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Citation	Journal of Materials Research (2011), 26(02): 306-310
Issue Date	2011-01
URL	http://hdl.handle.net/2433/139440
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Type	Journal Article
Textversion	author

Application of Self-Assembling Photosynthetic Dye for Organic Photovoltaics

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ABSTRACT

We have developed novel photovoltaic systems composed of the fullerene derivative (6,6)-phenyl C₆₁ butyric acid methyl ester as electron acceptor with a second functional organic molecule in this case bacteriochlorophyll *c* as light-harvesting and photosensitizing part. It was found that heat treatment of a thin-film of bacteriochlorophyll *c* altered the morphological states of the aggregates and conductivity of the thin-film could be regulated through the annealing process. Blended fullerene derivative and bacteriochlorophyll *c* thin-films were fabricated on the surface of an indium-tin oxide/poly(ethylene dioxythiophene) doped with polystyrene sulfonic acid substrate layer and their photovoltaic properties characterized and evaluated. Formation of fullerene-coordinated bacteriochlorophyll *c* complex was confirmed by changes in the visible absorption spectra and by FT-IR. Such complexation promoted generation of photocurrent in the region of the Q_y band and the current density of the thin-film increased. A maximum incident photon-to-current conversion efficiency of 5.1% was attained at 745 nm.

KEYWORDS: biomimetic (assembly), self-assembly, photovoltaic

Introduction

Photosynthesis is one of the suggestive natural phenomena since the solar-energy conversion

efficiency is quite high in terms of almost the 100%-quantum efficiency of charge separation.

For example, bacteriochlorophylls (BChls) *c*, *d*, and *e* are the main light-harvesting pigments of green photosynthetic bacteria that self-assemble into nanostructures within the chlorosomes forming the most efficient antennas of photosynthetic organisms.¹ Recently, solar cells have attracted much attention relevant to global environmental issues. Particularly, utilization of organic semiconductors have become attractive as lightweight, flexible, and color-tunable materials, which are expected to lead to simple fabrication processes with the potential for ubiquitous utilization.² In this regard, we have developed photovoltaic systems composed of organic semiconductors of poly(3-hexylthiophene)s (P3HT) and fullerene derivative (6,6)-phenyl C₆₁ butyric acid methyl ester (PCBM).³ Currently, combination of novel polymer of poly[4,8bis-2-ethylhexyloxy-benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-4-heptylcarbonyl-thieno[3,4-b]thiophene-2,6-diyl] with PC₇₀BM resulted remarkable enhancement of the power conversion efficiency (*PCE*) of 7.7%.⁴ While Matsuo et. al. reported the columnar structured bulk-heterojunction solar cell based on synthetic tetrabenzoporphyrin and bis(dimethylphenylsilylmethyl)[60]fullerene showing relatively higher *PCE* of 5.2%.⁵ However, such new materials are prepared by complicated synthetic route in fairly small amounts. In this context, application of environmentally benign photosynthetic dyes for photovoltaic system is

promising in terms of biomimetic approach, which allows us to prepare in large amounts of various self-assembling chlorophyllous pigments in nature with tailored properties of highly efficient charge separation and light-harvesting through simple cultivation of organisms. In this context, self-assembling mimics of the natural chlorophylls,⁶ bacteriochlorophylls,⁷⁻⁹ and chlorins^{7,9} had already been applied for organic thin-film photovoltaics, but due to the spontaneous aggregation and very fast charge recombination, the device performance was rather modest. In order to regulate and adjust the self-aggregation of the photosynthetic dyes, we report here the novel application of photosynthetic dye of bacteriochlorophyll *c* (BChl *c*) as light-harvesting and/or photo-sensitizing part for the bulk heterojunction organic thin-film solar cell.

