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Fabrication and photovoltaic properties of fullerene and copper phthalocyanine derivative mixed Langmuir-Schaefer films

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Surface pressure-area isotherms of mixed floating film of fullerene (C_{60}) and tri-(2,4-di-*t*-amylphenoxy)-(8-quinolinolyl) copper phthalocyanine (CuPc) were investigated at different molar compositions at air-water interface. The shapes of these isotherms and estimated areas per molecule are shown dependent on the molar compositions. C_{60}/CuPc mixed multilayers were fabricated onto various solid substrates by using Langmuir-Schaefer (LS) technique, and characterized by UV-VIS spectroscopy, electrochemical and photoelectrochemical measurements respectively. Uniform LS films were formed when the molar composition was less than 1 : 1 (C_{60} : CuPc). UV-VIS spectroscopic measurements showed that there was no distinct interaction between phthalocyanine and C_{60} molecules at ground state either in solution or in solid films. However, electron transfer appears to have occurred between two kinds of molecules under light illumination. Photoelectrochemical study revealed that phthalocyanine and C_{60} mixed system could be a potential candidate for photovoltaic applications.

1. Introduction

Phthalocyanines (Pcs) are promising materials for their optoelectronic applications in photovoltaic cell, light-emitting diode, photosensors, and even microelectronics, due to their larger and flexible absorption as well as their electrical properties similar to inorganic semiconductors [1–3]. Most of Pcs are usually prepared in their pristine form. However, controlled doping is a prerequisite for the realization of the efficient organic-based devices [4]. Pcs possess a good electron-donating property since their large π-electron systems are easily ionized. The low ionization and high polarisation energies of Pcs are favourable to their charge transfer interactions with electron-accepting molecules. It was demonstrated earlier that the conductivity of Pcs was influenced by doping with strong electron-accepting molecules [3]. Pcs can be doped by adding organic acceptor molecules such as orthochloranil, tetracynoquinodimethane, dicyanodichloroquinon, and fullerene [5–11].

Fullerene (C_{60}) is a good π-electron acceptor and has been widely used as a dopant in organic systems [12]. It has been reported that C_{60} reacts readily with some strong donor molecules to form a charge-transfer complex, such as tetrathiafulvalene derivatives, ferrocene [13, 14]. However, charge transfer is difficult to occur between phthalocyanine (Pc) and C_{60} molecules at ground state because of the high electron affinity of C_{60} (2.65 eV) [15]. The discovery of photoinduced charge transfer in conducting polymer and C_{60} composite has provided a molecular approach to high-efficient photovoltaic devices. The photoinduced charge transfer across a donor-acceptor interface also provides an effective way to overcome premature carrier recombination in organic systems and thus to enhance their optoelectronic responses [16].

Ultraviolet photoelectron spectroscopic studies revealed that charge transfer is energetically possible between Pc and C_{60} molecules [9]. Thus photoinduced charge transfer is possible between Pc and C_{60}

molecules. It was reported that Pc and C_{60} molecules formed a phase-separated composite in their mixture [8]. As such composite is composed of donor (Pc) and acceptor (C_{60}) molecules, they can form donor-acceptor interfaces within a few nanometers in any point. Therefore, such composite may be a good material for photovoltaic applications [16]. In the spirit of the nature of Pc and C_{60} molecules as well as their photoinduced properties, an attempt has been made to fabricate mixed Langmuir-Schaefer (LS) films of C_{60} and tri-(2,4-di-*t*-amylphenoxy)-(8-quinolinolyl) copper phthalocyanine (CuPc) at various molar compositions. The surface pressure-area isotherms of mixed Langmuir films were also investigated at air-water interface. The optical, electrochemical and photoelectrochemical properties of mixed LS films were also investigated.

2. Experimental details

2.1. Materials

CuPc was a generous gift from Prof. Shiquan Xi (Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, China) [7]. C_{60} and other chemicals used herein were purchased from Aldrich. Quartz, mica and indium-tin oxide (ITO)-coated glass plates were used as the substrates for the deposition of C_{60}/CuPc composite LS films. These substrates were cleaned as usual procedures before their use.

