

Electron-withdrawing group modification of thermally-activated delayed fluorescence materials for blue OLEDs with high efficiency and durability

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論 文 内 容 の 要 旨

※論文要旨

Organic light-emitting diodes (OLEDs) have attracted a great deal of attention due to their superior advantages that are not provided by conventional inorganic light-emitting diodes (LEDs) and liquid crystal displays (LCDs). The features of OLEDs are the thinness and flexibility, utilizing the softness and low-temperature processing characteristics of organic materials, and the high image quality (high contrast and short response time) comes from the superior emission properties of organic emitters. This makes it possible to design high-quality displays and lighting in a variety of forms, regardless of whether flat, curved, rollable, or transparent. OLEDs are expected to be used in all parts of our daily lives in the near future. However, OLEDs have not yet established a competitive advantage over inorganic LEDs and LCDs in terms of power consumption, durability, and manufacturing costs at present. This prevents the OLED market from further expanding.

The key component that determines the power consumption and durability of OLEDs is the emitting materials. In order to obtain highly efficient electroluminescence (EL), it is essential to utilize an electrically generated triplet excitons as an EL because 25% of singlet and 75% of triplet excitons are directly generated according to the spin statistic law. As a next-generation high-efficiency luminescent material, our group extensively developed highly emissive molecules based on thermally-activated delayed fluorescence (TADF). TADF materials show 100% internal EL quantum efficiency (IQE) by the harvesting of triplet exciton as delayed fluorescence through the reverse intersystem crossing (RISC). So far, many TADF materials with IQE ~ 100% have been reported. However, the reports for deep-blue TADF materials are limited to only a few literatures and most of the blue TADF materials are actually sky-blue. In addition, blue TADF-OLEDs show a shorter device operational lifetime than those of green TADF-OLEDs. The half device operational lifetime (LT_{50}) of blue TADF-OLEDs is typically several hundred hours or less, while that of green TADF OLEDs is exceeding 1000 hours. Intensive researches are undergoing, but the guidelines for a molecular design satisfying all the requirements of high efficiency, durability, and blue light emission are insufficient.

The purpose of this thesis is to develop blue TADF materials with high photoluminescence quantum yield (PLQY) and durability by controlling HOMO-LUMO levels and the excited-state stability through the modification with an electron-withdrawing group on the electron donor moiety. A simple molecular modification that allows controlling the emission color, efficiency, and durability of blue emitters

contributes significantly to improving the performance of blue OLEDs. This thesis is organized as follows.

In **Chapter 1**, the background and motivation of this thesis are introduced.

In **Chapter 2**, I demonstrated a new strategy for a wide HOMO-LUMO energy gap to obtain blue-shifted emission. When I employ an electron donor moiety having a weak electron-donating ability, TADF materials having wide HOMO-LUMO gaps should be obtained. To demonstrate this strategy, I selected 2,4,5,6-tetra(9*H*-carbazol-9-yl)isophthalonitrile (**4CzIPN**) and 2,3,5,6-tetra(9*H*-carbazol-9-yl)terephthalonitrile (**4CzTPN**) as a platform. As an electron-withdrawing group for weakening the donor nature, I selected the trifluoromethyl (CF₃) group and introduced it to the 2,7- (β -) or 3,6- (γ -) position of all carbazoles (Cz) on **4CzIPN** and **4CzTPN**. The modification with the electron-withdrawing group on the donor moiety showed deepened HOMO levels of the emitters and blue-shifted emission. The modification position of the CF₃ group affected the color purity (full width at half maximum, FWHM), emission efficiency of emitters.

In **Chapter 3**, I used a platform of 2,3,4,5,6-penta(9*H*-carbazol-9-yl)benzotrile (**5CzBN**) to demonstrate the full and partial CF₃ modification strategies. **5CzBN** has been often used to demonstrate the new strategies, e.g. hetero-donor, and multi-donor strategies. Fully CF₃ modified emitter (**5CF5**), in which all Cz constituting **5CzBN** were modified with CF₃ groups, exhibited highly efficient deep blue emission, as predicted from the discussion in **Chapter 2**. On the other hand, the partially CF₃ modified **5CzBN** derivatives showed red-shifted emission. Interestingly, the modification position of CF₃ on Cz had a critical effect on their photostability in spite of their HOMOs were distributed on the unmodified Cz. The modification on the β -position enhanced the photostability but on the γ -position contrastingly worsened. The stability of the excited states also affected the device lifetime. **5CF1** having a CF₃ modified Cz at the *para*-position of the benzotrile showed higher external quantum efficiency (EQE) of 17.6% and 3.2 times longer LT₅₀ of 276 h than naked **5CzBN** (14.1%, 86 h).

In **Chapter 4**, partial CF₃ modification was applied to 2,3,5,6-tetra(9*H*-carbazol-9-yl)benzotrile (**4CzBN**). **4CzBN** is a deep-blue TADF material and can be expected to emit in blue even when the emission color is red-shifted by the partial CF₃ modification. **4CF1** in which one Cz of **4CzBN** was replaced by CF₃ modified Cz, showed blue emission with higher PLQY and photostability compared with **4CzBN**. The EQE and LT₅₀ of OLEDs using these emitters were 5.9% and 3 h for **4CzBN**, and 11.7% and 33 h for **4CF1**. I succeeded in the enhancement of the efficiency and lifetime of the blue TADF device with the partial modification strategy using the carbazole having CF₃ groups on its β -position.

Finally, **Chapter 5** concludes and summarizes this study.

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