the **CzPyBF**-based device showed the longest device lifetime due to the better photochemical property and more balanced carrier transport property. Since all three hosts are based on the dibenzofuran structure and lifetimes showed noticeable differences, it is a good opportunity to investigate other factors, e.g., photochemical and thermal stability, which may play a more crucial role in affecting device lifetime. We first examined the correlation between the photochemical stability of the host materials and their corresponding device stability. The photochemical stability of the neat films of four hosts was determined by continuous UV irradiation of 300-400 nm with an intensity of 25 mW cm⁻² (**Figure 4-21**). **1-BF** and **4-BF** neat films showed LT_{70} (70% of the initial luminance) of 12 and 15 h, respectively, which were more stable than those of **2-BF** and **mCBP** ($LT_{70} = 7$ h). Despite **4-BF**'s best photochemical stability, it shows the worst device stability. Considering the lower glass-transition temperatures (T_g s) of all **DBF**-based hosts (< 70 °C) compared with **mCBP** (90 °C) and their irreversible oxidation curves, it is anticipated that other factors, different from thermal and chemical stabilities, play a more important role in affecting device stability.

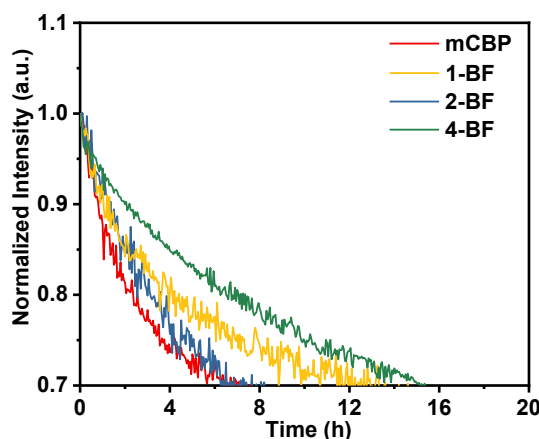


Figure 4-21. Photostability of neat films under continuous UV irradiation of 300-400 nm light with 25 mW cm^{-2} .

In Chapters 2 and 3, we have learnt that the HOD/EOD ratio is a good indicator for evaluating the carrier transporting properties of the device. The smaller the ratio is, the better the device stability we can achieve. The carrier transport properties of all devices have been estimated by fabricating hole-only and electron-only devices (HODs and EODs) (**Figure 4-22**). Interestingly, the descending order of HOD/EOD current density ratio at 12V was found to be **4-BF** (43:1) > **mCBP** (27:1) > **2-BF** (16:1) > **1-BF** (13:1), which, in turn, sufficiently accounted for the device stability (LT_{95}) order of **4-BF** (8 h) < **mCBP** (30 h) < **2-BF** (56 h) < **1-BF** (67 h). From the HOD and EOD of **1-BF**, the corresponding current densities were estimated to be 6.5 and 0.5 mA cm^{-2} , yielding the smallest ratio of 13. When the HOD/EOD ratio approaches 1, the carrier-transport properties are balanced, leading to carrier recombination in the middle of the emitting layer and better exciton recombination. Therefore, **1-BF** exhibited the most balanced hole- and electron-transport properties, resulting in prolonged device stability. Although the higher photochemical stability and more balanced carrier transport properties of **1-BF** and **2-BF** are the major reasons for their better stability, we do not rule out other possible factors, such as triplet-triplet and singlet-triplet annihilation, that may also affect the device lifetime. The data are summarized in **Table 4-5**.

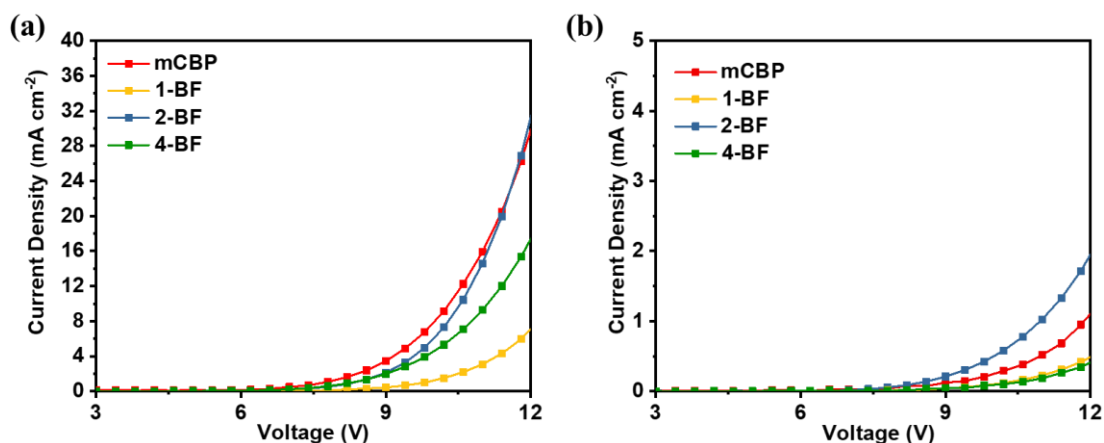


Figure 4-22. (a) Hole-only devices; (b) Electron-only devices for different hosts doped with 15 wt% of **4CzIPN**. Device structure of HOD: HATCN (10 nm)/Tris-PCz (30 nm)/15 wt% **4CzIPN**: host (30 nm)/Tris-PCz (50 nm)/Al (100 nm); EOD: T2T (40 nm)/15 wt% **4CzIPN**: host (30 nm)/T2T (10 nm)/Bpy-TP2 (40 nm)/LiQ (2 nm)/ Al (100 nm).

Table 4-5. Summary of hosts' photophysical properties and device performance of TADF OLEDs based on 15 wt% of **4CzIPN**.

Host	LT ₉₅ (h) ^a	Hole/Electron ratio ^b	T _g ^c (°C)	Neat film photostability LT ₇₀ (h)	Electrochemical stability
mCBP	30	27:1	90	7	irreversible
1-BF	67	13:1	57	12	irreversible
2-BF	56	16:1	67	7	irreversible
4-BF	8	43:1	68	15	irreversible

^a) Device lifetime at a constant current density of 3.3 mA cm⁻²; ^b) HOD/EOD current density at 12V; ^c) glass transition temperature.

4.4. Conclusion

In conclusion, three new DBF-based host materials, **1-BF**, **2-BF**, and **4-BF**, have been designed and synthesized. The regio-isomeric effect of three host materials on photophysical, electrochemical, thermal, and carrier transport properties has been studied. The excellent photochemical stability and bipolar carrier transporting properties of **1-BF** resulted in the most stable green TADF-OLEDs, even better than the reference **mCBP**-based OLED. In our future

study, we would like to realize the compatibility of high efficiency and long device lifetime by further modification of the **1-BF** structure. The findings in this chapter further solidified the relationship between carrier transporting properties and device stability.

Chapter 5

Efficient Host-free Delayed Fluorescence Organic Light-Emitting Diodes

5.1. Introduction

In the preceding chapters, we have systematically explored the design of host materials to address the critical requirements of thermally activated delayed fluorescence (TADF) organic light-emitting diodes (OLEDs). Through azasilane-, pyridine-, and dibenzofuran-based molecular frameworks, we demonstrated that rational host design can provide high triplet energy levels, balanced carrier-transporting properties, and superior stability, thereby improving device efficiency and durability. However, despite these advances, the host–guest strategy intrinsically suffers from limitations that are difficult to circumvent.