2.2. Formation of the composite LS films

Initially, C_{60} and CuPc were dissolved into benzene to obtain solutions with a concentration of 0.5 mmol/l and 0.1 mmol/l respectively. Such two different solutions were mixed together to obtain various resulting solutions. A commercial Langmuir trough of MDT Corp. (237 × 100 nm in size and 300 ml in volume) was used for surface pressure-area isotherm measurement and film deposition. An appropriate volume solution, depending on the concentration and molar composition, was spread onto an aqueous subphase (Milli-Q water with a resistivity of 18.2 MΩcm). After the complete evaporation of spreading solvent, the floating film was compressed to record the surface pressure-area isotherms, as well as to deposit the films. The stability of Langmuir film was investigated at different surface pressures for different molar compositions. The fabrication of composite LS films was carried out at a surface pressure of 30 mN/m in all cases with a barrier compression rate of 50 mm^2/min. Different numbers of layers were transferred onto various solid substrates by LS technique.

2.3. UV-VIS spectroscopic measurement

UV-VIS absorption spectra of C_{60}/CuPc (1 : 1) composite LS films deposited onto quartz plate were recorded using an UV-VIS-NIR spectrometer (model V-570, JASCO).

2.4. Electrochemical and photoelectrochemical measurements

The electrochemical measurements were carried out using a Potentiostat/Galvanostat (EG&G PARC, model 263A). A standard electrochemical cell with three-electrode configuration was employed, where a glass/ITO/LS film acted as a working electrode, a platinum wire as a counter, and Ag/Ag^+ as a reference electrode. 0.1 mol/l tetrabutylammonium tetrafluoroborate (TBATFB) acetonitrile solution was used as the supporting electrolyte. The standard three-electrode configuration was also employed for the photoelectrochemical measurements. A white light of 100 watts was illuminated with a distance of 10 cm away from the working electrode. The switch-on and switch-off of the light were controlled manually.

3. Results and discussion

3.1. Surface pressure-area isotherms

Fig. 1 depicts the surface pressure-area (π-A) isotherms of Langmuir film of C_{60}/CuPc composite at different molar compositions. The isotherm measurements reveal a similar condensed shape for all the isotherms. In general, the stability of Langmuir film is usually associated with a high collapse pressure, a steep increase in the condensed phase and a small hysteresis in the compression-relaxation cycle [17,18]. As can be seen in Fig. 1, all the isotherms possess a high collapse pressures up to 70 mN/m and a steep increase in the condensed phase. The area per molecule can be estimated by extrapolating the solid region of π-A isotherm to zero pressure. The estimated areas per molecule of C_{60} and CuPc are found to be 26 and 97 $Å^2$ respectively. C_{60} molecules tend to form ill-defined films of three-dimensional aggregates rather than a monolayer at air-water interface, and the expected theoretical area

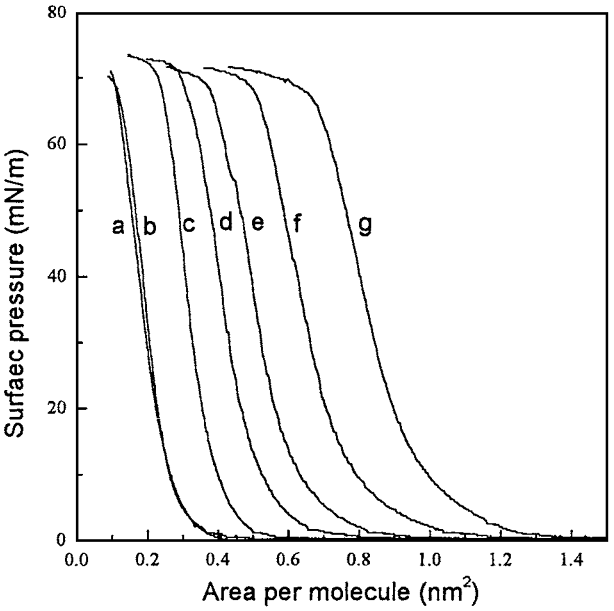

Figure 1 Surface pressure-area isotherms of various C_{60}/CuPc mixed Langmuir films obtained at air-water interface at room temperature: (a) C_{60}, (b) C_{60} : CuPc = 9 : 1, (c) C_{60} : CuPc = 7 : 3, (d) C_{60} : CuPc = 1 : 1, (e) C_{60} : CuPc = 3 : 7, (f) C_{60} : CuPc = 1 : 9, (g) CuPc).

