

# Investigation of the Photoelectrochemistry of C<sub>60</sub> and Its Pyrrolidine Derivatives by Monolayer-Modified SnO<sub>2</sub> Electrodes

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A monolayer of a C<sub>60</sub> mixture with arachidic acid (1:1) and C<sub>60</sub>-pyrrolidine derivatives [C<sub>60</sub>(C<sub>3</sub>H<sub>6</sub>NR); R = H (**1**), C<sub>6</sub>H<sub>5</sub> (**2**), *o*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> (**3**), and *o*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub> (**4**)] were successfully obtained at the air/water interface and deposited onto solid substrates with transfer ratios of about 0.90 ± 0.05 at 30 mN·m<sup>-1</sup> by the Langmuir–Blodgett (LB) technique. The photoelectrochemical investigation of these compounds on SnO<sub>2</sub> electrodes was carried out. The photocurrent was determined under nitrogen atmosphere because oxygen can suppress the photocurrents. Results showed that electrons flow from the electrolyte through LB film to SnO<sub>2</sub> and a chemical energy conversion occurs together with the photoelectric conversion. Positive bias voltage, electron donor, the incident light intensity, and the electron-repulsion groups in the derivatives are beneficial factors for generating higher photocurrent. The quantum yields vary from 0.015 to 0.069 for C<sub>60</sub> and its derivatives **1–4**.

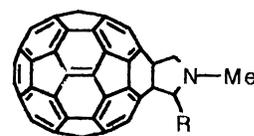
## Introduction

In the past 6 years, a rich “three-dimensional” chemistry of spherical and polyfunctional all-carbon molecules has been developed.<sup>1–3</sup> Investigations reveal that fullerenes and their derivatives, so-called fulleroids or organofullerenes, exhibit a variety of remarkable properties, for instance, superconductivity and molecular magnetism as well as catalytic and biological activity.<sup>2,8</sup> One of the most realistic applications seems to be the development of specific electronic devices.<sup>3c</sup> When the cast films on metal electrode surfaces, C<sub>60</sub> can act as an n-type semiconductor though the dark current is at least 1 order of magnitude larger than the photocurrent.<sup>4</sup> The bandgap of solid C<sub>60</sub> as a semiconductor is about 2 eV, and the conductivity can be varied between <10<sup>-7</sup> and 10 S/cm by doping.<sup>3b</sup> On the other hand, fullerenes and their derivatives are good electron acceptors and can be successively reduced up to six steps.<sup>5</sup> Polyvinyl carbazole doped with C<sub>60</sub> was shown to be a photoconductor, in which holes in the carbazole valence band act as the charge carriers and the C<sub>60</sub> molecules act as the photoactive electron acceptors.<sup>6</sup> When C<sub>60</sub> and C<sub>70</sub> are embedded within a lipid membrane, they act both as photosensitizers for efficient electron transfer from a donor and mediators for electron transport across the membrane.<sup>7</sup> In this process, electron transfer from the fullerene anions formed at the reductant interface occurs through fullerene aggregates in which the charges transfer by hopping and ultimately reach the oxidizing entities at the opposite interface.<sup>8</sup>

The monolayer film of the fullerenes is very sensitive to vibration, easy to aggregate, and very difficult to be transferred onto solid substrates<sup>9</sup> due to the very high hydrophobicity of the rigid ball-shape molecules.<sup>10</sup> It has been discovered that the introduction of polar atoms, such as nitrogen or oxygen, into the close-caged molecule can not only enhance their Langmuir film stability but also improve their monolayer transformation ability, in which the derivatives molecules really stand at the air/water interface. The monolayers were transferred

onto hydrophilically pretreated quartz substrates to form high-quality LB films, which has been demonstrated in previous work.<sup>11</sup> Besides, fullerenes and their derivatives can also form stable mixed Langmuir films with long-chain fatty acids or alcohols.<sup>9d,10a,c</sup> These mixed films could be easily transferred onto solid substrates with a uniform transfer ratio. However, the limiting area of the 1:1 mixed Langmuir films was much smaller than that it should be (around 93 Å<sup>2</sup>/molecule). In addition, solvents and the concentrations of spreading solutions also play an important role in making high-quality LB monolayers.<sup>10d</sup>

