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Osaka University

Doctoral Dissertation

Study on mesogenic-phthalocyanine-based bulk
heterojunction solar cells with donor-acceptor
phase-separated structures

液晶性フタロシアニンを用いたドナー—アセプタ相分離構造を有するバ
ルクヘテロ接合太陽電池に関する研究

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Abstract

A study on photovoltaic properties of octaalkylphthalocyanine (C_nPcH₂)-based bulk heterojunction (BHJ) organic solar cells (OSCs) with donor and acceptor phase-separated structures is reported. The effects of processing additives on the donor and acceptor phase separation and crystallization of BHJ materials are investigated and the high photovoltaic performances of the OSCs are achieved with the optimum donor and acceptor phase separation and crystallization of BHJ materials. Furthermore, the optical and electronic properties, structures, and stability of C_nPcH₂ are evaluated.

Chapter 1: Introduction

The purpose and overview of the dissertation is given. The general background of BHJ OSCs and their mechanism are also introduced. The fundamental properties, such as the optical and electronic properties, of mesogenic-phthalocyanine are briefly described.

Chapter 2: Effects of processing additives on donor and acceptor phase separation, crystallization and photovoltaic performances of solar cells

Studies on the effects of processing additives on the donor and acceptor phase separation, crystallization, and photovoltaic performance of BHJ OSCs made of 1,4,8,11,15,18,22,25-octahexylphthalocyanine (C₆PcH₂) and [6,6]-phenyl-C₆₁ butyric acid methyl ester ([60]PCBM) via spin-casting are reported. By incorporating various solvents as processing additives to a volume of a few percent, the separation of donor and acceptor phases in C₆PcH₂: [60]PCBM thin films, which is discussed by taking the photoluminescence (PL) quenching, Davydov splitting at the Q-band of the absorbance spectra and the surface nanomorphology into consideration, is promoted, and the crystallinity of the discotic C₆PcH₂ molecules with hexagonal structures is reinforced. The BHJ OSCs with the optimum phase-separated BHJ materials and high crystallinity of the discotic C₆PcH₂ molecules demonstrate the high power conversion efficiency (PCE) of 4.2%.

Chapter 3: Roles of fullerene in photovoltaic properties of solar cells

The C₆PcH₂: [60]PCBM-based BHJ OSCs demonstrated the relatively high PCE of 4.2%, and the external quantum efficiency (EQE) at Q band of phthalocyanine close to 60%, by utilizing

processing additives. However, the EQE at around 500 nm was limited due to the low absorption of both C6PcH₂ and [60]PCBM. By using asymmetric fullerene derivatives, [6,6]-phenyl-C₇₁ butyric acid methyl ester ([70]PCBM), the EQE of the OSCs at around 500 nm is improved from 8% to 24%, and the short-circuit current density increases from 8.1 to 10.2 mA/cm². An open-circuit voltage of 0.96 V is achieved by a using fullerene derivative with a high lowest unoccupied molecular orbital. Furthermore, the effects of blend ratios on the photovoltaic properties of BHJ OSCs utilizing C6PcH₂ were also discussed.

Chapter 4: Alkyl substituent length dependence of photovoltaic performance of solar cells

Alkyl substituent length dependences of photovoltaic performance of BHJ OSCs utilizing CnPcH₂ mixed in [70]PCBM are studied. By shortening the alkyl substituents, stacking of the discotic CnPcH₂ columns is probably changed from 2-D rectangular lattices to pseudo-hexagonal structures, and Davydov splitting at the Q-band of CnPcH₂ absorbance spectra decreases, which results in the balance of hole and electron mobilities and the deeper highest occupied molecular orbital energy levels. As a result, the photovoltaic performance of CnPcH₂-based BHJ OSCs is improved by shortening the alky substituent length.

Chapter 5: Mechanism of degradation and improvement of stability on mesogenic-phthalocyanine-based solar cells

Mechanism of degradation and improvement of stability on mesogenic-phthalocyanine-based solar cells are studied. C6PcH₂-based cells demonstrate higher stability than the cells fabricated using poly(3-hexylthiophene) without any ambient dependence. Furthermore, one found that the chemical bonds of two pyrrole aza nitrogens as well as the four mesobridging aza nitrogens with neighboring carbons in the C6PcH₂ molecule are broken after irradiation with a solar simulator, which affected the device lifetime. On the other hand, the C₆₀ thin films and the oxidized layers play an important role as blocking layers that prevent the diffusion of metal atoms into the active layer, resulting in the higher stability.

Chapter 6: Conclusion

The obtained results are summarized and the main conclusions are drawn.

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Chapter 1

Introduction

With the recent rise in the awareness of environmental issues, renewable energy sources have attracted considerable attention. In terms of photovoltaics, since the discovery of photoluminescence (PL) quenching, photoinduced charge transfer, and photoconduction enhancement in π -conjugated polymer-fullerene composite systems, bulk-heterojunction (BHJ) organic solar cells (OSCs) have been considered to be promising candidates for a light weight, flexible, large-area, low-cost, and renewable energy source [1-4]. Furthermore, a combination of material design, morphology control, structural insight, and device engineering has led to high-photovoltaic-performance BHJ OSCs with power conversion efficiencies (PCEs) reaching the 6–10% range [5, 6].

In terms of material design, donor materials are classified into two major groups: polymer and small-molecule-based semiconductors. Despite the high PCE reported for polymer BHJ OSCs, one found that for a given polymer structure, batch-to-batch variations in solubility, molecular weight, polydispersity, and purity can lead to the different processing properties and performance [7]. On the other hand, active layers in solution-processed small-molecule BHJ OSCs consist of well-defined molecules of intermediate dimensions. The higher molecular precision, relative to the statistically determined nature of synthetic polymers, can circumvent the aforementioned batch-to-batch variations. More reproducible fabrication protocols and a better understanding of molecular structure-property relationships are therefore anticipated.

