学 位 論 文 審 査 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 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. However, challenges remain for the rod-coil polymers approaches, because LEDs based on rod-coil polymers suffer from much lower performance than those fabricated from the fully conjugated copolymers. To provide a fundamental comprehension of improving flexible LED performance using rod-coil polymers, the author studied benefits of PF-based rod-coil polymers in flexible LEDs in this dissertation.

In Chapter 1, the author summarized 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.

In Chapter 2, the author described 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. In this study, PF-based flexible LED featuring a pair of TCEs comprising a thin percolation network of Cu/Ag nanofibers inlaid in the surface layer was fabricated. The flexible TCEs were bendable and exhibited a high transmittance (T) of 82 percent and a low sheet resistance (Rs) of 102 Ω sq^{-1} (the best value was 7.85 Ω sq^{-1}), which were then successfully applied to poly(9,9-di-*n*-octyl-2,7-fluorene) (PFO) LED. The results indicated that flexibility and stability of LED device can be improved by highly flexible conductive electrodes, which highlighted a potential of TCE in the future development of flexible LED. However, on the other hand, the results in this chapter also indicated that further investigation into an intrinsic and ductile emissive polymer is required for achieving great flexibility of the device. Exploring the synthesis of conjugated polymers with high flexibility and photoluminescence quantum yield (PLQY) is of great importance for their applications in LED.

In Chapter 3, the author proposed a combination of poly[2,7-(9,9-di-*n*-hexylfluorene)]-*block*-poly(*n*-butyl acrylate) (PFN_{24}-*b*-PBA_{90}) rod-coil BCPs and perovskite quantum dots ($CsPbBr_3$ QDs), namely, $CsPbBr_3$@PFN_{24}-*b*-PBA_{90}, for the preparation of high luminance light down-converter LED through electrospinning. A coil block (i.e., PBA) was coupled with PFN to produce the block copolymers (BCPs) through click reaction in order 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 demonstrated a novel strategy for achieving color-tunable property without complicated multilayer structures in flexible LEDs.

In Chapter 4, the author proposed a smart one-pot synthesis of poly(9,9-di-*n*-hexyl-2,7-fluorene)-*block*-poly(ϵ-decanolactone) (PF_{18}-*b*-PDL_n) (n = 13, 24, and 36, repeating units) BCPs and highlighted 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 PF_{18}-*b*-PDL_n BCPs with low dispersity were synthesized in high yields using a newly developed one-pot synthetic route without complicated process and purification. Second, the author discovered that the coil-segment (PDL) induced high exciton binding energy (EBE) due to the low-dielectric constant, thus allowing a high PLQY. Third, when the BCP with the optimized coil block ratio was applied as an emissive layer of touch-responsive LEDs, it showed 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 demonstrated a novel one-pot synthesis of PF-based polymers to accelerate the design and fabrication of LED with ultrahigh efficiency and flexibility.

Throughout this dissertation, the author successfully provided detailed insight and fundamental comprehension of improving flexible LED performance by using PF-based polymers. Such knowledge will greatly contribute to the future development of PF-based rod-coil BCPs for various potential applications in wearable LEDs. In conclusion, this dissertation can be recognized to be awarded a Ph.D. degree in Chemical Sciences and Engineering.