Here we wish to report the film formation properties of a series of C<sub>60</sub>-pyrrolidines derivatives C<sub>60</sub>(C<sub>3</sub>H<sub>6</sub>NR) (where R = H (**1**), C<sub>6</sub>H<sub>5</sub> (**2**), *o*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> (**3**), and *o*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub> (**4**)) and



R = H (**1**), -C<sub>6</sub>H<sub>5</sub> (**2**), *o*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> (**3**) and *o*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub> (**4**)

the photocurrent generation from the monolayer modified SnO<sub>2</sub> electrodes of these compounds (abbreviated as Fuller-SnO<sub>2</sub> electrodes). The dependencies of the photocurrents on some factors have been studied which may enhance or decrease the magnitude of the observed photocurrent, mainly, the bias voltage, the electron donor and acceptor in the electrolyte, and the light intensity as well as the electron attracting–repulsing effect of substituent groups bridged to C<sub>60</sub> by pyrrolidines. The mechanism of generating photocurrent is proposed, and a chemical energy conversion should take place together with the photoelectronic conversion.

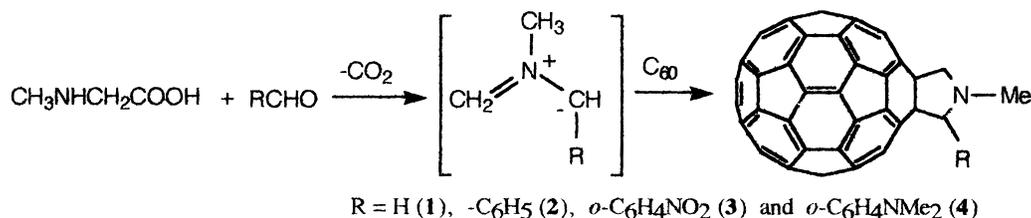
## Experimental Section

**Materials.** The C<sub>60</sub>/C<sub>70</sub> mixture was prepared in our lab according to the graphite-arc vaporization method.<sup>12</sup> Pure C<sub>60</sub> was obtained by a chromatographic separation method, in a purity of >99.9% (detected by HPLC<sup>13</sup>). The pyrrolidine

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## SCHEME 1



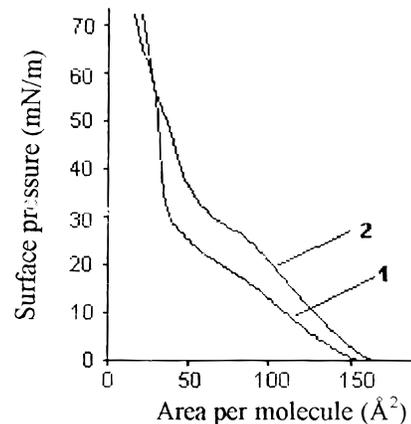
derivatives **1–4** were synthesized by a 1,3-dipolar addition to C<sub>60</sub> of the decarboxylated iminium ion formed from aldehyde (RCHO, R = H, C<sub>6</sub>H<sub>5</sub>, *o*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>, and *o*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>) and *N*-methylglycine by following a procedure slightly modified from that described by Maggini et al.<sup>14a</sup> The structures of **1–4** were characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR (400 MHz Bruker, CS<sub>2</sub>, 310 K)<sup>14b</sup> as shown in Scheme 1.

Methylviologen diiodide (MV<sup>2+</sup>) was synthesized by the reaction of 4,4'-bipyridyl with excess methyl iodine in refluxing ethanol for 6 h. The product was filtered and washed with ethanol four times, then dried in vacuum. The NMR spectrum indicated that the product was highly pure. Arachidic acid (AA) was purchased from Aldrich Co. The electrolytes were (*n*-Bu)<sub>4</sub>NPF<sub>6</sub> and KCl for electrochemical and photoelectrochemical experiments, respectively. The former was purchased from Aldrich Co. and the later from Beijing Chemical Factory. L<sup>(+)</sup>-Ascorbic acid (AsA) was from Medicine Manufacture in Shanghai and was recrystallized from water before use. The solvents, dichloromethane and chloroform (AR), were purchased from the Chemical Factory of Beijing. Deionized water purified by passing through an EASYpure RF compact ultrapure water system (Barnstead Co., U.S.) was used in all experiments.