Liquid crystals have been demonstrated as a novel type of small-molecule semiconductors for solution-processed BHJ OSCs [8-10]. In general, typical structures of mesogenic molecules are of “rodlike” and “disklike” types, which are known as calamitic and discotic liquid crystals, respectively. For discotic liquid crystals, the mesogenic molecule consists of a rigid core with a π -electronic conjugation system and alkyl substituents at peripheral or nonperipheral positions. While the core parts play an important role in electronic conduction, the flexible parts definitively attribute the self-assembling nature. In addition, the flexible parts have made such alkylated π -electronic conjugation systems much more attractive for “wet processing” thin-film devices due to their good solubility in common organic solvents. Recently, we have demonstrated high hole and electron drift mobilities in the crystalline phase of a mesogenic phthalocyanine derivative, 1,4,8,11,15,18,22,25-octahexylphthalocyanine (C6PcH₂) [9]. Moreover, C6PcH₂ exhibits not only

excellent processability in the form of thin films but also appropriate electronic characteristics for OSCs, such as a deep highest occupied molecular orbital (HOMO) energy level, a relatively small band gap, and strong optical absorption. Despite these attractive characteristics, OSCs with an active layer composed of C6PcH₂ mixed with [6,6]-phenyl-C₆₁ butyric acid methyl ester ([60]PCBM) showed the relatively low PCEs owing to poor BHJ-separated phases and the low external quantum efficiency (EQE) at around 500 nm [10].

In this dissertation, we mainly focused on investigating effects of processing additives and blend ratios on nanoscale phase separation, crystallization and photovoltaic performances of BHJ OSC utilizing C6PcH₂. Furthermore, the alkyl substituent length dependence of the photovoltaic performances of the OSCs was investigated, and the low EQE at around 500 nm was improved by employing asymmetric [6,6]-phenyl-C₇₁ butyric acid methyl ester ([70]PCBM). Otherwise, the mechanism of degradation and the stability of the BHJ OSCs were studied.

The outline of this dissertation is as follows. The remainder of this chapter will be assigned to introduce the fundamental concepts used in this dissertation: namely they are categorization of the solar cell technologies, photovoltaic principles, and properties and application of phthalocyanine. Chapter 2 devotes to investigate the effects of processing additives on the donor and acceptor phase separation, crystallization, and photovoltaic performance of the BHJ OSCs utilized discotic C6PcH₂ mixed with [60]PCBM. The BHJ OSCs with the optimum donor and acceptor phase separation and crystallization of the BHJ materials, achieved by adding 0.2% v/v of DIO to the BHJ blend solution, exhibited the high PCE of 4.2%. By using the optimum donor and acceptor phase separation and crystallization of the BHJ materials, the roles of fullerene derivatives in the photovoltaic properties of the BHJ OSCs utilizing C6PcH₂ and the dependences of optical and electronic properties, structures, and photovoltaic performance of BHJ OSCs utilizing C_nPcH₂ mixed [70]PCBM on the length of alkyl substituents will be investigated in chapters 3 and 4, respectively. In chapter 5, the high stability as well as the mechanism of degradation of C6PcH₂: [60]PCBM BHJ OSCs will be discussed. The main results obtained in each chapter will be summarized in chapter 6 and future prospects will be discussed.

1.1 Solar cell

New power generation and storage equipment, ranging from batteries to power plants, must be continually developed and manufactured to meet the ever increasing demand for electrical power around the globe for a wide variety of applications. Solar cells have the ability to meet some of these power demands by directly converting sunlight into electricity and can potentially generate power anywhere there is light. Since, Alexandre-Edmond Becquerel first observed the photovoltaic effect in an electrolyte solution in 1839 and the modern era of solid-state solar cells was ushered in with developments at Bell Labs in 1954, numerous solar cell technologies were developed at this point [11, 12]. In this dissertation, we will focus on the understanding and development of one of these technologies, organic solar cells.

1.2 Current solar cell technologies

Many solar technologies exist with varying degrees of development, and organic solar cells are one of the newer classes of these technologies. This section will briefly discuss the main solar cell technologies at present to help put the role of organics in context. The most commercially available solar cell technologies can be divided into two main groups: crystalline and multicrystalline silicon and inorganic thin films. After these two main groups, there are several emerging technologies that have not yet seen broad commercial availability but still been heavily investigated in the laboratory for future application, including GaAs, concentrator, dye-sensitized, and organic thin-film solar cells.

Solar cells based on crystalline and multicrystalline silicon are by far the most developed and produced of all the solar cell technologies. The development of silicon solar cells greatly benefited from the large-scale effort to understand and process silicon as a semiconductor for electronics and integrated circuits. In silicon solar cells, a photon is absorbed to generate a free hole and electron that are separated and collected to generate current [11]. PCEs, which define the percent of incoming light power converted into electrical power, up to 25% and 20.4% have been demonstrated in crystalline and multicrystalline silicon solar cells, respectively [13]. While silicon is by far the leading solar cell technology, there are still many areas for improvement either with advances in silicon or with other material systems. First, high-purity silicon is generally expensive and slow to grow. Because silicon is an indirect band-gap semiconductor and has a weaker absorption compared to other semiconductors, thicker layers of silicon are generally required compared to other materials [12]. For these and other reasons, the silicon alone accounts for nearly 50% of the cost of a completed solar module. To circumvent some of these limitations and potentially achieve lower costs

per produced power, technologies are also being developed that can use less material either by having thinner active layers based on thin films or smaller active layers with light from a large area concentrated onto the small cell.

Inorganic thin-film solar cells are the basis for nearly all of the presently available commercial solar cells that are not based on crystalline and multicrystalline silicon. Inorganic thin-film solar cells attempt to reduce the expensive cost of wafers in silicon cells by using thin films of semiconductors that are usually deposited onto a supporting substrate. The active layers are only a few microns thick but can still absorb significant amounts of light because of strong absorption in the materials. More impurities in the semiconductors can be tolerated since charges have a shorter distance to travel through the thin films [12]. Deposition and processing of thin-film materials also uses lower temperatures compared to silicon. Lower active material volume, purity, and processing temperatures can all lead to lower cost per area for thin-film solar cells, though it generally comes with a tradeoff of efficiency relative to crystalline and monocrystalline silicon. The net effect is a cost per Watt that is competitive with silicon. The leading material platforms for inorganic thin-film cells are amorphous silicon (a-Si), Cu(InGa)Se₂ (CIGS), and CdTe with highest efficiencies of 10.1%, 19.6%, and 19.6%, respectively [13].