Experimental

Chlorobium tepidum was grown and its chlorosomes were isolated by using methods similar to those previously reported¹⁰ with slight modification. Cultivation was carried out at 40°C under continuous illumination of 20 W fluorescent light to the surface of a 20 L PET bottle for 10 day. The extraction, isolation and purification of BChl *c* (Figure 1) from *Chlorobium tepidum* were carried out according to a modification of the method of Ishii *et. al.*¹¹ Ten volumes of methanol were added to the cell, and the extracts were filtered through diatomaceous earth that

had been previously washed with acetone. This extraction procedure was repeated three times for complete extraction of the pigments. The extracts were combined and dried *in vacuo*. The pigment mixture was dissolved in acetone and was filtered through Avicel FD-101 (crystalline cellulose; Asahi-Kasei Co., Ltd.) in order to remove water-soluble materials. Then *n*-hexane was added to the acetone solution to precipitate BChl *c*. Acetone was removed by evaporation, and precipitate of BChl *c* was washed with *n*-hexane to remove carotenoids (mainly chlorobactene) and bacteriopheophytin until the filtrate was colourless. The precipitate of BChl *c* was redissolved in acetone and filtered again through the cellulose column for purification. The obtained BChl *c* homologues were analyzed by high performance liquid chromatography (HPLC) using a ODS column (COSMOSIL 5C18-AR-II, 4.6 × 10 mm, Nacalai tesque Co. Ltd. Column temperature at 40 °C) with a mobile phase of 9 : 1 (v/v) methanol : water at a flow rate of 1.5 mL/min. Figure 2 shows HPLC traces of the mixture of BChl *c* homologues grown and obtained from *Chlorobium tepidum* in this work. Fraction 1 is assigned to *R*[E, E]BChl *c*,¹¹ in which relative peak area was 69% as compared with the other peak areas of fraction 2 and 3. While fraction 2 is *R*- and *S*[P, E]BChl *c* (28%), and 3 is *S*[I, E]BChl *c* (3%), respectively.¹¹

Indium-tin oxide (ITO) on glass substrate ($5 \Omega/\text{cm}^2$) with an aluminum wire as electrode were purchased from Geomatec Co. Ltd. and Nilaco Co. Ltd. The ITO substrate was sonicated with purified water, acetone, and ethanol, respectively. After air- and blow-drying, poly(ethylene dioxythiophene) doped with polystyrene sulfonic acid (PEDOT: PSS, Clevios P, KC Starck) was spin-coated at 4000 rpm onto the substrate. The active layer of the blended BChl *c*

and PCBM in chloroform was spincoated at 1500 rpm. Finally the Al electrode was deposited through thermal evaporation.

Energy conversion efficiency was measured under 1 sun of AM 1.5 illumination by using simulated solar light from a CEP 2000 illuminator (BUNKOH-KEIKI Co., Ltd.). The light intensity of the illumination source was calibrated by using a standard silicon photodiode (BS 520, BUNKOH-KEIKI Co., Ltd.). The Absorption properties were measured by UV-vis spectrophotometry (Shimadzu UV 2450).

Results and discussion

BChl *c* thin-film

Aggregated BChl *c* forms rod like structure through coordination of 3¹ hydroxyl or 13¹ ketocarbonyl group of one BChl *c* to the Mg center of another BChl *c*.¹² Absorption spectra of BChl *c* thin-films showed similar profiles (Figure 3) to that of the aggregates found for the chlorosome.

FT-IR spectra of BChl *c* thin-film showed a broad peak at 1643 cm⁻¹, which is assigned to the coordinative bonding.¹¹

Through annealing at 100°C or 150°C for 6 min, the absorption peak of Q_y band of BChl *c* thin-film was remarkably shifted from 722 nm to 735 nm as shown in Figure 3. On the other hand, annealing at 200°C resulted blue shift of Q_y band from 722 nm to 684 nm. This result implies that heat treatment of the thin-film alters the morphological states of the aggregated BChl *c*. Consequently, heat treatment at 100°C and 150°C promoted growth of the molecular assemblies, while thermal decomposition of them were proceeded by the heat treatment at 200°C.

Atomic force microscope (AFM) images of the thin-film before and after the annealing process also support the results of the absorption spectral changes. As shown in Figure 4, a microdomain with *ca* 400 nm of diameter was observed in the case of the heat treatment at 100°C and 150°C in addition to the as-prepared (*viz.* not annealed) one. On the other hand, after annealing at 200°C, such microdomain remarkably decreased.

A BChl *c* thin-film was fabricated onto the surface of ITO/PEDOT:PSS substrate by spin-coating method as shown in Figure 5.