First, doping processes require precise control over concentration to prevent aggregation-caused quenching (ACQ) and to ensure consistent emission spectra. Slight deviations can result in efficiency loss, color instability, and batch-to-batch variation.^{71–73} Second, host materials, often being small organic molecules, possess relatively low glass transition temperatures. This renders them prone to morphological changes under operational heating, ultimately leading to reduced device lifetime. Third, intermolecular host–guest interactions can introduce additional non-radiative pathways and complicate device optimization. These inherent issues raise the question of whether the use of hosts is indispensable for TADF-OLEDs.

An attractive alternative is to develop host-free (non-doped) TADF architectures, where the emitting layer consists of neat films of TADF emitters. Such an approach would dramatically simplify device fabrication, reduce the number of variables in device optimization, and potentially enhance device stability by eliminating host–guest mismatch. The major challenge for this strategy lies in achieving high photoluminescence quantum yields (PLQYs) in neat films, where intermolecular interactions are often exacerbated. Thus, molecular design that suppresses aggregation and accelerates exciton up-conversion is indispensable for enabling efficient host-free devices.^{74,75}

Against this background, we investigated the sky-blue TADF emitter **HDT1**, which had previously shown high PLQYs in both solution and doped films.⁷⁶ To further enhance its neat-film performance, a new derivative, **36Me-HDT1**, was designed by introducing sterically hindered 3,6-dimethylcarbazole units. This modification was expected to suppress detrimental intermolecular interactions, reduce delayed lifetime, and enhance the rate of reverse intersystem crossing (RISC). By comparing **HDT1** and **36Me-HDT1**, we aimed to establish clear design principles for developing efficient host-free emitters.

HDT1 is based on the heterodonor strategy, utilizing carbazole and diphenylcarbazole. Compared with diphenylcarbazole, unsubstituted carbazole is less sterically bulky. Moreover, it has been found that by substituting the 3,6-positions of carbazole, the TADF properties are fairly enhanced. Thus, a

new sky-blue TADF emitter **36Me-HDT1** was designed by replacing the carbazole in **HDT1** with 3,6-dimethylcarbazole. The chemical structures of **HDT1** and **36Me-HDT1** are shown in **Figure 5-1**.

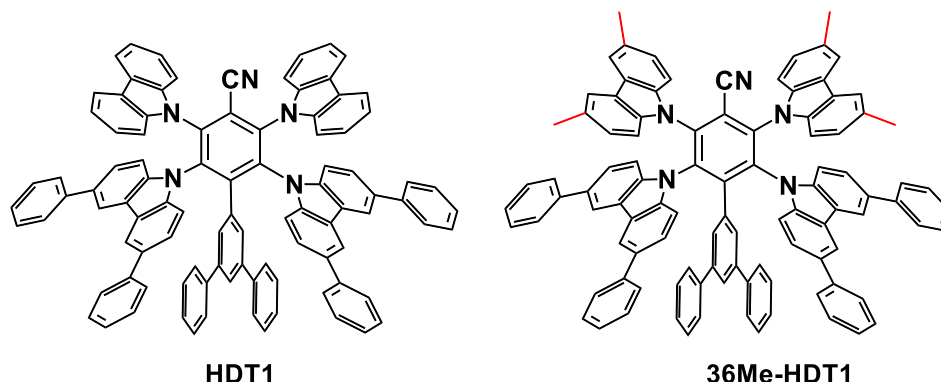


Figure 5-1. The chemical structures of **HDT1** and **36Me-HDT1**.

5.2. Synthesis

2DMCz2FBN was synthesized using the following methods. Under nitrogen atmosphere, 3,6-dimethyl-9H-carbazole (390 mg, 2 mmol) was dissolved in dry THF (30 mL) in a two-neck round-bottom flask equipped with a condenser. The reaction mixture was cooled to 0 °C, then NaH (80 mg, 2 mmol) was added. The reaction mixture was slowly warmed to room temperature and stirred for half an hour. After that, 2,3,5,6-tetrafluoro-5'-phenyl-[1,1':3',1''-terphenyl]-4-carbonitrile (403 mg, 1 mmol) was added, and the reaction was stirred for 1 hour. Then, the reaction was warmed to room temperature for 16 hours. The reaction was quenched with water, and the precipitate was filtered off. The crude product was purified by column chromatography. Yield: 603 mg (80%). ^1H NMR (500 MHz, Acetone- d_6): δ = 8.07 (s, 1H), 8.01 (s, 4H), 7.98 (s, 2H), 7.77 (d, 4H, 8.0 Hz), 7.41-7.52 (m, 10H), 7.32 (d, 4H, 8.0 Hz), 2.52 (s, 12H). ^{19}F NMR (471 MHz, Acetone- d_6): δ = -115.6 (s, 2H) (**Figure 5-2** and **5-3**). MS (APCI) calcd. for $\text{C}_{53}\text{H}_{37}\text{F}_2\text{N}_3$: m/z = 753.9; found: 754.5 $[\text{M}+1]^+$.

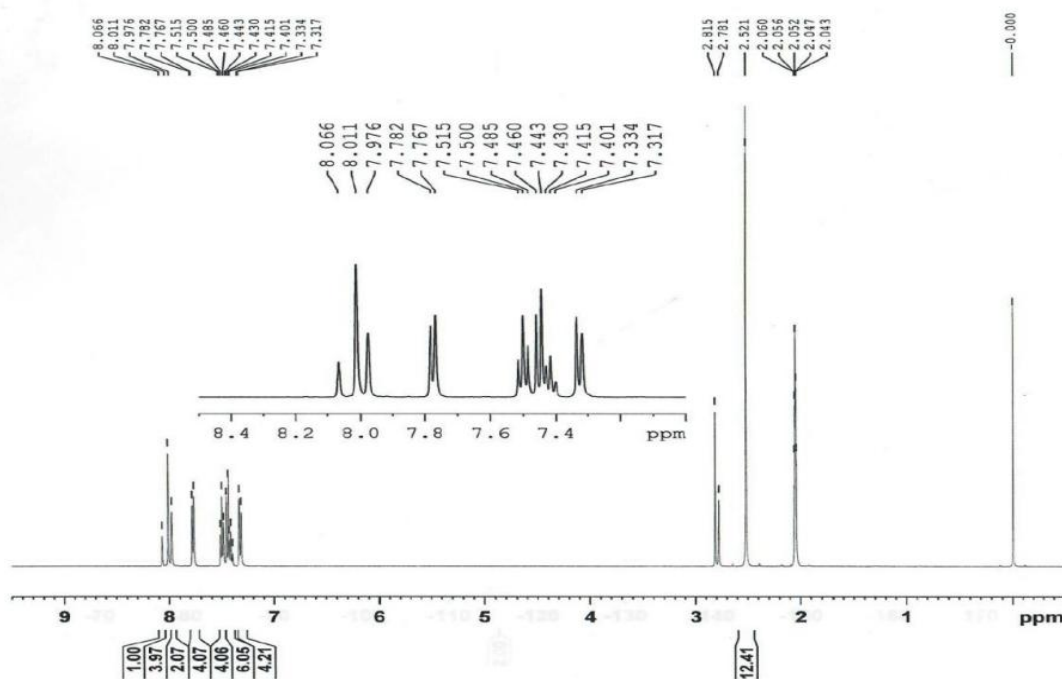


Figure 5-2. ¹H NMR of 2DMCz2FBN.