TABLE I Comparison between the experimental and theoretical values of area per molecule at various molar compositions of C_{60}/CuPc composite

	C_{60}	C_{60} : CuPc 9 : 1	C_{60} : CuPc 7 : 3	C_{60} : CuPc 1 : 1	C_{60} : CuPc 3 : 7	C_{60} : CuPc 1 : 9	CuPc
Experimental value (Å^2)	26	27	39	52	62	77	97
Theoretical value (Å^2)		33.1	47.3	61.5	75.7	89.9	

per molecule should be at least 86.6 Å^2 [19]. The measured area per molecule of 26 Å^2 is consistent with most of the previous reports [20], suggesting that C_{60} molecules form aggregates at the air-water interface. Our earlier study reveals that the area per molecule of CuPc is about 116 Å^2 when chloroform was used as the spreading solvent [21], which is larger than the area when benzene was used. The π-π interaction between CuPc and benzene molecules induces the formation of more aggregates of CuPc molecules, which results in smaller area per molecule. In fact, it has been demonstrated that C_{60} and CuPc molecules form independent domains in mixed films, that is, they form a phase-separated composite [8]. With an increase in the surface pressure, two kinds of molecules around the domains aggregated further leading to much larger aggregates. It can be seen from Table I that the experimental values of estimated area per molecule of C_{60}/CuPc composite at different molar compositions is less than their corresponding theoretical values. These results suggest that the two kinds of molecules tend to aggregate further after being mixed together for their strong intermolecular π-π interactions.

C_{60} floating film is not easy to be deposited onto various substrates, whereas CuPc has been proven a good film-forming material [7, 19]. Therefore, it is possible to deposit easily C_{60} films along with CuPc molecules. The inset in Fig. 2 shows that the C_{60}/CuPc (1 : 1) composite can be deposited successfully onto quartz slide. When the molar compositions are less than 1 : 1(C_{60} : CuPc), it is easy to deposit these composite films. When the molar ratios are larger than 1 : 1, it is also possible to deposit the composite films, even for composite (9 : 1) films. However, with an increase in the number of layers, the transfer ratio decreases, and the resulted films are not homogeneous.

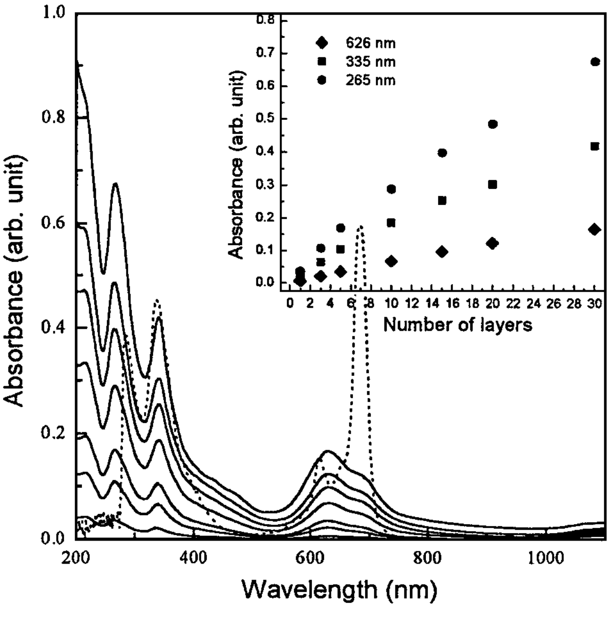

Figure 2 Evolution of UV-VIS spectra of C_{60}/CuPc (1 : 1) mixed LS films deposited onto a quartz slide at 30 mN/m with the number of layers. The dotted line donates UV-VIS spectrum of C_{60}/CuPc (1 : 1) composite benzene solution. The inset shows the absorption maxima at 626, 335 and 265 nm as a function of the number of layers. The linear increase indicates that equal amounts are deposited in each deposition cycle.

3.2. Absorption spectra

Fig. 2 depicts the optical spectra of C_{60}/CuPc (1 : 1) composite LS films deposited onto quartz plate as a function of the layers. It reveals three sharp absorption bands at 265, 335 and 626 nm, besides a feeble peak at 218 nm, as well as two shoulder peaks around 460 and 682 nm. C_{60} shows three absorption peaks at about 221, 264 and 354 nm in solution phase [22]. After being transferred onto solid substrates, C_{60} shows four characteristic absorption bands at 218, 267, 343 and 456 nm [23]. Therefore, the observed characteristic peaks at 218 and 265 nm can be attributed to C_{60} aggregates. The peaks at 630 and 682 nm are due to the π-π^* transition centred on the macrocycle of CuPc molecules, which are the Q bands of dimer and monomer of phthalocyanine molecules respectively [7]. At the same time, CuPc shows a Soret band around 345 nm, so the observed peak at about 335 nm could be due to the overlap of Soret band of CuPc and 343-nm band of C_{60} molecules. Since no extra features were observed when the two kinds of molecules were mixed together either in solution or in solid films, it can be deduced that there is no indication of charge transfer at ground state. The inset of Fig. 2 shows the optical absorption magnitude increases gradually with the increase in the number of layers, which reveals the uniformity in the deposition process.