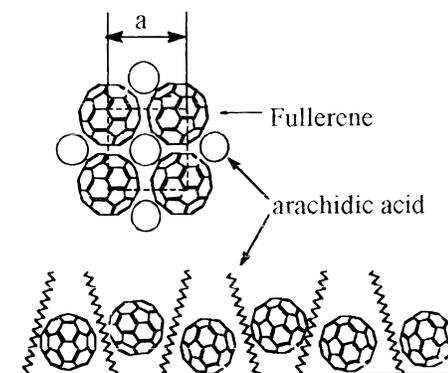
**Preparation of LB Films.** A NIMA 622 computer-controlled Langmuir trough (U.K.) was used for the formation of the fullerenes monolayers. It took about 1 h to spread a chloroform solution of C<sub>60</sub>/AA or its derivatives (10<sup>-6</sup>–10<sup>-5</sup> mol·L<sup>-1</sup>) onto an ultrapure water subphase (20 ± 1 °C, pH 5.60, >18 Ω). After the evaporation of the solvent over 15 min, the surface pressure–area ( $\pi$ -A) isotherms were recorded. The monolayer was deposited onto the hydrophilic pretreated transparent SnO<sub>2</sub> glass substrates with a lateral resistance of 50 Ω at a rate of 5 mm/min (vertical dipping) at a constant surface pressure of 30 mN·m<sup>-1</sup>. Typical transfer ratios were 0.90 ± 0.05.

**Electrochemical Measurements.** Cyclic voltammetry was recorded on a PAR-270 Electrochemical Analysis System (U.S.). A three-electrode configuration was used throughout. A polished platinum electrode (0.5 mm diameter) was used as working electrode. The counter electrode and the reference were a platinum wire and a Ag/AgCl electrode, respectively. All measurements were performed in a 0.1 mol·L<sup>-1</sup> dichloromethane solution of (*n*-Bu)<sub>4</sub>NPF<sub>6</sub> at -10 °C under a nitrogen atmosphere. The concentrations of C<sub>60</sub> and its derivatives ranged from 10<sup>-4</sup> to 10<sup>-3</sup> mol·L<sup>-1</sup>.

**Photoelectrochemical Measurements.** The photoelectrochemical studies was performed by using a model 600 voltammetric analyzer (CH Instruments Inc., U.S.) and a 500 W xenon lamp (Ushio Electric, Japan). A variety of filters (Toshiba, Japan) with certain band passes were used to obtain different wavelengths. The intensities of incident beams were standardized by a power and energy meter (Sciencetech 372, Boulder Co., U.S.). The IR light was filtered throughout the experiment with a Toshiba IRA-25S filter (Japan). To eliminate the influence of oxygen, all experiments were carried out under a nitrogen atmosphere. At least eight Fuller-SnO<sub>2</sub> electrodes were fabricated to test the reproducibility of photocurrent data under each conditions.



**Figure 1.** Surface pressure–area isotherms of C<sub>60</sub>/arachidic acid (**1**) and the derivative **4** [C<sub>60</sub>(C<sub>11</sub>H<sub>16</sub>N<sub>2</sub>)] (**2**) at the air/water surface.



**Figure 2.** Possible packing arrangement of C<sub>60</sub> and arachidic acid on the air/water surface.

## Results and Discussions

**Fabrication of Fuller-SnO<sub>2</sub> Electrodes.** The  $\pi$ -A isotherm of C<sub>60</sub>/AA (Figure 1) shows that the film can sustain more than 70 mN·m<sup>-1</sup> surface pressure and has a limiting molecular area of 87.9 Å<sup>2</sup>/molecule. Expansion and recompression of a previously compressed film reveals very little hysteresis up to the point at which the expansion initiated (for less than about 55 mN·m<sup>-1</sup>) without visible patchy domains on subphase. This suggests that the film on the aqueous subphase is a uniform and high-quality monolayer. Supposing that the molecules of C<sub>60</sub> and arachidic acid were in an ideal arrangement on the air/water interface (Figure 2), then the projection of the molecules onto the water surface forms a square lattice with a lateral length *a*; the calculated area per molecule is *a*<sup>2</sup>. This yields nearest-neighbor distances of 9.4 ± 0.6 Å for C<sub>60</sub> or arachidic acid molecules. Considering that arachidic acid has limiting area of 20 Å<sup>2</sup>/molecule, the calculated nearest-neighbor distance of 9.4 ± 0.6 Å is slightly smaller than of the ideal monolayer of C<sub>60</sub>/AA (11.2 ± 0.4 Å). This fact suggests that the C<sub>60</sub> molecules are squeezed into the hydrophobic long chains in a certain extent at such a surface pressure.

