Highly Efficient Photocurrent Generation from a Self-Assembled Monolayer Film of a Novel C_{60}-Tethered 2,5-Dithienylpyrrole Triad

Kyoung-Soo Kim, Mun-Sik Kang, Hong Ma, and Alex K.-Y. Jen*

Department of Materials Science and Engineering, University of Washington, Seattle, Washington 98185-2120

Received April 27, 2004. Revised Manuscript Received August 17, 2004

A C_{60}-tethered 2,5-dithienylpyrrole triad was synthesized and the self-assembled monolayer (SAM) on a gold electrode was prepared. The three-electron reduced C_{60} radical anions of the triad in both solution and SAM film at room temperature were detected. The redox kinetics between the C_{60} moieties and the gold electrode is faster compared to that of the C_{60} SAMs with nonconjugated flexible bridge/anchor systems, as determined by smaller peak splitting in the cyclic voltammogram. The photocurrent generated in a (Au/C_{60}-triad/MV^{2+}/Pt) cell upon irradiation of light is exceptionally large (3200 nA/cm^2) with high quantum yield (51%). The electron-rich characteristics of the molecule and the rigid conjugated molecular framework stabilize the C_{60} radical anions generated during electrochemical reduction and lead to remarkable enhancement of photocurrent generation.

Introduction

Due to its unique three-dimensional structure and high degree of π-electron delocalization, C_{60} and its functional derivatives are studied extensively to understand and utilize their interesting photochemical, photophysical, and electrochemical properties.[1−3] In particular, C_{60}-based thin films have potential applications in photoconductivity, superconductivity upon doping with alkali metals, nonlinear optics, and biological activity.[4] The successful technological application of these thin films relies heavily on novel syntheses to modify C_{60} with desired functional groups as well as the ability to form highly ordered arrangements on a surface. Self-assembly is a superior approach to achieve thin-film materials because self-assembled monolayers (SAMs) are formed spontaneously by chemisorption, yielding robust and well-defined structures on chosen substrates.[5] Conjugated molecules with covalently bonded fullerenes have been reported to form a long-lived charge-separated state via photoinduced electron transfer.[6] Therefore, various attempts have been made to develop photovoltaic cells with functionalized C_{60}s on electrodes, taking advantage of the structural regularity of SAMs.[7] Recently, Imahori et al. have reported large photocurrent generation in their oligothiophene-linked C_{60} SAMs on a gold electrode with high quantum efficiency.[8] More recently, we discovered in our laboratory that the self-assemblies of 4-mercaptophenyl-9-anthrylacetylene (MPAA) and MPAA−C_{60} (where C_{60} is covalently attached at the 10-position of anthracene in MPAA) on Au(111) form a highly ordered two-dimensionally staked array through the interplay of strong intermolecular $\pi-\pi$ stacking and chemisorptive thiol−gold interactions.[9] In addition, the SAM of MPAA−C_{60} on gold electrode also demonstrated efficient photocurrent generation upon illumination with white light.[10] Although both of these results showed very promising photocurrent generation, most C_{60}−molecular

---

* To whom correspondence should be addressed. E-mail: ajen@u.washington.edu.

(1) (a) Mirkin, C. A.; Caldwell, W. B. *Tetrahedron* **1996**, *52*, 5113. (b) Prato, M. *Top. Curr. Chem.* **1999**, *199*, 173. (c) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789.

(2) (a) Guldi, D. M.; Prato, M. *Acc. Chem. Res.* **2000**, *33*, 695 and references therein. (b) Arbogast, J. W.; Foote, C. S.; Kao, M. *J. Am. Chem. Soc.* **1992**, *114*, 2277. (c) Shi, X.; Caldwell, W. B.; Chen, K.; Mirkin, C. A. *J. Am. Chem. Soc.* **1994**, *116*, 11598. (d) Hatano, T.; Ikeda, A.; Akiyama, T.; Yamada, S.; Sano, M.; Kanekiyo, Y.; Shinkai, S. *J. Chem Soc., Perkin Trans. 2* **2000**, *5*, 909.

(3) (a) Beckers, E. H. A.; Hal, P. A.; Dhanabalan, A.; Meskers, S. C. J.; Knol J.; Hummelen, J. C.; Janssen, R. A. J. *J. Phys. Chem. A* **2003**, *107*, 6218. (b) Guildi, D.; Huie, R. E.; Neta, P.; Hungerbuhler, H.; Asmus, K. D. *Chem. Phys. Lett.* **1994**, *223*, 511. (c) Maggini, M.; Dono, A.; Scorrano, G.; Prato, M. *J. Chem. Soc., Chem. Commun.* **1995**, 843. (d) Echegoyen, L.; Echegoyen, L. E. *Acc. Chem. Res.* **1998**, *31*, 593.

