

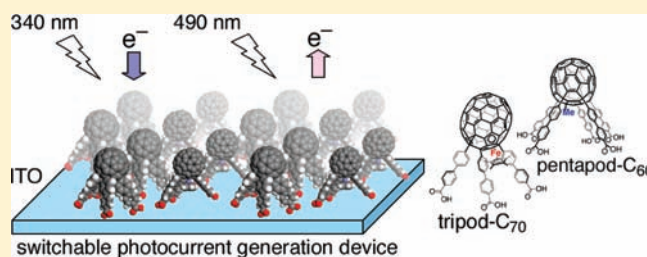
# Molecular Photoelectric Switch Using a Mixed SAM of Organic [60]Fullerene and [70]Fullerene Doped with a Single Iron Atom

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**S** Supporting Information

**ABSTRACT:** We describe a photoswitch fabricated on indium tin oxide (ITO) as a self-assembled monolayer (SAM) of two fullerene molecules, a purely organic [60]fullerene that generates an anodic current and a [70]fullerene doped with a single iron atom. This device generates a bidirectional photocurrent upon irradiation at 340 and 490 nm. The new [70]fullerene iron complex bearing three rigid carboxylic acid legs,  $\text{Fe}[\text{C}_{70}(\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{COOH})_3]\text{Cp}^*$ , generates only a cathodic current upon photoexcitation between 350 and 700 nm, whereas the organic [60]fullerene absorbs at wavelengths shorter than 500 nm. The quantum efficiency of the photocurrent generation by the mixed SAM is comparable to that of a single-component SAM, indicating that the individual diode molecules on ITO generate photocurrents independently with little cross talk.



## INTRODUCTION

Molecular design and hierarchical structural control of molecular assembly are the major challenges in the study of molecular photoelectronics.<sup>1–6</sup> For instance, a molecular photoswitch first requires two molecular photodiodes that generate photocurrents along the molecules in opposite directions<sup>7,8</sup> and then requires these molecules to work independently upon irradiation at two different wavelengths after controlled fabrication on an electrode surface. We previously reported that a [60]fullerene photodiode **1** (part a of Figure 1) on indium tin oxide (ITO) generates only an anodic photocurrent upon irradiation at <500 nm (part c of Figure 1) and that doping of such a molecule with a single iron atom reverses the current-generating ability.<sup>9</sup> To fabricate a photoswitch with **1** in hand, we need another photodiode that generates only a cathodic current at a wavelength of >500 nm (cf., part d of Figure 1).

We report here that a mixed self-assembled monolayer (SAM) made of  $\text{C}_{60}(\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{COOH})_3\text{Me}$  (**1**) and  $\text{Fe}[\text{C}_{70}(\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{COOH})_3]\text{Cp}^*$  (**2**) (part b of Figure 1 and Scheme 1;  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) generates a bidirectional photocurrent of approximately +8 and –8 nA/cm<sup>2</sup> upon irradiation at 340 and 490 nm, respectively (part f of Figure 1). The quantum efficiency of the photocurrent generation by the mixed SAM is on the same order of that of a single-component SAM, and the current density was 10 times larger than those (<1 nA/cm<sup>2</sup>) previously reported for devices using flexible molecules.<sup>7,8</sup> We ascribe the high efficiency of photocurrent generation to the wide separation of the molecules on the substrate surface (because of the bulky  $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{COOH}$  legs; as seen in parts a and b of Figure 1), as previously shown in a scanning tunneling microscope study.<sup>10</sup>

