Preparation and Photoelectrochemical Properties of Gold Electrodes Modified with [60]Fullerene-Linked Oligothiophenes

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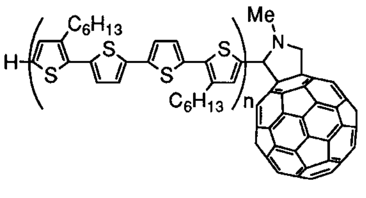
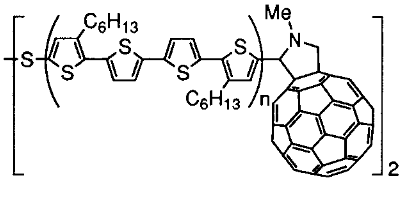
[60]Fullerene-linked quater- and octithiophenes with a disulfide anchoring group have been synthesized, and a photovoltaic cell with a gold electrode modified with the octithiophene derivative showed a large photocurrent under illumination of visible light.

Oligomeric materials with conjugated π-electronic systems have attracted considerable interest during recent years because they are potentially important candidates for a broad range of applications in the rapidly growing field of molecular electronics such as molecular wires and switches.[1] Recently, we have reported a series of [60]fullerene-linked oligothiophenes **1** and found that efficient photoinduced intramolecular energy transfer in toluene[2] and electron transfer in more polar solvents take place from the oligothiophene to the C_{60}.[3] The highly efficient electron transfer in **1** has prompted us to investigate their application to a photovoltaic cell based on a self-assembled monolayer (SAM). SAMs have been very widely investigated as ordered molecular layers at the molecular level, and, in particular, photoelectrochemical properties of the SAMs of donor-acceptor linked photoactive molecules on a metal electrode have aroused considerable attention not only as artificial photosynthetic mimics but also as potential candidates for molecule-based optoelectronic devices.[4] We here would like to report the synthesis of [60]fullerene-linked oligothiophenes **2** and **3** with a disulfide anchoring group and photoelectrochemical properties of their SAMs on a gold electrode.[5]

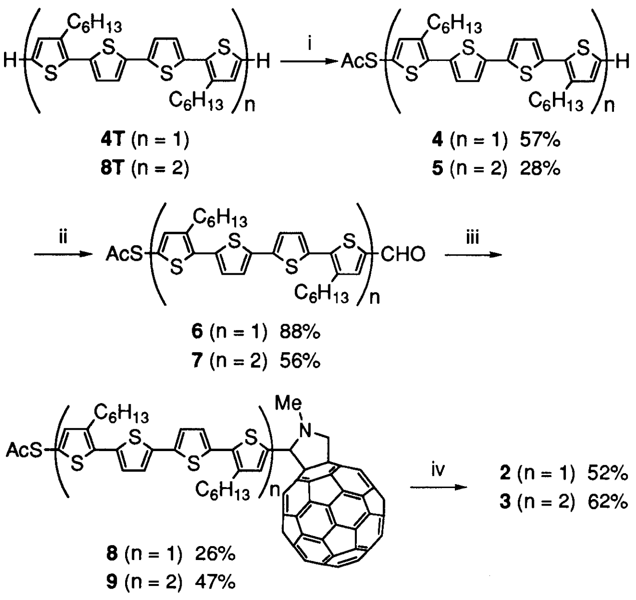


1 (n = 1–3)



2 (n = 1)
3 (n = 2)

The fullerene-linked oligothiophene disulfides were synthesized according to Scheme 1. Dihexylquaterthiophene **4T** and tetrahexyloctithiophene **8T**[2] were lithiated with butyllithium and treated successively with elemental sulfur and acetyl chloride to give acetylthioquaterthiophene **4** (57% yield) and acetylthiooctithiophene **5** (28% yield), respectively. These acetylthio derivatives were converted to the formyl derivatives **6** (88%) and **7** (65%) by the Vilsmeier reaction, and then treated with C_{60} and *N*-methylglycine in toluene[6] to give the corresponding fullerene-linked oligothiophenes **8** (26%) and **9** (47%). Mild alkaline hydrolysis of **8** and **9** afforded the desired fullerene-linked oligothiophene disulfides **2** (52%) and **3** (62%).[7]



