EFFECTIVE STRATEGIES FOR EFFICIENT EXCIPLEX EMISSION IN ORGANIC LIGHT-EMITTING DIODES

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GENERAL INFORMATION

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ABSTRACT

This paper presents a comprehensive investigation into the optimization of exciplex emission in organic light-emitting diodes (OLEDs). Through a systematic exploration of various combinations of hole-transporting materials (HTMs) and electron-transporting materials (ETMs), we elucidate critical factors influencing exciplex formation and its impact on OLED performance. Our analysis focuses on estimating the energy band gap of exciplexes, guiding the selection of appropriate material combinations. Experimental observations reveal distinct exciplex emission profiles and lifetime characteristics for different HTM/ETM combinations, providing valuable insights into exciplex formation dynamics. Importantly, we emphasize the significance of ensuring that the HTM/ETM combination possesses a higher triplet energy bandgap than the exciplex to optimize OLED performance and enhance energy efficiency. Overall, this study contributes to the advancement of OLED technology by offering effective strategies for achieving efficient exciplex emission, with implications for lighting, displays, and other applications

1. INTRODUCTION

In recent years, significant strides have been made in the development of efficient organic light-emitting diodes (OLEDs) through the utilization of two innovative techniques: exciplex and thermally-activated delayed fluorescence (TADF). A crucial aspect of TADF lies in the requirement of a minimal energy band gap between the first triplet excited state and the first singlet excited state (ΔE_{ST}), facilitating the capture of triplet excitons through reverse intersystem crossing. Similarly, achieving a small ΔE_{ST} is also pivotal in the exciplex technique, wherein it is generated through through-space intermolecular charge transfer between a hole-transporting material (HTM) and an electron-transporting material (ETM). What's noteworthy is that exciplex formation can be readily induced using commercially available materials. Generally, an exciplex can be created either through a bilayer structure employing both HTM and ETM, or by directly blending an HTM with an ETM. The latter method typically yields higher exciplex production rates. In principle, the energy band gap of an exciplex is dictated by the energy-level difference, implying that it could be tailored by selecting appropriate materials (Hu et al., 2020). Nevertheless, effective systems for achieving efficient exciplex emission remain somewhat scarce even to this day. Therefore, the focus of this study is to delve deeper into the exploration of effective systems for achieving efficient exciplex emission in OLEDs (Ying et al., 2022).

Our approach involves a multifaceted investigation encompassing both experimental and theoretical methodologies. Experimentally, we intend to synthesize and meticulously characterize various HTMs and ETMs, taking into account critical material properties such as electron affinity, ionization potential, and molecular architecture. Subsequently, we plan to fabricate OLED devices employing these materials, either in bilayer configurations or through direct blending, to facilitate exciplex formation (Wang et al., 2021; Zhang et al., 2021).

We will harness the power of theoretical modeling and computational simulations to forecast the energy level alignment and charge transfer dynamics between HTMs and ETMs (Chi et al., 2022). This computational insight will serve as a guiding principle in the rational design of material combinations with favorable exciplex properties. By meticulously exploring a wide array of material combinations and device architectures, we aim to unravel the key determinants that augment exciplex emission efficiency in OLEDs. Ultimately, our findings hold the promise of catalyzing the advancement of next-generation OLED technologies, characterized by enhanced performance and energy efficiency (Vipin et al., 2021).

2. EXPERIMENT

Material synthesis and characterization: HTMs (hole-transporting materials) and ETMs (electron-transporting materials) were synthesized according to established procedures. The materials were characterized using various techniques such as nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry, and elemental analysis to confirm their structures and purity.

Device fabrication: OLED devices were fabricated using a standard procedure. Indium tin oxide (ITO)-coated glass substrates were cleaned, followed by deposition of a hole injection layer (HIL) and a hole transport layer (HTL) by thermal evaporation. The HTM/ETM mixture was deposited as the emissive layer (EML), followed by the deposition of an electron transport layer (ETL) and a cathode. The devices were encapsulated to prevent degradation.

Characterization of OLED devices: The fabricated OLED devices were characterized using various techniques. Current-voltage-luminance (IVL) measurements were performed to assess the electrical properties, including current density, luminance, and efficiency. Photoluminescence (PL) spectra were recorded to analyze the emission characteristics of the devices. Time-resolved measurements, such as transient photoluminescence and transient electroluminescence, were conducted to study the exciton dynamics and device kinetics.

Exciplex formation and lifetime measurements: Exciplex formation in the OLED devices was investigated through photoluminescence measurements under different excitation conditions. Time-resolved PL measurements were conducted to determine the excited-state lifetimes of the devices. The exciplex emission profiles and decay kinetics were analyzed to elucidate the mechanisms governing exciplex formation and emission.