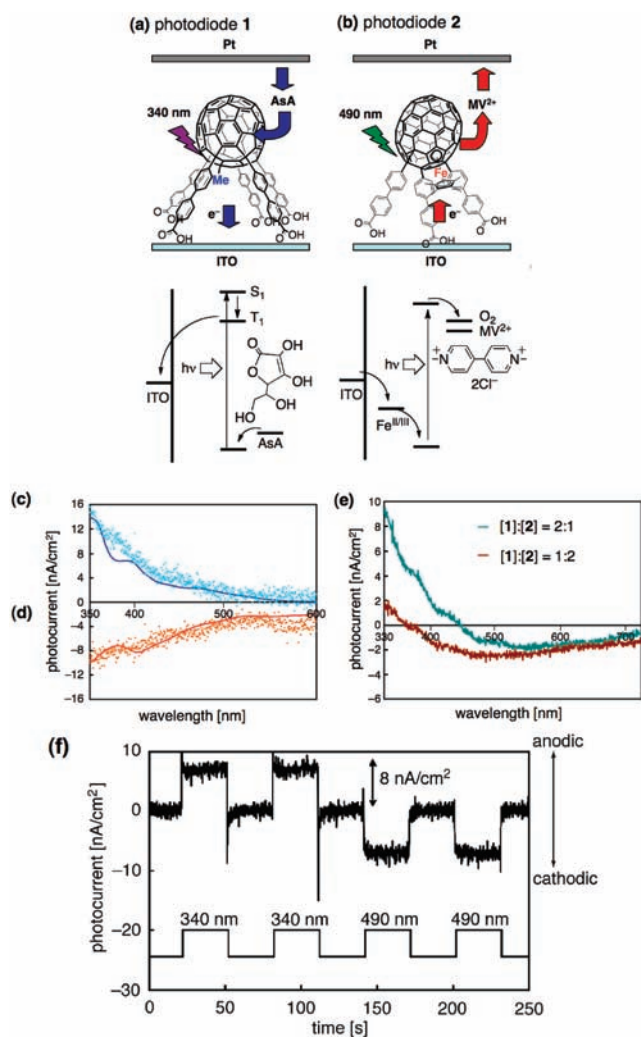
## RESULTS AND DISCUSSION

**Synthesis and Electrochemical Properties of Tripod C<sub>70</sub> Derivatives.** We investigated the availability of a [70]fullerene derivative that generates only a cathodic current. We first found that the lower symmetry of [70]fullerene allows us to introduce three  $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{COOH}$  addends (Scheme 1) and that these three legs can stably anchor the molecule on the ITO surface (cf., part b of Figure 1). Thus, we prepared  $\text{C}_{70}(\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CO}_2\text{Et})_3\text{H}$  (**3**) via regioselective 3-fold addition of an organocopper reagent ( $\text{CuC}_6\text{H}_4\text{C}_6\text{H}_4\text{CO}_2\text{Et}$ ),<sup>11</sup> and the product was further converted to  $\text{C}_{70}(\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CO}_2\text{H})_3\text{Me}$  (**7**),  $\text{Fe}[\text{C}_{60}(\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CO}_2\text{H})_5]\text{Cp}^*$  (**2**;  $\text{Cp}^* = \text{C}_5\text{Me}_5$ ), and  $\text{Ru}[\text{C}_{60}(\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CO}_2\text{H})_5]\text{Cp}^*$  (**8**) (Scheme 1).<sup>12,13</sup> The iron complex **5** exhibited reversible one-electron oxidation at 0.23 V and three-electron reduction at –1.03, –1.58, and –2.08 V (vs  $\text{Fc}/\text{Fc}^+$ ) (part a of Figure 2), and **6** showed a reversible oxidation peak at 0.57 V (Figure S1 of the Supporting Information). The Ru complex had a lower HOMO level than the Fe complex. Finally, we note that these compounds are stable on the shelf under air for years.

**Self-Assembled Monolayer Formation and Photocurrent Generation Properties of Tripod C<sub>70</sub> Derivatives.** To our satisfaction, the tripod [70]fullerenes formed stable SAMs on ITO and showed good photoresponses. An ITO electrode was immersed for several days in a 0.1 mM THF solution of **2**, **7**, and **8** to obtain the SAM-modified ITO electrodes. A cyclic voltammogram of **2** on ITO revealed a reversible one-electron oxidation

Received: April 7, 2011

Published: May 23, 2011

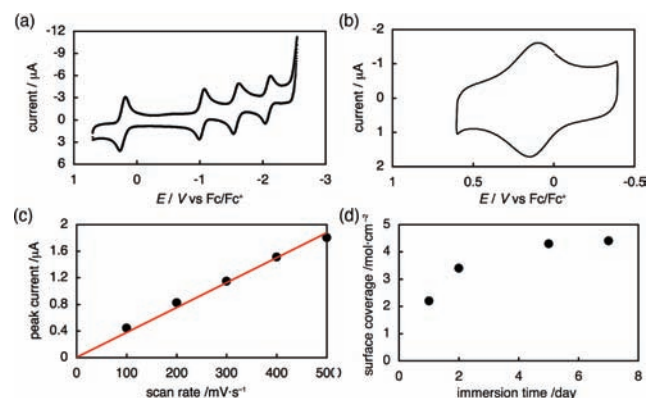
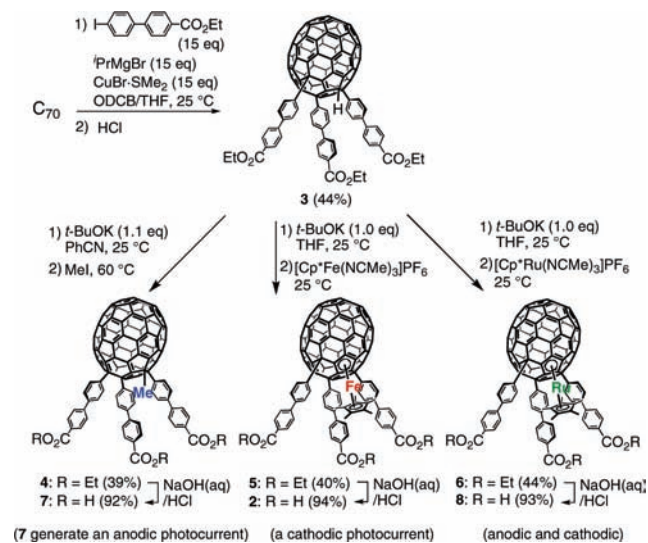


**Figure 1.** Mixed-component SAM of **1** and **2**, and its photocurrent-generation properties. (a, b) Schematic drawing with mechanisms for anodic and cathodic photocurrent generation by **1** and **2**, respectively. (c, d) Absorption spectra (solid line) and photocurrent action spectra (dots) of the mixed SAM of **1** and **2**. Positive and negative photocurrents refer to anodic and cathodic currents in the presence of only AsA (c) or  $MV^{2+}$  (d), respectively. (e) Photocurrent action spectra for the mixed SAM in the presence of both AsA and  $MV^{2+}$ . The action spectra changed when we changed the ratio of **1** and **2** used for the preparation of the SAM. (f) Photoswitching property of the mixed SAM of **1** and **2** in the presence of both AsA and  $MV^{2+}$  upon irradiation at 340 and 490 nm.  $[1]:[2] = 2:1$ .