Current-voltage profile of BChl *c* thin-film was measured in the range of -3 V and +3 V and summarized in Table 1. Current density increased with increasing temperature of annealing. Free-base (*viz.* Mg-free) BChl *c* showed the lowest conductivity. Therefore, molecular

assembling markedly improves the conductivity of the thin film. While as-prepared (*viz.* not annealed) and annealed thin-film at 100°C and 150°C exhibited rectification property, bipolar behaviour was observed in the case of the heat-treat films at 200°C. Consequently, conductivity of the thin-film can be regulated through heat-treatment by altering the morphology of the film.

Blended BChl *c* and PCBM thin-film

Blended BChl *c* and PCBM thin-films were spin-coated on the surface of an ITO/PEDOT:PSS substrate using CHCl₃ as the solvent (Figure 6) and their photovoltaic properties were characterized and evaluated.

The absorption spectra of blended BChl *c* and PCBM thin-films were measured and compared with a pristine BChl *c* thin-film as shown in Figure 7. A red shift of the Q_y band from 735 nm to 745 nm was observed after the addition of PCBM into BChl *c*. This spectral change is ascribed to the complexation of BChl *c* and PCBM. FT-IR measurements also support this result since a new absorption band at 1651 cm⁻¹ was observed when PCBM was blended with BChl *c* thin-film, which is assigned to the coordination bond between the O-atom of the C=O group in PCBM to Mg in BChl *c*.^{1,11}

Bulk heterojunction solar cells composed of ITO/ PEDOT: PSS/BChl *c* and PCBM/Al were fabricated and their photovoltaic properties were investigated. Weight ratios of BChl *c* and PCBM of 1:1, 1.25, 1.5, 1.75, and 2 were examined. Each cell exhibited low *PCE* ranging from $2.7 \times 10^{-2}\%$ to $6.2 \times 10^{-2}\%$, with short circuit current (J_{sc}) of 0.41-0.65 mA/cm², open circuit voltage (V_{oc}) of 0.33-0.40 V, and a fill factor (*FF*) of 0.24-0.27 as shown in Figure 8. Among these results, maximum J_{sc} and V_{oc} and the highest *PCE* were attained with [PCBM]/[BChl *c*] being 1.5.

The incident photon-to-current conversion efficiency (IPCE) profile of ITO/PEDOT:PSS/BChl*c* and PCBM/Al with various weight ratios of [PCBM]/[BChl *c*] are shown in Figure 9. The maximum IPCE value is 5.1% at 745 nm. This increase corresponds to an increase of short circuit current density. A remarkable increase in photocurrent at around 745 nm (Q_y band region) was observed in each blended BChl *c* and PCBM thin-film. This result implies that complex formation of BChl *c* and PCBM might be responsible for the increase in effective charge separation sites.

It is known that the V_{oc} of bulk heterojunction polymer solar cell is related to the difference between the highest occupied molecular orbital (HOMO) of the donor materials and the lowest unoccupied orbital (LUMO) of the acceptor material.^{13,14} When the charge transport path is not

appropriate, the internal resistance of the cell increases. In this work, increase of V_{oc} was attributed to the formation of an appropriate charge transport path through PCBM. Though the predominant factor of V_{oc} is still not clear, V_{oc} in this work might be related to the donor-acceptor morphology.

The self-assembling BChl *c* was utilized as a light harvesting and charge transporting materials. The accurate structure of molecular assembly is still obscure since the obtained BChl *c* composed of 3 homologues. However, the thin-films of BChl *c* showed interesting spectral changes caused by the addition of PCBM, which was assigned to the intermolecular coordination in the thin-films. Furthermore, a bulk heterojunction based on a blended BChl *c* and PCBM thin-film was fabricated and the device showed specific photovoltaic performance. The energy conversion efficiency of the cell increased remarkably through the complex formation of BChl *c* and PCBM in terms of the increase of effective charge separation site.

Consequently, though the optimizations of the weight ratios of BChl *c* and PCBM, and/or other conditions still have to be investigated, our self-assembling photosynthetic dye is able to form an effective light-harvesting part and such morphologically controllable aggregate can act as charge transporting path for organic thin-film solar cells.

