

Photoelectrochemical properties of gold electrodes modified with [60]fullerene-linked oligothiophenes

Yoshio Aso, Daigo Hirayama, Kazuo Takimiya, Tetsuo Otsubo, Taku Hasobe, Hiroko Yamada, Hiroshi Imahori, Shunichi Fukuzumi, and Yoshiteru Sakata
 Graduate School of Engineering, Hiroshima University
 Graduate School of Engineering, Osaka University
 CREST, Japan Science and Technology Corporation
 The Institute of Scientific and Industrial Research, Osaka University
 Kagamiyama, Higashi-Hiroshima 739-8527, Japan
 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan
 Mihoga-oka, Ibaraki, Osaka 567-0047, Japan

Photovoltaic cells based on metal electrodes modified with self-assembled monolayers (SAM) have aroused current attention in terms of mimic of photosynthetic electron transfer. Sophisticated donor-acceptor linked photoactive molecules have been actively developed and utilized for the cells generating large photocurrent. On the other hand, little attention has been paid to the structures of the SAMs themselves, which notably may affect the performance of the devices. Oligothiophenes are rigid rod-like π -conjugated molecules, which are ideal materials to be assembled on gold electrodes for efficient photocurrent generation when a thiol is attached as a terminal group. Here we report photocurrent generation from gold electrodes modified with [60]fullerene-linked quater- and octi-thiophenes **1** and **2** bearing a one-armed thiol anchor and with **3** and **4** bearing a tripodal rigid anchor, which is a rigid tetraphenylmethane core with three mercaptomethyl arms. The strategy to employ tripodal rigid anchor allows such molecules to be well-organized on the electrodes, thus leading to remarkable enhancement of the photocurrent generation as compared to the one-armed systems.

The cyclic voltammograms of SAMs **3**/Au and **4**/Au exhibited two well-resolved reversible cathodic waves at -0.66 V and -0.97 V corresponding to the successive one-electron reductions of the C_{60} moiety (Figure 1). The observation of these well-defined redox waves indicates that the molecules are strongly adsorbed on the surface due to three-point connection. In contrast to the three-point connected systems, the voltammograms of SAMs of **1** and **2** with one-point connection show poorly reversible waves (Figure 1), suggesting that the molecules are sparsely attached to the surface and tend to be detached during the reduction sweep. The Au/**3**/MV²⁺/Pt cell showed a cathodic photoelectrochemical response (Figure 2), and the cathodic photocurrent increases with increasing the negative bias of the gold electrode (Figure 3). The photocurrent density is much larger by a factor of about 190 than that observed for the Au/**1**/MV²⁺/Pt cell. The Au/**4**/MV²⁺/Pt cell also revealed a large photoelectrochemical response, and its photocurrent density is about 6 times as large as that observed for the Au/**2**/MV²⁺/Pt cell. The enhancement ratios of photocurrent much exceed the increased ratios of the surface coverages. The self-reliant standing of **3** and **4** on the gold surface probably suppress quenching of the excited states of the oligothiophene chromophore by intermolecular interactions and by the gold electrode, resulting in an increment in the photocurrent. The quantum yield of **4**/Au is approximately twice that of

3/Au, indicating that the long oligothiophene chain can facilitate the generation and charge transport of photocurrent.

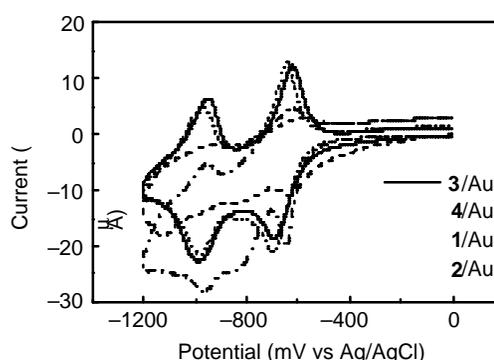
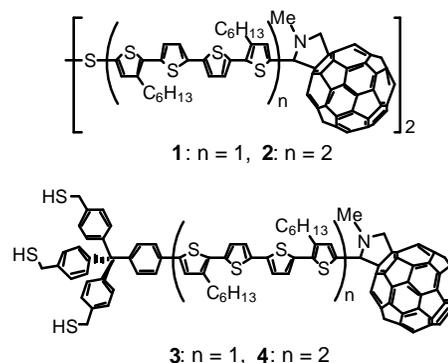


Figure 1. Cyclic voltammograms of the SAMs in CH_2Cl_2 containing $0.1 \text{ mol dm}^{-3} \text{ Bu}_4\text{NPF}_6$ as an electrolyte at scan rate of 100 mV s^{-1} .

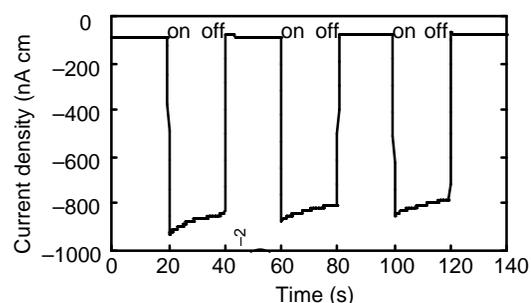


Figure 2. Photocurrent response of **3**/Au irradiated with 400 nm light (0.65 mW cm^{-2}) at -100 mV of bias vs Ag/AgCl.

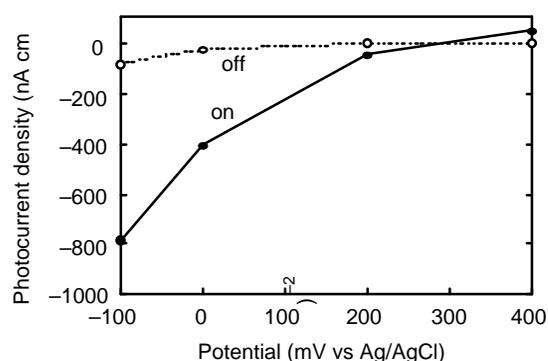


Figure 3. Photocurrent vs applied potential curves for **3**/Au when the 400 nm light (0.65 mW cm^{-2}) is on (solid line) and off (dotted line).