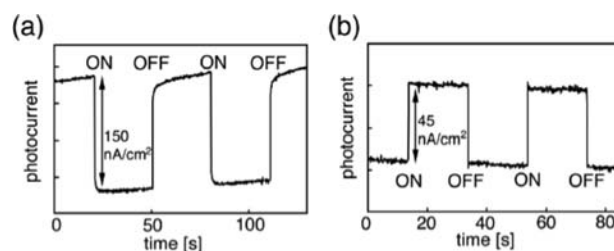
of the ferrocene moiety (part b of Figure 2) and provided evidence for the formation of the SAM on ITO (part c of Figure 2) with a coverage density of  $4.4 \times 10^{-11} \text{ mol} \cdot \text{cm}^{-2}$  (which was achieved after five days, part d of Figure 2). This density is comparable to that obtained for the pentapod [60]fullerene **1** ( $7.0 \times 10^{-11} \text{ mol} \cdot \text{cm}^{-2}$ )<sup>9</sup> and that based on the number of molecules per  $\text{cm}^2$  counted with STM.<sup>10</sup> AFM analysis also supported the SAM formation (Figure S2 of the Supporting Information).

Among the SAMs made of [70]fullerene **2**, **7**, and **8** that are photoresponsive up to 700 nm, only the SAM made with **2** generated the desired unidirectional cathodic photocurrent and showed a good ON/OFF response (part a of Figure 3,  $150 \text{ nA/cm}^2$

### Scheme 1. Synthesis of Tripod [70]Fullerenes



**Figure 2.** Electrochemical studies. (a) Cyclic voltammogram of **5** at  $25^\circ\text{C}$  (vs  $\text{Fc}/\text{Fc}^+$ ) at  $100 \text{ mV/s}$  in a  $0.1 \text{ M}$  THF solution containing  ${}^t\text{Bu}_4\text{NClO}_4$  as supporting electrolyte. (b) Cyclic voltammograms of **2/ITO** at a scan rate  $200 \text{ mV/s}$  at  $25^\circ\text{C}$  vs  $\text{Fc}/\text{Fc}^+$  in a  $0.1 \text{ M}$   $\text{CH}_3\text{CN}$  solution containing  ${}^t\text{Bu}_4\text{NClO}_4$  as supporting electrolyte. (c) Plots of the scan rate vs peak current of **2/ITO**. (d) Plots of the surface coverage of **2/ITO** vs immersion time.



**Figure 3.** Photocurrent-generation properties of the tripod  $C_{70}$  molecules. (a) Cathodic photocurrent generated from the SAM of **2** in the presence of  $MV^{2+}$  upon irradiation at  $400 \text{ nm}$ . (b) Anodic photocurrent from the SAM of **7** in the presence of AsA upon irradiation at  $400 \text{ nm}$ .

upon irradiation at  $400 \text{ nm}$  in the presence of  $MV^{2+}$ ) with no anodic current even in the presence of AsA. However, the

methyl 7, like **1**, generated a unidirectional anodic current and also showed a good ON/OFF response (45 nA/cm<sup>2</sup> upon irradiation at 400 nm in the presence of AsA, part b of Figure 3). The ruthenium 7 showed bidirectional photodiode behavior upon exposure to AsA and MV<sup>2+</sup> (Figure S3 of the Supporting Information) and hence is not suitable for the present purpose. Quantum yields of photocurrent generation of **2** (cathodic, -100 mV bias), **7** (anodic, 100 mV bias), **8** (anodic, 100 mV bias), and **8** (cathodic, -100 mV bias) were 8.2, 3.4, 2.1, and 1.3% respectively upon irradiation at 400 nm. These values are comparable to those obtained for the corresponding pentapod [60]fullerenes.<sup>3,9,14,15</sup> We therefore conclude that, like the five legs in **1**, the three legs in **2** can anchor the molecule stably on ITO.

In parts a and b of Figure 1, we show two diagrams accounting for the opposite behavior of **1** and **2**, which have been proposed previously for similar systems.<sup>9</sup> Part a of Figure 1 illustrates a mechanism for the anodic current generation by **1**, where **1** donates an electron to ITO from triplet photoexcited state. In the meanwhile, **1** is regenerated by accepting an electron from AsA. However, the photoexcitation of **2** results quickly in the intramolecular one-electron transfer from iron to the fullerene,<sup>16–18</sup> and the oxidized iron atom accepts an electron from the nearby ITO. Thus, the iron atom physically sandwiched between fullerene and ITO acted as a single-atom dopant and inverted the function of the fullerene photoreceptor.

**Photoelectric Switching Properties of the Mixed SAM of the Tripod C<sub>70</sub> and Pentapod C<sub>60</sub> Derivatives.** To approach the goal of photoswitching, we prepared a mixed SAM by immersion of a 2:1 mixture of **1** and **2** on ITO for five days and first studied its action in the presence of either AsA or MV<sup>2+</sup>. As shown in part c of Figure 1, this mixed SAM upon exposure to AsA generated an anodic current for wavelengths up to 550 nm, with the action spectrum in good agreement with the absorption spectrum of **1** (solid blue line). As shown in part d of Figure 1, in contrast, the same SAM generated a cathodic current upon exposure to MV<sup>2+</sup> up to 700 nm. The action spectrum also agreed with the absorption spectrum of **2** (solid red line).

