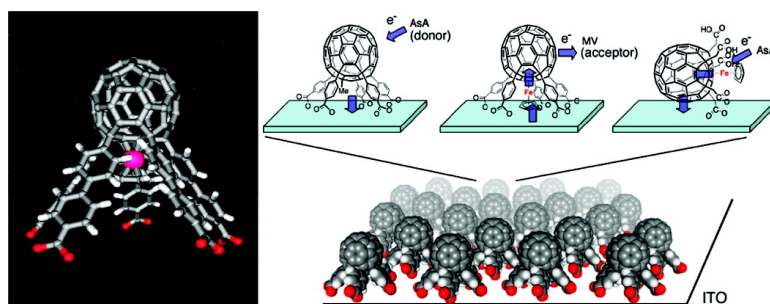


Photocurrent-Generating Properties of Organometallic Fullerene Molecules on an Electrode

Yutaka Matsuo, Katsuhiko Kanaizuka, Keiko Matsuo, Yu-Wu Zhong, Takahiro Nakae, and Eiichi Nakamura

J. Am. Chem. Soc., **2008**, 130 (15), 5016-5017 • DOI: 10.1021/ja800481d • Publication Date (Web): 15 March 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 8 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
 High quality. High impact.

Photocurrent-Generating Properties of Organometallic Fullerene Molecules on an Electrode

Yutaka Matsuo,* Katsuhiko Kanaizuka, Keiko Matsuo, Yu-Wu Zhong, Takahiro Nakae, and Eiichi Nakamura*

Nakamura Functional Carbon Cluster Project, ERATO, Japan Science and Technology Agency, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Received January 21, 2008; E-mail: matsuo@chem.s.u-tokyo.ac.jp; nakamura@chem.s.u-tokyo.ac.jp

Although the properties of molecules depend primarily on their molecular structure, they also depend heavily on the molecular orientation relative to the surroundings. In particular, two issues are crucial for the design of organic molecular electronic devices: how donor and acceptor modules are built into a molecule and how such molecules are oriented on an electrode.^{1–7} While the conventional design of molecular electronics has often called for the utilization of complex and flexible molecules, simple and rigid molecules are undoubtedly more desirable for studies on the relationship between molecular structure and the performance of molecular devices. With this issue in mind, we synthesized compact and rigid fullerene molecules bearing five anchoring legs (1–7, Figure 1), to which we can covalently attach an organic or a metallic group with a minimal change in the molecule's outer shape,^{8,9} deposited them as a self-assembled monolayer (SAM) on an indium–tin oxide (ITO) surface,^{10,11} and studied the photocurrent generated upon irradiation. Herein, we report that these devices exhibit a respectable quantum yield for photocurrent generation up to 18%, and, more importantly, the direction of the photocurrent can be changed not only by the molecular structure itself but also by changing the geometric configuration of the photoactive acceptor (fullerene) and donor (metal atom)¹² on the ITO surface. Thus, the observations showed an important correlation between molecular structure, molecular orientation, and device properties and will provide useful insights for the design of molecular arrays to be used in molecular electronics.^{13–15}

Molecules 1–7 (Figure 1a) have two important structural features in common.¹⁶ First, the structure resembles the Apollo lunar landing module and has a cavity between the five legs, with which the molecule can be bonded to the ITO surface with the aid of five carboxylic acid groups. Second, beneath the photoexcitable [60]fullerene, the pentapod structure forms a cavity that can accommodate a donor metal atom with negligible change in the outer profile of the molecule. The cavity structure can physically and electronically isolate the metal atom from the metal atoms in the neighboring molecules on the electrode. The cavity formed by the five biphenylene¹⁷ legs in 1–3 is big enough to accommodate easily a methyl group (1), an iron(II) atom (2, bucky ferrocene), or a ruthenium(II) atom (3, bucky ruthenocene).^{8,18–20}