3.3. Electrochemical properties

The electrochemical surveying of composite LS films deposited onto ITO-coated glasses at different molar compositions was carried out by using cyclic voltammetry. Fig. 3 shows cyclic voltammograms (CVs) of 30-layer C_{60}/CuPc (1 : 1) composite LS film at different scan rates in 0.1 mol/l TBATFB acetonitrile solution. The CV shows an oxidation peak at −380 mV when scanned at 50 mV/sec. C_{60} exhibits four well-separated quasireversible reduction peaks at −1.12, −1.50, −1.94 and −2.40 V versus ferrocene, as well as four corresponding reoxidation peaks in 1,2-dichlorobenzene solution [24]. The composite system does not show any well-defined peaks except the appearance of the new peak around −380 mV when C_{60} was mixed with CuPc forming 1 : 1 composite. It must be emphasised

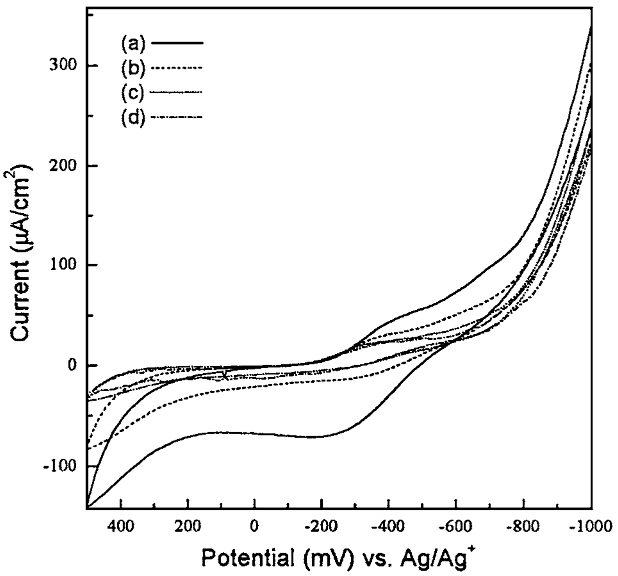

Figure 3 Cyclic voltammograms of 30-layer C_{60}/CuPc (1 : 1) mixed LS films on ITO-coated glass plate in 0.1 mol/l tetrabutylammonium tetrafluoroborate (TBA TFB) acetonitrile solution at different scan rates: (a) 100 mV/sec, (b) 50 mV/sec, (c) 20 mV/sec and (d) 10 mV/sec.

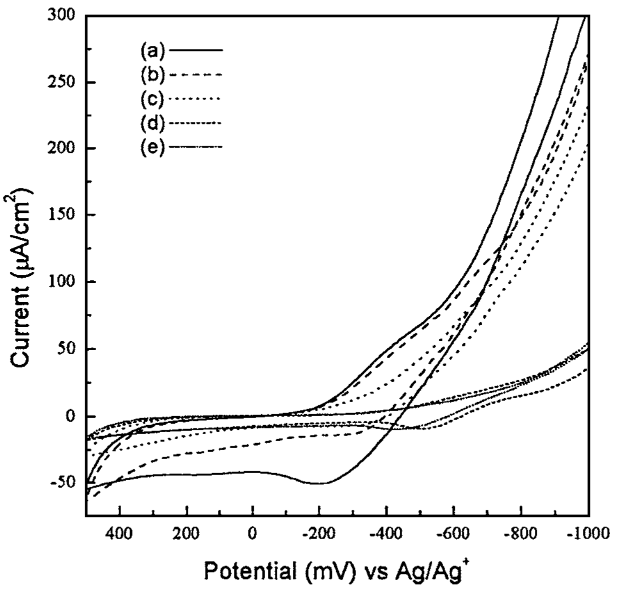

Figure 4 Cyclic voltammograms of 60-layer C_{60}/CuPc mixed LS films on ITO-coated glass plates in 0.1 mol/l TBA TFB acetonitrile solution at various molar compositions: (a) C_{60} : CuPc = 9 : 1, (b) C_{60} : CuPc = 7 : 3, (c) C_{60} : CuPc = 1 : 1, (d) C_{60} : CuPc = 3 : 7, (e) C_{60} : CuPc = 1 : 9.