Finally, we describe how the mixed SAM acts as a photoswitch. After considerable experimentation, we found that the use of a 2:1 mixture of **1** and **2** without bias voltage is optimum to obtain a good photoresponse. For instance, a 2:1 mixture allows the photocurrent to change from anodic to cathodic at a convenient wavelength of 450 nm, whereas a 1:2 mixture produces the change at 350 nm (part e of Figure 1). Thus, we used the 2:1 mixed SAM in the presence of a mixture of AsA and MV<sup>2+</sup> to find that it generates ca. 8 nA/cm<sup>2</sup> each of anodic/off/cathodic photocurrents upon irradiation with 340 nm light, none, and 490 nm light, respectively (part f of Figure 1).

Control experiments indicated that photodiodes **1** and **2** in the mixed SAM function independently of each other. Thus, we compared the cathodic photocurrent generation of the mixed SAM ([**1**]/[**2**] = 2:1) and a single-component SAM of **2** in the presence of both AsA and MV<sup>2+</sup> under 490 nm irradiation. The quantum yield of the photocurrent from the 2:1 mixed SAM was found to be comparable (1.4%, -20 mV bias; AsA and MV<sup>2+</sup>) to that of the SAM made of only **2** (1.6%, -20 mV bias; AsA and MV<sup>2+</sup>).

There is one obvious reason for the reduced quantum yields recorded for the mixed SAM as compared with the 8.2% yield obtained at -100 mV bias voltage at 400 nm, which is the use of 490 nm light for selective excitation of **2** in the presence of **1**. At

this wavelength of 490 nm, **1** absorbs some light and generates an anodic current, whereas the use of a longer wavelength is undesirable because the absorption of **2** becomes too weak.<sup>19</sup>

Overall, the results of the mixed SAM as well as the single component SAM of **1**<sup>9</sup> and **2** suggested a very small intermolecular cross talk between **1** and **2** in the mixed SAM. These observations are quite different from fast lateral charge hopping<sup>20</sup> across the film of [60]fullerene molecules bearing no spatial separator groups.

## CONCLUSIONS

In summary, we have synthesized a new tripod [70]fullerene iron complex **2** that absorbs light at a wavelength longer than 500 nm and demonstrated its utility as a photoswitch when used together with an organic [60]fullerene **1** that absorbs at wavelengths shorter than 500 nm. Taken together with a previous example of a single-component [60]fullerene photodiode,<sup>8</sup> the [70]fullerene iron complex has proven the viability of the concept of single-atom doping of molecular diodes. The [60] and [70]photodiode molecules were found to work independently in the mixed SAM to achieve much higher current densities than the reported devices,<sup>7</sup> which we ascribe to the formation of well-organized and robust assembly of the photodiode molecules on the ITO surface as well as the spatial separation of the molecules effected by the tailor-designed legs. With enhancement of the longer wavelength absorption by the use of a higher fullerene<sup>21</sup> or a metal–fullerene complex,<sup>22,23</sup> improvement in the quantum efficiency and an increase in the current density are expected.

## EXPERIMENTAL SECTION

**General.** All manipulations were carried out under nitrogen or argon atmosphere with standard Schlenk techniques. The water content of solvents was determined with a Karl Fisher moisture titration (MK-210, Kyoto Electronics Co.) to be less than 30 ppm. All reactions were monitored by HPLC (column, Cosmosil-Buckyprep, 4.6 × 250 mm, Nacalai Tesque; flow rate, 2.0 mL/min; eluent, toluene/*iso*-propanol; detector, Shimadzu SPD-M10Ayp). Preparative HPLC was performed on a Buckyprep column (20 × 250 mm) using toluene/*iso*-propanol as eluent (detected at 350 nm with an UV spectrophotometric detector, Shimadzu SPD-6A). Isolated yields were calculated on the basis of the starting fullerene compounds. All NMR spectra were measured with JEOL ECA-500 (500 MHz) instruments. Spectra are reported in parts per million from internal tetramethylsilane ( $\delta$  0.00 ppm) or residual protons of the deuterated solvent for <sup>1</sup>H NMR, and from solvent carbon (e.g.,  $\delta$  77.00 ppm for chloroform) for <sup>13</sup>C NMR. Mass spectra were measured on a JEOL LMS-T100LC APCI/ESI-TOF mass spectrometer.

**Materials.** Methyl viologen (MV) was purchased from Sigma-Aldrich Co. and used as received. *n*-Bu<sub>4</sub>NClO<sub>4</sub> for electrochemical measurement was purchased from Kanto Chemicals and used after recrystallization from ethanol. Na<sub>2</sub>SO<sub>4</sub> and ascorbic acid (AsA) were purchased from Kanto Chemicals and used as received. A THF solution of KO<sup>t</sup>Bu was purchased from Sigma-Aldrich Co. C<sub>60</sub>(C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>-COOH)<sub>5</sub>Me was prepared according to the previously reported procedure.<sup>9</sup> Transparent indium–tin oxide (ITO) electrode (10  $\Omega$ /cm<sup>2</sup>, ITO on glass plate) were obtained from GEOMATEC Inc. (Japan).

