Low-potential Electrosynthesis and Fluorescence Properties of Poly(9,9'-bifluorenylidene) in Boron Trifluoride Diethyl Etherate

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Electrosynthesized polyfluorene-based conjugated polymers (PFs) have been extensively researched since their discovery owing to their excellent fluorescence properties and one step fabrication process. However, most polyfluorenes have been obtained under high polymerization potentials over 1.2 V vs. Ag/AgCl, resulting in inevitable overoxidation and structural defects of the deposited polymer films, and thus imposing instability and long-term deterioration in optoelectronic properties. Herein, by the employment of a fused 9,9'-bifluorenylidene (BFY) as the initial monomer and boron trifluoride diethyl etherate (BFEE) as both the solvent and supporting electrolyte for the electropolymerization, we successfully achieved the low potential electrodeposition of a novel polyfluorene film for the first time at 0.9 V vs. Ag/AgCl. We demonstrate that the polymerization mechanism of BFY occurs dominantly at the 2,7 positions of the fluorene unit and forms an interconnected network of polyfluorene segments. The electropolymerization of BFY displays a sphere-type deposition process to produce a surface morphology of nanosphere clusters. We further explore the thermal degradation and electronic property evolution from monomer BFY to the deposited polymer, and find that the polymer exhibits a 100 nm-red shift in electronic absorption and significantly enhanced fluorescence intensity with a high quantum yield up to 0.78.

Keywords: conjugated polymers, electropolymerization, 9,9'-bifluorenylidene, boron trifluoride diethyl etherate, fluorescence

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