that the ITO layer is quickly oxidized at an applied potential of −2.5 V, even under nitrogen atmosphere. Therefore, we restricted our scan potential between 0.5 and −1.0 V. In fact, CuPc does not show any characteristic peaks in this potential range [21]. Therefore, it could be deduced that the appearance of such new peak is a result of interactions between C_{60} and CuPc molecules, which suggests that a low potential is required for electrons to move in the composite system. In order to verify the redox processes of composite LS films, the CVs of 30-layer LS films were recorded at different scan rates. The result conveys a surface confined system, i.e., the redox peak current increases linearly with the sweep rate [25]. Fig. 4 shows the CVs of mixed LS films at different molar compositions with a scan rate of 50 mV/sec, revealing a change in redox peaks with the doping level of C_{60}. As indicated, the oxidation peak shifts to potential that is more negative with an increase in the molar percentage of CuPc in mixed films (Table II), implying the electrochemical process is more electronegative when the molar ratio of CuPc decreases.

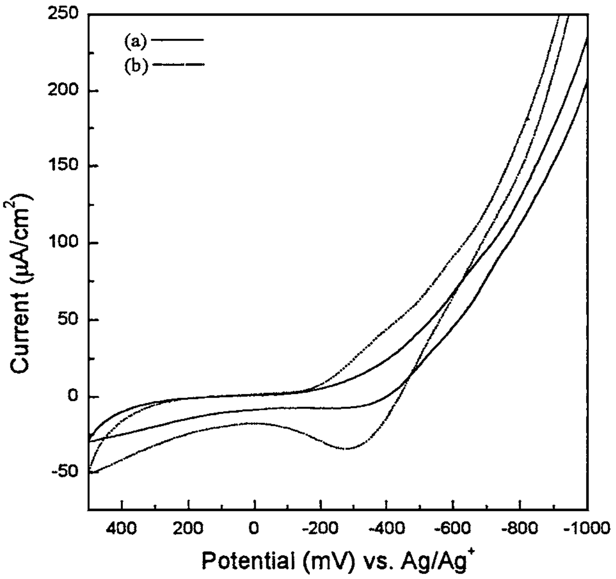

Figure 5 Cyclic voltammograms of 60-layer C_{60}/CuPc (1 : 1) mixed LS films on ITO-coated glass plate in 0.1 mol/l TBA TFB acetonitrile solution without (a) and with light illumination (b).

Fig. 5 shows the CVs of 60-layer C_{60}/CuPc (1 : 1) composite LS films without and with light illumination. The CV under illumination condition shows a similar feature to that of 30-layer composite LS films without illumination (as shown in Fig. 4 at 50 mV/sec). However, the current density of oxidation peak increases under illumination. Meantime, this peak shifts to potential that is more positive under illumination, as compared to that without illumination. The origin of this may lie in the electron transfer between C_{60} and CuPc molecules under illumination condition, whereas other researchers' and our previous studies suggested that the charge transfer from CuPc to C_{60} molecules is impossible at ground state [8, 9]. Therefore, the photoinduced charge transfer is possible to occur between CuPc and C_{60} molecules under illumination. C. Schlebusch *et al.* suggested that CuPc and C_{60} molecules share a weak intermolecular

TABLE II Comparison of the oxidation peak position at various molar compositions of 60-layer C_{60}/CuPc composite LS films

Composite system	C_{60} : CuPc 9 : 1	C_{60} : CuPc 7 : 3	C_{60} : CuPc 1 : 1	C_{60} : CuPc 3 : 7	C_{60} : CuPc 1 : 9
Peak position (mV)	−220	−360	−380	−440	−460