Numerous other solar cell technologies exist that are still not widely available commercially. The highest efficiencies have been demonstrated in cells based on GaAs for both single and multijunction devices. Multijunction solar cells use multiple layers that are tailored to more efficiently convert different portions of the solar spectrum based on the band gap of the layers. However, GaAs solar cells have generally been limited to space applications because of their higher cost [12]. The high cost of high efficiency cells can potentially be offset by concentrating a large area of sunlight onto a solar cell with a small area. Concentration can produce a large amount of power with only a small amount of semiconductor. Furthermore, higher efficiencies can be obtained under concentrated light compared to the standard one sun illumination [14]. Efficiencies of 44% have been obtained in multijunction solar cells under concentrated sunlight [13].

Two other technologies that have been garnering significant attention are based on organic materials. Dye-sensitized solar cells use an organic dye coating a porous electrode with large surface area to absorb light. Efficiencies of up to 11.9% have been achieved for dye-sensitized solar cells [13]. Another organic technology is thin-film solar cells based on solid-state organic semiconductors. Organic semiconductors can have their chemical and electrical properties tailored in numerous ways by modifying the chemical structures and can allow for new processing methods. Organics have great potential for light-weight, flexible devices fabricated with high-throughput processes from

low-cost materials in a variety of colors. Although organic semiconductors are still a relatively young field, the high PCEs of 10.7% are achieved [13].

1.3 Organic solar cells

Thin-film solar cells based on organic semiconductors are interesting for several reasons. Firstly, the electrical and chemical properties of organic semiconductors can be tailored by modifying the chemical structure of the compounds in endless combinations. Though specific design rules are still under investigation, the potential for tailoring molecules to different applications is great. Furthermore, the organic molecules have the potential to be cheaply synthesized without significant concern on the limit of raw materials. Next, organic semiconductors can be deposited in a number of low-temperature and high-throughput ways, such as evaporation and solution processing, that can lower manufacturing costs. Because organic materials can have high absorption coefficients, a layer of only a few hundred nanometers is often enough to absorb a large fraction of light in the material's absorption spectrum. The use of such thin layers reduces the amount of active material needed and also makes light-weight and flexible devices possible. For these and other reasons, OSCs have gained significant attention.

The first modern solid-state solar cell based on organic materials with a PCE close to or higher than 1% was developed by C. W. Tang during his time at Eastman Kodak [15]. Tang stacked a layer of copper phthalocyanine that donates electrons, or a donor, and a layer of perylene tetracarboxylic derivative that accepts electrons, or an acceptor, between the electrodes. When a photon is absorbed in an organic material, a bound electron-hole pair, called an exciton, is created and must be dissociated to contribute to the current. This architecture is commonly referred to as a planar heterojunction because the deposited layers can be idealized as stacked planes of different materials, as shown in Fig. 1.1(a). Vacuum thermal evaporation is the most common method of depositing the organic layers for planar-heterojunction devices. The exciton diffusion length is the average distance that an exciton travels before recombining and is critical in planar-heterojunction devices because a photogenerated exciton must travel a distance to the interface of donor and acceptor to be separated into a hole and electron. The short exciton diffusion lengths in most organic materials (on the order of tens of nanometers) limit the thickness of the organic layers. While thick layers are desired for high absorption, layers must also be sufficiently thin to prevent the excessive recombination because of the short exciton diffusion lengths.

To overcome some limitations by the small exciton diffusion length, the donor and acceptor layers can be blended together to minimize the distance, since an exciton must travel to reach the

interface of donor and acceptor. This structure is called a bulk heterojunctions since the heterojunction is dispersed throughout the bulk of the layer, as shown in Fig. 1.1(b). Hiramoto *et al.* first demonstrated the BHJ structure with a co-deposited layer of metal-free phthalocyanine (as donor) and a perylene tetracarboxylic derivative (as acceptor) between neat layers of the donor and acceptor [16].

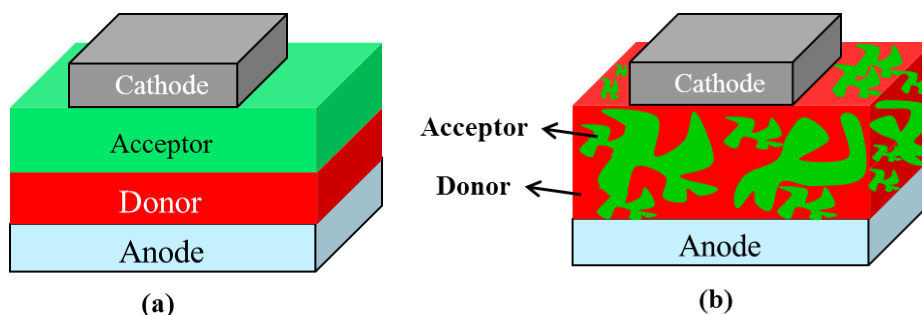


Fig. 1.1. Schematics of the basic structures for (a) planar-heterojunction OSCs and (a) BHJ OSCs.

Bulk heterojunctions also helped facilitate the transition to solution processing of the organic layers. Solution processing is attractive, because it might be more easily applied to large-scale, high-speed manufacturing processes, such as printing, compared to vacuum processing. The first solution-processed organic solar cells incorporating a blend for the active layer were demonstrated by blending the polymers MEH-PPV and cyano-PPV as donor and acceptor, respectively [17, 18]. The natural phase segregation of polymer blends was expected to create pathways to enhance carrier transport, and the work functions of the electrodes are thought to determine the extracted carrier type [17, 18]. Yu *et al.* showed that the acceptor polymer could be replaced with a soluble derivative of [60]PCBM, to yield devices with PCEs up to ~1.5% under low-intensity broadband illumination [4]. Much effort has been made of exploring new polymers and acceptors for BHJ OSCs to increase absorption and carrier transport. One of the most researched combinations to date is poly(3-hexylthiophene) (P3HT) blended with [60]PCBM, which reaches PCEs close to 5% [19, 20]. Recently, new donors with the absorption spectra that extend farther into the red part of the spectrum have been reported in blends with [70]PCBM yielding efficiencies greater than 5% [19].

The phase segregation in the composite thin films has become apparent as a major factor influencing overall device efficiency. Annealing of devices, changing the solvent and the drying speed of the film, and adding chemicals with selective solubility of the fullerene component to affect crystallization have been found to affect the phase segregation and the improvement of photovoltaic performance [19-21]. However, finding the optimum conditions can be very tedious and time

consuming. Researchers are taking advantage of the ability to solution process by demonstrating cells fabricated by various methods, such as screen printing, inkjet printing, gravure printing, brush painting, and even roll-to-roll printing [22-26].