**Synthesis of C<sub>70</sub>(C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>COOEt)<sub>3</sub>H (**3**).** A solution of 4-(4-ethoxycarbonyl-phenyl)phenyl iodide (0.90 g, 2.59 mmol) in 30 mL of THF was treated with isopropyl magnesium bromide (3.15 mL of 0.91 M solution in THF, 2.59 mmol) at -25 °C and stirred for 3 h. Copper(I) bromide dimethyl sulfide complex (550 mg, 2.59 mmol) was then added. After stirring for 10 min, a solution of C<sub>70</sub> (150 mg, 0.17 mmol)



in 20 mL of *o*-dichlorobenzene was added. The resulting mixture was stirred at room temperature until C<sub>70</sub> disappeared, as monitored by HPLC. The reaction was then quenched with 0.2 mL of saturated aqueous ammonium chloride solution and 30 mL of degassed toluene. The solution was filtered through a pad of silica gel and concentrated; 100 mL of hexane was then added. The resulting precipitate was collected after filtration and purified by preparative HPLC to afford 120 mg of the title compound in 44% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.38–1.44 (m, 9H, CH<sub>3</sub>), 4.36–4.45 (m, 6H, CH<sub>2</sub>), 4.53 (s, 1H, C<sub>70</sub>H), 7.56–7.63 (m, 8H, Ar), 7.67–7.70 (m, 4H, Ar), 7.76–7.77 (d, *J* = 8.60 Hz, 2H, Ar), 7.88–7.90 (d, *J* = 8.00 Hz, 2H, Ar), 7.97–7.99 (d, *J* = 8.60 Hz, 2H, Ar), 8.06–8.13 (m, 6H, Ar); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 14.09–14.10 (3C, CH<sub>3</sub>), 55.35, 56.01, 56.04, 59.85, 60.77, 60.81, 126.42, 126.63, 126.69, 127.28, 127.39, 127.70, 127.72, 127.78, 127.80, 128.12, 129.29, 129.38, 129.86, 129.88, 129.94, 130.65, 131.56, 131.78, 131.90, 131.96, 133.02, 133.06, 136.89, 138.50, 139.02, 139.31, 139.42, 139.46, 139.57, 140.54, 142.14, 142.18, 142.75, 142.94, 143.37, 143.92, 143.95, 144.02, 144.08, 144.47, 144.68, 144.86, 144.92, 145.03, 145.07, 145.28, 145.46, 145.67, 145.81, 146.24, 146.28, 146.58, 146.63, 146.97, 147.08, 147.23, 147.68, 147.81, 147.90, 148.10, 148.21, 148.28, 148.59, 148.66, 148.80, 148.90, 149.06, 149.18, 149.40, 149.50, 149.57, 149.85, 150.20, 152.18, 152.62, 153.88, 154.99, 155.66, 160.53, 166.03, 166.06; APCI-HRMS (+): Calcd. for C<sub>115</sub>H<sub>41</sub>O<sub>6</sub> [M<sup>+</sup>+H] 1517.2903, found 1517.2859.

**Synthesis of C<sub>70</sub>(C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>COOEt)<sub>3</sub>Me (4).** Compound 3 (77 mg, 0.05 mmol) was dissolved in 15 mL of degassed benzonitrile, followed by the addition of 0.05 mL of 1.0 M KO<sup>t</sup>Bu in THF (0.05 mmol). After stirring at room temperature for 10 min, 0.32 mL of iodomethane (5.0 mmol) was added. The reaction system was then heated to 60 °C and stirred for another 24 h. After cooling to room temperature, the mixture was filtered through a pad of silica gel and washed with toluene. Analytically pure product (30 mg, 39% yield) was obtained by preparative HPLC purification. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.38–1.46 (m, 9H, CH<sub>3</sub>), 1.54 (s, 3H, C<sub>70</sub>CH<sub>3</sub>), 4.36–4.46 (m, 6H, CH<sub>2</sub>), 7.51–7.52 (d, *J* = 8.55 Hz, 2H, Ar), 7.62–7.63 (d, *J* = 8.60 Hz, 4H, Ar), 7.70–7.72 (d, *J* = 8.05 Hz, 2H, Ar), 7.74–7.76 (d, *J* = 8.55 Hz, 2H, Ar), 7.79–7.81 (d, *J* = 8.55 Hz, 2H, Ar), 7.86–7.88 (d, *J* = 8.05 Hz, 2H, Ar), 8.03–8.07 (m, 4H, Ar), 8.11–8.15 (m, 4H, Ar), 8.18–8.20 (d, *J* = 8.00 Hz, 2H, Ar); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 14.33–14.37 (3C, CH<sub>3</sub>), 52.23, 55.61, 60.95, 61.07, 126.65, 126.84, 126.94, 127.07, 127.39, 128.20, 128.25, 129.01, 129.30, 129.65, 129.69, 130.01, 130.20, 130.23, 130.76, 131.16, 131.29, 131.79, 132.32, 133.53, 134.13, 134.30, 135.06, 137.43, 138.97, 139.82, 139.89, 140.03, 140.10, 140.30, 140.69, 141.28, 143.04, 143.54, 143.63, 143.69, 144.04, 144.37, 144.55, 144.69, 144.73, 144.89, 144.99, 145.04, 145.14, 145.49, 145.59, 145.69, 145.93, 146.33, 146.40, 146.89, 147.11, 147.20, 147.41, 147.56, 147.66, 147.71, 147.89, 148.01, 148.22, 148.36, 148.52, 148.74, 148.99, 149.21, 149.34, 149.43, 150.35, 150.42, 150.48, 150.60, 150.63, 151.06, 151.33, 151.81, 152.24, 153.13, 155.02, 166.36, 166.43.