Acknowledgements

We thank Prof. Hitoshi Tamiaki and Prof. Kaku Uehara for provision of *Chlorobium tepidum*. We also thank Dr. Yoshikazu Suzuki for FT-IR measurement.

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Figure Captions

Figure 1 BChl *c* R₇ = CH₃. R₈ = C₂H₅ (E), n-C₃H₇ (P), *iso*-C₄H₉ (I). R₁₂ = C₂H₅ (E), R₂₀ = CH₃.

Figure 2 HPLC traces of the mixture of BChl *c* homologues.

Figure 3 UV-vis absorption spectra of BChl *c* thin-film before and after the annealing at 100°C, 150°C, or 200°C for 6 min.

Figure 4 AFM images (5 μm square) of BChl *c* thin-film before and after the annealing at 100°C, 150°C, or 200°C for 6 min.

Figure 5 BChl *c* thin-film.

Figure 6 Blended BChl *c* -PCBM thin-film.

Figure 7 UV-vis absorption spectra of blended BChl *c* and PCBM thin-film.

Figure 8 Photovoltaic properties of ITO/ PEDOT: PSS/BChl *c* and PCBM/Al.

Figure 9 IPCE profile of ITO/ PEDOT: PSS/BChl *c* and PCBM/Al with various weight ratios of [PCBM]/[BChl *c*].

Table 1. Current densities of BChl *c* thin-film

Thin-film	Current density at -3 V (mA/cm ²)	I/V Profile
Free-base BChl <i>c</i> (no annealing)	2.31×10^{-1}	Rectification property
BChl <i>c</i> (no annealing)	6.00×10^{-1}	Rectification property
annealed (100°C) BChl <i>c</i>	4.71×10^0	Rectification property
annealed (150°C) BChl <i>c</i>	9.21×10^0	Rectification property
annealed (200°C) BChl <i>c</i>	7.44×10	Bipolar property

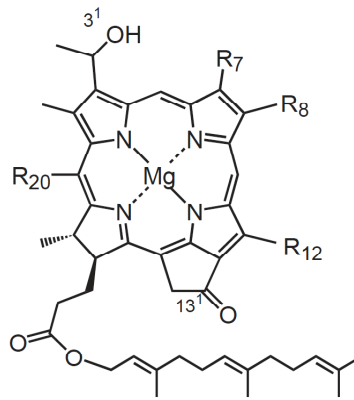


Figure 1 BChl *c* $R_7 = \text{CH}_3$, $R_8 = \text{C}_2\text{H}_5$ (E), $n\text{-C}_3\text{H}_7$ (P), *iso*- C_4H_9 (I). $R_{12} = \text{C}_2\text{H}_5$ (E), $R_{20} = \text{CH}_3$.

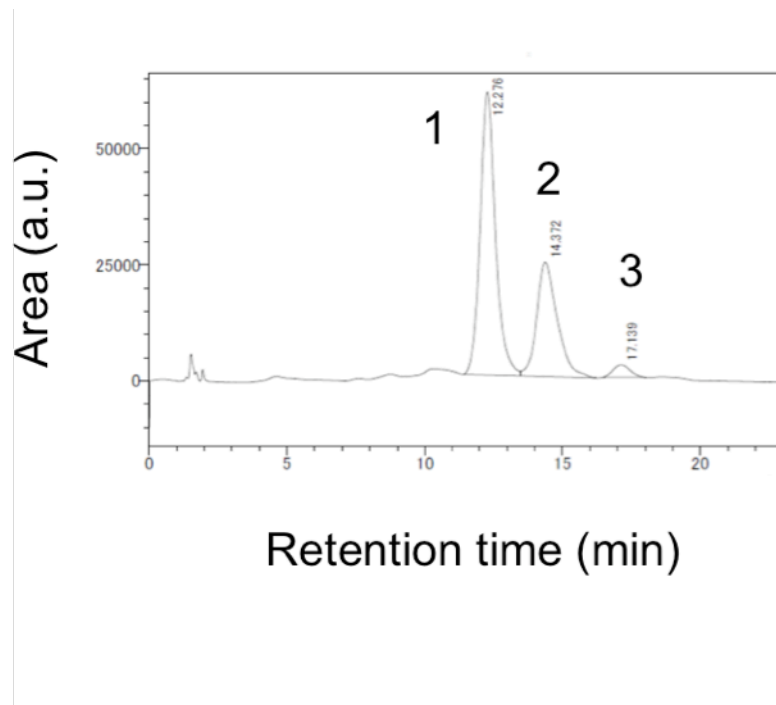


Figure 2 HPLC traces of the mixture of BChl *c* homologues.