1.4 Photovoltaic principles

This section will cover the basic electrical characteristics common to all solar cells. When measured in the dark, the current density–voltage (J – V) characteristics of most efficient inorganic and organic solar cells resemble the exponential response of a diode with high current in forward bias and small current in reverse bias. Under illumination, the device generates a photocurrent in the cell in addition to the diode behavior, and the J – V characteristic is ideally the superposition of the dark characteristic and the photocurrent. The J – V characteristics of an ideal device can be described by the Shockley equation with an additional photocurrent term, J_{ph}

$$J = J_0 \left[\exp\left(\frac{eV}{nkT}\right) - 1 \right] - J_{ph} \quad (1.1)$$

where J is the current density, V is the applied voltage, J_0 is the reverse saturation current density of the diode, e is the elementary charge, n is the ideality factor, k is the Boltzmann constant, and T is temperature [27]. In reality, the photocurrent will have a dependence on applied voltage, and the illumination can affect the characteristics of the diode.

Figure 1.2 depicts the J – V plot for a solar cell in the region of power generation. Power density, the product of voltage and current density, versus voltage is also plotted, and negative power indicates power generation. The most discussed performance parameters that can be found from the J – V curve of a device under a known illumination source are open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and PCE (or η).

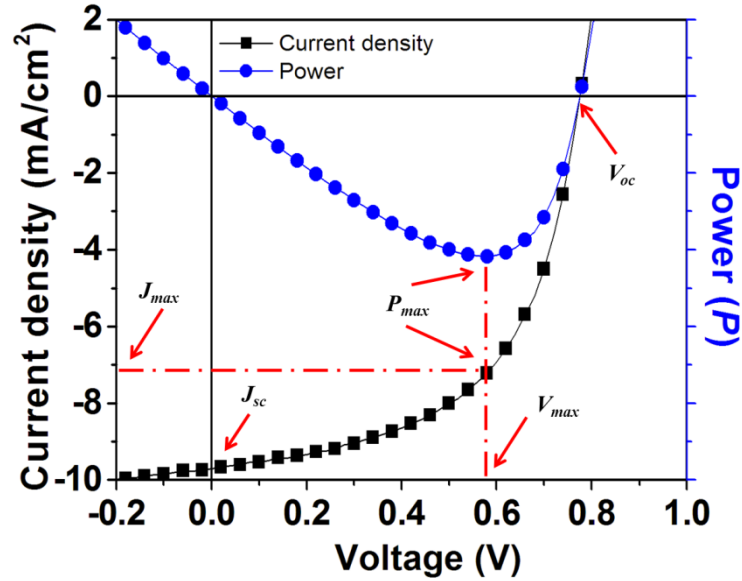


Fig. 1.2. Graphs of power and current density as a function of voltage for a solar cell along with parameters.

1.4.1 Open-circuit voltage

V_{oc} is the voltage across the solar cell when $J = 0$, which is the same as the device being open-circuited. Because $J = 0$ and power is the product of current and voltage, no power is actually produced at this voltage. However, the V_{oc} marks the boundary for voltages at which power can be produced. The V_{oc} can also be thought of as the point at which the photocurrent generation and dark current processes compensate one another.

1.4.2 Short-circuit current

J_{sc} is the current density when $V = 0$, which is the same conditions as the two electrodes of the cell being short-circuited together. Again, there is no power produced at this point, but the J_{sc} does mark the onset of power generation. In ideal devices, the J_{sc} will be the same as the photocurrent density J_{ph} . Although J_{sc} is technically a negative number with the conventions used here, discussions of different J_{sc} values will focus primarily on the magnitude of the value and treat it as a positive number, *e.g.*, a higher J_{sc} corresponds to a higher J_{ph} .

1.4.3 Fill-factor

While V_{oc} and J_{sc} mark the boundaries of power production in a solar cell, the maximum power density produced P_{max} occurs at the voltage V_{max} and current-density J_{max} where the product of J and

V is at a minimum (or maximum in absolute value), as shown in Fig. 1.2. Because of the diode behavior and additional resistance and recombination losses, $|J_{max}|$ and V_{max} are always less than $|J_{sc}|$ and V_{oc} , respectively. The fill factor FF describes these differences and is defined as

$$FF = \frac{J_{max} \times V_{max}}{J_{sc} \times V_{oc}} \quad (1.2)$$

FF is an indication of how close J_{max} and V_{max} come to the boundaries of power production of J_{sc} and V_{oc} , and also an indication of the sharpness of the bend in the exponential J - V curve that connects J_{sc} and V_{oc} . Since higher FF is related to higher maximum power, high FF is desired; however, the diode-like behavior of solar cells results in FF always being less than one. Devices with high $|J_{sc}|$ and V_{oc} can still have low FF , suggesting that something must be done to improve device quality.

1.4.4 Power conversion efficiency

The most discussed performance parameter of a solar cell is the PCE, and is defined as the percentage of incident irradiance I_L (light power per unit area) that is converted into output power. Because the point where the cell operates on the J - V curve changes depending on the load, the output power depends on the load. For consistency, the maximum output power is used for calculating efficiency. In equation form, the PCE, η is written

$$\eta = \frac{|J_{max}| \times V_{max}}{I_L} \times 100\% = \frac{FF \times |J_{sc}| \times V_{oc}}{I_L} \times 100\% \quad (1.3)$$

This form clearly shows that FF , J_{sc} , and V_{oc} all have direct effects on PCE. Furthermore, the area used to calculate J can affect PCE and should include inactive areas that are integral to the solar cell, such as grids and interconnects, when calculating efficiency for large area devices or modules.

PCE is important since it determines how effectively the space occupied by a solar cell is being used and how much area must be covered with solar cells to produce a given amount of power. Since larger areas require more resources to cover with solar cells, higher PCE is often desirable. However, there are tradeoffs between PCE and cost for each solar cell technology that must be balanced.

PCE is also very dependent on the power and spectrum of the light source since solar cells do not absorb and convert photons to electrons at all wavelengths with the same efficiency. To draw comparisons between various solar cells, a standard spectrum must be chosen for the calculation of PCE. Although the spectrum of the sunlight at the earth's surface varies with location, cloud coverage, and other factors, the AM1.5 G spectrum in Fig. 1.3 is the most commonly used standard spectrum for measuring and comparing the photovoltaic performance that are intended for outdoor use. Because of difficulties recreating this exact spectrum in the laboratory with standard lamps, PCE

measurements must often be corrected based on the EQE.