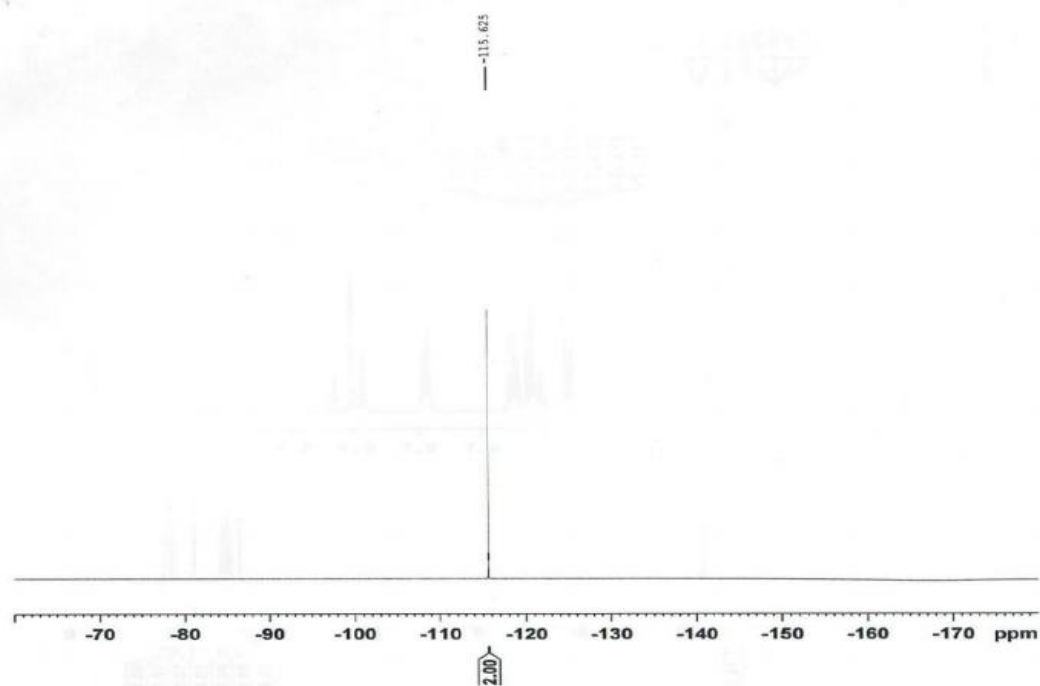


Figure 5-3. ¹⁹F NMR of 2DMCz2FBN.

36Me-HDT1 was synthesized with the following methods. Under nitrogen atmosphere, 3,6-diphenyl-9H-carbazole (957 mg, 3 mmol) was dissolved in dry THF (30 mL) in a two-neck round-bottom flask equipped with a condenser. The reaction mixture was cooled to 0 °C, then

NaH (120 mg, 3 mmol) was added. The reaction mixture was slowly warmed to room temperature and stirred for half an hour. After that, **2DMCz2FBN** (754 mg, 1 mmol) was added, and the reaction was stirred for 1 hour. Then, the reaction was heated to reflux for 16 hours. The reaction was quenched with water and the precipitate was filtered off. The crude product was purified by column chromatography. Yield: 1.1g (81%). ^1H NMR (500 MHz, CDCl_3): δ = 7.91 (s, 4H), 7.57 (s, 4H), 7.51 (d, 8H, 8.0 Hz), 7.42 (t, 8H, 8.0 Hz), 7.22–7.31 (m, 16H), 6.99–7.03 (m, 6H), 6.90 (t, 4H, 8.0 Hz), 6.79 (s, 1H), 6.72 (s, 2H), 6.21 (d, 4H, 8.0 Hz), 2.39 (s, 12H) (**Figure 5-4**). MS (APCI) calcd. for $\text{C}_{101}\text{H}_{69}\text{N}_5$; m/z = 1352.7; found: 1353.0 $[\text{M}]^+$.

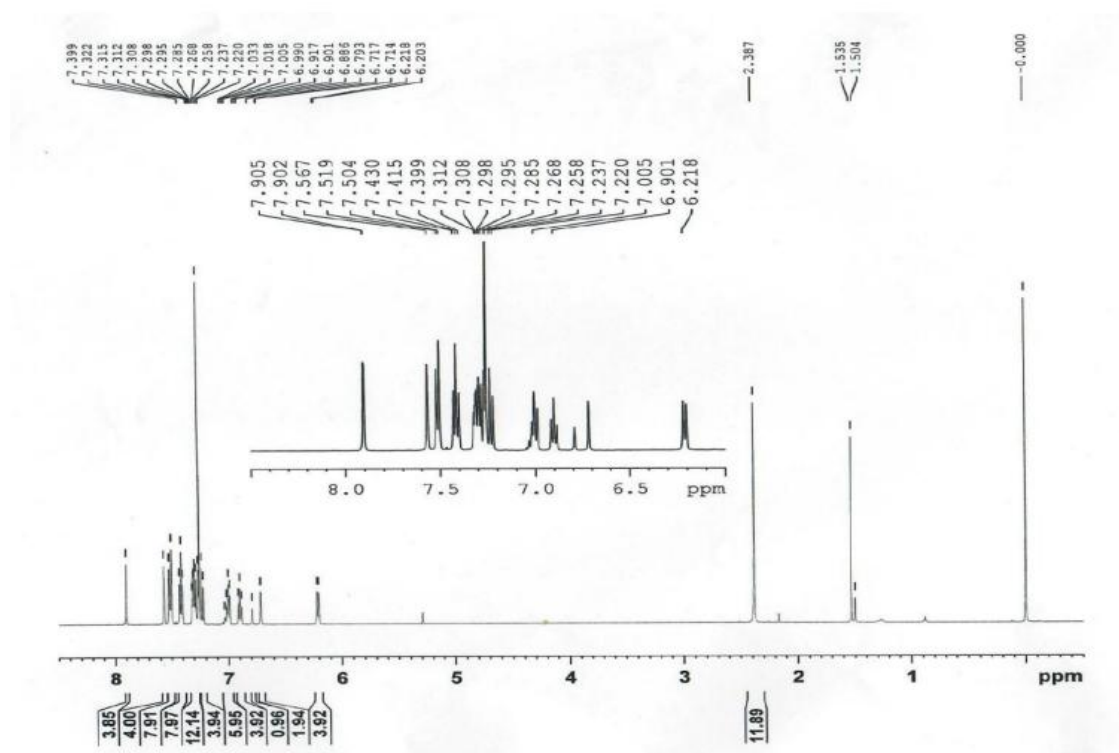


Figure 5-4. ^1H NMR of **36Me-HDT1**.

5.3. Results and Discussion

5.3.1. Theoretical Calculations

Time-dependent density-function theory (TD-DFT) calculations were carried out to determine their ground-state and the excited-state properties with the B3LYP/6-31G level of theory (**Figure 5-5**). In **36Me-HDT1**, although the LUMO remained localized on the central benzonitrile core, the HOMO of **36Me-HDT1** was localized on 3,6-dimethylcarbazole and 3,6-diphenylcarbazole, which is different from HDT1, with the HOMO localized only on two 3,6-diphenylcarbazole units.

