

# A Simplified Emissive Layer Strategy Utilizing Zero Radius of Intramolecular Energy Transfer Mechanism for High-Efficiency OLEDs

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## Abstract

A conventional exciplex emissive layer (EML) is composed of p-type and n-type hosts and dopants. Exciplex EML can enhance exciton utilization, leading to higher efficiency and operational stability. However, challenges remain in controlling the material mixing ration, maintaining uniformity during the processing steps, and addressing the high cost and the complex photophysical properties of the components. In this study, a novel 5,9-di([1,1'-biphenyl]-2-yl)-2'-(9H-carbazole-9-yl)3,7-dimethyl-5,5a,5a1,9,9a,16a-hexahydrospiro[5,9-diaza-16b-boraindeno[2,1-b]naphtho[1,2,3-fg]anthracene-11,9'-fluorene] (DABNA-Spiro-Cz), integrating a p-type host with a blue fluorescent dopant, has been designed and successfully synthesized. Within the DABNA-Spiro-Cz molecule, the p-type host and the blue fluorescent dopant are seamlessly integrated while maintaining their independent functional roles. An Exciplex is formed between the p-type host unit within the molecule and the n-type host, and the energy of the generated excitons is transferred to the dopant unit within the molecule. The successfully established zero-radius of intramolecular energy transfer in exciplex (ZETPLEX) mechanism not only simplifies the exciplex EML structure but also achieve a significantly higher external quantum efficiency (EQE) of 14.9% compared to conventional exciplex system organic light-emitting diodes (OLEDs). We present a novel pathway for high-efficiency blue OLEDs through the innovative ZETPLEX mechanism.

## Author Keywords

Organic emitting-diodes; Blue fluorescent; Exciplex; Fused emitter; Zero radius of intramolecular energy transfer mechanism.

## 1. Introduction

Enhancing exciton utilization is essential for achieving high-efficiency organic light-emitting layers (OLEDs). To improve exciton utilization, a multi-component emissive layer (EML) comprising a host and a dopant was first introduced in 1989 by Tang et al.(1) Excitons generated in the host are transported to the dopant, where they emit light. Recently, multi-component EMLs composed of p-type and n-type hosts along with a dopant in an exciplex system have been widely adopted. The exciplex system achieves high efficiency by demonstrating superior charge balance, attributed to the hole and electron injection and transport capabilities of the mixed hosts, and by enabling high exciton utilization through triplet harvesting from the exciplex state.(2-4)

The performance of multi-component EML is highly sensitive to the mixing ratio of their constituents, with emission characteristics varying accordingly. Additionally, in exciplex-dopant systems, the ratio of constituent materials significantly influences the energy transfer of excitons generated in the exciplex to the dopant. Therefore, precise control of the mixing ratio is crucial in multi-component EMLs.(5) However, due to the simultaneous mixing of multiple materials in a multi-component EML, accurately controlling the composition ratio poses significant challenges, leading to difficulties in the fabrication

process.(6)

The energy transfer process can occur through Förster resonance energy transfer (FRET), a long-range energy transfer mediated by electrostatic dipole-dipole coupling, and Dexter energy transfer (DET), a short-range energy transfer facilitated by electron exchange. Among these, the FRET process is particularly sensitive to the molecular distance between the host and the dopant.(7-9)

In a previous study, we reported the zero-radius of intramolecular energy transfer (ZRIET) mechanism, where the host and dopant are integrated within a single molecule, with each unit performing its role independently. The energy transfer occurring from the host unit to the dopant unit within the same molecule.(10) In this study, novel 5,9-di([1,1'-biphenyl]-2-yl)-2'-(9H-carbazole-9-yl)3,7-dimethyl-5,5a,5a1,9,9a,16a-hexahydrospiro[5,9-diaza-16b-boraindeno[2,1-b]naphtho[1,2,3-fg]anthracene-11,9'-fluorene] (DABNA-Spiro-Cz), which fuse a p-type host and a blue fluorescent dopant, was designed and successfully synthesized. In the DABNA-Spiro-Cz molecule the p-type host and the dopant unit are fully integrated, each performing their roles independently. An exciplex is formed between the p-type host unit within the DABNA-Spiro-Cz molecule and the n-type host, and the energy of the generated excitons is transferred to the dopant within the DABNA-Spiro-Cz unit. Unlike the conventional 3-component exciplex host and dopant system. The exciplex host and dopant system introduced with DABNA-Spiro-Cz allows exciton energy transfer within a single molecule. In other words, we have successfully demonstrated the implementation of the zero-radius of intramolecular energy transfer in exciplex (ZETPLEX) mechanism. Thanks to the ZETPLEX mechanism, both the FRET rate and efficiency are dramatically enhanced compared to the conventional 3-component EML composed of p-type and n-type hosts and a dopant. As a result, an EQE of 14.9% was achieved, surpassing the 12.2% EQE of devices with a 3-component EML, effectively simplifying the exciplex host and dopant system in the EML. Through the ZETPLEX mechanism, we present an innovative new pathway for high-efficiency OLEDs.

