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Large Photocurrent Generation of Gold Electrodes Modified with [60]Fullerene-Linked Oligothiophenes Bearing a Tripodal Rigid Anchor

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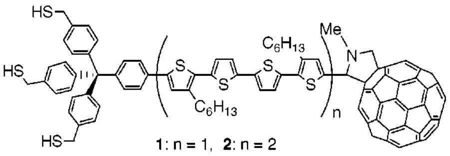
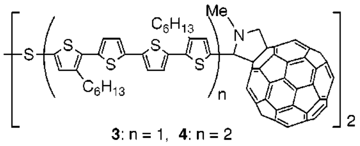
The preparation of fullerene-based thin films has been an active research field, with promise for practical applications to molecular devices and sensors.[1] In particular, self-assembled monolayers (SAM) of fullerenes have merited current attention from both fundamental and practical points of view.[2] In this context, donor-linked or functionalized fullerenes have frequently been fabricated on electrodes to develop photovoltaic cells.[3,4] However, it has still been difficult to control the structures of the SAMs themselves, which notably would affect the performance of the devices. Oligothiophenes are rigid rodlike π-conjugated molecules which are ideal materials to be densely packed normal to the electrodes when a thiol is attached as a terminal group. Oligothiophene-linked fullerenes have been reported to generate a long-lived charge-separated state via photoinduced electron transfer (ET).[5,6] Thus, oligothiophene-linked fullerenes with a thiol group at the end show great promise for being assembled on gold electrodes for efficient photocurrent generation.

We report herein newly designed [60]fullerene-linked quater- and octithiophenes (**1** and **2**) bearing a tripodal rigid anchor, which is a tetraphenylmethane core with three mercaptomethyl arms, allowing such molecules to be well-organized on the electrodes. A similar protocol using three-armed anchors for SAM formations on gold or TiO_2 was recently proposed,[7] but the practical advantage of such SAMs has not been demonstrated yet, to our knowledge. Our strategy to employ a tripodal rigid anchor has led to remarkable enhancement of the photocurrent generation [(Au/**1** or **2**/MV^{2+}/Pt cell)], as compared to the reference systems with one-armed anchoring compounds **3** and **4** [(Au/**3** or **4**/MV^{2+}/Pt cell)].[8] The compounds **1** and **2** were synthesized according to Scheme 1. 4-Aminophenyltris(4-methylphenyl)methane (**5**)[9] was first converted to the bromo derivative **6** by the Sandmeyer reaction, which was then brominated with 3 equiv of NBS to the tris(bromomethyl) derivative **7**, and finally treated with potassium thioacetate to afford the tris(acetylthiomethyl) derivative **8**. The Stille coupling reactions of **8** with tributylstannyl-substituted quater- and octithiophenes (**9** and **10**), prepared by a combination of lithiation and tributylstannylation of the corresponding oligothiophenes, gave **11** and **12**, respectively. They were converted to the formyl derivatives **13** and **14** by the Vilsmeier reaction, and then treated with C_{60} and *N*-methylglycine[10] to give the corresponding fullerene-linked oligothiophenes **15** and **16**. Mild alkaline hydrolysis of the acetyl protecting groups afforded the desired fullerene-linked oligothiophenes **1** and **2** with the free mercaptomethyl groups.

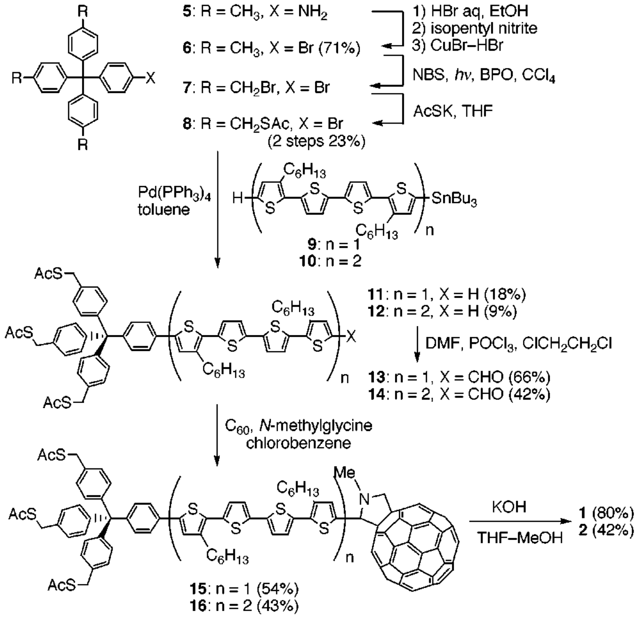


1: n = 1, **2**: n = 2



3: n = 1, **4**: n = 2

Scheme 1



SAMs of **1** (**1**/Au) and **2** (**2**/Au) were prepared by immersion of a hydrogen-frame-annealed Au(111)/mica substrate in their 2 × 10^{-5} mol dm^{-3} CH_2Cl_2 solutions at 25 °C for 24 h. The samples were rinsed with CH_2Cl_2 and EtOH, and then dried with a stream of nitrogen. To confirm the SAM formation, cyclic voltammetric experiments with the modified Au electrodes were carried out in CH_2Cl_2 containing 0.1 mol dm^{-3} of Bu_4NPF_6 as an electrolyte at scan rate of 100 mV s^{-1}. The cyclic voltammograms of **1**/Au and **2**/Au exhibited two well-resolved reversible cathodic waves at −0.66 and −0.97 V corresponding to the successive one-electron