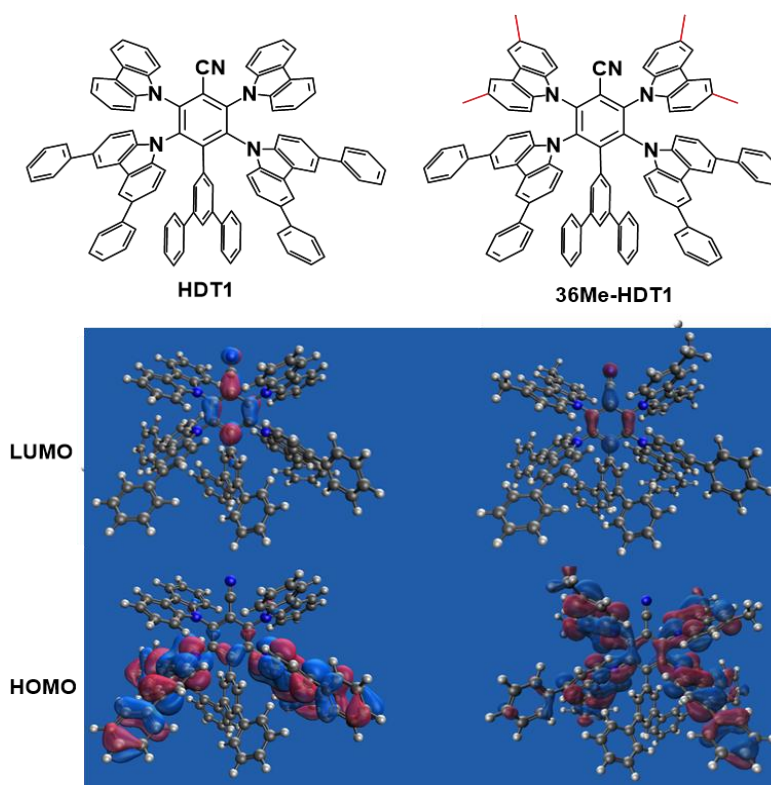


Figure 5-5. Chemical structures and DFT calculations of **HDT1** and **36Me-HDT1**.

5.3.2. Photophysical Study

The photophysical properties of **36Me-HDT1** were studied in toluene solution and summarized in **Table 5-1**. Expectedly, with increasing donor strength, the charge-transfer (CT) emission wavelength of **36Me-HDT1** was redshifted to 488 nm when compared with that of **HDT1** (477 nm) (**Figure 5-6**). The singlet energy levels of **HDT1** and **36Me-HDT1** were determined to be 2.90 and 2.81 eV, respectively.

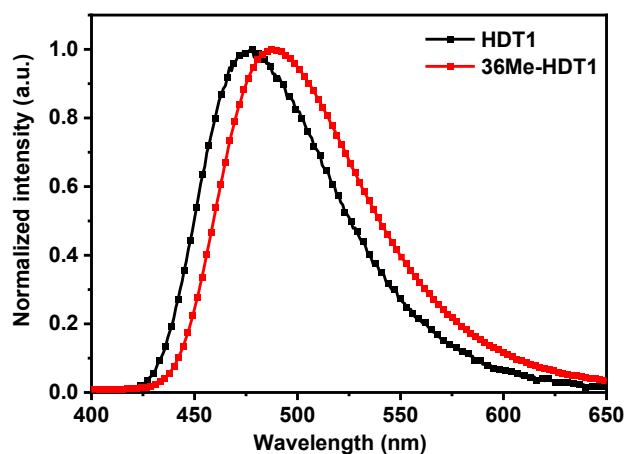


Figure 5-6. PL spectra of **HDT1** and **36Me-HDT1** in toluene at room temperature.

The phosphorescence spectrum was also recorded in toluene solution at 77 K. It has been found that **36Me-HDT1** showed structureless emission at 77 K (**Figure 5-7**). Besides, **36Me-HDT1** displayed a high photoluminescence quantum yield (PLQY) of 100% in degassed toluene solution (in aerated solution, the PLQY was only 12%).

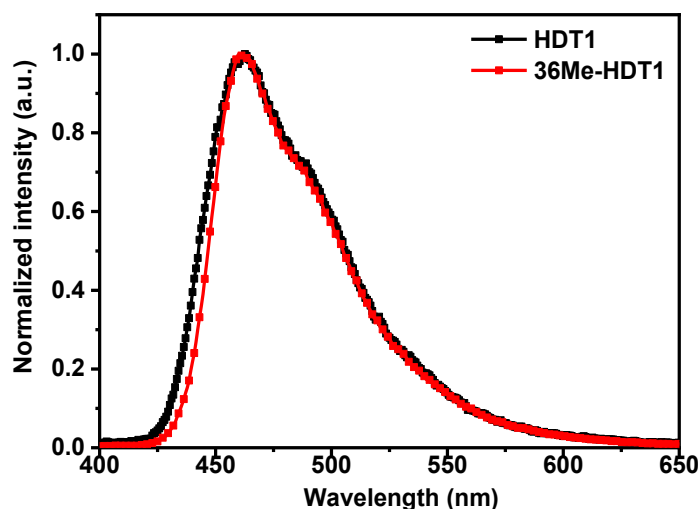


Figure 5-7. PL spectra of **HDT1** and **36Me-HDT1** in toluene at 77K.

The transient decay profile of **36Me-HDT1** was measured in toluene, in which the delayed lifetime (τ_d) was found to be 3.3 μs , which is much faster than that of **HDT1** (10.5 μs) (**Figure 5-8**). The rate constant of the reverse intersystem crossing process (k_{RISC}) was determined to be $1.4 \times 10^6 \text{ s}^{-1}$ (vs. $8.3 \times 10^5 \text{ s}^{-1}$ for **HDT1**).

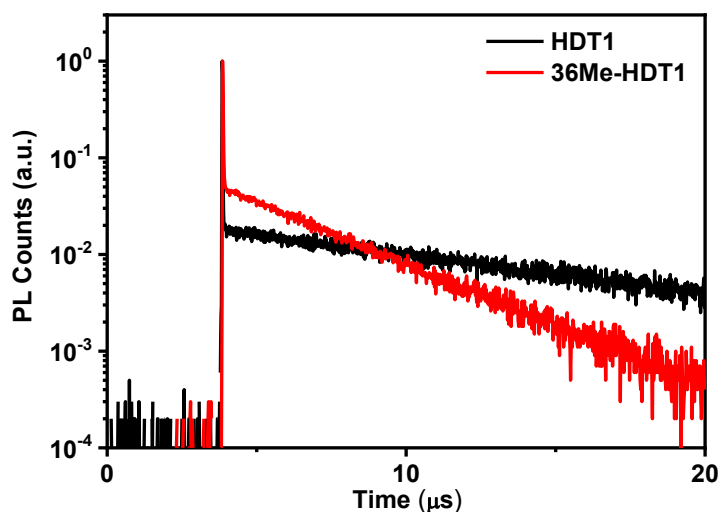


Figure 5-8. Transient decay profiles of **HDT1** and **36Me-HDT1** in degassed toluene.