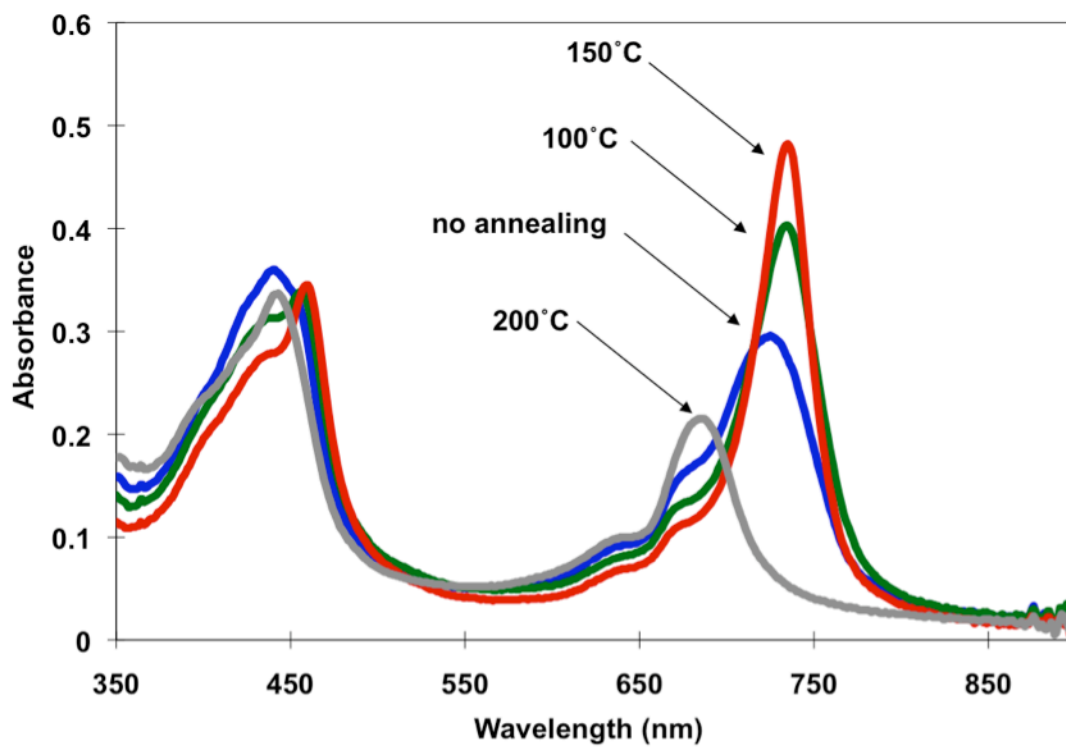


Figure 3 UV-vis absorption spectra of BChl *c* thin-film before and after the annealing at 100°C, 150°C, or 200°C for 6 min.