Computational modeling: The energy level alignment and charge transfer characteristics between HTMs and ETMs were theoretically modeled using computational methods. Density functional theory (DFT) calculations and molecular dynamics simulations were employed to predict the electronic structure and intermolecular interactions of the materials. Theoretical insights were compared with experimental data to validate the findings and provide a deeper understanding of the exciplex formation process.

3. RESULTS AND DISCUSSION

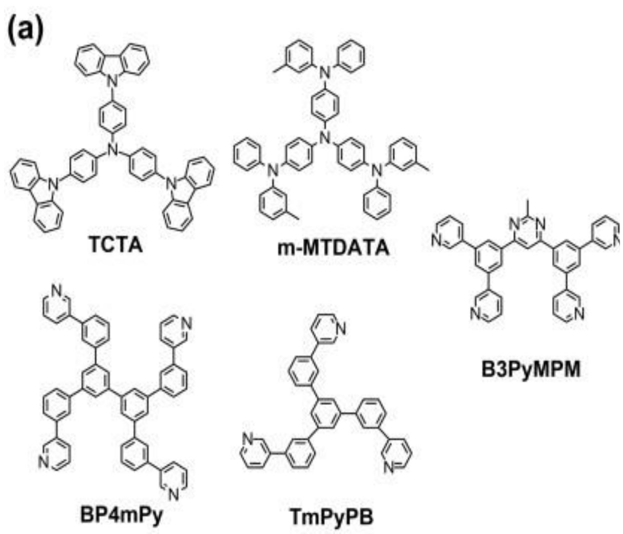
Understanding the energy band gap of exciplexes is pivotal in predicting their emission characteristics, as it relies on the energy difference between the lowest unoccupied molecular orbital (LUMO) of the electron-transporting material (ETM) and the highest occupied molecular orbital (HOMO) of the hole-transporting material (HTM). This relationship offers a rough estimate of the exciplex's emission color based on their respective energy levels. Drawing from previous literature, the LUMOs of BP4mPy, TmPyPB, and B3PyMPM were approximated to be around 2.57 eV, 2.73 eV, and 3.20 eV, respectively. Likewise, the HOMOs of TCTA and m-MTDATA were estimated at approximately 5.80 eV and 5.10 eV. Calculating the LUMO/HOMO differences yielded values of 4.09 eV for TCTA: BP4mPy, 2.37 eV for m-MTDATA: TmPyPB, and 1.90 eV for m-MTDATA: B3PyMPM.

We selected three combinations of HTM and ETM to foster exciplex formation. Specifically, TCTA and m-MTDATA served as the HTMs, while BP4mPy, TmPyPB, and B3PyMPM were chosen as the corresponding ETMs. These combinations were represented by samples labeled as B, G, and R, with their respective chemical structures and schematic energy level diagrams illustrated in Figure 1.

The analysis of the photoluminescence (PL) spectra and excited-state lifetime measurements of the thin-film samples, as presented in Figure 2, revealed intriguing differences. Sample B exhibited a narrower spectrum compared to samples G and R, suggesting a distinct exciplex emission profile. Moreover, samples G and R displayed a two-component decay in their lifetime measurements, indicating both prompt and delayed emissions, while sample B exhibited only a nanosecond-scale component.

As depicted in Figure 3(a), uncovered that both TCTA and BP4mPy possessed lower triplet energy bandgaps than the TCTA: BP4mPy mixture (sample B). This minimal energy difference ($\Delta EST \sim 0.1$ eV) corroborated the exciplex emission origin. Furthermore, the phosphorescence measurements (Figure 3(b)) unveiled a gradual decay in exciplex emission with extended delay times, accompanied by additional emissions resembling BP4mPy's phosphorescence. This observation provided concrete evidence of exothermic energy transfer.

Our findings underscore the significance of judiciously selecting HTM/ETM combinations to attain red, green, and blue emissions. Additionally, our photophysical results emphasize the necessity of ensuring that the HTM/ETM combination possesses a higher triplet energy bandgap than the exciplex to minimize energy loss to individual molecules. This study offers valuable insights into optimizing OLED performance through effective exciplex formation, paving the way for advancements in organic electronics.



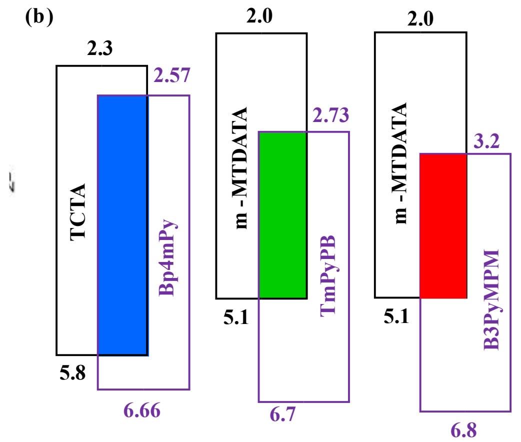


Figure 1. (a) Chemical structures of the materials; (b) the schematic energy level diagram.

