

Synthesis and Electrolytic Polymerization of the Ethylenedioxy-Substituted Terthiophene–Fullerene Dyad

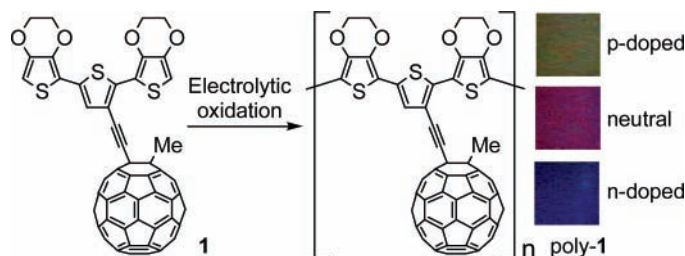
Tetsuya Yamazaki,[†] Yasujiro Murata,[†] Koichi Komatsu,^{*,†} Kazuaki Furukawa,[‡] Masao Morita,[‡] Norihiko Maruyama,[§] Takeshi Yamao,[§] and Shizuo Fujita[§]

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan, NTT Basic Research Laboratories, NTT Corporation, Atsugi, Kanagawa 243-0198, Japan, and International Innovation Center, Kyoto University, Kyoto 605-8501, Japan

komatsu@scl.kyoto-u.ac.jp

Received September 21, 2004

ABSTRACT



Two derivatives of ethylenedioxy-substituted terthiophene–fullerene dyads were newly synthesized as the precursors for polythiophene having fullerene side chains. By electrolytic oxidation of dyad 1, the charm-bracelet type polythiophene, poly-1, was obtained as a purple film, which showed electrochemical activity, electrochromism, and photoelectronic response.

Preparation of composite materials made of fullerene C₆₀ as a typical electron acceptor and π -donating polymers has been attracting great interest from the viewpoint of fundamental chemistry^{1,2} as well as practical applications.³ For the purpose of application, fixation of the C₆₀ cages on the π -conjugated polymer by covalent bonds is superior to simple mixing of the polymer and C₆₀ because phase separation and/or aggregation of each component can be prevented.⁴ Polythiophenes (PTs) are typical π -donating polymers, and

several PTs bearing fullerene subunits have been synthesized from bithiophene⁵ or from terthiophene⁶ monomers. Recently, oligothiophenes having C₆₀ as end group(s) have been prepared and their use for a photovoltaic device was reported.⁷ Compared with these PTs with absorption at 400–480 nm,^{5,6} poly(3,4-ethylenedioxythiophene) (PEDOT) absorbs at longer wavelength such as 610 nm⁸ with more

[†] Institute for Chemical Research, Kyoto University.

[‡] NTT Basic Research Laboratories, NTT Corp.

[§] International Innovation Center, Kyoto University.

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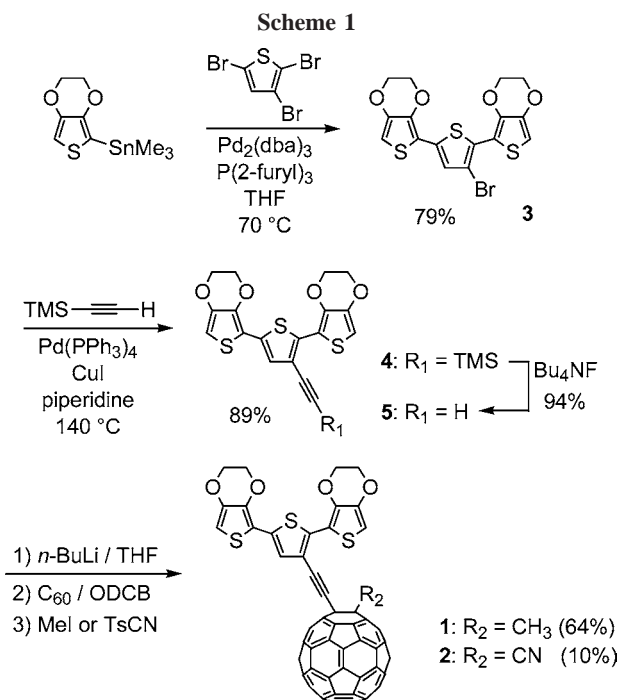
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efficient harvesting photons. Recently, EDOT has attracted more attention as the building block for π -conjugated systems, which have unique properties such as enhanced π -donor ability,⁹ low band gap,¹⁰ and electrochromic behavior.¹¹ Since the α - β and β - β mislinkage is forbidden by blocking the β positions of the thiophene units,⁸ the polymer PEDOT also has the advantage of having a regiochemically defined structure. Here, we report the synthesis and electropolymerization of two ethylenedioxy-substituted terthiophene derivatives having a C_{60} cage connected by a triple bond, as the donor-acceptor hybrid polymer. A nucleophilic addition of lithium acetylide was used to modify C_{60} , which can further introduce the second group of choice onto the C_{60} cage by electrophilic reaction.¹²