Table 5-1. Photophysical data of **HDT1** and **36Me-HDT1** in toluene

Material	λ_{PL} (nm)	PLQY (%) ^{a/c}	τ_{p} (ns) ^a	τ_{d} (μs) ^b	k_{RISC} (10^5 S^{-1})	S_1 (eV)	T_1 (eV)
HDT1	477	100 /12	8.1	10.5	8.3	2.90	2.88
36Me-HDT1	488	100 /21	11	3.3	1.4	2.81	2.79

^aPrompt lifetime; ^bdelayed lifetime; ^cmeasured in oxygen-saturated toluene.

The neat film photophysics properties were also studied. The emission maxima of neat films of **HDT1** and **36Me-HDT1** were gradually redshifted to 507 and 516 nm, respectively (Figure 5-9a). We measured the PLQYs of neat films of **HDT1** and **36Me-HDT1**, which were found to be 70% and 80%, respectively. The transient decay profiles of neat films were measured with τ_{ds} of 1.9 and 1.5 μs , respectively (Figure 5-9b).

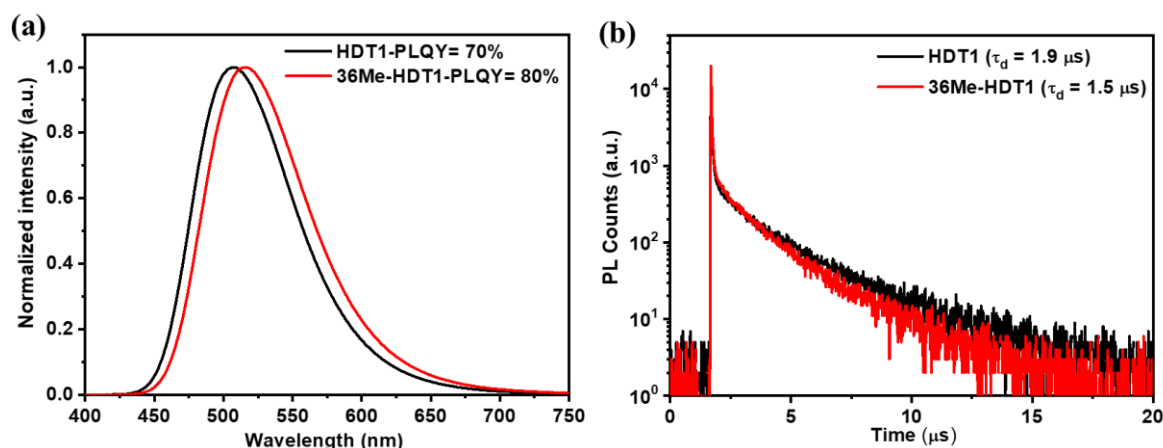


Figure 5-9. (a) PL spectra and (b) transient decay profiles of **HDT1** and **36Me-HDT1** neat films.

5.3.3. OLED Performance

We firstly fabricated doped TADF-OLEDs with the following configuration: ITO (100 nm)/HAT-CN (10 nm)/TrisPCz (30 nm)/mCBP (5 nm)/mCBP:20 wt% of **HDT1** (device A) or **36Me-HDT1** (device B) (30 nm)/SF3-TRZ (10 nm)/SF3-TRZ: 30 wt% Liq (20 nm)/Liq (2 nm)/Al (100 nm). The turn-on voltages of devices **A** and **B** were 3.2 and 3.4 V, respectively. Both devices **A** and **B** achieved maximum EQEs of 22.7% and 26.9%, respectively. At 1000 cd m^{-2} , the EQEs of **A** and **B** were found to be 16.4% and 22.5%, respectively. The smaller roll-off of device **B** was attributed to the higher k_{RISC} , which significantly reduced the

accumulation of triplet excitons within the device. Consistent with the PL study, the emission maxima of devices **A** and **B** at 1000 cd m^{-2} were found to be 485 and 493 nm, respectively, with full-width at half-maximum values of 80 and 79 nm. The device data are presented in **Figure 5-10** and **Table 5-2**.

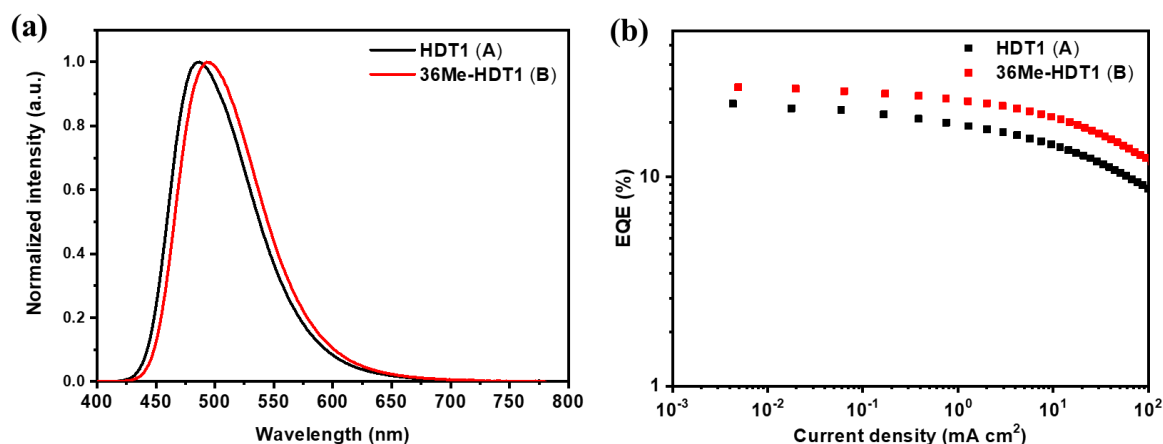


Figure 5-10. Doped devices with 20 wt% of the TADF emitter. (a) EQE versus luminance; (b) emission spectrum at 1000 cd m^{-2} .

Given the high PLQY values observed in neat films, non-doped TADF OLEDs were fabricated with a similar structure to devices **A** and **B**; only the emitting layer consisted of a neat film of **HDT1** (device **C**) or **36Me-HDT1** (device **D**). The turn-on voltage of devices **C** and **D** was found to be 3.2 and 3.6 V, respectively. Device **C**, based on **HDT1**, achieved an EQE_{max} of 16.5%, whereas device **D**, based on **36Me-HDT1**, resulted in a higher EQE_{max} of 21.3%. Due to aggregation, the efficiencies of both non-doped devices were lower than those of doped devices **A** and **B**; however, the resulting EQEs remained one of the best values amongst non-doped blue TADF OLEDs reported in the literature. As a result of aggregation, the emission wavelength of devices **C** and **D** was redshifted to 507 and 517 nm, respectively. The device data are presented in **Figure 5-11** and **Table 5-2**.