## 2. Results and Discussion

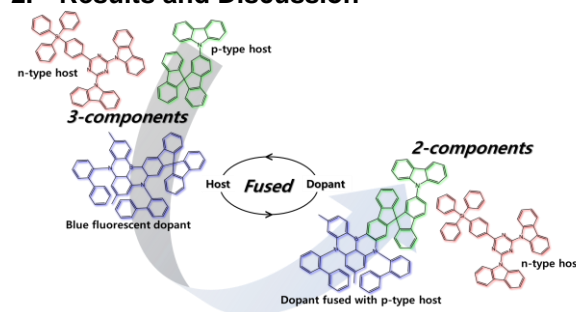
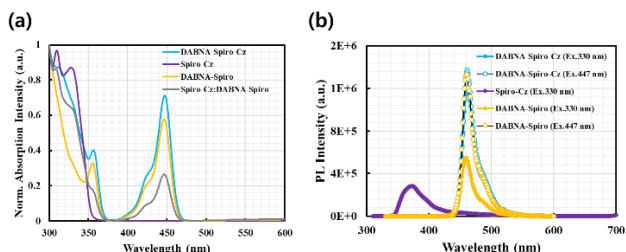


Figure 1. The concept of the ZETPLEX mechanism and the molecular design of DABNA-Spiro-Cz.

To implement the ZETPLEX mechanism, 9-(9'-spiro[fluoren]-2-yl)-9H-carbazole (Spiro-Cz) was designed and synthesized as the p-type host, while 5,9-di([1,1'-biphenyl]-2-yl)-3,7-dimethyl-5,5a,5a1,9,9a,16a-hexahydrospiro[5,9-diaza-16b-boraindeno[2,1-b]naphtho[1,2,3-fg]anthracene-11,9'-fluorene] (DABNA-Spiro) was developed as the blue fluorescent dopant. These two components were fused to create the DABNA-Spiro-Cz molecule. The molecular structures of Spiro-Cz, DABNA-Spiro-Cz, along with the concept of the ZETPLEX mechanism, are presented in **Figure 1**. Spiro-Cz consists of a fundamental carbazole moiety with p-type characteristics and a spiro structure designed for fusion.(11) DABNA-Spiro is composed of a DABNA core exhibiting multi resonance thermally activated delayed fluorescence (MR-TADF) properties, combined with a spiro moiety for fusion.(12)

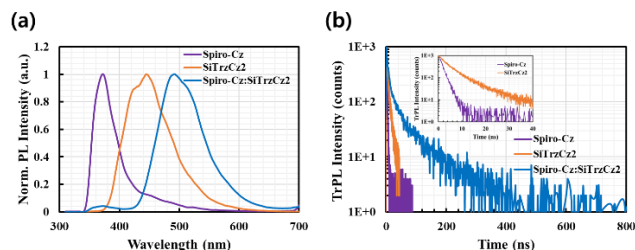


**Figure 2.** (a) The UV-vis absorption spectra of Spiro-Cz, DABNA-Spiro, and DABNA-Spiro-Cz and (b) their PL spectra at different excitation wavelengths. All samples were prepared in toluene solution at  $2 \times 10^{-6}$  M.

**Figure 2** presents the photophysical properties of the newly synthesized materials. The strong UV-vis absorption spectra below 330 nm in these materials originate from the  $\pi$ - $\pi^*$  transition of the spiro moiety.(13) The absorption peak at 447 nm observed in both DABNA-Spiro and DABNA-Spiro-Cz is associated with the DABNA core. The absorption spectrum of the 1:1 mixture of Spiro-Cz and DABNA-Spiro exhibits features including the peak below 330 nm from Spiro-Cz and the peaks at 356 nm and 447 nm from DABNA-Spiro. The absorption spectra of the mixture and DABNA-Spiro-Cz are nearly identical, indicating that Spiro-Cz and DABNA-Spiro are fully integrated within the DABNA-Spiro-Cz molecule without the emergence of any new spectral features.