The synthetic route for dyads **1** and **2** is shown in Scheme 1. Thus, ethynylterthiophene **5** was prepared by Stille

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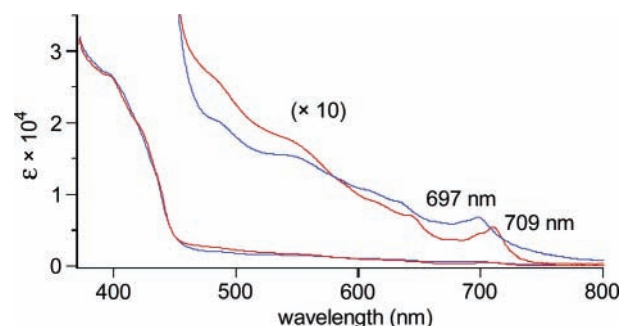


Figure 1. UV-vis spectra of **1** (red line) and **2** (blue line) in CS_2 .

coupling and Sonogashira coupling in good yields from 2-(trimethylstannyl)-3,4-ethylenedioxythiophene^{11c} followed by desilylation. The lithium acetylide generated from ethynylterthiophene **5** was added to a solution of C_{60} in *o*-dichlorobenzene (ODCB) at room temperature. The resulting ethynylated fullereryl anion was treated with either methyl iodide or tosyl cyanide to give fullerene-terthiophene dyad **1** or **2**, respectively. The structure of **1** was determined as the 1,2-adduct of C_{60} with C_s symmetry by ^1H and ^{13}C NMR, MS, IR, and UV-vis spectroscopy: the ^{13}C NMR spectrum exhibited 42 signals in the sp^2 carbon region and the UV-vis spectrum indicated an absorption maximum at 709 nm (Figure 1). The UV-vis spectrum of **2** was quite similar to that of **1** (Figure 1), indicating that there is no interaction between the donor and acceptor moieties in the ground state. Unfortunately, the extremely low solubility of **2** did not allow its further characterization.

The redox behavior of **1** was investigated by cyclic voltammetry (CV) in ODCB (glassy carbon (GC), 0.1 M Bu_4NBF_4 , scan rate 0.1 V s^{-1}). As shown in Figure 2a, an irreversible anodic peak and three reversible cathodic waves were observed at the first scan, corresponding to oxidation of the terthiophene unit and reduction of the C_{60} moiety ($E_{\text{pa}} +0.49$ and $E_{1/2} -1.14, -1.53,$ and $-2.08 \text{ V vs Fc/Fc}^+$). Compared with unsubstituted terthiophene-fullerene dyads ($E_{\text{pa}} +0.82$),⁶ the oxidation potential was found to be significantly lower,^{11a,13} indicating an enhanced donor ability of the terthiophenic system and high planarity characteristic of oligo-EDOTs.¹⁴

Application of repetitive scans between $+0.7$ and -2.5 V resulted in the increase in intensity of three cathodic waves and an anodic wave (Figure 2a). This clearly indicates that an electroactive polymer film is formed and deposited on the working electrode by the electropolymerization of the terthiophene unit retaining C_{60} subunits. The small redox peaks around $E_{\text{pa}} -0.3$ and $E_{\text{pc}} -0.9 \text{ V}$ should be ascribed to a redox process involving transfer of the electrolyte.¹⁵