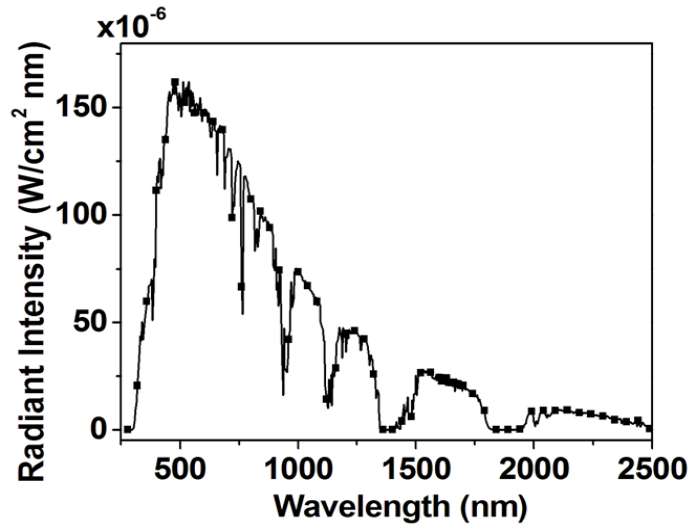


Fig. 1.3. Solar radiant spectra (AM1.5, 100 mW/cm²).

1.4.5 External quantum efficiency

EQE of a device is the fraction of incident photons converted into current and depends on wavelength. One reason for the wavelength dependence is that the absorption in the active layers is a function of wavelength. Another reason, especially in inorganic solar cells, is that the location where a photon is absorbed in a device can also affect the probability of the resulting charges being collected or being lost.

J_{sc} can be estimated from the EQE and the spectral irradiance of the light source by integrating the product of the EQE and the photon flux density. For the standard AM1.5 G spectrum, the calculation is

$$J_{sc} = \int_0^{\infty} eEQE(\lambda) \frac{\lambda}{hc} E_{\lambda}^{AM1.5G}(\lambda) d\lambda \quad (1.4)$$

where $E_{\lambda}^{AM1.5G}$ is the spectral irradiance of the AM1.5 G spectrum, λ is the wavelength, h is Planck's constant, c is the speed of light, and e is the elementary charge. If the EQE was measured at low light intensities, then this calculation will only be accurate if the J_{sc} is a linear function of irradiance, as is expected for ideal devices. Otherwise, EQE must be measured with a dc bias light source that generates a photocurrent in the device similar to what is expected under AM1.5 G.

1.5 Introduction to phthalocyanine: Properties and application

Phthalocyanines possess great chemical and thermal stability, with the unsubstituted derivatives

being able to withstand temperatures of up to ca. 400 °C without decomposing and are also resistant to strong acid and alkaline conditions [28]. These main properties rendered phthalocyanines as popular pigments and colourants [28]. They are very versatile compounds and most of their applications derive from the exploitation of their molecular and bulk properties. A more detailed description of the properties relevant to this project will be discussed.

1.5.1 Optical properties

Phthalocyanines are widely known for their intense blue-green colour as a result of the aromatic 18 π -electron system which they possess. The extended conjugation in the ring produces low energy π - π^* transitions which are detected in two main regions of the UV-Vis spectrum. These are denominated Q and Soret bands (or B band), with the main absorption occurring in the Q-band region. Metallated phthalocyanines exhibit a characteristic single Q-band which appears in the red/near-infrared region of the spectrum (670-720 nm) giving the phthalocyanines their characteristic blue/green colour. Metal-free phthalocyanines are usually characterised on the other hand by a split Q-band signal, arising from the reduced symmetry in the molecular structure compared to the metallated phthalocyanines (D_{2h} for metal-free phthalocyanines and D_{4h} for the metallated phthalocyanines). The split signals are usually designated as Q_x and Q_y . Vibrational overtones can also be detected in the visible region and appear as minor absorptions near the main Q band.

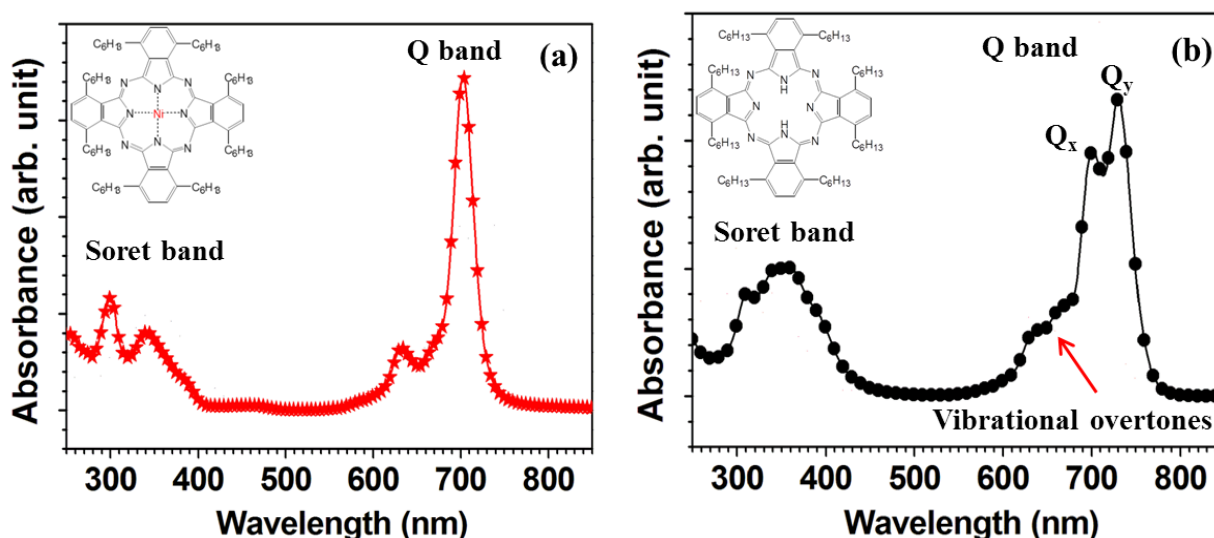


Fig. 1.4. Absorbance spectra of (a) metallated phthalocyanines and (b) metal-free phthalocyanines in solution.