(4) (a) Prato, M. *J. Mater. Chem.* **1997**, *7*, 1097. (b) Diederich, F.; Gómez-López, M. *Chem Soc. Rev.* **1999**, *28*, 263 and references therein. (c) Boutorine, A. S.; Tokuyama, H.; Takasugi, M.; Isobe, H.; Nakamura, E.; Helene, C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2462. (d) Hebard, A. F.; Rosseinski, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. *Nature* **1991**, *350*, 600. (e) Holczer, K.; Klein, O.; Huang, S.-M.; Kaner, R. B.; Fu, K.-J.; Whetten, R. L.; Diederich, F. *Science* **1991**, *252*, 1154. (f) Haddon, R. C. *Acc. Chem. Res.* **1992**, *25*, 127. (g) Rosseinsky, M. J. *J. Mater. Chem.* **1995**, *5*, 1497. (h) Tutt, L. W.; Kost, A. *Nature* **1992**, *356*, 225. (i) Kajzar, F.; Taliani, C.; Danieli, R.; Rossini, S.; Zamboni, R. *Chem. Phys. Lett.* **1994**, *217*, 418.

(5) (a) Ulman, A. *An Introduction to Ultrathin Organic Films*; Academic Press: San Diego, CA, 1991. (b) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.

(6) (a) Segura, J. L.; Martín, N. *J. Mater. Chem.* **2000**, *10*, 2403−2435. (b) Fujitsuka, M.; Ito, O.; Yamashiro, T.; Aso, Y.; Otsubo, T. *J. Phys. Chem. A* **2000**, *104*, 4876−4881. (c) van Hal, P. A.; Knol, J.; Langeveld-Voss, B. M. W.; Meskers, S. C. J.; Hummelen, J. C.; Janssen, R. A. J. *J. Phys. Chem. A* **2000**, *104*, 5974−5988. (d) Fujitsuka, M.; Matsumoto, K.; Ito, O.; Yamashiro, T.; Aso, Y.; Otsubo, T. *Res. Chem. Intermed.* **2001**, *27*, 73−88.

(7) (a) Imahori, H.; Azuma, T.; Ajavakom, A.; Norieda, H.; Yamada, H.; Sakata, Y. *J. Phys. Chem. B* **1999**, *103*, 7233. (b) Imahori, H.; Norieda, H.; Yamada, H.; Nishimura, Y.: Yamazaki, I.; Sakata, Y.; Fujuzumi, S. *J. Am Chem. Soc.* **2001**, *123*, 100. (c) Imahori, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y. *J. Phys. Chem. B* **2000**, *104*, 2099. (d) Dominguez, O.; Echegoyen, L.; Cunha, F.; Tao, N. *Langmuir* **1998**, *14*, 821.

(8) Hirayama, D.; Takimiya, K.; Aso, Y.; Otsubo, T.; Hasobe, T.; Yamada, H.; Imahori, H.; Fukuzumi, S.; Sakata, Y. *J. Am. Chem. Soc.* **2002**, *124*, 532.

10.1021/cm049322i CCC: $27.50

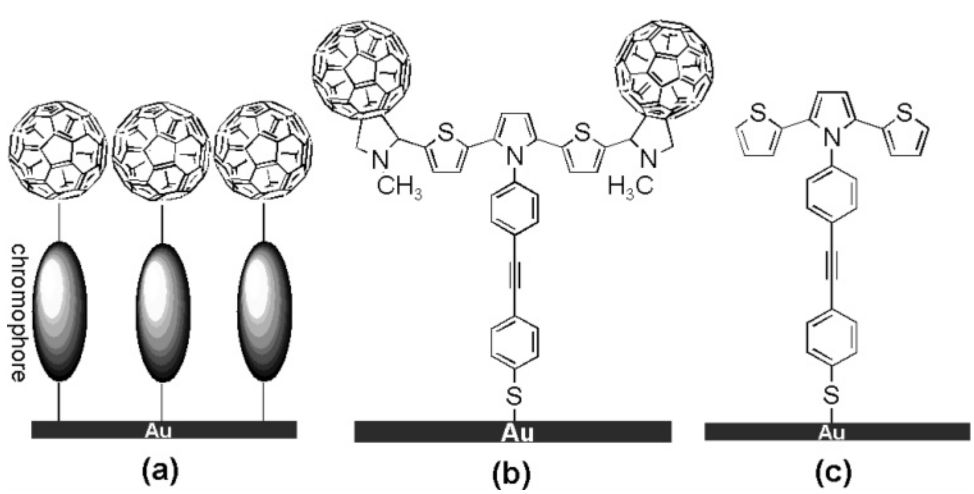


Figure 1. Schematic representations of SAMs: (a) since chromophores are embedded inside the film, light absorption by the chromophore is limited; (b) the C_{60}s and the chromophores are spatially separated, making exposing the chromophores to light irradiation; (c) control.