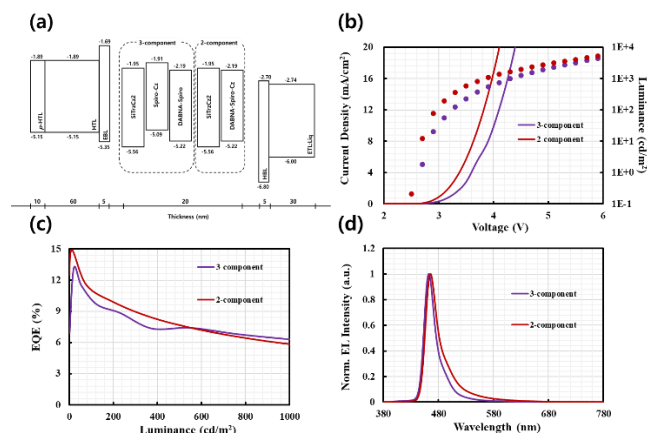
To determine whether the fully fused molecule allow the Spiro-Cz and DABNA-Spiro units to function independently while enabling intramolecular energy transfer, PL spectra were compared by exciting the materials at wavelengths. When DABNA-Spiro-Cz was excited at 330 nm, corresponding to the absorption peak of Spiro-Cz, and at 447 nm, corresponding to the absorption peak of DABNA-Spiro, it consistently exhibited PL spectra characteristic of DABNA-Spiro. The observation of the PL spectrum corresponding to DABNA-Spiro at both excitation wavelengths indicates that intramolecular energy transfer occurs from the Spiro-Cz unit to the DABNA-Spiro unit within the DABNA-Spiro-Cz molecule. Additionally, when DABNA-Spiro and DABNA-Spiro-Cz were excited at 447 nm, their PL intensities were neatly identical. However, when excited at 330 nm, the PL intensity of DABNA-Spiro-Cz was nearly twice as high as that of DABNA-Spiro. At 330 nm, the PLQY of DABNA-Spiro and DABNA-Spiro-Cz are 56.8% and 61.2%, respectively, showing only a small difference. Therefore, the significant difference in PL intensity is not due to the difference in PLQY.

The enhanced PL intensity of DABNA-Spiro-Cz arise from the effective ZRIET occurring within the fused molecule.(10)



**Figure 3.** (a) The PL spectra and (b) the Transient PL data of Spiro-Cz, SiTrzCz2, and mixed film of Spiro-Cz and SiTrzCz2.

To establish an EML with an exciplex system, the PL spectra and transient PL curves of the p-type host Spiro-Cz and the n-type host 9,9'-(6-(4-(triphenylsilyl)phenyl)-1,3,5-triazine-2,4-diyl)bis(9H-carbazole) (SiTrzCz2) were compared with those of a mixed film of Spiro-Cz and SiTrzCz2 as shown in **Figure 3**. When an exciplex is formed, a red shift in the PL spectra is observed in the mixed film compared to the individual films.(14) The mixed film of Spiro-Cz and SiTrzCz2 exhibits a red-shifted PL spectrum compared to the individual films and shows a significantly longer decay time in the transient PL curve. These results strongly indicate the formation of an exciplex between Spiro-Cz and SiTrzCz2.



**Figure 4.** (a) Device structures, comparison of (a)  $J$ - $V$ - $L$  characteristics, (c) EQE curves, (d) EL spectra of 3-component device and 2-component device.

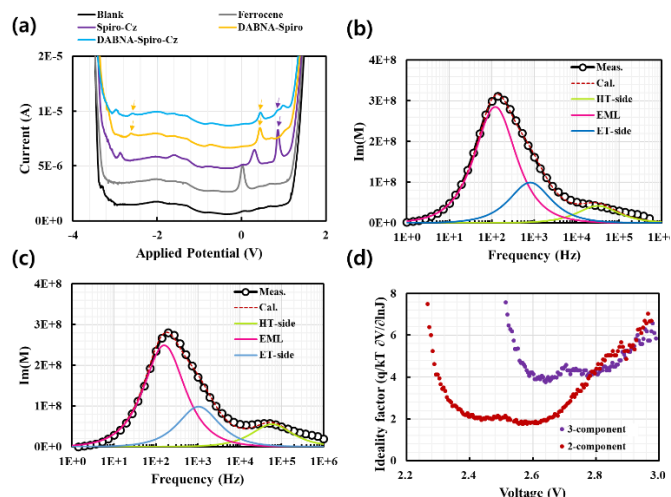
The performance of a 2-component EML device using DABNA-Spiro-Cz and a conventional 3-component EML device with an exciplex system are compared and presented in **Figure 4**. The EMLs of the fabricated devices are the only differing components, while all other configurations remain the same. The 3-component EML consists of SiTrzCz2 and Spiro-Cz mixed on a 1:1 ratio and DABNA-Spiro doped at 2 wt.%. The 2-component EML is composed of SiTrzCz2:DABNA-Spiro-Cz at a 10 wt.% concentration. The concentrations of the materials in each EML are optimized conditions. The 2-component device demonstrates superior charge injection and transport capabilities compared to the 3-component device. The EQE of the 3-component device is 13.1%, while the EQE of the 2-component device is 14.9%, indicating better efficiency performance in the 2-component