Scheme 1. Reagents and conditions: i) 1) *n*-BuLi, THF, –30 °C, 1 h, 2) S, –50 °C then rt, 3 h, 3) AcCl, –50 °C then rt, overnight; ii) DMF–$POCl_3$, dichloroethane, rt, 12 h; iii) C_{60}, *N*-methylglycine, toluene, reflux, 19 h; iv) K_2CO_3, MeOH–toluene, rt, 3 h.

The electronic absorption spectra of **2** and **3** in chlorobenzene showed two strong absorption bands in the ultraviolet/visible region; **2**: 330 nm (log ε: 4.97) and 397 nm (4.88), **3**: 331 nm (5.01) and 451 nm (5.13). The short wavelength absorption is characteristic of the *N*-methylpyrrolidine derivative of C_{60}.[2,6] The long wavelength absorption is assigned to the oligothiophene moiety and red-shifted with extension of the chain length. In the visible region, the absorption due to the oligothiophene is much stronger relative to the C_{60}, showing that the oligothiophene is a major absorber of visible photons.

Monolayers of **2** and **3** were prepared by immersion of the Au(111)/mica substrate in their saturated $CHCl_3$ solutions ($< 1 \times 10^{-5}$ mol dm^{-3}) at 25 °C for 24 h. After soaking, the samples were rinsed in $CHCl_3$ and EtOH and then dried with a stream of nitrogen. In order to estimate the surface coverage, cyclic voltammetric experiments using the modified Au electrodes were carried out in CH_2Cl_2 containing 0.1 mol dm^{-3} Bu_4NPF_6 as an electrolyte at the scan rate of 100 mV s^{-1}. The voltammograms of **2** and **3** on Au (hereafter, **2**/Au and **3**/Au) showed a peak at –0.73 V (vs Ag/AgCl), which corresponded to the first reduction of the C_{60} moiety. The adsorbed amount of -S-**8T**-C_{60} on Au is calculated from the charge of the reduction peak to be 9.3×10^{-11} mol cm^{-2}, which corresponds to the occupied area of 180 $Å^2$ $molecule^{-1}$. In contrast, the corresponding reduction peak of **2**/Au is considerably small compared with that of **3**/Au, and the calculated surface coverage of -S-**4T**-C_{60} is ca. 2.2×10^{-11} mol cm^{-2} (750 $Å^2$ $molecule^{-1}$), indicating a loosely packed structure of the SAM. Assuming that the molecules of -S-**8T**-C_{60} are packed perpendicularly to the gold surface, the occupied area of one molecule is estimated on the basis of an MM2 optimized geometry as 160 $Å^2$, which is consistent with the experimental value. On the other hand, the large occupied area of -S-**4T**-C_{60} suggests a flat-lying structure of the molecules onto the gold surface. It is thus speculated that increasing attractive intermolecular interactions between the alkyl side chains as well as the long oligothiophenes may be responsible for the formation of the densely packed structure in **3**/Au.[8]

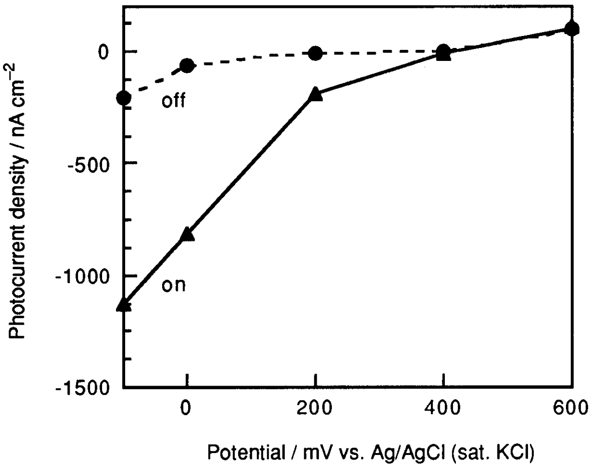


Figure 1. Photocurrent vs. applied potential curves for the **3** on Au electrode when the 440 nm light is on (▲) and off (●).