According to our previous photophysical study of the excited states of simpler bucky ferrocenes and ruthenocenes,¹² 1 will generate a triplet excited state with a microsecond lifetime upon photoexcitation, the ferrocene 2 will generate a charge-separated state with a picosecond lifetime through very rapid electron donation from the iron(II) atom to the fullerene moiety, and the ruthenocene 3 will show an intermediate behavior to generate both a triplet state and a charge transfer state. The crystal

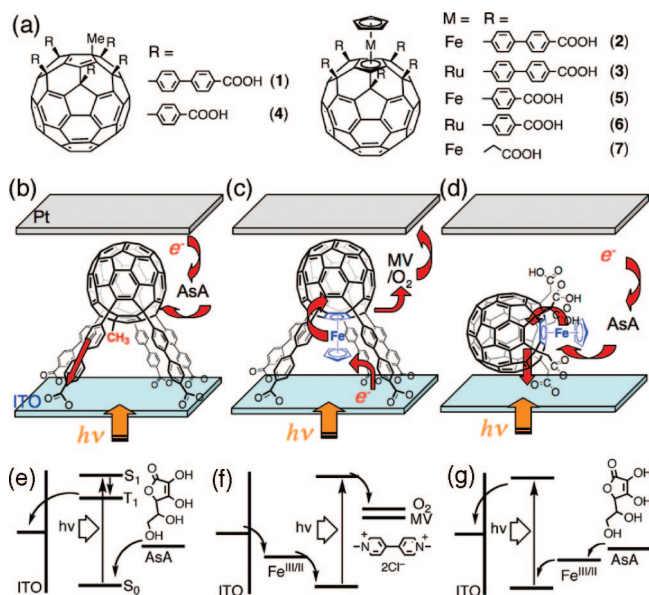


Figure 1. (a) Structures of the molecules used in this study. (b–d) Plausible geometric configurations and schematic representations of photocurrent generation for 1, 2, and 7. (e–g) Orbital diagrams for photocurrent generation for 1, 2, and 7, respectively.

structure shows that the methylene ferrocene 7²¹ cannot stand upright on ITO because the methylene legs are so short that the bulky ferrocene group protrudes from the cavity.

To study the structure/activity relationship, we formed SAMs of 1–7 on an ITO electrode by immersing the electrode in a THF solution of the compound until the surface coverage became constant (about 3 days, 0.07–0.1 nmol/cm² for 1–3, which is the range expected for monolayer coverage assuming complete flatness of ITO; Supporting Information)²² and then rinsing with THF. The corresponding ethyl esters did not bind to ITO at all, indicating the importance of the carboxylic acid groups for SAM formation. The photocurrent generation properties of the molecules attached to an ITO electrode (with a platinum counter electrode) were examined under two different conditions: one by the use of ascorbic acid (AsA) as a sacrificial electron donor electrolyte placed between the electrodes, and another by the use of molecular oxygen/methyl viologen (MV) as an electron acceptor, both studied with a bias voltage between 0 and \pm 0.1 V. The performance of the device function was evaluated on the basis of the number of electrons generated per photon absorbed by the molecules (quantum yield ϕ , %). Agreement of the action spectra of the molecules (400–600 nm) with their absorption spectra indicated that the fullerene molecules are the photoactive species (Supporting Information).

Table 1. Quantum Yield of Anodic and Cathodic Photocurrent (φ_a and φ_c)^a

compound	anodic current, φ_a , %		cathodic current, φ_c , %	
	no bias	0.1 V bias	no bias	-0.1 V bias
1	7.2 ± 0.8	14.4 ± 1.5	0	0
2	0	0	3.6 ± 0.4	6.3 ± 0.7
3	8.9 ± 0.9	14.9 ± 1.5	6.0 ± 0.6	10.2 ± 1.0
4	7.7 ± 0.8	17.1 ± 1.8	0	0
5	0	0	2.8 ± 0.3	4.3 ± 0.5
6	9.1 ± 1.0	18.1 ± 1.9	<1	<1
7	2.0 ± 0.2 ^b	NA ^c	0	0

^a Quantum yield was measured for 400 nm irradiation. ^b The fullerene SAM coverage of the ITO surface was very low for this compound, and the SAM was unstable during the measurement. ^c Not available because the SAM rapidly degraded even when a small bias voltage was applied.

