Synthesis of Fluorene-Based Polymer for Optoelectronic Application

Tok J.\textsuperscript{1} and Lai Y.H.\textsuperscript{2}

Department of Chemistry, Faculty of Science, National University of Singapore
10 Kent Ridge Road, Singapore 117546

ABSTRACT

Organic light-emitting diodes (OLEDs) are now considered to be the only flat-panel technology with the potential to pose a realistic challenge to liquid crystal displays (LCDs). Recently, significant effort has been devoted to synthesis of new light emitting polymers due to their potential applications as active materials for organic electroluminescent display. The conjugated polymers possess a number of very interesting optical and electronic properties and are one of the most promising materials for use in organic electroluminescent displays. An attempt to synthesize a fluorene-based polymer with cumulenic linkage at C9 position of fluorene was done for the study of its possible use in blue OLED.

INTRODUCTION

Fluorene-based polymers are blue light emitting and have drawn significant interest because they show highly efficient photoluminescence and electroluminescence, excellent thermal and oxidative stability, and good solubility in organic solvents. The rigidity of the fluorene core is beneficial for improving the quantum efficiency, and systematic tuning of the structure of the central linkage by introducing different substituents at the C9 position of fluorene provides new possibilities for probing the properties of the polymers. The synthesis of a cumulenic linkage at C9 to another fluorene was attempted (Scheme 1) due to its planarity, for which the improvement in quantum yield of photoluminescence and the ability to retain the morphological stability of the polymer can be studied. In addition, the extensive resonance delocalization of cumulenes is highly favourable.

Scheme 1. Synthetic route of template (1,4-bisbiphenylenebutatriene)

With 1,4-bisbiphenylenebutatriene as the core structure, an attempt to synthesize a fluorene-based polymer via Heck coupling (Scheme 2) was done.

\textsuperscript{1} Student
\textsuperscript{2} Associate Professor
Scheme 2. Synthetic route of fluorene-based π-conjugated polymer

EXPERIMENTAL

All experiments with air or moisture sensitive compounds were carried out under argon or nitrogen. Commercially available starting materials were used as received. NMR spectra were measured in CDCl$_3$ solution on 300 MHz Bruker ACF 300 with tetramethylsilane as an internal reference. EI mass spectrometry was done on a micromass 7034E mass spectrometer. All melting points were taken in a capillary melting point apparatus.

Synthesis of Fluorenone (1) and 2,7-Dibromo-fluoren-9-one (5)

Representative procedure: Fluorene (2.0g, 12.0 mmol) in a solution of sodium dichromate in acetic acid and water was refluxed for 0.5 hour. More acetic acid was added, and the solution was refluxed 2.5 additional hours. The reaction mixture was poured into water. The solid, which precipitated, was filtered. Recrystallization from ethanol gave the product. (1) Yield: 2.08 g (96 %), yellow crystals. $^1$H-NMR: $\delta$ 7.26 – 7.32 (m, 2H), 7.45 – 7.53 (m, 4H), 7.65 – 7.67 (d, 2H). MS (EI): m/z 180.1. Mp: 82.4 – 83.2°C (lit. 82 – 83°C). Anal. Calcd for C$_{13}$H$_{8}$O: C, 86.65; H, 4.47. Found: C, 86.48; H, 4.43. (5) Yield: 1.98 g (95 %), yellow solid. $^1$H-NMR: $\delta$ 7.37 – 7.40 (d, 2H), 7.61 – 7.64 (d, 2H), 7.77 (s, 2H). MS (EI): m/z 337.6. Mp: 200.7 – 201.6°C (lit. 201 - 202°C). Anal. Calcd for C$_{13}$H$_{6}$Br$_2$O: C, 46.20; H, 1.79; Br, 47.28.