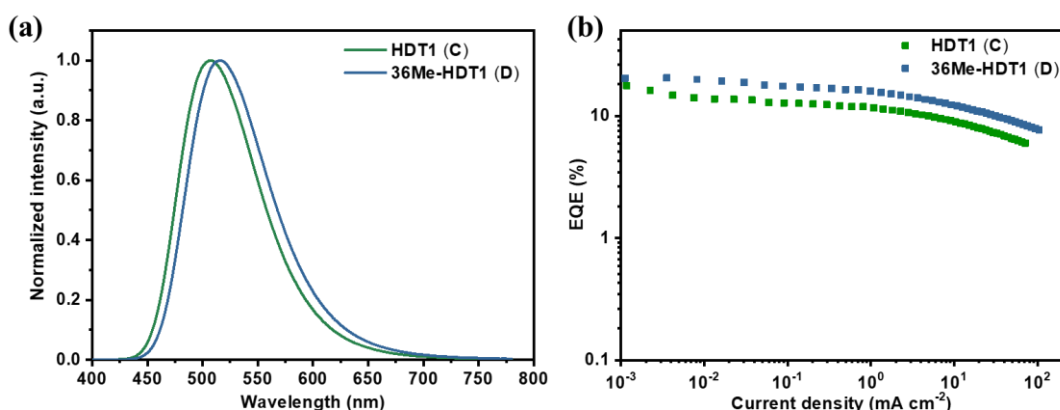


Figure 5-11. Non-doped devices of **HDT1** and **36Me-HDT1** (a) emission spectra at 1000 cd m^{-2} ; (b) EQE versus luminance.

Table 5-2. Device performance of device A–D.

Device	EML	Voltage (V) ^a	λ_{EL} (nm) ^b	L_{max} (cd/m^2) ^b	CE (cd/A) ^c	PE (lm/W) ^d	$\text{EQE}_{\text{max/100/1000}}$ (%)
A	20 wt% HDT1	2.8	486	46539	52.8	55.3	22.7/19.8/16.4
B	20 wt% 36Me-HDT1	3.0	493	70181	68.4	67.2	26.9/25.0/22.5
C	100 wt% HDT1	3.2	507	12038	46.2	45.4	16.5/12.4/10.4
D	100 wt% 36Me-HDT1	3.6	517	24761	62.6	51.8	21.3/17.3/14.8

^a At 1 cd m^{-2} ; ^b at 1000 cd m^{-2} ; ^c maximum current efficiency; ^d maximum power efficiency.

5.4. Conclusion

In this chapter, we demonstrated the feasibility of efficient host-free TADF OLEDs by combining rational molecular design and careful device engineering. Through steric modification of a sky-blue TADF emitter, **36Me-HDT1** achieved faster exciton dynamics and higher neat-film PLQY, leading to host-free devices with EQEs exceeding 21%—a record among reported non-doped TADF OLEDs. This finding paves a new way for the construction of highly efficient non-doped TADF OLEDs.

Chapter 6

Summary and Future Prospective

6.1. Summary

In this study, we have systematically designed and synthesized a series of azasiline-, pyridine-, and dibenzofuran-based host materials and blue TADF emitter. Their photophysical, electrochemical, and thermal properties in solution and thin-film states were investigated. By applying these newly synthesized host materials, the efficiency, stability, and driving voltage of green TADF-OLEDs improved significantly; moreover, a non-doped blue TADF-OLED achieved an EQE of 21.3%, one of the highest EQEs among all non-doped devices.

In Chapter 2, azasiline was introduced as a novel structural unit for the design of high-triplet-energy hosts. Two silicon-containing hosts, **2SiPh** and **2SiPy**, were synthesized and fully characterized. Both hosts exhibited high triplet energies (~ 3.2 eV), making them suitable for green/blue TADF emitters. Device studies using the green emitter **4CzIPN** revealed that the **2SiPh**-based device achieved a maximum EQE of 16.6%, whereas the **2SiPy**-based device showed a lower EQE of 8.2% due to severe hole trapping. The device lifetimes of LT_{95} were 2.3 h and 2.2 h for **2SiPh** and **2SiPy**, respectively (Figure 6-1). The short device lifetime is due to unbalanced carrier transport properties, as confirmed by HODs/EODs studies.

In Chapter 3, with reference to a common *p*-type host material, **mCBP**, three novel host materials based on a pyridine unit, **mCBP-1N**, **CzPyPhCz**, and **CzPyBF**, were systematically designed to improve stability efficiently. The green TADF-OLEDs were fabricated with these three new hosts. EQE_{max} s of green OLEDs were

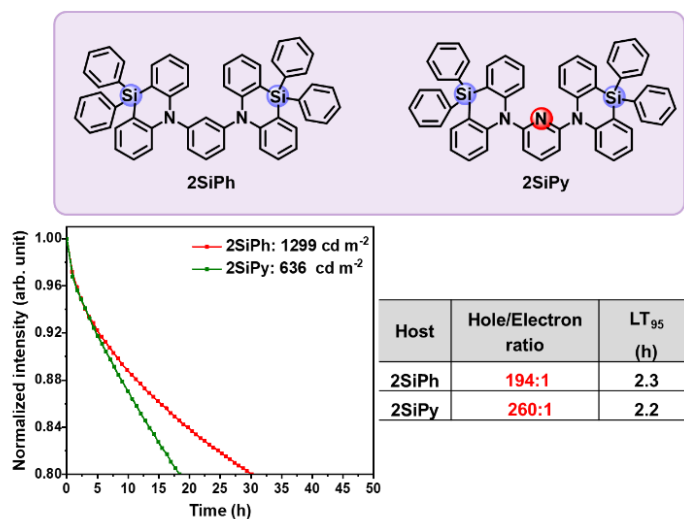


Figure 6-1. HOD/EOD ratio and device lifetime of **2SiPh** and **2SiPy**-based green devices.

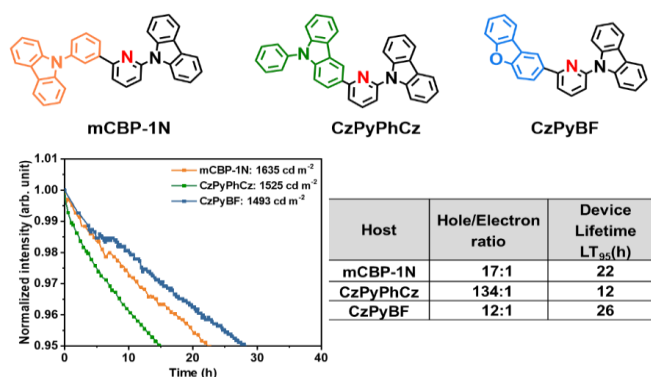


Figure 6-2. HOD/EOD ratio and device lifetime of pyridine-based green devices.

20.3 and 14.0% for **CzPyBF** and **mCBP** hosts, respectively. Further, high EQEs of 19.2 and 12.9% were maintained even at 1000 cd m^{-2} . Most importantly, the device lifetime of the **CzPyBF** host achieved LT_{95} of 26 h, which is 1.5 times longer than that of **mCBP** (15 h) (**Figure 6-2**). The outperformed device stability of the **CzPyBF**-based device was attributed to more balanced carrier transporting properties, which was confirmed by the smallest HOD/EOD ratio (12:1 for **CzPyBF**). Unexpected lower turn-on voltages were achieved by using the **CzPyPhCz** green device. With host engineering, we simultaneously improved the TADF-OLEDs with lower turn-on voltages, higher EQEs, and longer device lifetimes.