The  $\pi$ -A isotherms of all fullerene derivatives indicate that these molecules can form stable monolayers on an aqueous

TABLE 1: Comparison of Interfacial Properties of C<sub>60</sub> and Its Derivatives

compd	spreading solution (mmol·L <sup>-1</sup> )	A <sub>0</sub> <sup>b</sup> (Å <sup>2</sup> )	π <sub>max</sub> <sup>c</sup> (mN·m <sup>-1</sup> )	deposited condition		transferability or transfer ratio	ref
				model	treatment		
C <sub>60</sub>	CS <sub>2</sub> /CH <sub>2</sub> Cl <sub>2</sub> (0.1)	94.2	~73	vertical	either	x	9c
C <sub>60</sub> /IA <sup>a</sup>	benzene	7	>45	horizontal	hydrophobic	yes	10b
C <sub>60</sub> O	CS <sub>2</sub> /CH <sub>2</sub> Cl <sub>2</sub> (<0.1)	95.9	~73	vertical	hydrophobic	x	9c
				horizontal	hydrophobic	yes	9c
C <sub>60</sub> (C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> )	CS <sub>2</sub> /CH <sub>2</sub> Cl <sub>2</sub> (7.6 × 10 <sup>-2</sup> )	89	>40	vertical	hydrophilic	0.85 ± 0.05	11a
C <sub>60</sub> /AA	CHCl <sub>3</sub> (8.8 × 10 <sup>-3</sup> )	87.9	>70	vertical	hydrophilic	0.90 ± 0.05	this work
C <sub>60</sub> (C <sub>3</sub> H <sub>7</sub> N) (1)	CHCl <sub>3</sub> (7.8 × 10 <sup>-3</sup> )	93.4	>60	vertical	hydrophilic	0.90 ± 0.05	this work
C <sub>60</sub> (C <sub>9</sub> H <sub>11</sub> N) (2)	CHCl <sub>3</sub> (6.8 × 10 <sup>-3</sup> )	97.8	>60	vertical	hydrophilic	0.90 ± 0.05	this work
C <sub>60</sub> (C <sub>9</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> ) (3)	CHCl <sub>3</sub> (8.5 × 10 <sup>-3</sup> )	96.6	>60	vertical	hydrophilic	0.90 ± 0.05	this work
C <sub>60</sub> (C <sub>11</sub> H <sub>16</sub> N <sub>2</sub> ) (4)	CHCl <sub>3</sub> (9.5 × 10 <sup>-3</sup> )	96.7	>60	vertical	hydrophilic	0.90 ± 0.05	this work

<sup>a</sup> IA: icosanoic acid. <sup>b</sup> A<sub>0</sub>: the limiting molecular area. <sup>c</sup> π<sub>max</sub>: the collapse pressure.

subphase due to the introduction of hydrophilic functional groups. The limiting molecular area of compound **1** is in good agreement with that for C<sub>60</sub>O,<sup>9c</sup> but the others are slightly larger (Table 1). The nearest-neighbor distances are calculated as follows. Assuming that the substituents of the fullerene derivatives are attracted toward the water and that the projection of the molecules onto the water surface forms a triangular lattice of circular objects of radius *r*, the calculated area per molecule is  $2\sqrt{3}r^2$ , thus the nearest-neighbor distances of the derivatives **1**, **2**, **3**, and **4** are  $10.4 \pm 0.5$ ,  $10.6 \pm 0.5$ ,  $10.6 \pm 0.5$ , and  $10.6 \pm 0.5$  Å, respectively. They are slightly larger than that of C<sub>60</sub>.<sup>8a,c</sup> This indicates that the films are really monolayers and the phenyl group occupied a small area on the monolayers. The π–A isotherms of expansion and recompression also show the same results as C<sub>60</sub>/AA, suggesting that the induced hydrophilic groups really enhance the stability of these Langmuir films.

#### Photocurrent Generation from Fuller-SnO<sub>2</sub> Electrodes.

The experimental results show that C<sub>60</sub> and its derivatives have very similar photoelectric responsibilities. To describe conveniently, the derivative **4** (C<sub>60</sub>(C<sub>11</sub>H<sub>16</sub>N<sub>2</sub>)) is chosen as a representative to discuss below because its SnO<sub>2</sub> electrode can give the largest photocurrent among them.