**Synthesis of C<sub>70</sub>(C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>COOH)<sub>3</sub>Me (7).** Compound 4 (15.0 mg, 0.01 mmol) and 0.30 mL of 0.5 M NaOH in MeOH (0.15 mmol) were added to 5 mL of toluene. The mixture was heated to 60 °C and stirred for 2 h. After cooling to room temperature, the precipitate was collected by filtration and washing with toluene. The solid obtained was then treated with 1 mL of 1 M HCl aqueous solution. After filtration and washed with water, the obtained solid was dried for 6 h at 60 °C under vacuum (13.0 mg, 92% yield). <sup>1</sup>H NMR (500 MHz, THF-*d*<sub>8</sub>): δ 1.29 (s, 3H, C<sub>70</sub>CH<sub>3</sub>), 7.57–7.59 (d, *J* = 8.00 Hz, 2H, Ar), 7.69–7.71 (d, *J* = 8.55 Hz, 2H, Ar), 7.79–7.80 (d, *J* = 8.00 Hz, 4H, Ar), 7.86–7.91 (m, 4H, Ar), 8.01–8.04 (m, 4H, Ar), 8.09–8.11 (d, *J* = 8.60 Hz, 4H, Ar), 8.15–8.17 (d, *J* = 8.00 Hz, 4H, Ar); <sup>13</sup>C NMR (125 MHz, THF-*d*<sub>8</sub>): δ 53.12, 56.80, 127.22, 127.33, 127.44, 127.64, 127.78, 127.86, 128.31, 128.76, 128.90, 129.08, 129.12, 129.67, 129.94, 130.47, 130.71, 130.80, 130.99, 131.14, 131.16, 131.35, 131.42, 132.03, 132.07, 132.59, 132.68, 133.21, 134.39,

135.06, 135.15, 135.91, 138.12, 138.26, 139.83, 140.69, 140.75, 140.88, 141.06, 141.10, 141.56, 141.81, 142.25, 143.27, 144.46, 144.57, 144.71, 144.82, 144.93, 145.06, 145.19, 145.46, 145.56, 145.79, 145.92, 146.06, 146.41, 146.63, 147.10, 147.26, 147.78, 147.97, 148.05, 148.40, 148.50, 148.74, 148.82, 148.88, 149.09, 149.21, 149.34, 149.49, 149.60, 149.93, 150.15, 150.35, 151.17, 151.49, 151.71, 151.80, 151.90, 152.63, 152.92, 153.27, 153.97, 155.18, 167.40; APCI-HRMS (+): Calcd. for C<sub>110</sub>H<sub>31</sub>O<sub>6</sub> [M<sup>+</sup>+H] 1447.2121, found 1447.2088.

**Synthesis of Fe[C<sub>70</sub>(C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>COOEt)<sub>3</sub>]Cp\* (5).** To a dark-brown suspension of 3 (84 mg, 0.055 mmol) in THF (25 mL) was added a 1 M THF solution of <sup>t</sup>BuOK (0.055 mL, 0.055 mmol) at room temperature. The suspension turned dark brown solution immediately, then [Cp\*Fe(NCMe)<sub>3</sub>]PF<sub>6</sub> (60 mg, 0.13 mmol) was added. After stirring for 1 h, the volatile materials were removed under reduced pressure. The crude mixture was diluted with toluene and filtered through a pad of silica gel and concentrated. Purification by preparative HPLC afforded 38 mg of 5 in 40% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.05 (s, 15H, Cp\*), 1.42–1.45 (t, 6H, 2CH<sub>2</sub>CH<sub>3</sub>), 1.58–1.61 (t, 3H, CH<sub>2</sub>CH<sub>3</sub>), 4.40–4.44 (q, 4H, 2CH<sub>2</sub>CH<sub>3</sub>), 4.58–4.62 (q, 2H, CH<sub>2</sub>CH<sub>3</sub>), 7.80–7.81 (d, *J* = 8.05 Hz, 4H, aromatic), 8.07–8.09 (d, *J* = 8.0 Hz, 4H, aromatic), 8.42–8.43 (d, *J* = 8.0 Hz, 2H, aromatic), 8.76–8.77 (d, *J* = 8.0 Hz, 2H, aromatic); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 9.96 (C<sub>5</sub>CH<sub>3</sub>), 14.36 (2CH<sub>2</sub>CH<sub>3</sub>), 14.54 (CH<sub>2</sub>CH<sub>3</sub>), 57.20, 58.65, 61.31 (2CH<sub>2</sub>CH<sub>3</sub>), 61.58 (CH<sub>2</sub>CH<sub>3</sub>), 81.96 (C<sub>5</sub>), 88.14, 90.94, 128.72, 129.55, 129.73, 129.92, 130.11, 130.42, 130.45, 131.65, 132.14, 133.31, 136.05, 137.73, 139.19, 142.51, 144.11, 144.62, 144.75, 144.92, 145.04, 145.96, 146.18, 146.28, 146.32, 146.41, 146.60, 146.97, 147.01, 147.16, 147.40, 148.52, 148.63, 148.76, 148.79, 148.93, 149.60, 149.66, 150.22, 151.03, 156.70, 159.69, 166.11, 166.39; APCI-HRMS (+): Calcd. for C<sub>125</sub>H<sub>54</sub>O<sub>6</sub>Fe [M<sup>+</sup>] 1706.3270, found 1706.3205.