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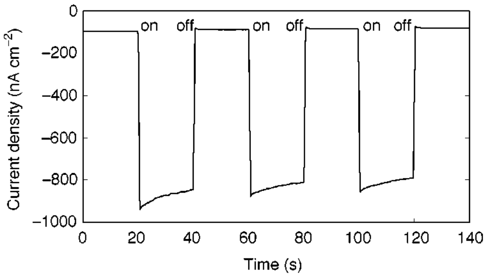

Figure 1. Photocurrent response of **1**/Au irradiated with 400 nm light (0.65 mW cm^{-2}) at −100 mV of bias vs Ag/AgCl.

reductions of the C_{60} moiety (Figure S2). The observation of these well-defined redox waves indicates that the molecules are strongly adsorbed on the surface very probably due to three-point connection. In contrast to the three-point connection systems, the voltammograms of SAMs of **3** (**3**/Au) and **4** (**4**/Au) with one-point connection show poorly reversible waves, suggesting that the molecules are sparsely attached to the surface and tend to be detached during the reduction sweep. On the basis of the integrated charge of the first reduction peak, surface coverages (Γ) are calculated as follows: **1**/Au, 1.7×10^{-10} mol cm^{-2}; **2**/Au, 1.6×10^{-10} mol cm^{-2}; **3**/Au, 3.5×10^{-11} mol cm^{-2}; **4**/Au, 8.9×10^{-11} mol cm^{-2}.[11] The small surface coverage for **3**/Au is due to its lying structure. Judging from the other three surface coverages, it turns out that the three-armed molecules **1** and **2** are more densely adsorbed than the one-armed molecule **4**. In addition, it is worth noting that the adsorbed amounts of **1** and **2** are virtually the same, independent of the oligothiophene length. These results indicate that the three-armed anchor molecules can stand up on the surface by themselves, forming highly ordered SAMs.

Photoelectrochemical measurements were performed in an argon-saturated 0.1 mol dm^{-3} Na_2SO_4 solution containing 5×10^{-3} mol dm^{-3} of methyl viologen (MV^{2+}) as an electron carrier using the modified Au electrode as a working electrode and a platinum counter electrode at −100 mV bias against an Ag/AgCl reference electrode under illumination of 400 nm light for **1**/Au or 440 nm for **2**/Au, which is mainly absorbed by the oligothiophene chromophore. The Au/**1**/MV^{2+}/Pt cell showed a cathodic photoelectrochemical response as shown in Figure 1. The amount of generated photocurrent for **1**/Au (*close to 1 mA* in Figure 1) is remarkable as compared to several nA scale usually observed for this type of photovoltaic cells.[12] The action spectrum of the Au/**1**/MV^{2+}/Pt cell (Figure S3) roughly agrees with the absorption spectrum on the gold electrode (Figure S4). The cathodic photocurrent increases with an increase of the negative bias of the gold electrode (Figure S5).

On the basis of the reported photodynamics of the oligothiophene-[60]fullerene dyads,[6] together with the results on similar photoelectrochemcial cells,[4] we can conclude that photoexcitation of the quaterthiophene chromophore first induces ET from the quaterthiophene to the C_{60} moiety to generate a net vectorial electron flow from the gold cathode to the Pt counter electrode via MV^{2+} with the aid of applied bias. The photocurrent density is much larger by a factor of about 190 than that observed for the Au/**3**/MV^{2+}/Pt cell. The Au/**2**/MV^{2+}/Pt cell also revealed a large photoelectrochemical response, and its photocurrent density is about 6 times as large as that observed for the Au/**4**/MV^{2+}/Pt cell. The enhanced photoresponses of **1**/Au and **2**/Au are primarily attributable to the densely packed SAMs. However, it is interesting to note that the enhancement ratios of the photocurrent much exceed the increased ratios of the Γ values. The self-reliant standing of **1** and **2** on the gold surface probably may suppress quenching of the excited states of the oligothiophene chromophore by intermolecular interactions and by the gold electrode, leading to increasing the photocurrent. The quantum yields of **1**/Au and **2**/Au were estimated based on the number of absorbed photons being 17 ± 7% and 35 ± 8%, respectively.[13] The remarkably large quantum yield for **2**/Au as compared to the value for **1**/Au indicates that the long oligothiophene chain can facilitate the generation and charge transport of photocurrent.

In summary, we have demonstrated an important role of the tripodal rigid anchor in preparing well-organized SAMs of [60]-fullerene-linked long oligothiophenes on the electrode to construct highly efficient photovoltaic cells.

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Supporting Information Available: The experimental procedures and spectral data for all new compounds, cyclic voltammograms, absorption spectra, and action spectra of the SAMs. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) The occupied areas per molecule of **1**/Au and **2**/Au agree largely with the calculated areas, assuming **1** and **2** are well-packed on the gold surface with a perpendicular orientation.

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(13) Photocurrent density/nA cm^{-2} (absorbance): **1**/Au, 783 (0.006 at 400 nm); **2**/Au, 1570 (0.006 at 440 nm). For comparison, it was estimated that the quantum yield of **3**/Au was less than 0.1% and that of **4**/Au was about 5%.

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