*The Wavelength of Incident Light.* The photocurrents are very low when visible incident light is used, and the absorbency of the SnO<sub>2</sub> electrode increases very sharply at wavelengths below 320 nm. Since the electronic absorption spectra of Fuller-films on quartz substrate show that the absorbencies in the near-ultraviolet part are several times higher than those in the visible part,<sup>11a,c</sup> the light beam of the wavelength at  $355 \pm 30$  nm was chosen as the exciting source. The action spectra prove that the photocurrent with the wavelength of  $355 \pm 30$  nm as incident light is really several times higher than that with visible light (Figure 3).

*Effect of Oxygen.* Oxygen can quench the triplet state of the fullerenes<sup>8b,15a,b</sup> and suppress >95% of the photocurrent.<sup>7b</sup> These processes occur for the derivatives since the electronic structure of C<sub>60</sub> is retained in its derivatives and the similar photoelectrochemical responses of C<sub>60</sub> and its derivatives were observed when oxygen exists. From our experimental results, oxygen can not only suppress the magnitude of photocurrent but also redirect the flow of electrons. Consequently, all experiments were carried out under nitrogen.

Under the condition of a nitrogen atmosphere, an anodic pulse photocurrent up to 120 nA was observed when the Fuller-SnO<sub>2</sub> electrode was illuminated under a light intensity of 3.4 mW·cm<sup>-2</sup> with a  $355 \pm 30$  nm light beam as the exciting source (after transmitting the SnO<sub>2</sub> electrode). Also, the photocurrent rose gradually to an equilibrium value ranging from 19 to 38 nA in a 1.0 mol·L<sup>-1</sup> KCl electrolyte solution without any bias voltage (Figure 4). The equilibrium values can increase to 65–92 nA if nitrogen is kept bubbling when the photocurrent is being determined.

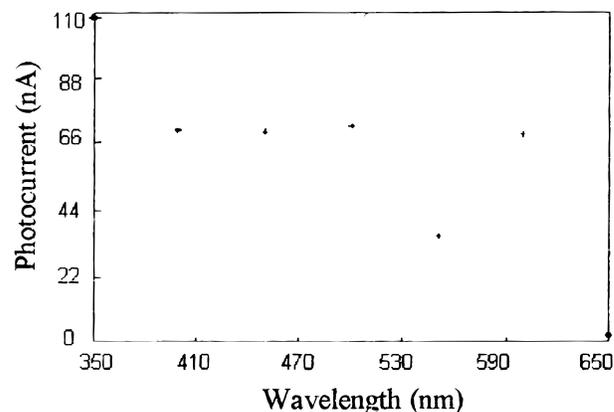


Figure 3. Representative actions spectrum of the Fuller-SnO<sub>2</sub> electrode (derivative **4**). The photocurrents and the intensities of different wavelengths are all normalized.

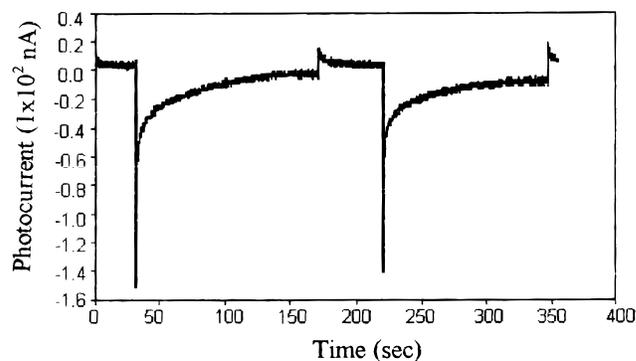
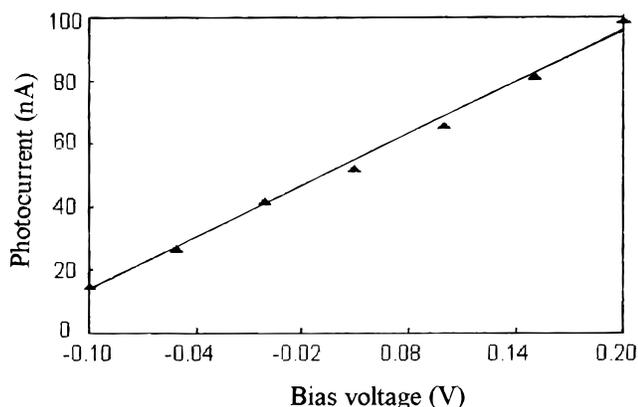