device. The EL spectra of both devices are identical to the PL spectrum of DABNA-Spiro. However, the EL spectrum of the 2-component device exhibits a slightly broader characteristics, which is attributed to the excimer features of DABNA-Spiro-Cz due to its high doping concentration of 10 wt.%. Despite the high doping level, the performance of the 2-component device outperforms the 3-component device because the ZRIET mechanism, within DABNA-Spiro-Cz can be successfully extended to the ZETPLEX mechanism.

In the 2-component EML, the Spiro-Cz unit within the DABNA-Spiro-Cz molecule forms an exciplex with SiTrzCz2, and the energy of the generated excitons is transferred to the DABNA-Spiro unit within the DABNA-Spiro-Cz molecule. The successful implementation of ZETPLEX in the 2-component EML device not only simplifies the exciplex-dopant system but also reduces the fabrication challenges associated with maintain the uniformity of multi-component EMLs, while demonstrating superior performance. The performance of the fabricated devices is summarized in **Table 1**.

**Table 1.** EL performances of fabricated devices.

Device	Voltage [V]	Luminance [cd/m <sup>2</sup> ]	EQE <sub>max</sub> [%]	CIE <sub>x</sub> /CIE <sub>y</sub>	λ <sub>max</sub> [nm]
3-component	4	656.84	13.1	0.137/0.109	463
2-component	3.73	872.36	14.9	0.151/0.190	466

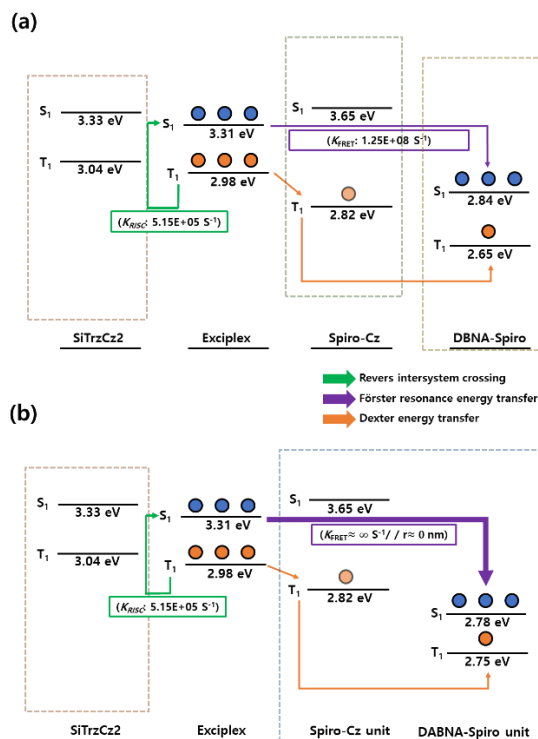


**Figure 5.** (a) DPV curves of Spiro-Cz, DABNA-Spiro, and DABNA-Spiro-Cz, (b-c) the bode plot of modulus measured at 0.001 mA/cm<sup>2</sup> and fitting data of 3-component and 2-component devices, and (d) ideality factors extracted from 3-component device and 2-component device.

