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Synthesis and Characterization of a New Polyfluorene Derivative with Well-Defined Conjugation Length

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We report on a new polyfluorene derivative which has nonlinear main backbone and well-defined conjugation length of three flourene units. The polymer was synthesized via Suzuki coupling reaction of 9,9`-dihexyl-2,7-fluorenediboronic acid and 2-bromofluorene connected by an alkyl ring which is perpendicular to the plane of the fluorene unit.

Keywords polyfluorene; Suzuki coupling; conjugation length

INTRODUCTION

Since the first fabrication of the polymer light emitting devices (PLEDs) by Cambridge group [1], extensive researches have been carried out in the field of PLEDs. Recently, PLEDs based on PPV type conjugated polymers have achieved a high level performance with regard to efficiency, brightness, and lifetime [2]. However, because no PPV derivatives can emit blue light, there are still demands of efficient blue emitting polymers for full color display.

Polyfluorene derivatives have received much attention as blue light emitting conjugate polymers due to their high photoluminescence quantum efficiencies and thermal stability [3]. Although polyfluorene derivatives have various intrinsic advantages, there are still problems to be solved for the blue device application. Polyfluorene derivatives have

a linear backbone that easily allows the fluorene units to be aggregated. It results in red-shifted emission bands in 500 nm region with a quite broad shape and a low quantum efficiency.

In order to overcome this problem, we synthesized a new fluorene monomer that is 2-bromofluorene dimmer connected by a spiro type alkyl ring which is perpendicular to the plane of the fluorene plane. This ring structure is expected to prevent formation of the chain aggregation. In addition, the monomer consists of two isomers, one has two 2-bromofluorene unit in the same direction and the other has that in opposite direction, which is expected to further suppress the polymer chain aggregation.

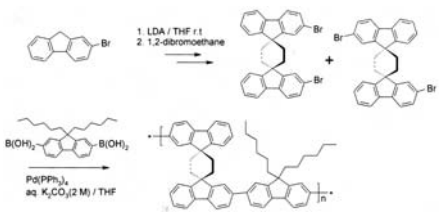

FIGURE 1. Synthetic scheme of a new polyfluorene derivative.

EXPERIMENTAL

All starting materials were obtained from Aldrich Chemical Co. and used without further purification except THF which was dried by refluxing over calcium hydride. 9,9'-dihexyl-2,7-fluorenediboronic acid was synthesized by the well-known method [3].

Dispiro[1,1',4,4'-bis(2-bromofluorene) cyclohexane] (DBFC) To a solution of 4.94 g (20 mmol) of 2-bromofluorene in THF at room temperature under nitrogen, 11 ml (22 mmol) of lithium

diisopropylamide (2 M in heptane/tetrahydrofuran/ethylbenzene) was added dropwise. The solution was stirred at room temperature for 1 h and 0.86 ml of 1,2-dibromoethane (10 mmol) was added dropwise to the mixture at room temperature. The solution was stirred for 1 h and all the procedures were repeated. The mixture was poured into water and extracted with ether. The organic extracts were dried over magnesium sulfate and evaporated. The residue was purified by column chromatography (silica gel, hexane) to provide 2.5 g of the product as a sticky liquid. ^{1}H-NMR (300 MHz, $CDCl_3$, ppm): δ 7.76 (d, 2H), 7.64 (d, 2H), 7.43 (d, 2H), 7.31 (m, 4H), 7.15 (s, 2H), 7.01 (d, 2H), 1.69 (s, 8H)

Polymerization (PDBFC3) 0.77 g (1.43 mmol) of BDFC, 0.60 g (1.43 mmol) of boronic acid and 0.04 g (2 mol %) of $(PPH_3)_4Pd(0)$ were dissolved in a mixture of 30 ml of THF and 15 ml of aqueous 2 M K_2CO_3. The solution was refluxed with vigorous stirring for 60 h under nitrogen. The reaction mixture was extracted with ether and the organic extracts were dried over magnesium sulfate and evaporated. The polymer dissolved in chloroform was precipitated by methanol and collected. 1H-NMR (300MHz, CDCl3, ppm) δ 7.98-7.58 (m, 12H), 7.42 – 7.26 (m, 6H), 7.08 (d, 2H), 2.10 (m, 4H), 1.82 (m, 8H), 1.1 (m, 16H), 0.8 (m, 14H)

RESULTS AND DISCUSSION

We synthesized BDFC via intramolecular cyclization of two fluorene units. From the mechanism, BDFC may consist of two isomers with the same ratio. We polymerized BDFC and 9,9'-dihexyl-2,7-fluorenediboronic acid as a comonomer via Suzuki coupling reaction [4]. From the polymer structure, not only intrinsic monomer composition, but also crankshaft shape linkage of the polymer could help to suppress the polymer chain aggregation. In PBDFC films, no crystalline phase was found under a polarizing optical microscope.

The photoluminescence spectra of PDBFC and poly(dihexyl

fluorene) as a reference are shown in Fig. 2. As expected, PDBFC showed emission bands in shorter wavelength region (λ_{max} = 420 nm) than the fully conjugate polymer and emission above 500 nm region was negligible.

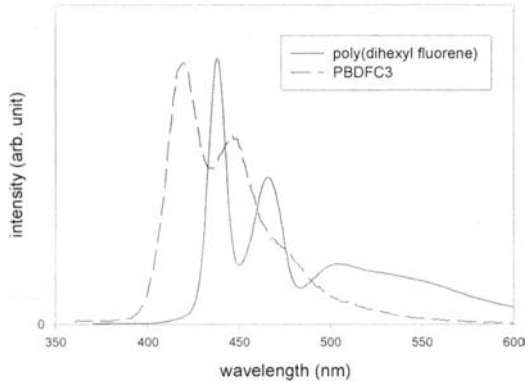

FIGURE 2. PL spectra of PDBFC3 and poly(dihexyl fluorene) films

In conclusion, we successfully synthesized a new blue emitting polymer which has nonlinear kinked backbone and well-defined conjugation length of three fluorene units. Due to its complex backbone structure, the polymer showed good solubility in common solvents such as chloroform and toluene and did not show aggregation peaks. The maximum emission of the polymer film occurs at 420 nm. The device characterization of the polymer is under investigation.

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