The molar extinction coefficient of these compounds is also uniquely high, rendering them ideal compounds for inks and dyes [29]. Their first use after their discovery was as blue and green

light-resistant pigments and dyes in the paper and textile industries because of their high thermal, chemical, and photochemical stabilities [30]. Currently they are still being manufactured worldwide on a large scale as inks, textile dyes, and plastic colorants provide the basis for most blue-green paints in the automotive industry [28].

The absorption peak in the Q-band region can undergo a bathochromic or hypsochromic shift due to several factors such as the metal ion inserted into the cavity of the phthalocyanine, the addition of substituents at peripheral or non-peripheral positions of the molecule and the type of solvent used. The insertion of a metal in the phthalocyanine macrocycle may result in an excitation transfer between the metal's d-orbitals and the phthalocyanine ligands [31].

On the other hand, the structural modifications in the macrocycle are the main contributors that give rise to the wide range of colours of phthalocyanines that have been synthesised up until now [29, 32]. The functionalization of the phthalocyanine periphery usually produces a bathochromic shift of the Q-band with respect to the Q-band of the unsubstituted phthalocyanine, with the peripheral and non-peripheral positions having different effects [33]. Different substituents also affect the degree of shifting, due to electron-donating effects raising the energy levels of the HOMO orbitals. Also, by extending the π -system, it is even possible to induce a shift of the Q-band well into the near-IR region [33, 34].

Historically, phthalocyanines found themselves known primarily as materials that excelled as dyes and pigments due to their optical properties but their use was limited due to their poor solubility. Once the chemistry of phthalocyanines evolved, it was possible to functionalize these materials to give organic-solvent soluble derivatives that enable exploitation of their other properties and expand the scope of their applications into the novel field of optoelectronics.

The intense absorption in the visible region, the Q band, results from the $a_{1u}-e_g$, $\pi-\pi^*$ transition, generating an orbitally doubly degenerate state, 1E_u , in metal phthalocyanines of D_{4h} symmetry. In the metal-free phthalocyanines, the symmetry is lowered to D_{2h} and the excited state is split into two components usually termed Q_x and Q_y . These then are the two principal 670-720-nm-region absorptions in the mononuclear species.

The theory of interaction between phthalocyanine and between porphyrin molecules has been discussed in the literature, especially in the context of cofacial diporphyrins and chlorophyll dimers, aggregated porphyrins, and oxo-bridged porphyrins, and is generally based on exciton coupling [35].

The exciton coupling is proportional to the magnitudes of the transition moments, inversely proportional to the cube of their separation, and has angular dependence. In D_{4h} symmetry, two pairs of doubly degenerate states will then arise, with transitions to the two upper, in-phase coupled states

allowed (these will be blue-shifted relative to the mononuclear case), and transitions to the lower out-of-phase combinations being forbidden. In the D_{2h} symmetry of the metal-free derivatives, the Q_x and Q_y states will split and the coupling will result in a pair of nondegenerate in-phase higher energy combinations (Q_{y+}, Q_{x+}) and a pair of lower energy outof-phase combinations (Q_{y-}, Q_{x-}) (Fig. 1.5). This theory specifically precludes any overlap between the molecular orbitals of each component. The ground state of the binuclear system corresponds with that of the mononuclear unit but may be stabilized by van der Waals's interaction energy.

In the low symmetry of the real binuclear molecules (tilted and slipped conformations etc.), transitions to both the higher and the lower energy combinations can be expected, yielding intensity both blue- and redshifted with respect to the mononuclear case. A range of energies is anticipated for the in-phase and out-of-phase combinations, arising from the various conformations. At room temperature a Franck-Condon electronic excitation will see a summation of all the dynamic conformations which exist in solution. Without discussing the added complexities of solvent effects varying from mononuclear to binuclear species, a broad absorption is predicted, shifted to the blue of the mononuclear absorption and possessing a broad weak tail to the red. Superimposed on this envelope will be the two Q peaks of species in which the two halves of the molecule are sufficiently uncoupled to be regarded simply as two independent mononuclear species tied together.

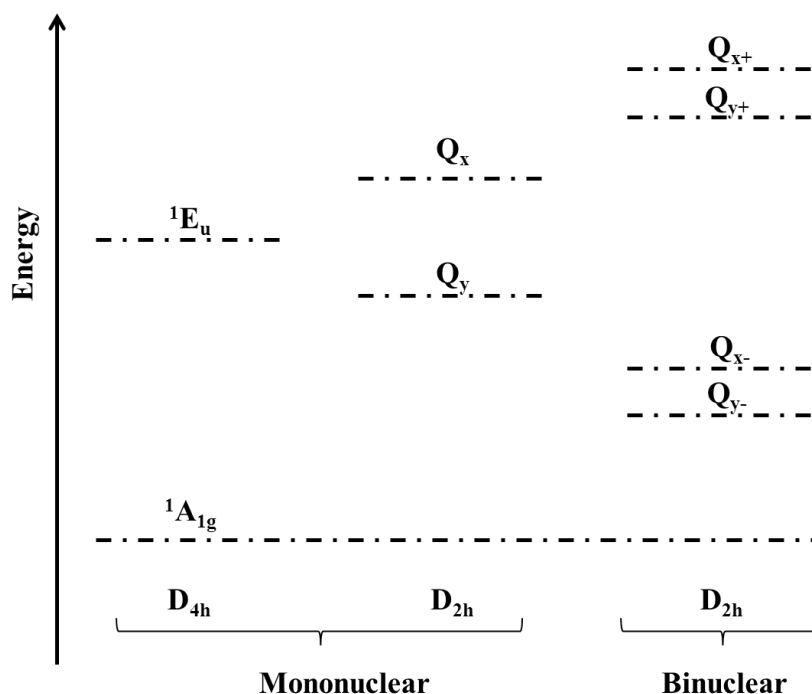


Fig. 1.5. A qualitative orbital energy diagram for exciton coupling.

1.5.2 Semiconductive properties

A semiconductor can be defined as a material that presents electrical conductivity due to either electron flow or “hole” transfer at a magnitude between that of a conductive and an insulating material. This conductivity is roughly established between 10^3 and 10^{-8} S/cm. In simple terms, the conductivity present in these materials arises from the transfer of electrons across the electronic structure of the materials. In a conductive material the electron transfer occurs when the electrons are excited from the ground-state valence band to the conduction band. The energy needed to provide this excitation depends on the energy gap present between these two bands. The size of this gap, as shown in Fig. 1.6, is what determines if a material is a conductor, semiconductor or insulator.