**Synthesis of Fe[C<sub>70</sub>(C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>COOH)<sub>3</sub>]Cp\* (2).** Compound 5 (15 mg, 0.0095 mmol) and 0.30 mL of 0.5 M NaOH in MeOH (0.15 mmol) were added to 5 mL of toluene. The mixture was heated to 60 °C and stirred for 2 h. After cooling to room temperature, the precipitate was collected by filtration and washing with toluene. The solid obtained was then treated with 1 mL of 1 M HCl aqueous solution. After filtration and washed with water, the obtained solid 2 was dried for 6 h at 60 °C under vacuum (14 mg, 94% yield). <sup>1</sup>H NMR (500 MHz, THF-*d*<sub>8</sub>): δ 1.16 (s, 15H, Cp\*), 7.75–7.77 (d, *J* = 8.55 Hz, 4H, Ar), 7.79–7.81 (d, *J* = 7.45 Hz, 4H, Ar), 7.95–7.93 (d, *J* = 8.60 Hz, 4H, Ar), 8.02–8.04 (d, *J* = 8.00 Hz, 2H, Ar), 8.07–8.08 (d, *J* = 8.05 Hz, 4H, Ar), 8.19–8.23 (m, 4H, Ar), 8.83–8.85 (d, *J* = 8.00 Hz, 2H, Ar); APCI-HRMS (+): Calcd. for C<sub>119</sub>H<sub>42</sub>O<sub>6</sub>Fe [M<sup>+</sup>] 1622.2331, found 1622.2330.

**Synthesis of Ru[C<sub>70</sub>(C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>COOEt)<sub>3</sub>]Cp\* (6).** To a dark-brown suspension of 3 (40 mg, 0.026 mmol) in THF (5 mL) was added a 1 M THF solution of KO<sup>t</sup>Bu (0.026 mL, 0.026 mmol) at room temperature. The suspension turned dark brown solution immediately, then [Cp\*Ru(NCMe)<sub>3</sub>]PF<sub>6</sub> (31.7 mg, 0.062 mmol) was added. After stirring for 1 h, the volatile materials were removed under reduced pressure. The crude mixture was diluted with toluene and filtered through a pad of silica gel and concentrated. The product was separated by chromatography on silica gel (CS<sub>2</sub> only) afforded 19.5 mg of 6 in 44% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.22 (s, 15H, Cp(CH<sub>3</sub>)<sub>5</sub>), 1.39–1.41 (t, 6H, CH<sub>3</sub>), 1.45–1.48 (t, 3H, CH<sub>3</sub>), 4.37–4.41 (q, 4H, CH<sub>2</sub>), 4.44–4.47 (q, 2H, CH<sub>2</sub>), 7.57–7.59 (d, *J* = 8.05 Hz, 4H, Ar), 7.61–7.63 (d, *J* = 8.00 Hz, 4H, Ar), 7.72–7.73 (d, *J* = 8.05 Hz, 4H, Ar), 7.86–7.88 (d, *J* = 8.60 Hz, 2H, Ar), 7.91–7.92 (d, *J* = 8.00 Hz, 2H, Ar), 8.10–8.11 (d, *J* = 8.05 Hz, 4H, Ar), 8.24–8.26 (d, *J* = 8.05 Hz, 2H, Ar), 8.61–8.62 (d, *J* = 8.00 Hz, 2H, Ar); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 10.27, 14.33, 14.39, 57.07, 58.42, 61.01, 61.12, 87.47, 126.94, 127.16, 127.29, 127.32, 129.25, 129.51, 129.74, 130.04, 130.15, 130.31, 131.60, 132.14, 133.36, 134.16, 138.00, 139.23, 139.30, 139.63, 142.33, 142.43, 142.51, 144.24, 144.55, 144.67, 144.74, 144.86, 145.11, 146.01, 146.42, 146.54, 146.90, 147.29, 147.44, 147.51, 147.75, 148.70, 148.90, 148.95, 149.81, 150.16,

150.92, 156.62, 160.53, 166.34, 166.41; APCI-HRMS (+): Calcd. for  $C_{125}H_{54}O_6Ru [M^+ + H]$  1753.3042, found 1753.3077.