dyad or triad systems reported so far have C_{60}s attached linearly to either donor or acceptor segments causing one of the active segments to be embedded when they form a SAM film, which may limit their light harvesting properties (Figure 1a). Our strategy to enhance their light absorption ability is to attach a C_{60} at both ends of an electron-rich 2,5-dithienylpyrrole chromophore to prevent C_{60} from blocking the chromophore core so that more light can be absorbed by the chromophore. In this structure, the C_{60}s and the chromophore are spatially separated, which increases the molecule's efficiency in light harvesting (Figure 1b).

Here we report a newly synthesized rigid C_{60}-tethered 2,5-dithienylpyrrole triad, describing its synthesis, electrochemical properties, and highly efficient photocurrent generation in SAMs. The π-conjugated 2,5-dithenylpyrrole was chosen as a donor segment, whereas the C_{60} acts as an acceptor. The phenylethynyl moiety was chosen to provide a rigid framework in the molecular structure for forming a stable and conducting footing in the SAM. It is also expected that the use of more electron-rich 2,5-dithienylpyrrole may further extend the lifetime of the charge-separated state of the system, since the oxidation potential of the dithienylpyrrole is lower (ca. +0.7 V vs SCE) than that of its ter-thiophene analogues (ca. +0.95 V vs SCE).[11] Photocurrent generation from a SAM film of the new C_{60} triad on a gold electrode is remarkably efficient compared to those of the previously studied C_{60} dyad or triad systems.[12]

Experimental Section

Buckminsterfullerene (C_{60}) was purchased from Bucky USA and used as received. All other reagents were purchased from Aldrich and used without further purification unless otherwise indicated. ^1H NMR spectra were recorded on an AF 300 (300 MHz) spectrometer with the solvent proton signal as standard. Mass spectra were recorded on a JEOL HX-110 mass spectrometer or Bruker biflex III MALDI-TOF MS.

Synthesis of 1,4-Di-thiophene-2-yl-butane-1,4-dione (2). Compound **2** was synthesized by following the procedures reported in ref 17.[17]

1-(4-Bromo-phenyl)-2,5-di-thiophene-2-yl-1H-pyrrole (3). A three-neck round-bottomed flask equipped with a Dean–Stark trap, a reflux condenser, and a nitrogen inlet was charged with 2.5 g (10 mmol) of 1,4-di-thiophene-2-yl-butane-1,4-dione (**2**), 2.58 g (15 mmol) of 4-bromoaniline, 10 mmol of acetic acid, and 40 mL of benzene. This reaction mixture was stirred and refluxed for 72 h under nitrogen. Evaporation of the benzene, followed by column chromatography (SiO_2, eluting with 25% ethyl acetate in hexane) gave the targeted compound[18] (pale yellow crystals). Yield 67%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.54 (dd, 2H), 7.17 (d, 2H), 7.10 (dd, 2H), 6.85 (dd, 2H), 6.54 (dd, 2H), 6.52 (s, 2H). MS (FAB): *m/z* 287 (MH^+).

2,5-Di-thiophen-2-yl-1-(4-trimethylsilanylethylnyl-phenyl)-1H-pyrrole. A round-bottomed pressure tube was charged with 1-(4-bromo-phenyl)-2,5-di-thiophene-2-yl-1*H*-pyrrole (3) (1.93 g, 5 mmol), dichlorobis(triphenylphosphine)palladium (II) (0.14 g, 0.2 mmol), copper (I) iodide (0.038 g, 0.2 mmol), tri-*tert*-butylphosphine (0.2 g, 1 mmol), diisopropylethylamine (20 mL), and THF (50 mL). The reaction tube was degassed and back-filled with nitrogen, and then trimethylsilylacetylene (4 mL, 28 mmol) was added. The reaction mixture was stirred at 50 °C (oil-bath temperature) for 28 h. After the solvent was removed, the residue was diluted with methylene chloride and washed with a saturated solution of ammonium chloride followed by brine. The aqueous phases were extracted with methylene chloride and the combined organic phases were dried over anhydrous magnesium sulfate, filtered, and concentrated. The resulting residue was purified by flash column chromatography (SiO_2, eluting with hexane then 20% ethyl acetate in hexane) to afford analytically pure product (pale yellow powder). Yield 53%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.53 (dd, 2H), 7.17 (d, 2H), 7.09 (dd, 2H), 6.85 (dd, 2H), 6.54 (dd, 2H), 6.51 (s, 2H), 0.27 (s, 9H). MS (FAB): *m/z* 404 (MH^+).