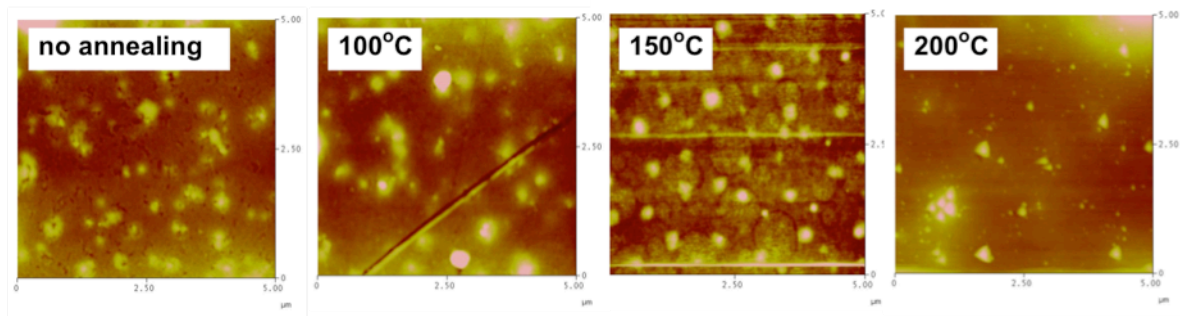


Figure 4 AFM images ($5 \mu\text{m}$ square) of BChl *c* thin-film before and after the annealing at 100°C , 150°C , or 200°C for 6 min.

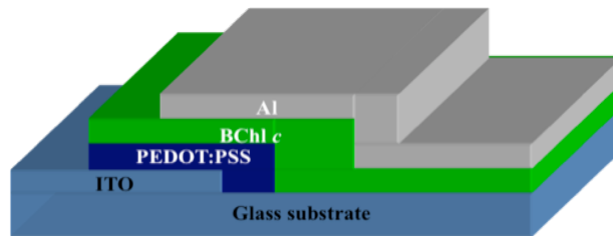


Figure 5 BChl *c* thin-film.

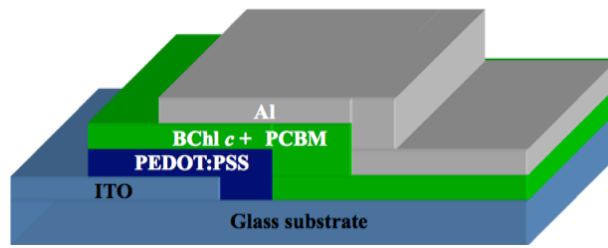


Figure 6 Blended BChl *c* -PCBM thin-film.

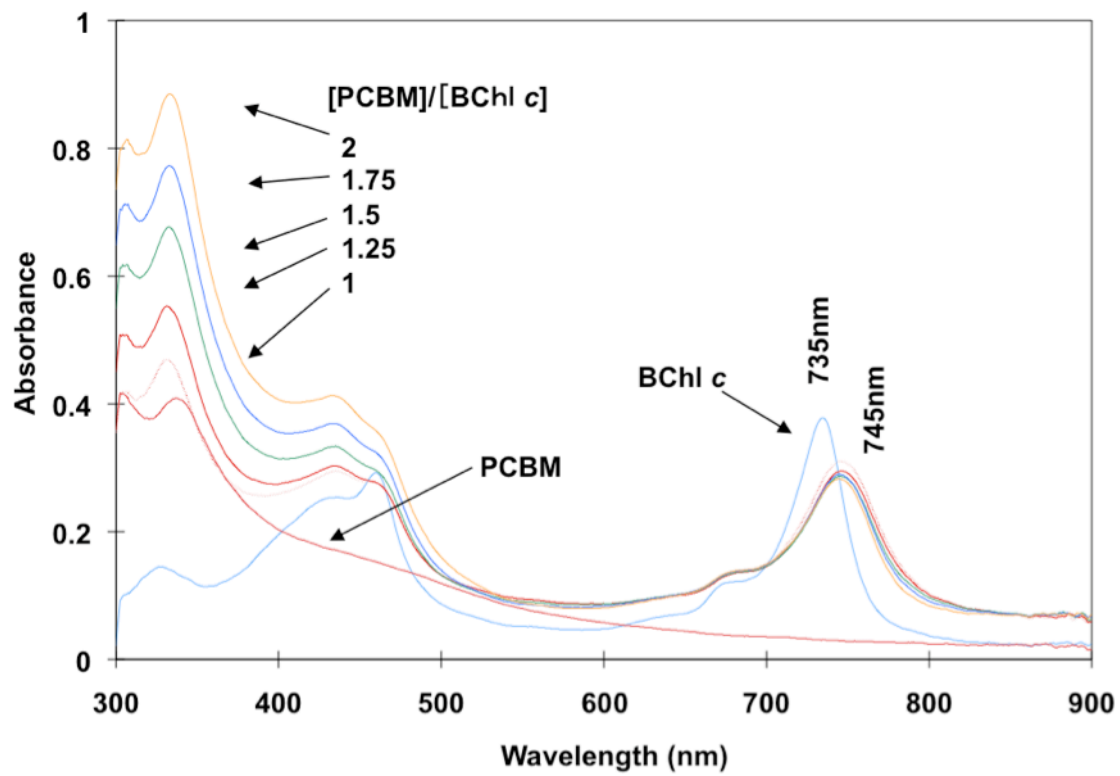


Figure 7 UV-vis absorption spectra of blended BChl *c* and PCBM thin-film.