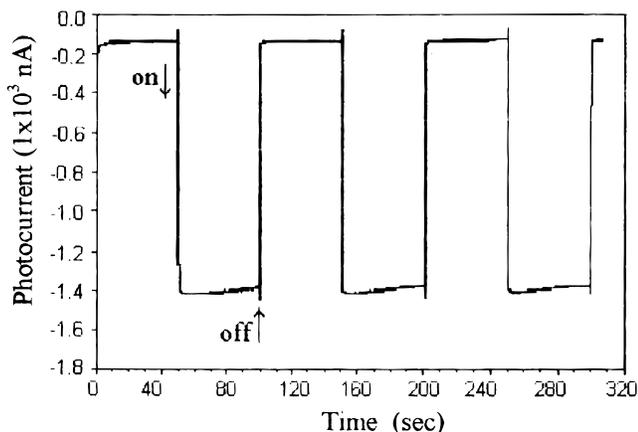
Figure 4. Representative photocurrent for the derivative **4** obtained under N<sub>2</sub> atmosphere without bubbling when the Fuller-SnO<sub>2</sub> electrode was first illuminated.

The monolayer film shows a stable photoelectronic response for tens of times switching on and off the light, and the attenuation is not very large compared with the initial photocurrent (ca. 0.01 of decay rate) after keeping in 1.0 mol·L<sup>-1</sup> KCl electrolyte for 3 days. The photoelectronic responses of uncoated SnO<sub>2</sub> electrodes and more than eight SnO<sub>2</sub> electrodes coated by arachidic acid were studied to probe their contributions to the photocurrent. A stable anodic photocurrent ranging from 12 to 20 nA under a  $355 \pm 30$  nm light beam was obtained. These values are smaller than the photocurrent generated from the Fuller-SnO<sub>2</sub> electrode, revealing that C<sub>60</sub> and its derivatives are the main contributors causing the change of photocurrent.

*Effect of Bias Voltage and Light Intensity.* To probe the electron-transfer process between the SnO<sub>2</sub> electrode and the Fuller film, the effect of bias voltage was investigated. There is a linear relationship with a slope of 0.27 nA·mV<sup>-1</sup> between the observed photocurrent and the bias voltage in the range -0.10 to 0.20 V vs SCE (Figure 5). The anodic photocurrent



**Figure 5.** Effluence of bias voltage to the photocurrent generation from the Fuller-SnO<sub>2</sub> electrode of the derivative **4** with N<sub>2</sub> bubbling and an irradiation of 3.4 mW/cm<sup>2</sup>.



**Figure 6.** Representative photocurrent obtained from the Fuller-SnO<sub>2</sub> electrode of the derivative **4** under N<sub>2</sub> atmosphere with 0.1 V bias voltage and 15 mmol·L<sup>-1</sup> ascorbic acid in the electrolyte solution.

increases as the positive bias of the electrode increase, and vice versa. This shows that the electrons flow from the electrolyte through the LB film to the electrode.

A good linear relationship between the photocurrent and the light intensities (from 0.9 to 10.3 mW/cm<sup>2</sup>) is observed. The photocurrent increases along with the light intensity increase. No saturation state was observed because the filter and the SnO<sub>2</sub> glass absorbed more than 90% of the intensity of the exciting light and such an intensity cannot supply enough photons to make all molecules active and contribute to the photocurrent.

**Effect of Electron Donor and Acceptor.** The effect of the electron acceptor (AsA) and donor (MV<sup>2+</sup>) also certifies the direction of electron transfer. As the well-known electron donor ascorbic acid was added into the electrolyte solution (1.0 mol·L<sup>-1</sup> KCl solution), the photocurrent increases in direct proportion with the concentration of AsA in lower range (<1.9 mmol·L<sup>-1</sup>) with a slope of 120–200 nA·(mmol·L<sup>-1</sup>)<sup>-1</sup>, then turns to a nonlinear relationship, and finally levels off at a higher concentration (started at ca. 15.6 mmol·L<sup>-1</sup>). A horizontal photocurrent of the modified electrode of compound **4** as well as C<sub>60</sub> and other derivatives was obtained with 15.6 mmol·L<sup>-1</sup> AsA and a 0.1 V bias voltage as shown in Figure 6.