Photoelectrochemical measurements were performed in an argon-saturated 0.1 mol dm^{-3} Na_2SO_4 solution containing 5×10^{-3} mol dm^{-3} methyl viologen (MV^{2+}) as an electron carrier using the modified Au electrode as a working electrode, a platinum counter electrode, and an Ag/AgCl reference electrode. The Au/**3**/MV^{2+}/Pt cell showed a photoelectrochemical response under illumination of 440 nm light (22 mW cm^{-2}) as shown in Figure 1. An increase in the cathodic photocurrent with an increase of the negative bias to the gold electrode demonstrates that a photocurrent flows from the gold electrode to the counter electrode through the electrolyte. In contrast, no apparent photocurrent was detected for **2**/Au in accordance with its loosely packed structure.

The photocurrent generation of **3**/Au may be explained as follows. Photoinduced charge-transfer first occurs from the photo-excited oligothiophene to the C_{60} moiety. The resulting $C_{60}^{\bullet-}$ transfers an electron to diffusing methyl viologen molecules, which can carry the charge to the counter electrode. On the other hand, the oligothiophene$^{\bullet+}$ gains an electron from the gold cathode, resulting in the recovery of the initial state, and thus a net vectorial electron flow relay functions. Although further studies are necessary to clarify the exact mechanism and the quantum efficiency of the photocurrent generation system, the sufficiently large photocurrent observed for **3**/Au despite its relatively simple dyad system[9] indicates that long oligothiophenes are promising charge-carrying molecular wires as well as donor building blocks for molecular photoelectric systems.

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7 All new compounds were characterized by spectroscopic measurements and elemental analyses. Selected data for **2**: a brown powder from CS_2/hexane; mp 175 °C (decomp); ^1H NMR (400 MHz, $CDCl_3$:CS_2 = 1:1) δ 0.81–0.88 (m, 12H), 1.21–1.39 (m, 24H), 1.57–1.66 (m, 8H), 2.72–2.80 (m, 8H), 2.94 (s, 6H), 4.23 (d, J = 9.7 Hz, 2H), 4.96 (d, J = 9.7 Hz, 2H), 5.16 (s, 2H), 7.00 (d, J = 3.9 Hz, 2H), 7. 01 (s, 2H), 7.01 (d, J = 3.9 Hz, 2H), 7.08 (d, J = 3.9 Hz, 4H), 7.22 (s, 2H); UV-Vis (chlorobenzene) λ_{max}/nm (log ε) 330 (4.97), 397 (4.88), 705 (2.85). **3**: a reddish brown powder from CS_2/hexane; mp 138 °C (decomp); ^1H NMR (400 MHz, $CDCl_3$:CS_2 = 1:1) δ 0.84–0.90 (m, 24H), 1.22–1.41 (m, 48H), 1.57–1.70 (m, 16H), 2.72–2.80 (m, 16H), 2.94 (s, 6H), 4.23 (d, J = 9.7 Hz, 2H), 4.95 (d, J = 9.7 Hz, 2H), 5.15 (s, 2H), 6.95 (s, 4H), 6.99 (d, J = 3.8 Hz, 2H), 7.00 (d, J = 3.8 Hz, 2H), 7.01 (d, J = 3.8 Hz, 2H), 7.03 (s, 2H), 7.04 (d, J = 3.8 Hz, 2H), 7.07 (d, J = 3.8 Hz, 2H), 7.08 (d, J = 3.8 Hz, 2H), 7.11 (d, J = 3.8 Hz, 4H), 7.21 (s, 2H); UV-Vis (chlorobenzene) λ_{max}/nm (log ε) 331 (5.01), 451 (5.13), 704 (2.85).

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