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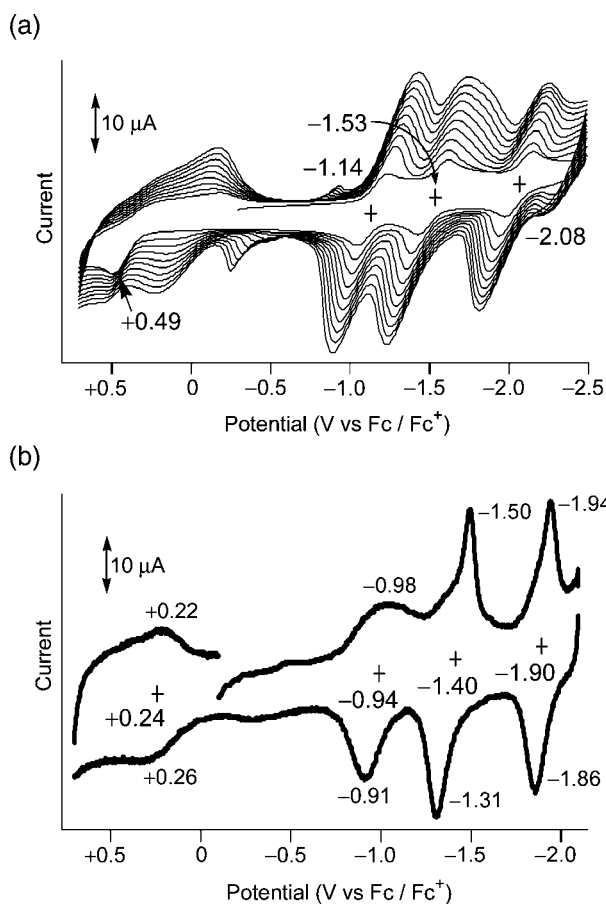


Figure 2. Cyclic voltammograms (0.1 M Bu₄NBF₄, scan rate 0.1 V s⁻¹) of (a) dyad **1** in ODCB and (b) poly-**1** on a glassy carbon electrode in MeCN.

The CV in MeCN (0.1 M Bu₄NBF₄) of the poly-**1** film electrodeposited on the GC working electrode exhibited a voltammogram with one anodic wave and three cathodic waves at $E_{1/2}$ +0.24 and $E_{1/2}$ -0.94, -1.40, and -1.90 V, respectively (Figure 2b). This oxidation wave was also shifted to less positive potential than that of a polymer film obtained by electropolymerization of the unsubstituted terthiophene-C₆₀ dyad (E_{pa} +0.63).⁶ The first reduction peak of the C₆₀ cage at -0.98 V is broad, which could be due to reorganization of the film structure taking place during the formation of the monoanionic species.¹⁶

A clear electrochromism was observed when CV was conducted on the poly-**1** film deposited on an indium-tin oxide (ITO) electrode. The absorption spectra of poly-**1** on the ITO electrode recorded at different potentials are shown in Figure 3. The neutral polymer, which was purple in color, showed a broad absorption band corresponding to the π - π^* transition of PEDOTs at 580–600 nm at a potential of -0.6 V (Figure 3, red line). When an oxidation potential was applied to this polymer at +0.4 V, the 600-nm band disap-

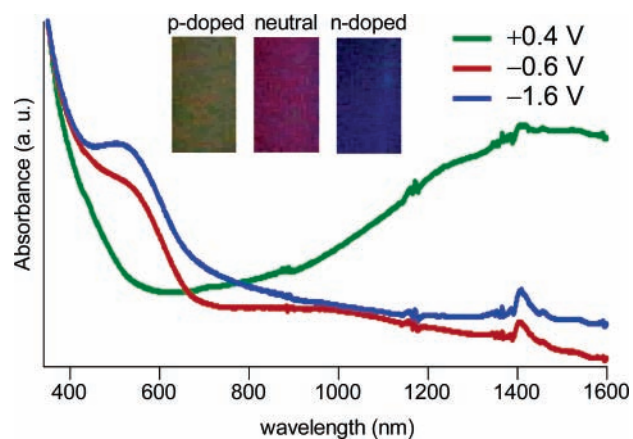


Figure 3. Electronic absorption spectra of poly-**1** film on an ITO electrode at various applied potentials in MeCN (0.1 M Bu₄NBF₄, V vs Fc/Fc⁺). The peak at around 1400 nm is attributed to an absorption of the ITO electrode.

peared with the concomitant development of a new broad peak at around 1500 nm corresponding to the typically observed absorption of the cationic or p-doped state of PEDOT polymers,¹¹ which resulted in color change of the poly-**1** film to green (Figure 3, green line). On the other hand, at -1.6 V corresponding to the second reduction of the C₆₀ moiety (Figure 3, blue line), the absorption band in the visible region centering at 550 nm grew up with the color change of the film to bluish purple. This color change is characteristic of that observed upon reduction of C₆₀ derivatives as has been reported for a C₆₀-charm-bracelet-type polythiophene.^{5b}

Although the color change was reversible in the potential range between +0.4 and -1.2 V, it became irreversible beyond the stage of the second reduction of C₆₀ (-1.6 V), and the bluish purple film was peeled off from the glass electrode. This is attributed to disintegration of the ITO substrate itself because a clear voltammogram of the poly-**1** film with three reduction waves has been observed at the potential range of +0.7 to -2.1 V, when a GC electrode was employed instead of an ITO electrode (Figure 2b).

