

Electrochemical Synthesis of Polythiophene Derivative Bearing Periodic C₆₀ Pendants and Its Fundamental Electronic Properties

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INTRODUCTION

Fullerene C₆₀ is known to have a unique electronic structure among organic materials, which makes it useful as an electron acceptor for many organic electronic devices. Since the electron transfer between C₆₀ and π -conjugated polymers are very fast, their composites are expected to become high-efficiency organic solar cells. Recently, poly-*p*-phenylenvinylene derivative-C₆₀ derivative composite has been developed to show good performance as an organic solar cell with a 2.5% power conversion efficiency.[1] Further increase of the efficiency could be achieved if the C₆₀ derivative would be dispersed in the film without aggregation.

The idea is attained by means of molecular design of the polymer.[2,3] We prepared terthiophene derivative **1** bearing C₆₀ on the thiophen ring in the middle as shown in Figure 1. Monomer **1** can be electrochemically polymerized to yield polymer **2**, bearing a C₆₀ pendant every three units of thiophene ring in the backbone. We report the detail syntheses of the films of **2** as well as their fundamental electronic properties such as electronic absorption spectra and HOMO and LUMO energy levels.

EXPERIMENTAL

An *o*-dichlorobenzene solution of **1** (0.5 mM) with tetra-*n*-butylammonium tetrafluoroborate (0.1 M) was used for electrochemical experiments by using ALS600 potentiostat with reference and counter electrodes of Ag/Ag⁺ and Pt, respectively. The cyclic voltammetry (CV) curve was recorded using a working electrode of glassy carbon. The electrochemical synthesis of **2** was conducted on indium-tin-oxide (ITO) working electrode (~1 cm²). The film thickness, which was measured by Dektak 3030, was controlled by monitoring the consumed charge by chronocoulometry technique. The absorption spectra were recorded by using Hitachi U3500 spectrophotometer. The HOMO levels were determined by using Rikei Keiki AC-1 photoelectron spectrometer.

RESULTS AND DISCUSSION

Figure 2 shows a repetitive CV curve for **1**. It shows clear C₆₀ reduction/oxidation peaks in the negative potential area. At a positive potential of 0.75 V, **1** is electrochemically polymerized to yield **2** on the working electrode surface. The proportional increase of C₆₀ reduction/oxidation peak current was clearly observed as the number of CV cycle increased, which indicated that the electrochemical polymerization proceeded quantitatively.

The film was grown on ITO next. Typically, 1.0 V was applied on ITO for several minutes to 1h, and we could obtain a good film up to ~1 μ m thickness on ITO.

The syntheses of **2** were also successful on the surface of PEDOT-PSS and Baytron-P (H.C.Starck) coated ITO as well as of electrochemically polymerized film of EDOT on ITO.

The AC-1 measurements determined two independent values of 5.1 and 5.5 eV for **1**, which are respectively assigned to the HOMO level of C₆₀ pendant and terthiophene derivative. By contrast, the HOMO level of **2** was determined to 5.1 eV. As the polymerization proceeded, the HOMO level of ter-thiophene derivative became unstable and overlapped with that of C₆₀.

The HOMO-LUMO gaps estimated by UV absorption spectra were 2.8 and 1.8 eV for terthiophene and C₆₀ units for **1**. It was not clear for **2** from its dispersive absorption spectrum without characteristic structures. However, we can reasonably assume the gap less than that of **1** of 2.8 eV. The schematic band diagrams for **1** and **2** are thus drawn, which is useful for the design of organic solar cell device based on **2**. We preliminarily observed photocurrent from **2** using wet cells. Further experiments on wet cells as well as solar cells are ongoing.

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REFERENCES

- [1] S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, J. C. Hummelen, *Appl. Phys. Lett.* **2001**, 78, 841.
- [2] News & Views, *Nature Materials* **2003**, 2, 360.
- [3] B. Joussetme, P. Blanchard, R. Levillain, R. de Bettignies, J. Roncali, *Macromolecules* **2003**, 36, 3020.

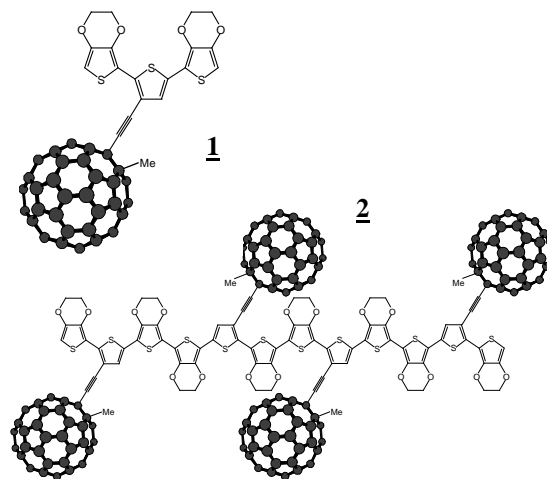


Figure 1 Structures of monomer **1** and polymer **2**.

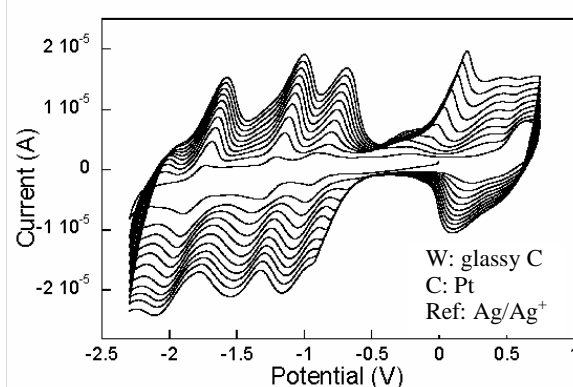


Figure 2 CV monitoring of the synthesis of **2**.