The photocurrent can be repeated for tens of times switching on and off the light, and the attenuation is also very small, coincident with the results obtained under no AsA and no bias voltage. It is worthy to notice that the equilibrium values of photocurrent are almost the same regardless of aeration or not.

An opposite effect is observed for the addition of the electron acceptor methylviologen diiodide (MV<sup>2+</sup>) to the electrolyte. Without bias voltage, the photocurrents decrease sharply when the concentration is less than 2 mmol·L<sup>-1</sup>. Results indicate that MV<sup>2+</sup> not only attenuates the anodic photocurrent but also redirects the flow of electrons when the concentration is up to 20 mmol·L<sup>-1</sup>.

From the above results, it can be concluded that positive bias voltage and electron donor as well as light intensity are beneficial factors for generating photocurrent and that the electrons flow from the electrolyte through the LB films to the electrodes.

**Photocurrent Generation Mechanism.** Photoinduced electron transfer investigations show that C<sub>60</sub> and its derivatives give very high yields of the triplet state under irradiation at 355 nm as a result of very high rate of intersystem crossing from the singlet state.<sup>8,15</sup> <sup>3</sup>C<sub>60</sub> is a powerful electron acceptor with a reduction potential near 1.14 V vs SCE.<sup>16</sup> The reduction potential of compounds **1–4** should also be near 1.14 V vs SCE. The reasons are that (1) the redox potentials of compound **1–4** are ca. 0.1 V negative shifts with C<sub>60</sub> (as shown in Table 2), which means that derivatives **1–4** retain the electronegative property of its parent fullerene, and (2) the triplet energies of the derivatives (1.50 eV) are very close to that of C<sub>60</sub> (1.57 eV).<sup>8b,15a,b,17</sup> Another important aspect of the photoinduced electron-transfer process of fullerenes is that the triplet state can be efficiently quenched by oxygen.<sup>8,15</sup>

Therefore, when the Fuller-SnO<sub>2</sub> electrode is illuminated without an electron donor, the Fuller molecules are excited to the singlet and transfer to the triplet very quickly. Then the excited Fuller molecules are reduced to anions by water and oxygen is produced because the <sup>3</sup>E<sub>red</sub> (the reduced potential of the triplet state) of the Fuller molecules is higher than the E<sub>O<sub>2</sub>/H<sub>2</sub>O</sub> (0.66 V<sub>SCE</sub> as pH is 5.60). After that the electrons transfer from the Fuller triplet-state anions to the holes in the valence band of SnO<sub>2</sub>. As a result, the electrons transfer from electrolyte through film to the SnO<sub>2</sub> electrode. More details of mechanism are still being investigated.

The oxygen molecules produced in the photoelectronic response process quench the photoactive Fuller-molecules, and a suppressed photocurrent is thus obtained. This causes the equilibrium values of photocurrent without bubbling nitrogen to be lower due to the concentration of oxygen in the electrolyte rising up. As the electron donor, AsA, is added, the molecules of AsA take precedence to give electrons to the Fuller molecules because of the lower potential E<sub>(ox)/(red)</sub> (-0.21 V<sub>SCE</sub>). In this case, the equilibrium photocurrent is independent of aerating or not since there is no suppressed factor.

**The Effect of Different Substituent Groups on Photocurrent Generation.** Due to the fact that arachidic acid was used for improving the stability of C<sub>60</sub> film, part of the SnO<sub>2</sub> electrode surface is occupied by the arachidic acid molecules and some C<sub>60</sub> molecules are squeezed into the hydrophobic long chains

**TABLE 2: E<sup>1/2a</sup> (V vs Ag/AgCl) by Cyclic Voltammetry<sup>b</sup> of C<sub>60</sub> and Its Derivatives **1–4****

compd	C <sub>60</sub>	C <sub>60</sub> (C <sub>3</sub> H <sub>7</sub> N) ( <b>1</b> )	C <sub>60</sub> (C <sub>9</sub> H <sub>11</sub> N) ( <b>2</b> )	C <sub>60</sub> (C <sub>9</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> ) ( <b>3</b> )	C <sub>60</sub> (C <sub>11</sub> H <sub>16</sub> N <sub>2</sub> ) ( <b>4</b> )
E <sup>0/1-</sup>	-0.50	-0.61	-0.61	-0.64	-0.63
E <sup>1-/2-</sup>	-0.88	-0.96	-0.99	-1.03	-1.00
E <sup>2-/3-</sup>	-1.33	-1.51	-1.51	-1.42	-1.52

<sup>a</sup> E<sup>1/2</sup> is the reduced potential from state 1 to state 2. <sup>b</sup> vs Ag/AgCl in a 0.1 mol·L<sup>-1</sup> dichloromethane solution of Bu<sub>4</sub>NPF<sub>6</sub> at -10 °C. Scan rates = 200 mV/s.