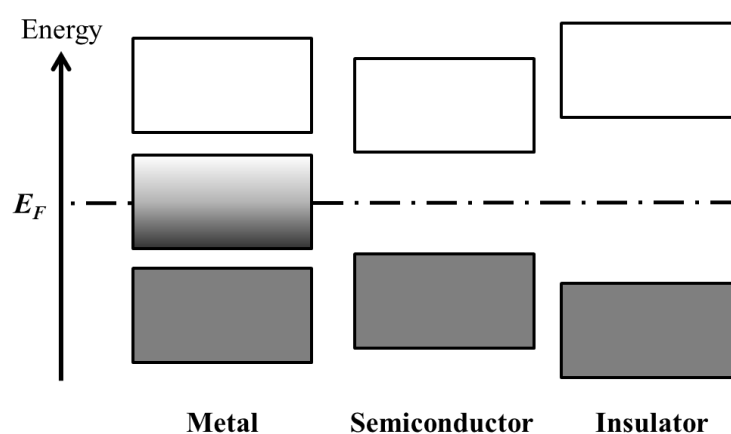


Fig. 1.6. Diagram of the electronic band structure of metals, semiconductors and insulators.

There are two types of semiconductor materials due to the fact that the electron flow can be carried out in two different ways. In the case of n-type semiconductors free-electrons are considered to “move” across covalent bonds through the conduction band. On the other hand, when an electron is excited to the conduction band it will leave a “hole” in the valence band. In this case a neighboring electron can move into this space and subsequently leave another void in its place and so on, making it appear as if the “hole” is moving, behaving like a positive-charged particle.

Most of organic compounds in the solid state have no conductive properties. However, this does not hold for those with conjugated π -electron systems that pack in the solid state in a manner that allows for interaction of the other π clouds of adjacent molecules. Phthalocyanines often meet those requirements and exhibit some levels of conductivity that provide the basis for their use in organic semiconductor devices.

Phthalocyanines were some of the first reported organic semiconductors, and together with other

polycyclic aromatic hydrocarbons they make up a large part of the charge-transfer complexes that present semiconductive properties.

The modifiable nature of phthalocyanines makes them excellent candidates for their use in optoelectronic devices as they can be easily processed as thin films. Unsubstituted phthalocyanines have been made into films by means of vacuum deposition. This technique is not considered to be efficient, as most of the material is wasted. The problem can be overcome by modifying the phthalocyanine structure to make it more soluble and thus rendering it ideal for creating thin films using methods such as spin-coating, drop casting and ink jet printing.

Functionalized-phthalocyanine-based thin films are currently being used as the conductive layers in a wide range of optoelectronic devices, such as organic light-emitting diodes, OSCs, and organic field-effect transistors [36, 37].

1.5.3 Liquid crystal properties

Also known as the “fourth state of matter”, the liquid crystal phase (mesophase) is present between the solid and liquid phases and shares some properties of both states of matter. In liquids, the molecules exist in a highly disordered state in which all molecular directions are equivalent, therefore, no order is detected (isotropic). As we move towards the highly ordered crystal lattice, the molecules become completely anisotropic and arrange themselves in a fixed order and/or position.

In a liquid crystal, the molecules will arrange themselves due to anisotropic interactions to give a phase that presents some degrees of order either positional or orientational whilst preserving its fluidity (Fig. 1.7).

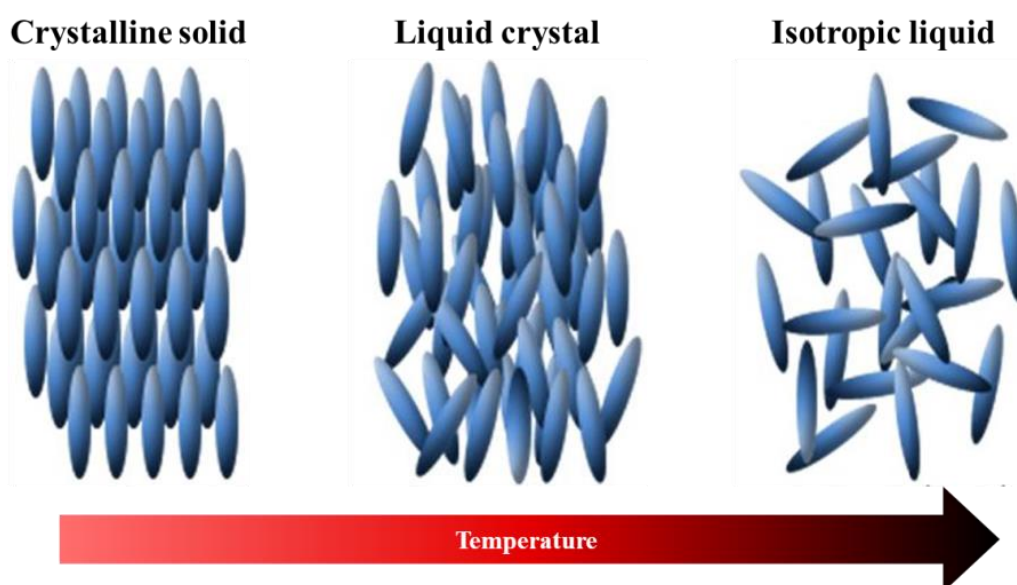


Fig. 1.7. Simplified diagrams of states of mater.

Molecular anisotropy is the main origin for the mesophase. This is due to the intermolecular interactions present in the material, which gives the molecules a preferred orientation or affinity to arrange in a certain direction. Particularly, each molecule presents a predominant axis that provides the direction in which the molecules will tend to arrange themselves by, with the shape of the molecule determining the predominant axis/directional order of the liquid crystal phase.

Liquid crystals can be divided into two main groups: thermotropic and lyotropic. While thermotropic liquid crystal has a stable mesophase at a specific temperature range, whilst lyotropic mesophases only occur upon the addition of a solvent to the liquid crystal material. The thermotropic liquid crystal can be sub-classified into calamitic and discotic liquid crystals. For the purpose of this research, we will focus solely on discotic-type liquid crystals.