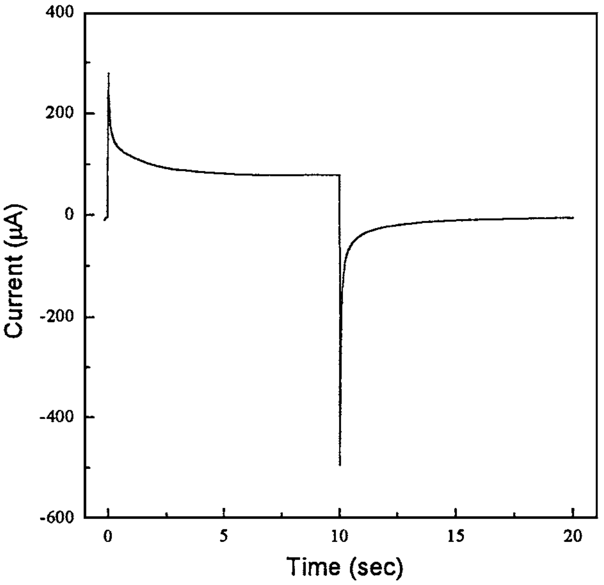

Figure 6 Oxidation and reduction current response of 60-layer C_{60}/CuPc (1 : 1) mixed LS films in 0.1 mol/l TBA TFB acetonitrile solution.

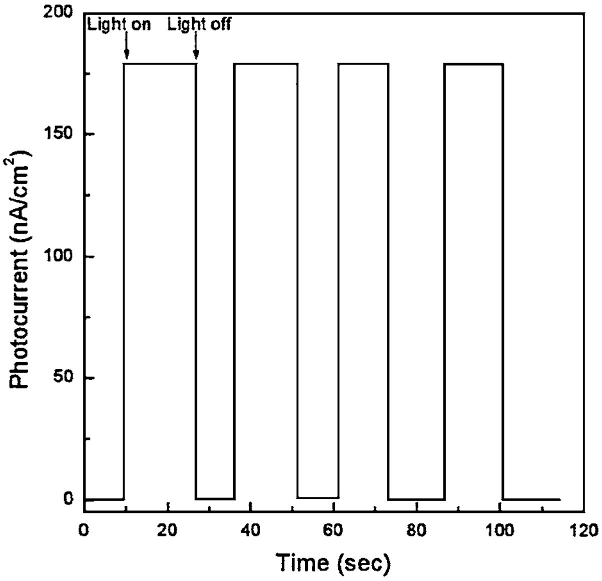

Figure 7 Photoeffect of 60-layer C_{60}/CuPc (3 : 7) mixed LS films. Photocurrent produced by an ITO/60-layer composite LS films in 0.1 mol/l TBA TFB acetonitrile solution. The potential of the working electrode was set at zero V versus Pt counter electrode.

interaction and the energy when an electron transfers from the valence band of CuPc to the highest occupied molecular orbital of C_{60} is only 0.8 eV [9, 26]. Under illumination condition, photoinduced electrons in CuPc will lower their energy by transferring to the C_{60}, and the photoinduced holes in C_{60} will lower their energy by transferring to the CuPc, so the photosensitivity is substantially enhanced in the mixed system. However, the redox responses shown in Fig. 6 evidence a slow redox process in the composite LS films.

3.4. Photoelectrochemical response measurements

For photocurrent response measurement, a 100 watts white lamp served as a source of whole wavelength was passed through ITO/composite LS films in an electrochemical cell. The stabilization of photocurrent was checked. The steady state electrochemical photocurrent was observed by applying potential from Potentiostat, and the photocurrent was measured. The uniform photocurrent was observed in each switch-on and switch-off condition for the electrode containing LS films. Fig. 7 shows the photocurrent transient for C_{60}/CuPc (3 : 7) composite LS films. Such figure depicts the photocurrent rise time is shorter than the time between light switch-off and switch-on for the composite LS films. A photoelectron study has shown that the presence of active species in the supporting solution, which exert significantly the role in the photocurrent. It is clarified that the open circuit voltage and short circuit current increase with the doping level of C_{60} in the composite systems (data not shown). This fact suggests that the device efficiency can be enhanced with the increase in the doping level of C_{60} in the composite films. Through these studies, an effective composite can be carefully selected, and the solid photovoltaic devices will be investigated further.

4. Conclusions

In summary, various experimental techniques indicated a uniform deposition of C_{60}/CuPc composite Langmuir-Schaefer films. The areas per molecule of composite floating films were found dependent on molar compositions. The experimental values of area per molecule are less than theoretical values, suggesting that two kinds of molecules form aggregates further in composite systems. When the molar compositions are less than 1 : 1 (C_{60} : CuPc), the composites can form films with good quality. UV-VIS spectra suggested that there is no electron transfer between phthalocyanine and C_{60} at ground state. However, electron transfer appears to have occurred under scan potential and light illumination. Photoelectrochemical investigation reveals that phthalocyanine and C_{60} composite system is a potential candidate for photovoltaic applications.

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