To further analyze the excellent performance of the 2-component device utilizing the ZETPLEX mechanism, impedance analysis and ideality factor analysis were performed and are presented in **Figure 5**. The HOMO/LUMO levels of Spiro-Cz, DABNA-Spiro, and DABNA-Spiro, experimentally determined through differential pulse voltammetry (DPV) measurements, are -5.09/-1.91 eV, -5.22/-2.19 eV, and -5.22/-2.19 eV, respectively. The HOMO/LUMO levels of DABNA-Spiro and DABNA-Spiro-Cz

are identical. Interestingly, the second oxidation potential peak corresponding to the HOMO-1 level of DABNA-Spiro-Cz is the same as the HOMO-1 level of Spiro-Cz, at -5.64 eV. From the perspective of electrical transport, the DPV measurement data of DABNA-Spiro-Cz suggest the presence of a dual channel, possessing transport characteristics of both Spiro-Cz and DABNA-Spiro. In the J-V characteristics shown in **Figure 4**, DABNA-Spiro in the 3-component EML act as a charge trap, while DABNA-Spiro-Cz in the 2-component EML does not appear to act as a charge trap. The bode plot of modulus was measured for both devices, and the data was fitted using a 3-resistance-capacitance model to compare the resistances of the hole transport (HT) side, EML electron transport (ET) side. The resistance values extracted from the EML show that the 3-component EML has a resistance of 743 kΩ, while the 2-component EML has a resistance of 501 kΩ. The smaller resistance value of the 2-component EML indicates efficient charge transport with slight charge trapping characteristics. Additionally, the HT-side resistance values for the 3-component and 2-component devices are 0.420 kΩ and 0.298 kΩ, respectively, which suggests that the 2-component device demonstrates excellent hole transport capability through the dual channel.

The ideality factor of the two devices shows that the 3-component device has a value close to 4, while the 2-component device has a significantly lower ideality factor. This suggests that the 3-component device undergoes trap-assisted recombination, whereas the 2-component device primarily exhibits dominant Langevin recombination. As a result, the 2-component device has dual electrical transport channels and demonstrates minimal charge trapping characteristics.



**Figure 6.** The schematic diagram of the energy transfer dynamics in (a) the 3-component EML and (b) the 2-component EML.

To gain a deeper understanding of the ZETPLEX mechanism, in the 2-component EML, the exciton dynamics of both the 3-component EML and the 2-component EML were analyzed and presented in **Figure 6**. Both EMLs operate based on an exciplex-dopant system, where singlet energy transfer predominantly occurs. This transfer is governed by the FRET process, and the FRET rate ( $k_{\text{FRET}}$ ) and efficiency ( $\eta_{\text{FRET}}$ ) follow the equations below:(15)

$$K_{\text{FRET}} = \frac{\eta_{\text{D}}}{\tau_{\text{D}}} \left( \frac{R_0}{r} \right)^6 \quad (1)$$

$$\eta_{\text{FRET}} = \frac{1}{\left( 1 + \left( \frac{r}{R_0} \right)^6 \right)} \quad (2)$$

where  $\eta_{\text{D}}$  is host's PLQY,  $r$  is host-dopant distance, and  $R_0$  is the FRET radius.

The calculated  $k_{\text{FRET}}$  and  $\eta_{\text{FRET}}$  for the 3-component EML are  $1.25 \times 10^8 \text{ s}^{-1}$  and 48%, respectively. In the case of the 2-component EML, both the donor and acceptor responsible for transferring the exciton energy generated within the exciplex are integrated into a single molecule. Consequently, the “ $r$ ” approaches zero, resulting in an exceptionally high  $k_{\text{FRET}}$  and and nearly 100%  $\eta_{\text{FRET}}$ .

The experimentally determined energy transfer characteristics of both EMLs highlight the superior energy transfer capability of the ZETPLEX mechanism, effectively demonstrating the enhanced performance of the 2-component device compared to the conventional 3-component device.

### 3. Summary

In this study, we successfully designed and synthesized DABNA-Spiro-Cz by integrating a p-type host and blue fluorescent dopant. From an electrical transport perspective, DABNA-Spiro-Cz exhibits a dual-channel structure and charge trap-free characteristics. Thanks to the innovative ZETPLEX mechanism, the energy of excitons generated in the exciplex is transferred through extremely fast and efficient FRET process. As a result, the 2-component device with the implemented ZETPLEX mechanism successfully simplifies the conventional 3-component device and achieves a higher EQE of 14.9%. The ZETPLEX mechanism enhances the efficiency of OLED processes and paves the way for a new path toward high-efficiency OLEDs.

### 4. Impact of Your Research

This study successfully designed and synthesized a molecule integrating a p-type host and a blue fluorescent dopant, thereby implementing the ZETPLEX mechanism. The ZETPLEX mechanism not only simplifies the existing exciplex-dopant system-based EML but also significantly enhances the energy transfer rate and efficiency. The ZETPLEX mechanism represents an innovative new concept in energy transfer, both from a materials and device perspective.

### 5. Acknowledgements

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