---

(9) (a) Zareie, M. H.; Ma, H.; Reed, B. W.; Jen, A. K.-Y.; Sarikaya, M. *Nano Lett.* **2003**, *3*, 139. (b) Kang, S. H.; Ma, H.; Kang, M.-S.; Kim, K.-S.; Jen, A. K.-Y.; Zareie, M. H.; Sarikaya, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1512.

(10) Kang, M.-S.; Kang, S. H.; Ma, H.; Kim, K.-S.; Jen, A. K.-Y. Manuscript in preparation.

(11) (a) Ferraris, J. P.; Skiles, G. D. *Polymer* **1987**, *28*, 179. (b) Ferraris, J. P.; Newton, M. D. *Polymer* **1992**, *33*, 391.

(12) (a) Hirayama, D.; Yamashiro, T.; Takimiya, K.; Aso, Y.; Otsubo, T.; Norieda, H.; Imahori, H.; Sakata, Y. *Chem. Lett.* **2000**, 570–571. (b) Otsubo, T.; Aso, Y.; Takimiya, K. *J. Mater. Chem.* **2002**, *12*, 2565.

(13) Ogura, K.; Yanai, H.; Miokawa, M.; Akazome, M. *Tetrahedron Lett.* **1999**, *40*, 8887.

(14) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798.

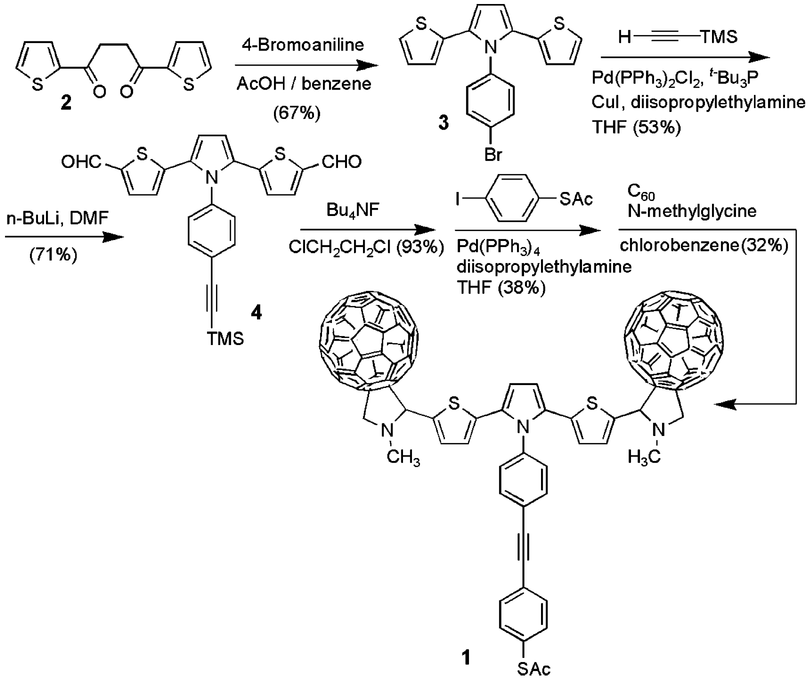
(15) Imahori, H.; Azuma, T.; Ozawa, S.; Yamada, H.; Ushida, K.; Ajavakom, A.; Norieda, H.; Sakata, Y. *Chem. Commun.* **1999**, 557.

(16) Lahav, M.; Heleg-Shabtai, V.; Wasserman, J.; Katz, E.; Willner, I.; Durr, H.; Hu, Y. Z.; Bossmann, S. H. *J. Am. Chem. Soc.* **2000**, *122*, 11480.

(17) Ogura, K.; Yanai, H.; Miokawa, M.; Akazome, M. *Tetrahedron Lett.* **1999**, *40*, 8887.

(18) The Benzoin–Stetter reaction with 4-iodoaniline was not successful. The reaction gave only polymeric black tar-like compound that could not be dissolved in any solvent. No attempt has been made to identify the product.

