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Design of fluorescent blue light-emitting materials based on analyses of chemical structures and their effects

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ABSTRACT

Organic light-emitting diodes (OLEDs) have been successfully commercialized in the mobile phone market, and considerable effort is currently being devoted to applying OLEDs in other commercial applications such as televisions (TVs) and lighting. OLED displays are becoming the mainstream of next-generation displays to replace the liquid crystal display (LCD). Many technological advances are needed to apply OLEDs in TVs and lighting, but the development of fluorescent materials that emit short-wavelength blue light is especially essential for the future use of OLED displays. Usable fluorescent blue light-emitting materials must not only emit a deep blue light but also be thermally stable, highly efficient and have a long lifetime. There has been recent progress in research on blue fluorescent materials, and a resulting plethora of information. These results require a systematic organization to decipher the relationships between chemical structure and OLED device performance. We aim to address this need in the current review by systematically classifying blue fluorescent materials from a conceptually new "core-side" perspective, summarizing features that increase efficiency to improve OLED device performance, and providing a practical guideline for studying new blue fluorescent materials. This article summarizes the chemical structures and efficiency characteristics of selected 126 blue fluorescent materials. Systematic studies based on chemical structure and increased efficiency effects are necessary to develop highly efficient deep-blue fluorescent materials, and such studies on blue fluorescent materials are expected to become more prevalent in the fields of TV and lighting, as well as future flexible displays. Also, a systematic classification and understanding of the materials that have already been reported will aid the development and study of new light-emitting materials through quantitative and qualitative approaches.

Contents

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1. Introduction

Organic light-emitting diodes (OLEDs) have attracted considerable attention in both academic and industrial circles since the pioneering work of Tang et al. in 1987 [1]. OLEDs have recently been commercialized in the mobile phone market, and intensive attempts are being made to apply them in the television (TV) and lighting markets as well. Accordingly, OLEDs are becoming a mainstream of next-generation displays. The relative importance of OLEDs, compared to existing liquid crystal displays (LCDs), derive from their many advantages, such as flexibility, self-emission, full-color emission, low driving voltage, and fast response time [2–7].

While the development of OLED process technologies is needed for OLEDs to become dominant in markets such as TV and lighting, the development of a red, green and blue (RGB) light emitter with high electroluminescence (EL) efficiency, good thermal properties, and long device lifetime as well as pure color coordinates is also essential for making a high-performance device. Many conjugated organic molecules have been synthesized and reported to exhibit electroluminescence, with the wavelengths of the emitted light ranging from red to green and blue. A phosphorescent material that emits red light with $CIE_{x,y}$ coordinates (1931 Commission Internationale de L'Eclairage *x*, *y* coordinates) of (0.66, 0.34) and with a long lifetime of more than 900,000 h (half lifetime@ 1000 cd/m^2) at 24 cd/A has recently been developed. A phosphorescent emitter of green light with $CIE_{x,y}$ coordinates of (0.34, 0.62) and a lifetime of 400,000 h (half lifetime@ 1000 cd/m^2) at 78 cd/A, has also been achieved [8]. However, the best results reported for a blue fluorescence material are a relatively short lifetime of only 10,000 h at 9.0 cd/A and $CIE_{x,y}$ coordinates of (0.14, 0.12) [9,10]. The development of highly efficient long-lifetime emitter of blue light with high color purity has not yet been achieved. It is difficult to produce highly efficient emitters of blue light with long device lifetimes because, with wide band gaps, their electronic levels are unlikely to match the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the other OLED layers such as the hole-transporting layer (HTL) and the electron-transporting layer (ETL). These differences between the electronic levels result in an imbalance between the electron and hole carriers, a low EL efficiency and a short lifetime. To overcome the above issues, many attempts have focused on the development of fluorescent and phosphorescent materials that emit blue light. OLED devices based on phosphorescent emitters (PhOLED) have the advantage of a theoretical 100% internal quantum efficiency due to its harvesting of both singlet and triplet excitons. However, obtaining an efficient blue light-emitting phosphorescent material that also has a long lifetime remains a formidable challenge because of the following issue. Since OLED TVs require cool white color coordinates, the $CIE_{x,y}$ coordinates of the emitter of blue light must be 0.08 or below and the maximum EL wavelength should be no longer than 450 nm. In other words, the phosphorescence emission here requires the development of a deep blue light-emitting material in which the T_1 level participating in the emission is 2.75 eV or higher, and the S_1 level of the material is even higher in order to make the high T_1 level possible. Such a material is typically used as a dopant in PhOLED devices, and the dopant cannot be used by itself in the device. To achieve an OLED with high efficiency, the host and dopant materials should be used together since energy transfer from the host to dopant is needed. To make for a smooth energy transfer to the dopant, the band gap of the host material needs to be larger than that of the dopant. Moreover, the T_1 level of the host material must also be higher than that of the dopant. Considering that the S_1 level, which influences the band gap, is higher than the T_1 level, it is necessary to use a host material with a very wide band gap. Therefore, in PhOLED devices, charge balance, carrier injection and carrier transport become more difficult to attain for phosphorescent hosts and dopants with extremely wide energy band gaps.

On the contrary to the above, blue light-emitting fluorescent materials only use the S_1 level, without using the T_1 level as do phosphorescent materials, and hence do not require very high S_1 energy levels. Researchers have focused on blue fluorescent materials, and blue light has only been derived from fluorescence in actual products. In the development of fluorescent materials that emit blue light, in order to attain the generally regarded external quantum efficiency (EQE) value of 5%, another approach involving the use of triplet level for fluorescence emission has been recently investigated. The Adachi group developed a highly efficient fluorescent material using thermally activated delayed fluorescence (TADF). They achieved a very high efficiency of 19.5% but further development is still needed to improve the roll-off and longevity of the device. Common properties required for high-performance materials that emit blue light can be summarized as follows: (1) highly efficient electroluminescence; (2) blue light emission maximum wavelengths less than 450 nm; (3) a narrow full width at half maximum (FWHM), i.e., in the range of less than 60 nm, which produces low CIE y value of less than 0.15 for TVs and mobile phones; and (4) thermal stability and thin film properties for stable device operation and a longer device lifetime. Device lifetime will not be discussed further in this review since a specific life-time was not mainly provided in the papers.

To satisfy these conditions, blue light-emitting fluorescent compounds have been synthesized with particular combinations of core and side group structures. The core moiety is the basic central structure of the molecule and as such should display high fluorescence efficiency, while side groups substitute into the core and should help control the optical, thermal, and electrical properties of the compound. Such concepts for the core moiety and the side groups have not been systematically classified in a review, and neither have their performances. We therefore aim to review fluorescent materials that emit blue light from such a "core-side" perspective, and provide insightful information for new high-performance emitters of blue light. When designing a blue fluorescent material, a chemical component with high emission quantum efficiency is selected and placed at the center as the core of the molecule, and side groups are selected from diverse conditions to optimize the properties of the molecule to be synthesized. Performance of the final material is adjusted by