The quantum yield discussed below refers to the values upon light irradiation at 400 nm.

The measurements showed two very clear trends for molecules **1**, **2**, **3**, and **7** on ITO: one for the set of the three biphenylene molecules **1–3** and another for the pair of **1–3** and the methylene molecule **7** (Table 1, compounds **1–7** as listed in this order). The phenylene molecules **4**, **5**, and **6** showed behavior similar to that of their biphenylene analogue except for the lower performance in the cathodic section. The 17–18% quantum yield recorded for **4** and **6** is comparable to the best data reported for various fullerene/ITO photocurrent-generating systems.¹⁰

The methyl-capped biphenylene molecule **1** on ITO generated an anodic photocurrent (to ITO) in 7.2% quantum yield upon use of AsA as a sacrificial electron donor without bias voltage and in 14.4% quantum yield upon application of a 0.1 V bias. It generated no cathodic current when O₂/MV was used as an electron acceptor. In contrast, the ferrocene molecule **2** generated a cathodic current upon use of O₂/MV with up to 6.3% quantum yield but no anodic current upon use of AsA. The ruthenocene analogue **3** generated both anodic (up to 14.9%) and cathodic currents (up to 10.2%). In contrast to the biphenylene counterpart **2**, the ruthenocene **6** with the phenylene spacer generated mainly the anodic current. Similarly, the methylene ferrocene molecule **7** generated only an anodic current, albeit in a low quantum yield.

In Figure 1b–g, we show a series of diagrams of molecular orientations and molecular orbitals that accounts for the observed photocurrent generation behavior. Figure 1b,e illustrates a mechanism for the anodic current generation by **1**, for which only a triplet photoexcited state with a microsecond order lifetime is available.¹² Thus, a triplet photoexcited state of **1** accepts an electron to its lower singly occupied orbital from the low-lying HOMO of the ambient AsA and donates an electron to ITO.

Figure 1c,f illustrates a mechanism for the cathodic current generation by **2** in the presence of O₂/MV. Photoexcitation of the fullerene moiety generates a charge-separated state with a picosecond lifetime by rapid electron transfer from the ferrocene group.¹² Because the pentapod structure forces the cationic ferrocene group to be sandwiched between the fullerene and the ITO surface, ITO supplies an electron to the ferrocene group faster than to the fullerene group, the overall result being the generation of a cathodic photocurrent.

The molecular orientation of the biphenylene ruthenocene **3** must be the same as that for ferrocene **2** (Figure 1c). We therefore ascribe the ambivalent behavior of **3** to the ability of

bucky ruthenocenes to generate both triplet and charge-separated states.¹² A fraction of the molecules on ITO go to the triplet excited state and behave like the methyl-capped molecule **1**, while another fraction of the molecules goes to the charge-separated state and behaves like ferrocene **2**.

We ascribe the anodic photocurrent observed for the methylene ferrocene **7** to the inability of **7** to stand upright on the ITO surface and propose Figure 1d,g to describe a possible mechanism. Here, the ferrocene group is not sandwiched between fullerene and ITO but instead exposed directly to the electrolyte. The ferrocene therefore accepts an electron from AsA rather than from ITO and hence generates only the anodic current. We consider that a similar situation also exists in the phenylene molecules **5** and **6**, which generates the cathodic current with low and very low efficiency, respectively. Molecular models suggest that the bottom cavity created by the phenylene groups can accommodate the ferrocene and ruthenocene moieties with some and considerable difficulty, respectively. Thus, these molecules may be unable to stand perfectly upright on the ITO surface.^{16,18}

In summary, we have shown that the nanometer-sized, rigid molecular structure of [60]fullerene is useful for the synthesis of compact, pentapod molecular structures and for construction of photocurrent-generating devices on an ITO surface. The properties of the devices indicated that we can change the properties both by chemical modification of the interior area of the molecules without significant change to the outer profile of the molecules and by changing the geometric configuration of the photoactive acceptor (fullerene) and the donor (metal atom) on the ITO surface.