Scheme 1. Synthesis of C_{60}-Tethered 2,5-Dithienylpyrrole Triad



2,5-Bis(5-formyl-thiophen-2-yl)-1-(4-trimethylsilanylethynyl-phenyl)-1*H*-pyrrole (4). To an ice/salt-cooled mixture of 2,5-di-thiophen-2-yl-1-(4-trimethylsilanylethylnylphenyl)-1*H*-pyrrole (4.1 g, 10 mmol) and 2,2,6,6-tetramethylpiperidine (3.53 g, 25 mmol) in dry THF, *n*-butyllithium (1.6 M, 25 mmol) was added under nitrogen with stirring. After the mixture was stirred for 30 min, it was cooled to −78 °C with an acetone/dry ice bath, and a solution of anhydrous DMF (30 mmol) in dry THF was added. After stirring the mixture at that temperature for an hour, it was slowly brought up to room temperature and stirred for another hour. The reaction mixture was then poured into a water/diethyl ether mixture and the aqueous phase was extracted several times with diethyl ether. The combined organic fractions were dried over anhydrous magnesium sulfate, filtered, and concentrated to afford greenish yellow crystals. Subsequent purification by flash column chromatography (SiO_2, eluting with 10% ethyl acetate in hexane) resulted in pure 2,5-bis(5-formyl-thiophen-2-yl)-1-(4-trimethylsilanylethynyl-phenyl)-1*H*-pyrrole (fine green crystals with strong fluorescence). Yield 71%. ^1H NMR (300 MHz, $CDCl_3$): δ 9.71 (s, 2H), 7.56 (d, 2H), 7.41 (d, 2H), 7.25 (d, 2H), 6.75 (s, 2H), 6.57 (d, 2H), 0.27 (s, 9H). MS (FAB): *m/z* 460 (MH^+).

1-(4-Ethynyl-phenyl)-2,5-bis-(5-formyl-thiophen-2-yl)-1*H*-pyrrole. In a round-bottomed flask 2,5-bis(5-formyl-thiophen-2-yl)-1-(4-trimethylsilanylethynyl-phenyl)-1*H*-pyrrole (**4**) (2.3 g, 5.0 mmol) was dissolved in THF and cooled to 0 °C. Tetrabutylammonium fluoride (1.5 equiv, 1.0 M in THF) was added, and the reaction was stirred for 6 h. The reaction mixture was then subjected to an aqueous workup and the aqueous phase was extracted with methylene chloride. Combined organic fractions were washed with water, dried over anhydrous magnesium sulfate, then concentrated. The crude product could be used without further purification. Purification by flash column chromatography (SiO_2, eluting with 10% ethyl acetate in hexane) gave pure 1-(4-ethynyl-phenyl)-2,5-bis-(5-formyl-thiophen-2-yl)-1*H*-pyrrole (fine greenish red crystals with strong fluorescence). Yield 93%. ^1H NMR (300 MHz, $CDCl_3$): δ 9.69 (s, 2H), 7.57 (d, 2H), 7.39 (d, 2H), 7.22 (d, 2H), 6.71 (s, 2H), 6.55 (d, 2H), 3.21 (s, 1H). MS (FAB): *m/z* 388 (MH^+).

Thioacetic acid 4-{4-[2,5-bis-(5-formyl-thiophen-2-yl)-pyrrol-1-yl]-phenylethynyl}-phenyl ester. A round-bottomed thick-wall pressure tube was charged with 1-(4-ethynylphenyl)-2,5-bis-(5-formyl-thiophen-2-yl)-1*H*-pyrrole (0.33 g, 0.85 mmol), terakis(triphenylphosphine) palladium (0.06 g, 0.05 mmol), diisopropylethylamine (10 mL), THF (20 mL), and thioacetic acid *S*-(4-iodo-phenyl)ester[19] (0.24 g, 0.85 mmol). The reaction tube was degassed and back-filled with nitrogen and then sealed. The reaction mixture was stirred at 50 °C (oil-bath temperature) overnight. After the solvent was removed, the residue was diluted with methylene chloride and washed with a saturated solution of ammonium chloride and then brine. The aqueous phases were extracted with methylene chloride several times and the combined organic phases were dried over anhydrous magnesium sulfate, filtered, and concentrated. The resulting residue was purified by flash column chromatography (SiO_2, eluting with hexane then 15% ethyl acetate in hexane) to afford pure thioacetic acid 4-{4-[2,5-bis-(5-formyl-thiophen-2-yl)-pyrrol-1-yl]-phenylethynyl}-phenyl ester. Yield 38%. ^1H NMR (300 MHz, $CDCl_3$): δ 9.69 (s, 2H), 7.61 (d, 2H), 7.41 (d, 2H), 7.32 (d, 2H), 7.22 (dd, 4H), 6.71 (s, 2H), 6.58 (d, 2H), 2.43 (s, 3H). MS (FAB): *m/z* 538 (MH^+).