Synthesis of 9-Ethynyl-9H-fluoren-9-one (2)

9-Fluorenone (3.32 g, 18.45 mmol) was dissolved in 50 ml of THF, the solution was cooled below 0°C using dry ice in acetone, and a solution of ethynylmagnesium bromide (2.6 g, 20 mmol) in 40 ml of THF was added dropwise. The reaction mixture was warmed to room temperature and then stirred for 2.5 h. Afterward the solution was poured onto 100 ml of saturated NH$_4$Cl solution and extracted with three 25 ml portions of diethyl ether, and the combined organic extracts were dried over sodium sulfate. After the solvent was removed under vacuum, the residue was purified by means of column chromatography (diethyl ether:petroleum ether = 20:80). The white compound can be obtained from the third fraction. Yield: 1.77 g (46.6 %), white crystals. $^1$H-NMR: $\delta$ 2.48 (s, 1H), 7.25 – 7.44 (m, 4H), 7.61 – 7.64 (d, 2H), 7.70 – 7.72 (d, 2H). MS (EI): m/z 206.0. Mp: 107.5 – 108.5°C (lit. 111 - 112°C). Anal. Calcd for C$_{15}$H$_{10}$O: C, 87.36; H, 4.89. Found: C, 87.44; H, 4.66.
Synthesis of Bis(9-hydroxy-9H-fluoren-9-ylylethynyl)-9H-fluoren-9-ol (3) and 2,7-Dibromo-9-(9-hydroxy-9H-fluoren-9-ylylethynyl)-9H-fluoren-9-ol (6)

Representative Procedure: 9-Ethynyl-9H-fluoren-9-ol (0.25 g, 1.22 mmol) was dissolved in 10 ml of THF, and the solution was cooled below 0°C using dry ice in acetone. tert-BuLi (1.5 ml, 1.7 M in pentane, 2.55 mmol) and, after 30 min, 0.25 g of 2,7-Dibromo-fluoren-9-one (1.39 mmol) as well as 1.25 ml of TMEDA (10 mmol) were added, and the reaction mixture was brought to room temperature. Refluxing the solution for 1 h completed the reaction. Quenching was carried out with 3 ml of water, and the solvent was evaporated. The residue was washed with hot petroleum ether and recrystallized from acetone/petroleum ether. Yield: 0.24 g (51.0 %), white crystals. 1H-NMR: δ 2.23 (s, 2H), 7.33 – 7.43 (m, 8H), 7.61 – 7.64 (d, 4H), 7.70 – 7.74 (d, 4H). MS (EI): m/z 385.9. Mp: 227.5 – 228.7°C (lit. 228°C).

Synthesis of 1,4-Bisbiphenylenebutatriene (4)

Potassium iodide (0.14 g, 1.2 mmol) and Bis(9-hydroxyfluorenyl-9-yl)ethyne (0.15 g, 0.4 mmol) were added to 50 ml of ethanol and the solution was heated to reflux. 1 ml of concentrated sulphuric acid was then added and the mixture was refluxed for 4 hours. The mixture was concentrated in vacuo, poured into water and extracted using dichloromethane. The organic layer was washed with water until neutral to litmus, and the solvent was evaporated. Crude yield: 0.06 g (45 %), yellow crystals. 1H-NMR: δ 6.80 – 6.85 (d, 2H), 7.27 – 7.68 (m, 10H), 8.01 – 8.03 (d, 2H), 10.83 – 10.86 (d, 2H).

RESULTS AND DISCUSSION

Compound 4 was first synthesized to study the feasibility of using it as a core structure for the synthesis of 10. Unlike alkyl-substituted cumulenes, which are usually colourless, 4 has...
intense absorptions in the visible region of the spectrum, thus is yellow. This indicates that the
electrons in fluorene are conjugated with the cumulene backbone, and is further enhanced by the
planarity. However, the yield was too low for recrystallization due to the multi-step synthesis,
whereby the yield of each step is approximately less than 50%. Therefore, pure 4 was not
obtained and could not be fully characterized. In the synthesis of 6, the high reactivity of butyl
lithium posed as a problem. As it is able to react with the carbonyl group, alcoholic group and
bromide on 5, the stoichiometry must be exactly two times of the number of moles of 5, such
that it will not react with the bromide by the selection of the reactivity. However, it is difficult
to use an exact amount of butyl lithium as it is a suspension in pentane, which was not totally
homogenous. As a result, excess of butyl lithium could have cleaved off bromide, thus the
product could not be fully characterized as the expected 6. It is also possible that protons
cleaved from acetylenic or alcoholic group could have reacted with bromide. Due to the failure
to obtain 6, 7 and 11 could not be synthesized subsequently. Even so, the synthesis of the
substituents that was intended for Heck coupling with 7 was still carried out as experiments
were done concurrently. However, 10 was not done due to its unstable nature, which could only
be done if 7 was obtained. Hence, the synthesis of the fluorene-based polymer failed.

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