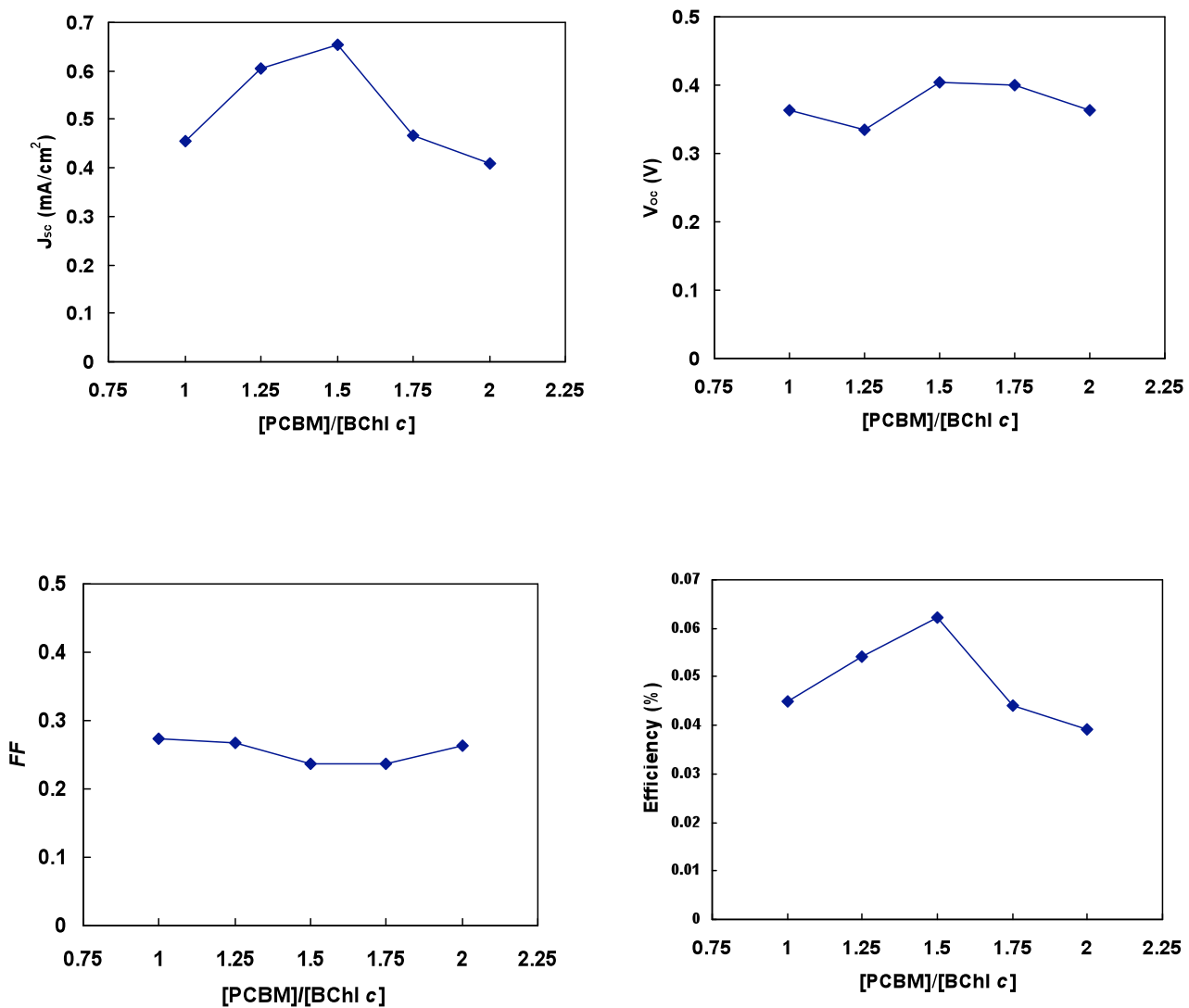


Figure 8 Photovoltaic properties of ITO/ PEDOT: PSS/BChl *c* and PCBM/Al.