C_{60}-Tethered Triad 1. A solution of thioacetic acid 4-{4-[2,5-bis-(5-formyl-thiophen-2-yl)-pyrrol-1-yl]-phenylethynyl}-phenyl ester (50 mg, 0.09 mmol), finely ground sarcosine (*N*-methylglycine, 0.07 g, 0.72 mmol), and C_{60} (0.26 g, 0.36 mmol) in chlorobenzene (60 mL) was stirred and refluxed for 19 h under nitrogen. At the completion of reaction, the mixture was cooled to room temperature. The insoluble solid was filtered and washed with toluene. The filtrate and the washing were combined and concentrated. The crude product was purified by flash column chromatography on silica gel, using toluene, 15% toluene in CS_2, and 20% ethyl acetate in toluene as eluents to afford targeted C_{60}-tethered triad 1 as brown solid. Yield 32%. ^1H NMR (300 MHz, $CS_2/CDCl_3$): δ 7.47 (d, 2H), 7.36 (d, 2H), 7.18 (dd, 4H), 6.94 (d, 2H), 6.72 (s, 2H), 6.48 (d, 2H), 5.34 (s, 2H), 5.11 (d, 2H), 4.36 (d, 2H), 3.18 (s, 6H), 2.43 (s, 3H). MS (MALDI-TOF): calcd for $C_{154}H_{29}N_3OS_3$, *m/z* = 2031.1; found, *m/z* = 2031.2 (M^+).

Results and Discussion

The procedure for the synthesis of the C_{60}-tethered 2,5-dithienylpyrrole triad **1** is summarized in Scheme 1. 1,4-Bis(2-thienyl)-1,4-butanedione, **2**, which was obtained via a Stetter reaction with 2-thiophenecarboxaldehyde and a Mannich base,[13] was reacted with

---

[19] Price, D. W.; Tour, J. M. *Tetrahedron* **2003**, *59*, 3131.

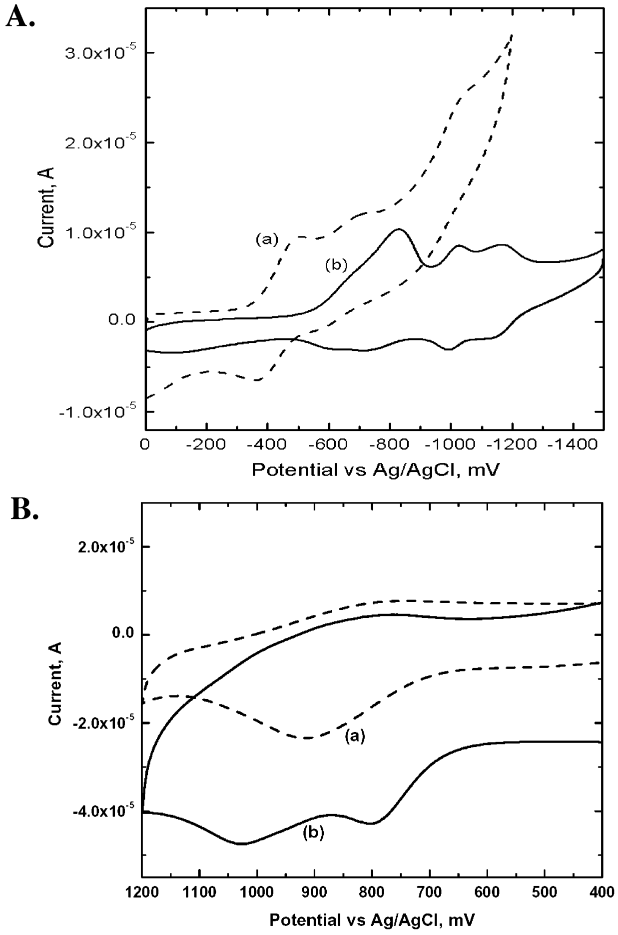


Figure 2. Cyclic voltammograms of (A) cathodic reduction and (B) anodic oxidation; (a) **1** in solution and (b) **1**/Au SAM in a solvent mixture of toluene/acetonitrile (4:1) containing 0.1 M Bu_4NPF_6 as electrolyte at a sweep rate of 100 mV s^{-1}.

