

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

フー, ヤンメイ

<https://hdl.handle.net/2324/7443416>

出版情報 : Kyushu University, 2025, 博士 (工学), 課程博士
バージョン :
権利関係 :



氏 名 : HU YANMEI

論 文 名 : Design and Synthesis of Hosts and Emitters - From Photophysical Studies to Device Applications in Organic Light-Emitting Diodes
(有機 EL におけるホスト材料および発光材料の設計・合成と光物性評価およびデバイス応用に関する研究)

区 分 : 甲

論 文 内 容 の 要 旨

Despite substantial progress in organic light-emitting diodes (OLEDs), blue OLEDs are still predominantly based on fluorescent emitters, which suffer from limited efficiency. Since the introduction of thermally activated delayed fluorescence (TADF) in 2012, TADF emitters have attracted considerable attention owing to their ability to theoretically achieve 100% internal quantum efficiency while using purely organic materials. Although high efficiencies have been demonstrated for red and green TADF-OLEDs, the operational lifetime of blue TADF-OLEDs remains unsatisfactory, representing a major obstacle to their further development and practical application. One of the fundamental challenges arises from the intrinsically high triplet energy required for blue emission, together with the limited availability of host materials that can simultaneously provide high triplet energy, chemical stability, and appropriate charge-transport properties. Moreover, the operational lifetime of OLEDs is governed by multiple factors, including exciton density, molecular stability, and charge recombination dynamics. Among these factors, balanced hole and electron transport in the emissive layer is indispensable for achieving long device lifetime, as it suppresses carrier accumulation, mitigates exciton-polaron and exciton-exciton annihilation processes, and stabilizes the recombination zone.

In this dissertation, the design and synthesis of novel host materials with high triplet energies and improved carrier-transport balance are systematically investigated, primarily focusing on green TADF-OLEDs, where device stability can be reliably evaluated without the severe constraints imposed by deep-blue emission. Through stepwise molecular modification and comprehensive investigation of intrinsic and extrinsic host properties, OLEDs with high efficiency, reduced driving voltage, and enhanced operational stability were achieved. Furthermore, this work is extended to alternative device architectures, including host-free emissive layers for blue TADF-OLEDs, to explore viable strategies toward efficient blue 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), indicating the great

potential for green/blue TADF emitters. Devices using the green emitter 4CzIPN revealed that the 2SiPh-based device achieved a EQE_{max} of 16.6%, whereas the 2SiPy-based device showed a lower EQE of 8.2% due to the stronger interaction between 2SiPy and 4CzIPN. The device lifetimes of LT₉₅ were 2.3 h and 2.2 h for 2SiPh and 2SiPy, respectively. 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 20.3 and 14.0% for CzPyBF and mCBP hosts, respectively. Most importantly, the device lifetime of the CzPyBF host achieved LT₉₅ of 26 h, which is 1.5 times longer than that of mCBP (15 h). 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. The green 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 LT₉₅ of 67 h, followed by 2-BF (56 h), both outperforming mCBP (30 h), whereas the 4-BF-based device degraded rapidly with an LT₉₅ of only 8 h. 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.

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. 36Me-HDT1-doped OLEDs achieved a EQE_{max} 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.