Design of Luminophores for Efficient Exciton Interconversion and Their Application in Organic Light-Emitting Diodes

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論 文 名　：Design of Luminophores for Efficient Exciton Interconversion and Their Application in Organic Light-Emitting Diodes
（効率的な励起子相互変換のための発光材料の設計と有機発光ダイオードへの応用）

区　　分　：甲

論 文 内 容 の 要 旨

The science and technology of organic light-emitting diodes (OLEDs) have advanced steadily over the past three decades since the first discovery in 1987. OLEDs are now widespread, present in smartphones, watches, and televisions, and offer advantages such as being light-weight, high-contrast, and flexible. Thermally activated delayed fluorescence (TADF) has emerged as a promising and viable electroluminescence (EL) technology for producing highly efficient and stable blue OLEDs. In principle, TADF-OLEDs are capable of boosting internal EL quantum efficiency (η_{int}) to ~100% by harvesting all electro-generated excitons through efficient reverse intersystem crossing (RISC) from non-radiative lowest excited triplet (T_1) to radiative lowest excited singlet (S_1) states by thermal activation. However, there are still significant challenges to realizing the practical use of TADF in terms of emission color purity and efficiency of exciton interconversion. Therefore, this dissertation focuses on the molecular design of blue TADF materials with efficient exciton interconversion and narrowband emission and their applications in OLEDs.

In Chapter 2, phenoxaborin and xanthone-cored TADF emitters with quadrupolar electronic structures were developed to exhibit sub-microsecond TADF lifetimes as short as 650 and 970 ns, respectively, while preserving high fluorescence quantum yields. By extending the El-Sayed rule to the quadrupolar π-systems, the contribution of doubly degenerate charge-transfer excited states induced by dual donor units could enhance the spin–orbit coupling (SOC) between them, leading to a spin-flip acceleration between the excited triplet and singlet states. This electronic feature was advantageous for mitigating exciton annihilation processes in the emission layer, thereby reducing the efficiency roll-offs in OLEDs. Consequently, a high external EL quantum efficiency (η_{ext}) over 20% could be retained, even under operating the device at a high luminance of 1000 cd m^{-2}.

In Chapter 3, a material design of linear *cis*-quinacridone (*cis*-QA) derivatives was suggested as delayed fluorescence luminogens. In contrast to the widely studied traditional *trans*-isomers, the functionality of *cis*-QA and its derivatives remain unexplored and unclarified. Through combined computational and experimental investigations, it was revealed that *cis*-QA derivatives could function as fascinating narrowband deep-blue delayed fluorescence emitters for OLEDs. The best-performing deep-blue OLEDs incorporating these *cis*-QA luminogens achieved high η_{ext} of up to 19.0% and high color purity with chromaticity coordinates of (0.13, 0.14).

In Chapter 4, it was demonstrated that strategically fusing indole moieties to the periphery of a simple multiple resonance (MR) skeleton allows for further emission spectral narrowing. Moreover, a combination of photophysical analyses and computational simulations revealed that π-extended indolocarbazole moieties promote fluorescence radiative decay and singlet−triplet spin interconversion. Consequently, the OLED based on a doubly indolo-fused MR-TADF emitter showed narrowband sky-blue EL with a full width at half maximum of 21 nm (0.11 eV), as well as high maximum external EL quantum efficiency of 25.9% with an alleviated efficiency roll-off behavior.

In Chapter 5, highly efficient blue TADF molecules combining 1,8-dimethylcarbazole as a weak donor (D) unit with a triazine-based acceptor (A) core were developed. Unlike unsubstituted carbazole, 1,8-dimethylcarbazole could effectively induce intermolecular twisting between the D–A linkages, thus enhancing the TADF properties. Moreover, a quadrupolar D–A–D-type blue TADF molecule exhibited superior photoluminescene and EL properties to a dipolar D–A-type counterpart. TADF-OLEDs based on the D–A–D-type emitter featuring the versatile 1,8-dimethylcarbazole–triazine conjugates displayed a brilliant blue EL emission and furnish a maximum η_{ext} as high as 21.2% with CIE color coordinates of (0.16, 0.27).

In Chapter 6, the dissertation is summarized, and perspectives are discussed.