An atomic force microscopy (AFM) was conducted for the surface of the poly-**1** film. Particles of 200–300 nm in diameter were observed (Figure 4a) together with up-and-downs with about 20–30 nm height in the cutout view (Figure 4b). These particles are considered to be formed by anionic electrolytes (BF₄⁻) acting as the cores during the polymer growth in the oxidative polymerization.¹⁷

Photoelectrochemical measurements were performed in a 0.1 M Na₂SO₄ aqueous solution containing 5 mM methyl viologen by using the poly-**1**-deposited ITO electrode as a working electrode and a platinum counter electrode. Robust and stable poly-**1** films up to 300 nm in thickness were successfully fabricated on ITO by electrochemical polymerization as described above. Figure 5 shows a typical

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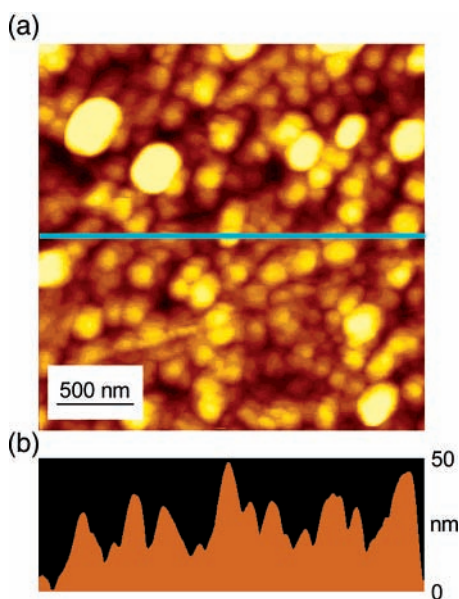


Figure 4. AFM images of (a) the surface and (b) the cutout view (along blue-line in (a)) of the poly-1 film deposited on an ITO electrode.

photocurrent response under irradiation with a halogen lamp (50 mW/cm^2) at -100 mV bias against an Ag/Ag^+ reference electrode. As shown, a significant cathodic photocurrent was observed compared to those of similar photovoltaic cells.^{5d,18} This can be attributed to the efficient trapping of electrons from the excited states of PEDOT by C_{60} moieties as a strong acceptor, which leads to the effective generation of holes that readily transport along the PEDOT backbone. Thus, when a UV light was used, the wavelength of which is more advantageous for PEDOT excitation, a several times stronger photocurrent was observed. These are still preliminary results,

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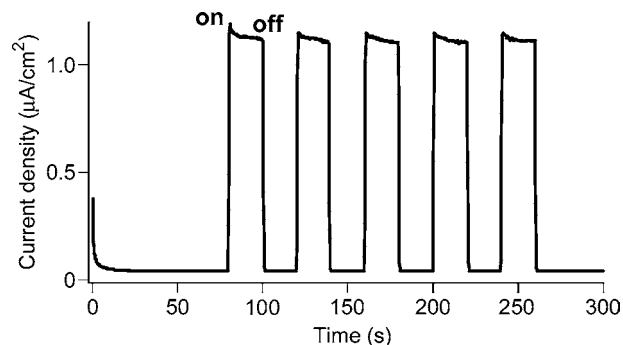


Figure 5. Photocurrent response of poly-1/ITO irradiated with a halogen lamp at -100 mV of bias vs Ag/Ag^+ in $0.1 \text{ M Na}_2\text{SO}_4$ aqueous solution containing 5 mM methyl viologen.

and the efficiency would be further increased by optimizing the device design and measurement conditions.

In summary, we synthesized novel ethylenedioxy-substituted terthiophene–fullerene dyads **1** and **2** with a triple bond connector. The electrochemical oxidation of dyad **1** by repetitive CV scans gave a corresponding polymer on the electrode. Poly-**1** was electroactive on both p- and n-dope states and exhibited electrochromism. A preliminary study revealed a photoelectrochemical response, which implies the potential of this type of compounds for the realization of organic solar cells.

Acknowledgment. This work was supported by the Integrative Industry–Academia Partnership (IIAP) including Nippon Telegraph and Telephone Corp., Pioneer Corp., Hitachi, Ltd., Mitsubishi Chemical Corp., Rohm Co., Ltd., and Kyoto University.

Supporting Information Available: Detailed descriptions of experimental procedures for the synthesis of compounds **1–5** and NMR data for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL048081H