**Synthesis of Ru[C<sub>70</sub>(C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>COOH)<sub>3</sub>]Cp\* (8).** Compound 6 (10.5 mg, 0.0060 mmol) and 0.30 mL of 0.5 M NaOH in MeOH (0.15 mmol) were added to 5 mL of toluene. The mixture was heated to 60 °C and stirred for 2 h. After cooling to room temperature, the precipitate was collected by filtration and washing with toluene. The solid obtained was then treated with 1 mL of 1 M HCl aqueous solution. After filtration and washed with water, the obtained solid 8 was dried for 6 h at 60 °C under vacuum (9.9 mg, 93% yield). <sup>1</sup>H NMR (500 MHz, THF-*d*<sub>8</sub>): δ 1.29 (s, 15H, Cp\*), 7.72–7.80 (m, 12H, Ar), 7.97–7.99 (d, *J* = 8.60 Hz, 2H, Ar), 8.06–8.11 (m, 6H, Ar), 8.19–8.21 (d, *J* = 8.60 Hz, Ar), 8.65–8.66 (d, *J* = 8.00 Hz, 2H, Ar); <sup>13</sup>C NMR (125 MHz, THF-*d*<sub>8</sub>): δ 10.68, 58.36, 59.68, 88.72, 127.70, 127.92, 128.30, 128.73, 128.90, 129.67, 130.24, 130.50, 130.80, 131.06, 131.19, 132.53, 133.10, 134.26, 135.73, 138.81, 140.27, 140.45, 140.78, 143.03, 143.24, 143.34, 145.23, 145.41, 145.67, 145.87, 146.02, 146.91, 147.25, 147.44, 147.81, 148.13, 148.38, 148.56, 149.03, 149.59, 149.83, 149.88, 150.65, 150.86, 151.15, 151.83, 157.82, 162.23, 167.35, 167.43.

**Preparation of the SAMs.** Preparation of self-assembled monolayers (SAMs) of fullerene compounds was carried out using a simple dipping method: an ITO (25 mm × 25 mm, UV–O<sub>3</sub> treated before use) was immersed in a 0.1 mM THF solution of the fullerene derivatives at room temperature. Then the ITO was washed with THF and dried in an argon gas stream.

**Electrochemical Measurements.** Electrochemical measurements were carried out with a Hokuto HZ-5000 voltammetric analyzer. A glassy-carbon electrode was used as the working electrode. The counter electrode was a platinum coil, and the reference electrode was a Ag/Ag<sup>+</sup> electrode. Cyclic voltammetry (CV) was performed at a scan rate of 100 mV/s. The potential was corrected against Fc/Fc<sup>+</sup>.

**Characterization of the SAM.** Cyclic voltammetry of the ITO modified with fullerene derivatives was carried out using an ITO working electrode, a Pt wire counter electrode, and an Ag/Ag<sup>+</sup> reference electrode in a 0.1 M CH<sub>3</sub>CN solution containing <sup>n</sup>Bu<sub>4</sub>NClO<sub>4</sub> as supporting electrolyte in a standard one-compartment cell under argon. Figure indicates the dependence of the surface coverage on the period of immersion for assembly of 4 on the ITO electrode. Five days are needed to construct the saturated SAMs. The little difference between oxidation and reduction peak potential was observed and the peak current was found to be proportional to the scan rate. These are clear evidence for a single layer of the molecules on the electrode surface. The surface coverage was estimated from the area of the reversible redox process for the ferrocene part to be  $4.4 \times 10^{-11}$  mol/cm<sup>2</sup>.

**Measurement of Photocurrent Generation.** Photoelectrochemical measurements were carried out in a one-compartment cell, being irradiated with monochromatic excitation light (light intensity at 400 nm was  $207 \pm 5$  μW for systems of ITO electrodes). The photocurrent was detected with an HZ-5000 voltammetric analyzer.

In the case of the anodic system, 50 mM ascorbic acid (AsA) was added as a sacrificial electron donor in an argon-saturated 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution, and 50 mM methyl viologen (MV) was used as an electron acceptor in an oxygen-saturated 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution. Quantum efficiencies of anodic and cathodic current ( $\varphi_a$  and  $\varphi_c$ ) were obtained by the following equation,

$$\varphi = (i/e)/[I(1 - 10^{-A})]$$

where  $I = (W\lambda/hc)$ .  $I$  is the number of photons per unit area and unit time,  $A$  is the absorbance of the adsorbed dyes at  $\lambda$  nm,  $i$  is the photocurrent density,  $e$  is the elementary charge,  $W$  is the light power irradiated at  $\lambda$  nm,  $\lambda$  is the wavelength of light irradiation,  $h$  is the Planck constant, and  $c$  is the speed of light.  $A$  was estimated from the next equation,

$$A = \varepsilon c l$$

where  $\varepsilon$  was measured from the UV–vis spectrum of the compound in THF solution and  $c l$  was estimated from cyclic voltammogram.

Photocurrent switching experiments by the bicomponent SAM were carried out in the one-compartment cell described above. The current from the substrate was detected with the voltammetric analyzer described above. The concentrations of an electron donor, AsA, and an electron acceptor, MV, were 50 mM.

**Preparation of the Mixed-SAMs.** Preparation of mixed-self-assembled monolayers (mixed-SAMs) of two kind of fullerene compounds was carried out also using a simple dipping method: an ITO (as above) was immersed in the mixed solution of 1 and 2 (or 7 and FeC<sub>60</sub>(C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>COOH)<sub>5</sub>Cp). Total concentration of these compounds was also set at ca. 0.1 mM.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Photoelectrochemical data and AFM image of the modified ITO electrode. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## ■ ACKNOWLEDGMENT

This work was financially supported by Japan Society for the Promotion of Science (Funding Program for Next Generation World-Leading Researchers) and MEXT, Japan (KAKENHI, No. 22000008 and the Global COE program).

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(19) Another reason is that one cannot increase the quantum yield by relying on the use of bias voltage to enhance the quantum yield of the mixed SAM because the bias voltage shifts the anodic/cathodic tipping point toward shorter wavelengths than 450 nm making the photoswitching action less effective. One solution would be the use of a ferrocene complex of a higher fullerene that absorbs longer wavelength light, although such a compound is thus far unknown.

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