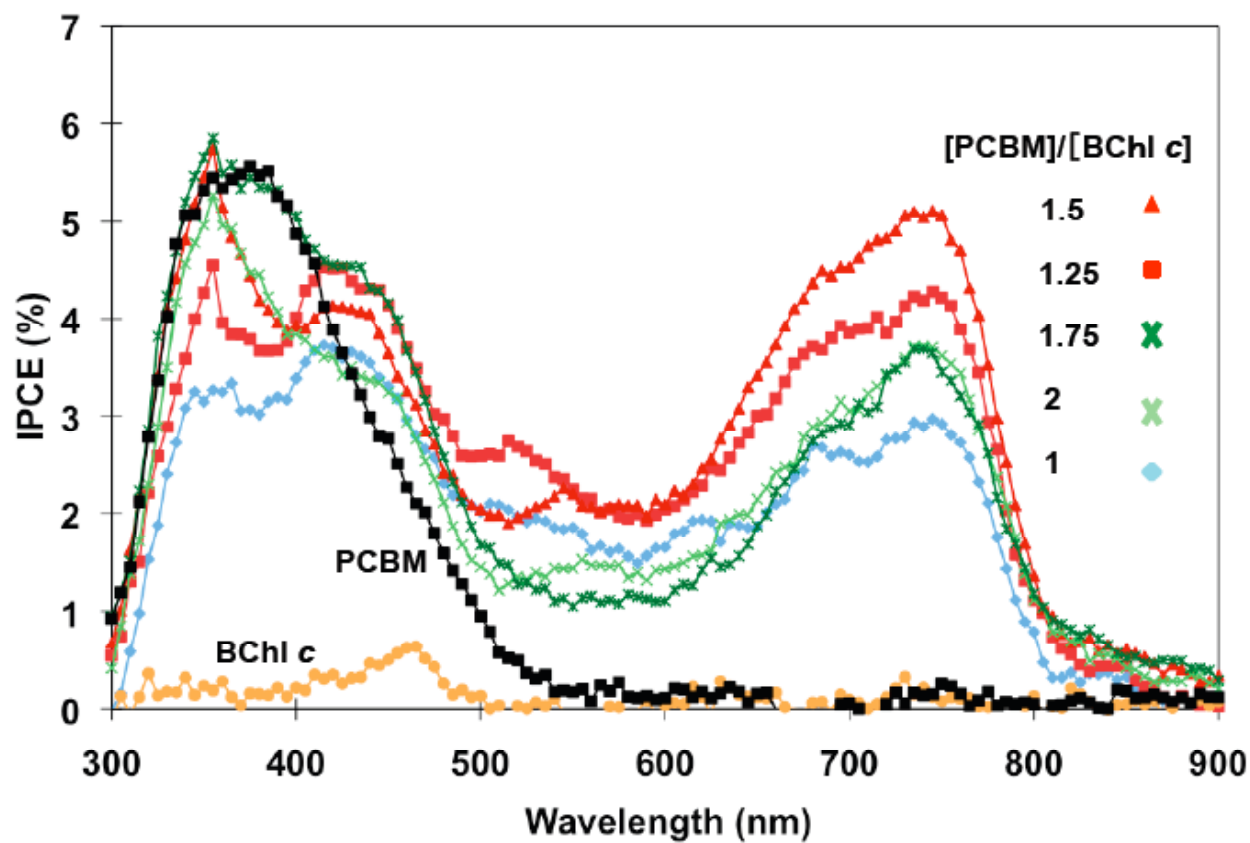


Figure 9 IPCE profile of ITO/ PEDOT: PSS/BChl *c* and PCBM/Al with various weight ratios of [PCBM]/[BChl *c*].