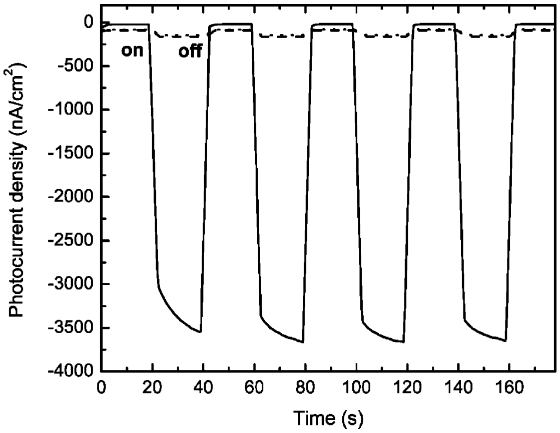


Figure 3. Photoelectrochemical responses of the [Au/1/MV^{2+}/Pt] cell (solid line), the [Au/MV^{2+}/Pt] cell (dotted line), and the [Au/control/MV^{2+}/Pt] (dashed line) cell upon irradiation with 0.85 mW cm^{-2} light (400 nm) on bias voltage of −100 mV vs Ag/AgCl.

bromoaniline in the presence of acetic acid under azeotropic conditions to yield 4-bromo-phenyl-2,5-dithienylpyrrole **3**. Compound **4** was prepared by Sonogashira reaction of **3** with (trimethylsilyl)acetylene followed by diformylation with *n*-BuLi/DMF. The trimethylsilyl group of **4** was first deprotected with Bu_4NF. The resulting phenylacetylene was coupled with 1-(*S*-acetylthio)-4-iodobenzene and then reacted with C_{60} using the Prato reaction condition[14] to afford the corresponding C_{60}-tethered 2,5-dithienylpyrrole triad **1**.

The SAM of the triad was prepared by immersing an Au substrate in a 200 μM solution of **1** in toluene at 25 °C for 48 h. Ammonium hydroxide solution was added to hydrolyze the acetyl protecting group. The thin-film sample was rinsed with toluene and ethanol, and then dried with a stream of nitrogen. The electrochemical properties of **1** and the **1**/Au film were evaluated using cyclic voltammetry (CV) in a solvent mixture containing toluene/acetonitrile (4:1) and 0.1 M Bu_4NPF_6 as electrolyte at a sweep rate of 100 mVs^{-1}. The SAM film of **1** on Au exhibited two irreversible redox waves at −0.70 and −0.83 V and two quasi-reversible waves at −1.02 and −1.16 V (E_p vs. Ag/AgCl) which are assigned to the reduction of the C_{60} moiety (Figure 2A). These peaks are slightly shifted to more negative potentials compared to those of **1** in solution. Although similar behavior was also reported previously for C_{60} SAMs,[7a] the detection of four reductive peaks of C_{60} in the molecular dyad or triad films at ambient temperature has not yet been reported because of the unstable nature of the three- or four-electron reduced C_{60} radical anion species. The value of the peak splitting ($\Delta E = \sim 110$ mV) is smaller than that of the C_{60} SAMs with nonconjugated flexible bridge/anchor groups,[7a,15] indicating faster redox kinetics between the C_{60} moieties and the gold electrode, possibly due to the rigid conjugated molecular framework. The SAM film of **1** on Au exhibited two irreversible waves at 0.80 and 1.02 V (E_p vs. Ag/AgCl) which are assigned to the oxidation of the pyrrolodithiophene moiety (Figure 2B). The calculated area per molecule is 122.6 Å², but the charge integration of the first reduction peak yields monolayer surface coverage (Γ) for **1**/Au of 7.1×10^{-11} mol cm^{-2} (233.6 Å² $molecule^{-1}$). This indicates that each molecule occupies a larger area on gold electrode than its dimension due to steric hindrance.

Photoelectrochemical experiments were carried out in a 0.1 M Na_2SO_4 aqueous electrolyte solution containing 50 mM of methyl viologen (MV^{+2}) acting as electron acceptor (mediator). Bare gold, a control molecule (Figure 1c), or a modified **1**/Au electrode (electrode area, 0.25 cm^2) was used as the working electrode along with a platinum counter electrode, and an Ag/AgCl reference electrode. A steady high cathodic current was generated immediately upon irradiation of the modified **1**/Au electrochemical cell with light. As shown in Figure 3, photochemical responses (on/off photoswitchable photocurrents) were recorded under illumination with a 400 nm monochromic light (0.85 $mWcm^{-2}$) at a bias voltage of −100 mV vs Ag/AgCl. The 400 nm light was chosen to maximize the absorption of the SAM **1**/Au (Figure 4). The observed value (3200 nA cm^{-2}) of photocurrent generated in the **1**/Au system is exceptionally large compared to the values from similar systems.[12,16] The large difference in photocurrent density generated from bare Au, control molecule/Au, and from **1**/Au is indicative of the involvement of both the chromophore and C_{60} moieties in the photoelectrochemical reaction.