In Chapter 4, the regio-isomeric effect of dibenzofuran-carbazole hosts was systematically studied through three positional isomers: **1-BF**, **2-BF**, and **4-BF**. All three hosts possessed high triplet energies suitable for exciton confinement. In green OLEDs with **4CzIPN**, the devices based on **1-BF**, **2-BF**, and **4-BF** achieved EQE_{max} of 13.3%, 14.6%, and 14.0%, respectively, which were comparable to the reference **mCBP** device (14.8%). Importantly, the device stability varied significantly among the isomers. The **1-BF**-based device showed the longest LT_{95} of 67 h, followed by **2-BF** (56 h), both outperforming **mCBP** (30 h), whereas the **4-BF**-based device degraded rapidly with an LT_{95} of only 8 h (**Figure 6-3**). Carrier-transport studies confirmed that **1-BF** and **2-BF** exhibited more balanced hole and electron transport, directly correlating with their superior device stability. This work clearly established the strong regio-isomeric effect in **DBF**-carbazole hosts and emphasized the importance of substitution position in tuning photophysical and device properties.

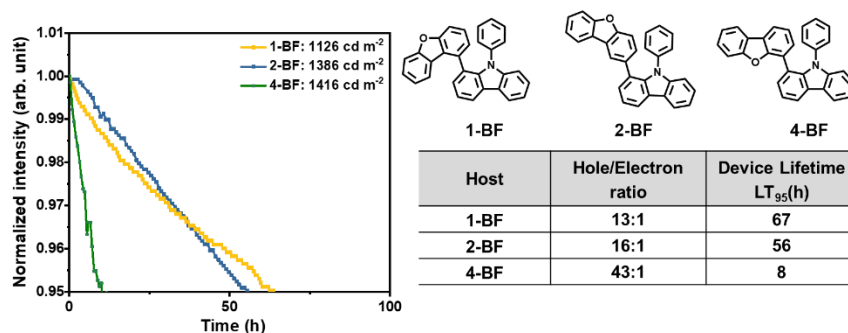


Figure 6-3. HOD/EOD ratio and device lifetime of **DBF**-based green devices.

In Chapter 5, the research focus shifted from host design to emitter engineering, exploring the potential of host-free OLEDs. A new TADF emitter, **36Me-HDT1**, was designed by introducing 3,6-dimethylcarbazole substituents to the previously reported **HDT1**. This structural modification enhanced donor strength, suppressed aggregation, and accelerated reverse intersystem crossing ($k_{\text{RISC}} = 1.4 \times 10^6 \text{ s}^{-1}$ for **36Me-HDT1** vs. $8.3 \times 10^5 \text{ s}^{-1}$ for **HDT1**).

Photophysical studies showed that neat films of **36Me-HDT1** retained a high PLQY of 80%. Device evaluations confirmed the advantage of this design: doped OLEDs achieved a maximum EQE of 26.9%, while host-free OLEDs based on neat films of **36Me-HDT1** realized an EQE of 21.3%, one of the highest reported among non-doped TADF-OLEDs. This work demonstrated that rational molecular design of emitters can enable efficient host-free OLEDs.

6.2. Future Perspective

According to the results discussed in Chapters 2-4, the device stability improves significantly when the ratio of HOD/EOD approaches 1. This is because a balanced carrier transport property facilitates the formation of a broader recombination zone, which is believed to reduce electrical stress in the emissive layer and lead to a lengthened operational lifetime (**Figure 6-4**). Since dibenzofuran-based hosts exhibit more balanced carrier transport and better photochemical stability, it is expected that incorporating additional dibenzofuran or triazine units will further lower the HOD/EOD ratio, ideally to 1.

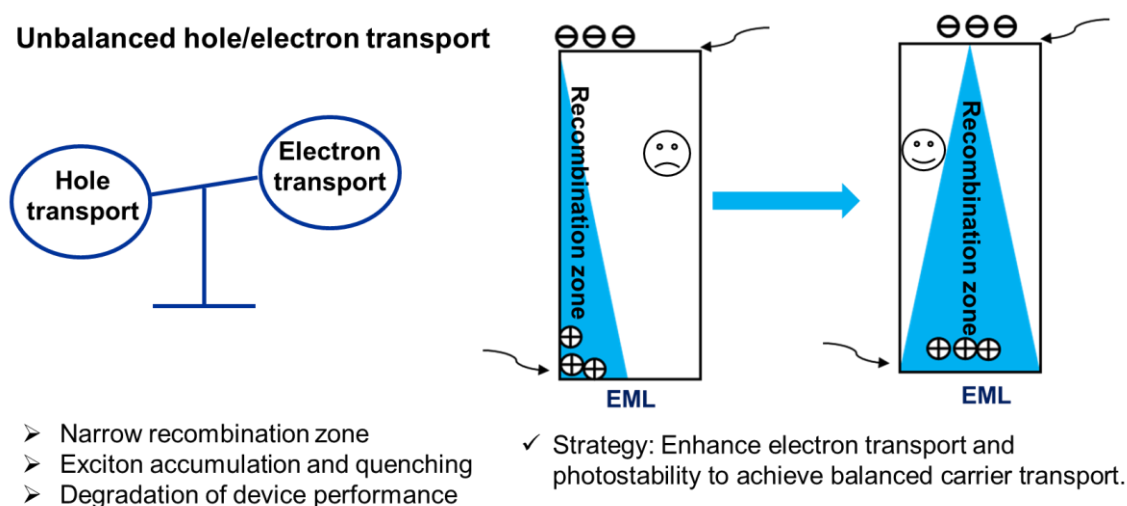


Figure 6-4. Control of recombination position and width by balancing hole and electron transport.

Inspired by the excellent performance of ambipolar host materials, two novel hosts, **BF-Cz** and **TRZ-BF**, were designed (**Figure 6-5**). Based on the outstanding performance of **1-BF**, an additional dibenzofuran unit was introduced into **BF-Cz**, with the expectation of further enhancing its thermal and photochemical stability. Nevertheless, because the hole-transporting ability of dibenzofuran-based hosts remains stronger than their electron-transporting ability, triazine (TRZ) was incorporated into **TRZ-BF** to improve electron mobility. Furthermore, the

large dihedral angles within these molecular frameworks are expected to maintain a high T_1 energy level, which is essential for their application in blue and green TADF-OLEDs.

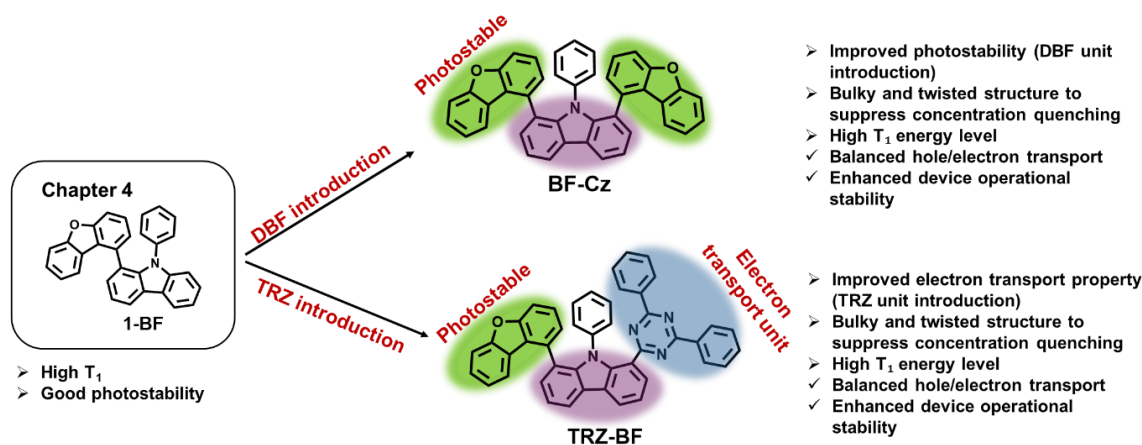


Figure 6-5. Design of ambipolar host materials based on our findings.

