Design of High-Performance Delayed Fluorescence Materials and Their Application in Organic Light-Emitting Diodes

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論 文 名　：　Design of High-Performance Delayed Fluorescence Materials and Their Application in Organic Light-Emitting Diodes
（高性能遅延蛍光材料の設計と有機発光ダイオードへの応用）

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論 文 内 容 の 要 旨

Chapter 1 describes the background and motivation of this dissertation. Full-color flat-panel displays and solid-state lighting sources based on organic light-emitting diodes (OLEDs) have attracted considerable research interest for over 30 years, because of their high contrast, flexibility, and potentially low manufacturing costs as well as bright and full-color light emissions from thin organic layers. In general, the light emission of excited organic molecules is classified as either fluorescence or phosphorescence. Although fluorescence materials have attracted attention because of their high color purity and high reliability, the internal quantum efficiency of conventional fluorescent OLEDs is limited to 25%, as the recombination of injected electrons and holes generates the lowest excited triplet (T_1) and singlet (S_1) states at a ratio of 3:1. This spin-statistical requirement limits the maximum external electroluminescence (EL) quantum efficiency of fluorescent OLEDs to less than 5%. Meanwhile, phosphorescence organometallic materials incorporating an iridium or platinum metal center are promising emitters for OLEDs because the internal quantum efficiency of nearly 100% can be attained by harvesting both 25% S_1 and 75% T_1 excitons for EL emission by accelerated intersystem crossing from the S_1 to T_1 states, owing to a strong spin–orbit coupling. As an alternative way, thermally activated delayed fluorescence (TADF) has recently gained increasing interest to produce highly efficient OLEDs since the achievement of the internal quantum efficiency close to unity by Uoyama et al. in 2012. Until this discovery, only phosphorescence organometallic materials were regarded as the sole candidates as emitters in high-efficiency OLEDs because phosphorescent OLEDs can achieve external EL quantum efficiency of over 20%. However, these phosphorescence materials still have some drawbacks: the rarity of the precious metals required for fabrication, toxicity, and difficulty in color rendering of the three primary colors (blue, green, and red), especially for blue emission. Purely organic TADF materials can utilize both S_1 and T_1 excitons for light emission without the use of any precious metal. Thus, TADF molecules can act as a class of next-generation organic light-emitting materials. Therefore, this dissertation focuses on molecular design for highly efficient TADF materials and their application in OLEDs.

In Chapter 2, luminescent wedge-shaped molecules, which comprise a central phthalonitrile or 2,3-dicyanopyrazine acceptor core coupled with various donor units, were designed and synthesized as TADF emitters. This set of materials allows systematic fine tuning of the band gap and exhibits TADF emission that cover the entire visible range from blue to red. Full-color TADF-OLEDs with high maximum external EL quantum efficiencies of up to 18.9% were achieved by employing these phthalonitrile and 2,3-dicyanopyrazine-based TADF emitters.

In Chapter 3, high-performance blue TADF emitters based on a central pyrimidine acceptor core with peripheral diphenylacridan donor units, have been developed. A design motif of highly twisted donor–acceptor–donor (D–A–D) architectures having a small singlet–triplet energy splitting allows for the production of efficient blue TADF with high photoluminescence (PL) quantum efficiencies exceeding 90%. An OLED based on the blue pyrimidine-based TADF emitter exhibited a high maximum external EL quantum efficiency of 20.8% and a high power efficiency of 31.5 lm W^{-1}.

In Chapter 4, a simple and versatile donor–acceptor (D–A) system combining acridan-based donors and pyrimidine-based acceptors has been developed as a new platform for high-efficiency deep-blue TADF emitters. The designed pre-twisted acridan–pyrimidine D–A molecules exhibited small singlet–triplet energy splitting and high PL quantum yields, functioning as efficient deep-blue TADF emitters. OLEDs utilizing these TADF emitters displayed bright blue electroluminescence with external EL quantum efficiencies of up to 20.4%, maximum current efficiencies of 41.7 cd A^{-1}, maximum power efficiencies of 37.2 lm W^{-1}, and the Commission Internationale de l'Éclairage (CIE) color coordinates of (0.16, 0.23). The design strategy featuring such acridan–pyrimidine D–A motifs can offer great prospects for further developing high-performance deep-blue TADF emitters and TADF-OLEDs.

In Chapter 5, a highly efficient blue emitter based on phenazaborin acceptor and spiroacridan donor units has been developed by weakening the intramolecular charge-transfer (ICT) effect. This new emitter exhibited efficient TADF properties with a high PL quantum efficiency of nearly 100% in its doped film. A blue-emitting OLED containing the phenazaborin derivative as a TADF emitter exhibited a high external EL quantum efficiency of 18.2% with CIE color coordinates of (0.15, 0.23).

In Chapter 6, new linear-shaped TADF emitters, which consists of a central terephthalonitrile acceptor core and three donor moieties linked by π-conjugated phenylene bridges, were designed and synthesized. A D–A–D type linear-shaped molecular architecture allows to exhibit efficient TADF properties as well as horizontally oriented dipoles against to a substrate in a host matrix, which induce efficient light-blue, green, and yellow emission with small singlet–triplet energy splitting values of less than 0.28 eV. Multilayer OLEDs based on these TADF emitters with a suitable host material exhibited both high internal quantum efficiencies of nearly 80% and extremely high light out-coupling efficiencies of over 30%, which lead to high maximum external EL quantum efficiencies of up to 23.4%.

In Chapter 7, novel bipolar host materials consisting of an electron-donating 9-phenylcarbazole unit and an electron-accepting triphenylphosphine oxide, triphenylphosphine sulfide, or 2,4,6-triphenyl-1,3,5-triazine unit linked by a non-conjugated cyclohexane core, have been developed. These bipolar host materials possess high glass-transition temperatures of over 100 °C and high lowest triplet values of approximately 3.0 eV. TADF-OLEDs employing these bipolar host materials with 1,2,3,5-tetrakis(carbazol-9-yl) -4,6-dicyanobenzene (4CzIPN) as a green TADF emitter achieved high external EL quantum efficiencies of up to 21.7% together with reduced efficiency roll-off characteristics. This is because of expansion of the charge-recombination zone within the emission layer arising from the bipolar charge transport ability of these host materials.

Chapter 8 summarizes this dissertation and introduces future perspectives.