Supporting Information Available: Procedures for the synthesis of new compounds **1–7**, crystallographic data for **5** (CIF file), SAM characterization, and details of the photocurrent measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Joachim, C.; Gimzewski, J. K.; Aviram, A. *Nature* **2000**, *408*, 541.
- Bach, U.; Lupo, D.; Comte, P.; Moser, J. E.; Weissörtel, F.; Salbeck, J.; Spreitzer, H.; Grätzel, M. *Nature* **1998**, *395*, 583.
- Saha, S.; Johansson, E.; Flood, A. H.; Tseng, H.-R.; Zink, J. I.; Stoddart, J. F. *Chem.-Eur. J.* **2005**, *11*, 6846.
- Yasutomi, S.; Morita, T.; Imanishi, Y.; Kimura, S. *Science* **2004**, *304*, 1944.
- Imahori, H.; Sakata, Y. *Adv. Mater.* **1997**, *9*, 537.
- Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40.
- Shirai, Y.; Cheng, L.; Chen, B.; Tour, J. M. *J. Am. Chem. Soc.* **2006**, *128*, 13479.
- Sawamura, M.; Kuninobu, Y.; Toganoh, M.; Matsuo, Y.; Yamanaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **2002**, *124*, 9354.
- Zhong, Y.-W.; Matsuo, Y.; Nakamura, E. *Org. Lett.* **2006**, *8*, 1463.
- Cho, Y.-J.; Ahn, T. K.; Song, H.; Kim, K. S.; Lee, C. Y.; Seo, W. S.; Lee, K.; Kim, S. K.; Kim, D.; Park, J. T. *J. Am. Chem. Soc.* **2005**, *127*, 2380.
- Yamada, H.; Imahori, H.; Nishimura, Y.; Yamazaki, I.; Ahn, T. K.; Kim, S. K.; Kim, D.; Fukuzumi, S. *J. Am. Chem. Soc.* **2003**, *125*, 9129.
- Guldi, D. M.; Rahman, G. M. A.; Marczak, R.; Matsuo, Y.; Yamanaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **2006**, *128*, 9420.
- Carroll, R. L.; Gorman, C. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 4378.
- Kubatkin, S.; Danilov, A.; Hjort, M.; Cornil, J.; Brédas, J.-L.; Stühr-Hansen, N.; Hedegård, P.; Bjørnholm, T. *Nature* **2003**, *425*, 698.
- Venkataraman, L.; Klare, J. E.; Nuckolls, C.; Hybertsen, M. S.; Steigerwald, M. L. *Nature* **2006**, *442*, 904.
- Crystal structure of **5** is stored in Supporting Information.
- Sawamura, M.; Kawai, K.; Matsuo, Y.; Kanie, K.; Kato, T.; Nakamura, E. *Nature* **2002**, *419*, 702.
- Matsuo, Y.; Kuninobu, Y.; Ito, S.; Nakamura, E. *Chem. Lett.* **2004**, *33*, 68.
- Toganoh, M.; Matsuo, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2003**, *125*, 13974.
- Hamasaki, R.; Matsuo, Y.; Nakamura, E. *Chem. Lett.* **2004**, *33*, 328.
- Nakae, T.; Matsuo, Y.; Nakamura, E. *Org. Lett.* **2008**, *10*, 621.
- Shi, X.; Caldwell, W. B.; Chen, K.; Mirkin, C. A. *J. Am. Chem. Soc.* **1994**, *116*, 11598.

JA800481D