学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Flexible Light-Emitting Diode Application of Polyfluorene-based Conjugated Polymers
（ポリフルオレン含有高分子材料のフレキシブル発光ダイオード応用）

Polyfluorene-based (PF-based) polymers, either as semiconductors themselves or as structure directors, are emerging as a promising class of materials for understanding and controlling processes associated with light-emitting diodes (LEDs). The extensive interest in conjugated polymers originates not only from their potential technological advantages but also from their ability to naturally self-assemble into periodic ordered nanostructures further affecting the performance of LEDs. Incorporating these self-assemble materials into optoelectronic device fabrication processes or directly into the device will lead to new insights into structure-property relationships and perhaps, ultimately, increases device efficiency. Flexible and wearable displays, one of the most desirable requisites of electronic devices, have emerged with PF-based rod-coil polymers as a technology for their capability to revolutionize device and fashion industries in collaboration with state-of-the-art electronics. Nevertheless, challenges remain for the rod-coil polymers approaches, because rod-coil polymers LEDs suffer from much lower performance than those fabricated on the fully conjugated copolymers. To achieve a fundamental comprehension of improving flexible LED performance by using rod-coil polymers, a simple overview of the methods used and the expected benefits of PF-based rod-coil polymers in flexible LEDs is given in this dissertation.

Chapter 1 outlines the theoretical background regarding LED, the current state of research on PF-based conjugated polymers, background in the relationship between the chemical structures of PF-based polymers and the optical and mechanical properties of the polymer thin film, theoretical details of the analytical parameters utilized in this dissertation, and the objective of the dissertation.

Chapter 2 describes the fabrication of the novel transparent conductive electrodes (TCEs) with copper (Cu)/silver (Ag) nanofibers (NFs) with core/shell nanostructures via using a combination of electrospinning (ES) and chemical reduction. The PF-based flexible LED features a pair of TCEs comprising a thin percolation network of Cu/Ag nanofibers inlaid in the surface layer. The resulting flexible TCEs, exhibit a high transmittance (T) of 82 percent, and a low sheet resistance (Rs) of 102 Ω sq-1 (the best value is 7.85 Ω sq-1) which is bendable, and can emit light when applied to poly(9,9-di-n-octyl-2,7-fluorene) (PFO) LED. The results indicated flexibility and stability could improve by highly flexible conductive electrodes. However, the great flexibility of the device requires further investigation into an intrinsic and ductile emissive polymer. Exploring the synthesis of conjugated polymers with high flexibility and photoluminescence quantum yield (PLQY) is of great importance for their applications in

LED. These results highlight a potential as an effective TCE to aid in the future development of flexible LED.

Chapter 3 demonstrates poly[2,7-(9,9-di-n-hexylfluorene)]-b-poly(n-butyl acrylate) (PFN24-b-PBA90) rod-coil BCPs with perovskite quantum dots (CsPbBr3 QDs), namely CsPbBr3@PFN24-b-PBA90 through electrospinning for preparation of high luminance light down-converter LED. A coil block PBA is introduced into block copolymers (BCPs) through click reaction to enhance overall stretchability. Furthermore, the LED' s color can be tuned by varying the QD/polymer ratios through the double fluorescence combination by only a single-layer fiber mat. In summary, this study demonstrates a novel strategy for achieving color-tunable property without complicated multilayer structures in flexible LEDs.

Chapter 4 proposes a smart one-pot synthesis of the poly(9,9-di-n-hexyl-2,7-fluorene)-block-poly(ε -decanolactone) (PF18-b-PDLn) (n = 13, 24, and 36, repeating units) BCPs and highlights three major aspects: facile synthesis of PF-based BCPs, investigation of high PLQY in conjugated BCP system, and development of highly efficient stable touch-responsive LEDs. First, a series PF18-b-PDLn copolymers are synthesized using a one-pot synthetic route for producing high yield and low dispersity surpassing the complicated process and purification. Second, the coil-segment (PDL) induces high exciton binding energy (EBE) due to low-electric constant and thus yields a high PLQY. Third, optimized the ratio of coil block in the conjugated BCP, as an emissive layer of touch-responsive LEDs, it shows ultrahigh stability that no obvious decrease in performance under 300 times on/off switch and possessed an ultrahigh external quantum efficiency (EQE) as 6 times higher than PF homopolymer. In summary, this study demonstrates a novel one-pot synthesis of PF-based polymers to accelerate the design and fabrication of LED with ultrahigh efficiency and flexibility.

Chapter 5 summarizes the results. Chapter 2 demonstrates the TCEs based on Cu/Ag core/shell NFs have considerable flexibility, transparency, and conductivity and can be applied to the flexible PF-based LEDs, thus demonstrating their practical utility. In Chapter 3, the author exhibits PF-based BCPs to achieve high stretchability as well as favorable fluorescent properties for versatile applications that require outstanding optical properties. Chapter 4 describes the conjugated BCPs importance with robust stretchable wearable LED fabrication and the one-pot smart synthesis is anticipated to achieve impressive breakthroughs in forming diverse rod-coil BCPs and wearable electronic fabrication. These results obtained from the present investigation offers detailed insight and fundamental comprehension of improving flexible LED performance by using PF-based polymers and contributes to the future development of PF-based rod-coil BCPs for various potential applications in wearable LEDs.