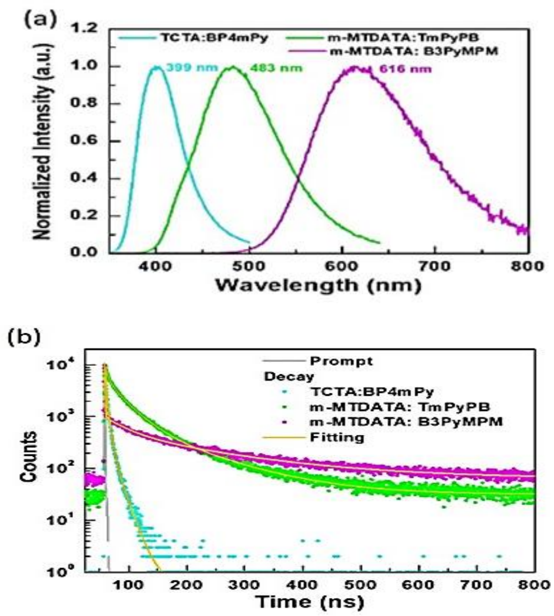
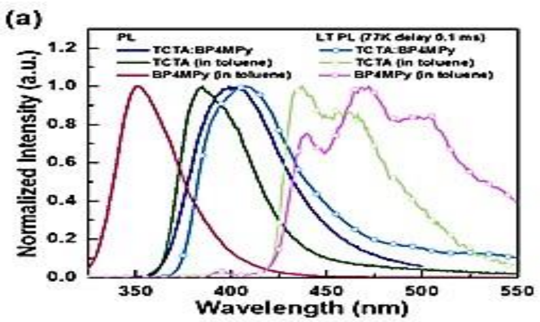
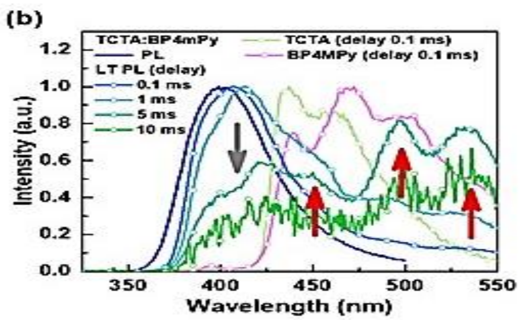


Figure 2. (a) The PL Spectra of sample A, B and C. (b). The decay characteristics of sample A,B and C





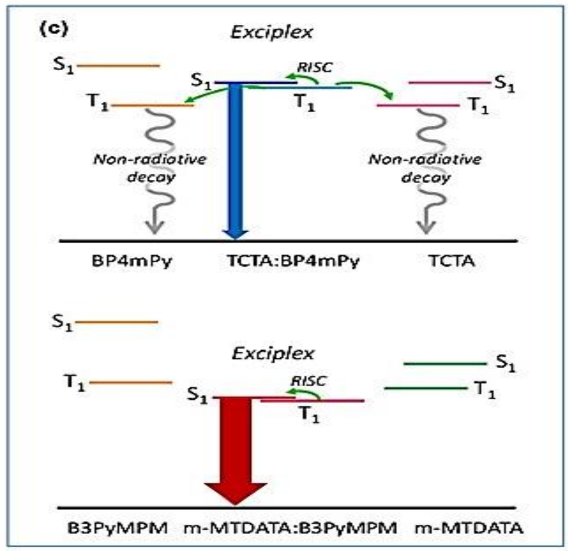


Figure 3. (a) The fluorescent and phosphorescent spectra of TCTA, BP4mPy, and sample B. (b) The phosphorescent spectra of sample B with different delay times. (c) The schematic diagram of energy tranfers in sample B and R

4. CONCLUSION

Our study into efficient exciplex emission in OLEDs has shed light on critical factors influencing their performance. By examining various combinations of hole-transporting materials (HTMs) and electron-transporting materials (ETMs), we have gained valuable insights into exciplex formation and its impact on OLED characteristics.

The experiment results highlight the importance of understanding the energy band gap of exciplexes, which is determined by the energy difference between the LUMO of the ETM and the HOMO of the HTM. This understanding allowed us to estimate the emission color of exciplexes and select appropriate material combinations for our study.

Through experimental analysis, we observed distinct exciplex emission profiles and lifetime characteristics for different HTM/ETM combinations. Samples exhibited a range of emission behaviors, including prompt and delayed emissions, providing valuable information about exciplex formation dynamics.

Our findings underscored the significance of ensuring that the HTM/ETM combination possesses a higher triplet energy bandgap than the exciplex to minimize energy loss to individual molecules. This insight is crucial for optimizing OLED performance and enhancing energy efficiency. The paper contributes to the advancement of OLED technology by elucidating effective strategies for achieving efficient exciplex emission. By leveraging the principles of exciplex formation and energy transfer, future OLED designs can be tailored to exhibit improved performance and color purity, paving the way for innovative applications in lighting, displays, and beyond.

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