There was a linear relationship between generated photocurrent density and light input power. The cathodic photocurrent increased monotonically with an increasingly negative bias applied to the gold electrode,

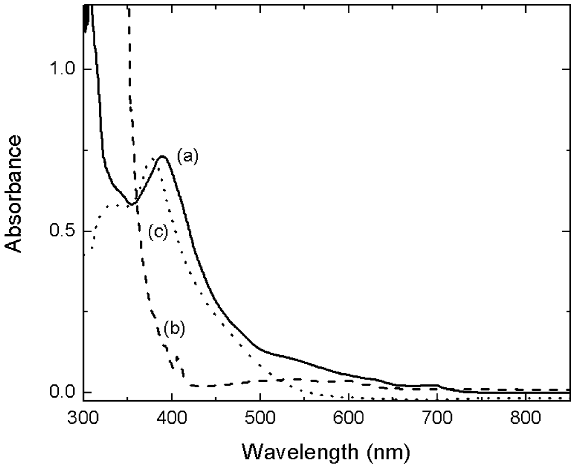


Figure 4. Absorption spectra of (a) triad **1**, (b) C_{60}, and (c) control molecule in toluene. Absorbance of control molecule was normalized for comparison.

which indicates that photocurrent flows from the gold electrode to the counter electrode through the SAM and the electrolyte. Following that the absorption spectrum of triad **1** exhibits decreased light absorption in a range of 350−600 nm, the action spectrum (Figure 5) of triad **1**/Au system shows decreased photocurrent density in that range of wavelength. The quantum yield based on the number of photons absorbed by **1** on a gold electrode was determined by using the input power, the photocurrent density, and the absorbance on gold electrode, and was estimated to be 51%,[20] which is much larger than that of the oligothiophene−fullerene dyad system[8] and is comparable to that of the ferrocene−porphyrin−fullerene triad system, which has the highest reported quantum yield.[6b]

We have designed and synthesized a new self-assembling C_{60}-tethered 2,5-dithienylpyrrole derivative with a rigid molecular framework. The detection of three-electron reduction of the C_{60} species both in solution and in a SAM film by electrochemical measurement has been demonstrated. Electron-rich characteristics of the donor molecule and faster redox kinetics between the C_{60} moieties and the gold electrode led to a large photocurrent generation in [Au/1/MV^{2+}/Pt] cell with high quantum efficiency. This design strategy is readily applicable to materials for highly efficient photovoltaic devices. The detailed photophysical studies along with development of practical applications for this material are currently underway and will be presented in due course.

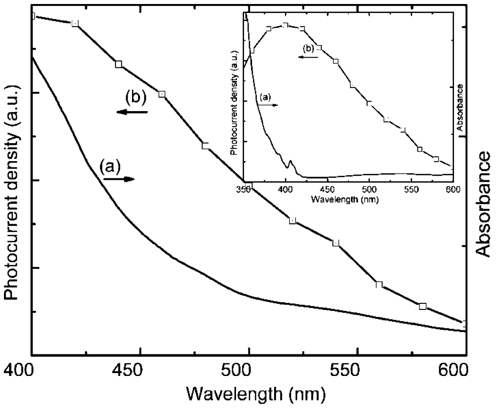


Figure 5. Absorption spectrum of (a) triad **1** and (b) action spectrum of [Au/**1**/MV^{2+}/Pt] cell. Inset: Absorption spectrum of (a) C_{60} and (b) action spectrum of [Au/**1**/MV^{2+}/Pt] cell.

Acknowledgment. We thank the Air Force Office of Scientific Research (AFOSR-BIC) and Army Research Office (ARO-DURINT) for their financial support.

CM049322I

---

[20] Quantum yield (ϕ) of photocurrent generation of the [Au/1/MV^{2+}/Pt] cell was calculated by following equation: $\phi = (i/e)/[I(1-10^{-A})]$, where $I = (W\lambda)/(hc)$, i is the photocurrent density, e is the elementary charge, I is number of photons per unit area and unit time, λ is the wavelength of light irradiated, A is absorbance of the adsorbed chromophores at λ, W is light power irradiated at λ, c is the light velocity, and h is the Planck constant. Absorbance (A) of the adsorbed chromophores at λ was calculated by assuming that the absorption coefficient of **1** on gold substrate is the same as that in solution and was estimated to be 0.0097.