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# Molecular Design, Synthesis, and Properties of Highly Efficient Thermally Activated Delayed Fluorescence Materials for Organic Light-Emitting Diodes

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Chapter 1 describes the background and motivation of this dissertation. Organic light-emitting diodes (OLEDs) have been drawing considerable attention for their practical applications in flexible displays and solid-state lighting sources for architectural or automotive lighting because of their unique advantages such as high electroluminescence (EL) efficiency, flexibility, high contrast, light weight, and low manufacturing costs. In OLEDs, electrically injected holes and electrons recombine to form singlet and triplet excitons in the ratio of 25% and 75%, respectively, according to spin statistics. Therefore, in conventional fluorescent OLEDs, only the lowest singlet ( $S_1$ ) excitons can be utilized for light emission because the lowest triplet ( $T_1$ ) excitons undergo a spin forbidden transition, resulting in nonradiative deactivation processes. Meanwhile, organometallic phosphorescent materials containing rare metals can effectively convert both  $S_1$  and  $T_1$  excitons into light emission. Despite their desirable EL characteristics, phosphorescent materials still have some drawbacks such as the rarity, toxicity, and high cost of the used rare metals. As an alternative, thermally activated delayed fluorescence (TADF) materials have recently emerged as a promising class of organic luminophores for the production of high-efficiency OLEDs without using rare metals. TADF emitters, which have a small energy difference ( $\Delta E_{ST}$ ) between the  $S_1$  and  $T_1$  states, enable efficient reverse intersystem crossing (RISC) from their  $T_1$  to  $S_1$  states via thermal activation, and hence lead to the high internal EL quantum efficiency close to unity. The basic design strategy for achieving such a small  $\Delta E_{ST}$  in donor-acceptor (D-A) molecules is to minimize the spatial overlap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), in accordance with reduced electron-exchange interactions, by localizing these orbitals on the donor and acceptor constituents, respectively. This dissertation focuses on molecular design, synthesis, and properties of highly efficient TADF materials for OLEDs.

In chapter 2, a new series of D-A molecules consisting of a xanthone acceptor unit coupled with different donor units was designed and synthesized. OLEDs employing a heavily doped emitting layer consisting of 75 wt%-TADF emitter doped in a host material exhibited considerably high external EL quantum efficiencies of up to 18% with suppressed concentration quenching characteristics. Concentration quenching of TADF molecules was found to be dominated by electron-exchange interactions for triplet excitons, as described by the Dexter energy-transfer model. This result is in marked contrast to conventional fluorescent and phosphorescent molecules, which involve the Förster energy-transfer mechanism. Owing to the short-range nature of electron-exchange interactions, even a small modulation in molecular geometric structures drastically affected the concentration-quenching behavior, leading to enhanced photoluminescence (PL) and EL properties.

In chapter 3, regioisomeric D-A molecules consisting of a xanthone acceptor unit and a *para*- or *meta*-linked tercarbazole donor unit were designed and synthesized as TADF emitters. These luminophores exhibited obvious twisted intramolecular charge transfer characteristics, as revealed by solvatochromism and

transient PL analyses. Blue OLEDs employing these TADF emitters showed high external EL quantum efficiencies of up to 14.4% with suppressed roll-off characteristics.

In chapter 4, new D–A molecules comprised of isobenzofuranone or chromone as an acceptor unit and spiroacridan as a donor unit, were designed and synthesized as blue TADF emitters. Their small  $\Delta E_{ST}$  values in the range of 0.08–0.11 eV could contribute to the fast RISC, leading to short triplet exciton lifetimes of less than 4  $\mu$ s. The OLEDs based on these TADF emitters exhibited high external EL quantum efficiencies of up to 16.2% with extremely suppressed efficiency roll-off characteristics even in their heavily doped and non-doped devices. From the detailed analysis of efficiency roll-off characteristics, the fast RISC for isobenzofuranone and chromone-based TADF emitters significantly suppressed singlet–triplet annihilation and triplet–triplet annihilation processes.

In chapter 5, donor–acceptor–donor (D–A–D) and D–A molecular systems containing oxadiazole or triazole as an acceptor unit and phenoxazine as a donor unit were developed. In toluene solution, the D–A–D molecules showed more efficient TADF and higher PL quantum efficiencies than D–A molecules. OLEDs utilizing D–A–D molecules displayed green and blue EL emission with external EL quantum efficiency of 14.9% and 6.4%, respectively.

In chapter 6, a series of acceptor–donor–acceptor molecules, comprising a dihydrophenazine donor unit coupled with various acceptor units was designed and synthesized. The emission color from green to orange,  $\Delta E_{ST}$  values ( $\sim$ 0–0.19 eV), and triplet exciton lifetimes (0.14–0.53  $\mu$ s) of these TADF materials could be controlled by changing the acceptor units. A green-emitting OLED based on the benzimidazole-based TADF emitter exhibited a external EL quantum efficiency of 12%, which is much higher than the theoretical limit of external EL quantum efficiencies in conventional fluorescent OLEDs.

Chapter 7 summarizes this dissertation and introduces future perspectives.