**TABLE 3: Values of Photocurrent (*I*, nA) and the Quantum Yields of the Fuller-SnO<sub>2</sub> Electrodes with the Electrolytes Containing 15 mmol·L<sup>-1</sup> AsA and Saturated N<sub>2</sub> under 0.1 V Bias Voltage**

electrode	C <sub>60</sub> /AA	1	2	3	4
<i>I</i> <sub>obs</sub> (nA)	270–430	450–600	550–750	500–700	1300–1900
<i>I</i> <sub>unit</sub> (nA·mm <sup>-2</sup> )	3.4–5.4	5.6–7.5	6.9–9.4	6.3–8.8	16.3–23.8
quantum yield (%)	1.2~1.9	1.9~2.6	2.4~3.2	2.2~3.0	5.6~8.2

to a certain extent at the surface pressure of 30 mN·m<sup>-1</sup>. The observed photocurrent should be a little higher than the ideal monolayer C<sub>60</sub>-SnO<sub>2</sub> electrode. But the value still can be used as a standard when the effect of different substituent groups on generation photocurrents for compounds 1–4 is taken into comparison.

The photocurrent ranges of C<sub>60</sub>/AA and its derivatives without bias voltage and electron donor are overlapped to quite an extent. This may due to the complex influence of the produced oxygen, the released rate of oxygen from the electrolyte solution, and the different adsorption abilities for oxygen on the surfaces of the Fuller-SnO<sub>2</sub> electrodes. Results show that positive bias voltage and electron donor as well as light intensity enhance generating stable photocurrents. Therefore, in order to test the capacities of generating photocurrents of each compound, the determining conditions were chosen as follows: a 1.0 mol·L<sup>-1</sup> KCl electrolyte solution containing 15 mmol·L<sup>-1</sup> ascorbic acid and saturated N<sub>2</sub> under 0.1 V bias voltage. Table 3 shows the values of photocurrent and the quantum yields of C<sub>60</sub>/AA and its derivatives with these conditions. The quantum yields were calculated according to the following formula:

$$\text{quantum yield} = \frac{\text{electron number of photocurrent}}{\text{photon number absorbed by the Fuller-SnO}_2 \text{ electrode}}$$

Results in Table 3 indicate that the photocurrent and the quantum yield obtained from C<sub>60</sub>-SnO<sub>2</sub> electrode are higher than what were reported by Hwang et al.<sup>7</sup> This difference results from the beneficial factors used here. What need to be emphasized is the electron attracting–repulsing effect of different substituent groups. The introduction of the ring of pyrrolidine can increase the values of photocurrent as compared with that of C<sub>60</sub> because the methyl on the nitrogen can act as an electron donor and cause more efficient electric charge separation than the parent fullerene. Values also show that the phenyl-substituted pyrrolidines promote photocurrent more effectively. Particularly for the compound 4, the photocurrent is more than twice that of other systems. This strongly supports that an efficient electron-donating group can efficiently enhance photoelectronic response. But, the electron-attracting group, –NO<sub>2</sub> in compound 3, does not show the effect expected on generating photocurrent as compared with compound 2.

## Conclusion

We have successfully transferred the monolayer films of C<sub>60</sub> and its pyrrolidines derivatives onto SnO<sub>2</sub> electrodes by the LB technique; their photoelectrochemistry behavior were observed. The photocurrents indicate that electrons flow from the electrolyte through the LB film to SnO<sub>2</sub>; therefore, a chemical energy conversion occurs together with the photoelectronic response. The derivatives can give higher photocurrents than C<sub>60</sub> itself, especially when efficient electron-donating groups exist. More investigation is in progress on the electron-transfer process and photocurrent generation of other Fuller-systems.

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## References and Notes

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