Moreover, a higher maximum EQE is always desirable, because a lower current density can be used to achieve the same brightness, thereby extending the device lifetime. Much effort has been devoted to the design and synthesis of hosts and emitters to tune their excited-state properties. In contrast to modulating photophysical properties for EQE improvement, achieving preferential horizontal orientation of the emitter molecules is an alternative approach to increase the out-coupling efficiency. With higher out-coupling efficiency (OC), the corresponding EQE will be enhanced. To achieve a higher OC value in a doped device, studies have been focused on the molecular design of emitters having preferential horizontal orientation (PHO); however, the molecular design of host materials affecting PHO of the emitter has rarely been reported in the literature. As a result, the study of host-induced PHO of the TADF emitter will be carried out. With a careful molecular design of hosts, I would expect the PHO of TADF can be maximized by the host material via host-host interaction, thereby leading to an enhanced EQE and longer device lifetime. 3',6'-Diphenyl-1,1':2',1''-terphenyl (4Ph) manifold has been proven to induce PHO of emitter.⁷⁷ I am going to incorporate the 4Ph unit onto **CzPyBF** in Chapter 3 and **1-BF** in Chapter 4 (**Figure 6-6**). It is expected that the 4Ph-modified hosts will exhibit PHO behavior, thus improving device performance in terms of both efficiency and stability.

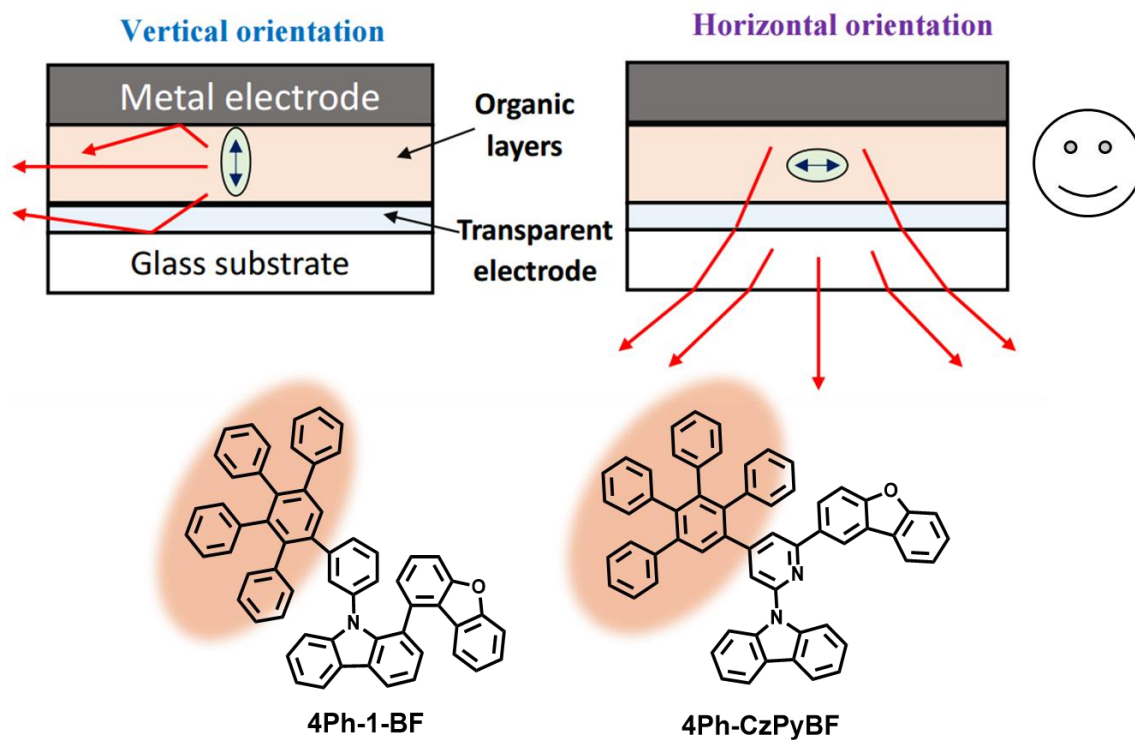
4Ph- induced preferential horizontal orientation

Figure 6-6. 4Ph-modified host materials aiming for PHO.

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List of Publications

- **Papers (first authorship)**

1. **Y. Hu**[#], A. Civil[#], Y. Li, G.N. Iswara, Y. Tsuchiya, C.-Y. Chan, C. Adachi, Judicious Design of Pyridine-Based Hosts for Stable, Efficient, and Low-Driving Thermally Activated Delayed Fluorescence Organic Light-Emitting Diodes. *Adv. Opt. Mater.* **2024**, *12*, 2302971.
([#]Equally contributed with A. Civil)
2. **Y. Hu**, G. N. Iswara, Y. Tsuchiya, and C. Adachi, Azasiline-based host materials for thermally activated delayed fluorescent organic light-emitting diodes. *Chem. Lett.* **2025**, *54*, 9.
3. X. Tan[#], **Y. Hu**[#], Y. Li, B. Cai, Y.-T. Lee, C. Adachi, C.-Y. Chan, Efficient host-free delayed fluorescence organic light-emitting diodes, *J. Mater. Chem. C*, **2025**, *13*, 16373.
([#]Equally contributed with X. Tan)
4. **Y. Hu**, Y. Li, C.-Y. Chan, Y. Tsuchiya, C. Adachi, Regio-isomeric Effect of Dibenzofuran-Based Host Materials on Photophysics and Device Performance in Organic Light-Emitting Diodes. *Chem. Lett.* **2026**, *55*, 1.

- **Joint papers**

1. Y.-T. Lee; C.-Y. Chan, N. Matsuno, S. Uemura, S. Oda, M. Kondo, R. W. Weerasinghe, **Y. Hu**, G. N. I. Lestanto, Y. Tsuchiya, Y. Li, T. Hatakeyama, C. Adachi, *Nat. Commun.* **2024**, *15*, 3174.

The list of presentations at international conferences

1. **Y. Hu**, A. Civil, Y. Li, G.N. Iswara, Y. Tsuchiya, C.-Y. Chan, C. Adachi, Judicious Design of Pyridine-based Hosts for Stable, Efficient, and Low-Driving Thermally Activated Delayed Fluorescence Organic Light-Emitting Diodes, Japan Society of Applied Physics (*JSAP Spring meeting-2024*), Tokyo, Japan (March 2024). (Poster)
2. **Y. Hu**, G. N. I. Lestanto, Y. Tsuchiya, C. Adachi, Azasiline-modified Host Materials for Thermally Activated Delayed Fluorescent Organic Light-Emitting Diodes, 15th International Conference on Optical Probes of Organic and Hybrid Semiconductors (OP2025), Fukuoka, Japan (September 2025). (Poster)

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