The first discotic liquid crystalline materials were discovered in 1977 by Chandrasekhar and other examples were later reported in 1982. This sub-class is formed by disk-shaped molecules in which either one of its molecular axes is shorter than the other. These disk-shaped materials can form different types of liquid crystal phases according to their position and ordering as shown in the diagram below, Fig. 1.8.

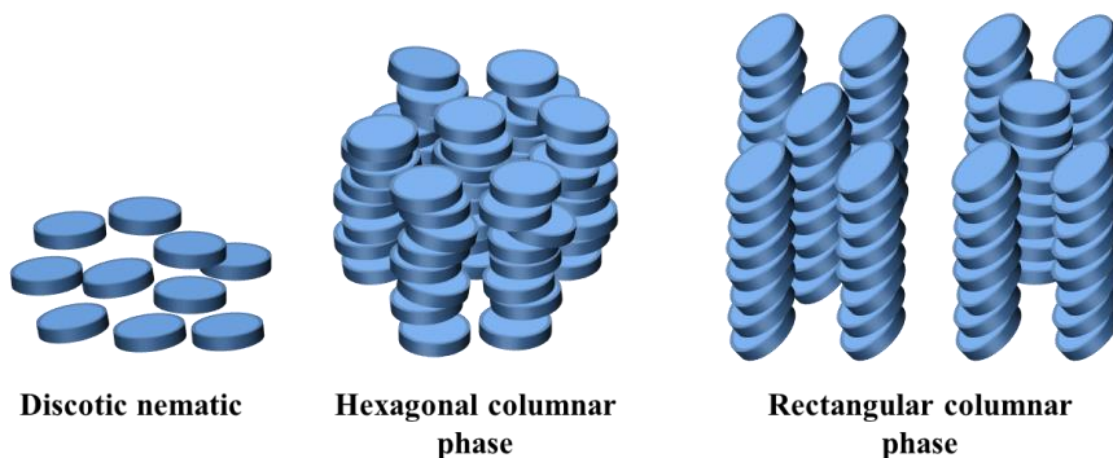


Fig. 1.8. Discotic liquid crystal classification.

The nematic mesophase arises when the molecules are arranged in a similar orientation in line with their longest axes. This arrangement lacks positional order, and therefore provides a high degree of fluidity in the system. When positional order is present however, the molecules will have a tendency to arrange themselves into columns and adopt a bi-directional lattice structure in either a rectangular or hexagonal form.

Phthalocyanines are known to be discotic mesogens. The most commonly known liquid crystalline materials are composed of an electron-rich aromatic core with aliphatic chains attached to

the periphery. Thus addition of aliphatic chains to the phthalocyanine nucleus was first investigated in the 1980's, when it was discovered that these flexible chains led to enhanced solubility in most organic solvents and most importantly promoted the columnar liquid crystal formation. Several groups investigated the effect that different substituents in the peripheral positions had on the formation of discotic mesophases. It was established that alkoxymethyl, alkoxy and alkyl chains led to columnar phase formation. The discotic liquid crystal behaviour was also investigated in the non-peripherally substituted phthalocyanines.

The study led by Cook *et al.* of the non-peripherally substituted macrocycles provided an in-depth understanding of the effect of the substituents on the mesogenic properties. Compounds with linear aliphatic chains of up to 18 carbons and a range of metals such as Cu, Co, Zn, Ni and Pd were investigated, but focus was set on chains of 5-10 carbons. These materials were found to display remarkable properties such as polymesomorphism in which some materials presented up to four different mesophases [38]. Further, examination of the properties of these liquid crystalline materials showed that the derivatives gave an excellent conductometric response to NO₂ whilst a different group used a thin-film of the octahexyl analogue for the development of a gas sensor.

1.5.4 Phthalocyanines for organic solar cells

In terms of OSC, the synthesis of stable low band gap polymers for efficient light-to-electricity conversion is a major challenge. OSCs employing polymer–fullerene heterojunctions have been shown to have the high PCEs [6]. However, most of the available conjugated polymers exhibit band gaps of ca. 2 eV. Therefore, there is a clear mismatch between the absorption spectrum of these macromolecules and the terrestrial solar spectrum, which extends to the near IR.

Phthalocyanines exhibit the high extinction coefficients around 700 nm where the maximum of the solar photon flux occurs for efficient photon harvesting, and many other features, that make them especially suitable for integration in light energy conversion systems. Phthalocyanines have the excellent stability, rich redox chemistry, *p*-type and also *n*-type semiconducting properties, and relative high charge carrier mobility. Therefore, phthalocyanines are among the most intensively studied dyes in this field. They are incorporated as antennas into photovoltaic devices usually in blends together with semiconducting polymers and/or acceptor counter partners such as fullerenes [15, 39].

Thus, a planar-heterojunction structured copper phthalocyanine (CuPc)/C₆₀ thin-film solar cell with Ag as the metal cathode with PCE of 3.5% has been described. Moreover, the PCEs exceeding 5.5% have been obtained by stacking in series two of these cells [40, 41]. The control of V_{oc} in

organic PV cells with multicharge separation interfaces (CuPc or ZnPc/C₆₀ and pentacene/C₆₀) by inserting an ultrathin metallated phthalocyanines layers, has been reported with PCEs reaching 2.04% [42]. OSCs using hexadecafluorophthalocyaninatocopper (CuF16Pc) as electron acceptor material and para-sexiphenyl as electron donor have been reported recently [43]. Doping-induced efficiency enhancement in organic photovoltaic devices has been described recently. By doping rubrene into CuPc/C₆₀-based solar cell, an exceptionally high PCE of 5.58% was achieved [44]. The performance improvement is mainly attributed to efficient light absorption by rubrene in the range of 460–530 nm, where two hosts have low absorbance, leading to more effective exciton formation. These findings motivate the use of fluorescent dyes for maximizing absorption spectral coverage, as well as increasing photon harvesting. Recently, Miyake has reported the high hole and electron drift mobilities in the crystalline phase of a mesogenic phthalocyanine derivative, C6PcH₂ and the BHJ OSCs utilizing the soluble phthalocyanine have reported with the PCEs exceeding 3.1% [9, 10].

Chapter 2

Effects of processing additives on donor and acceptor phase separation, crystallization and photovoltaic performances of solar cells

2.1 Introduction

In terms of BHJ OSCs, by intermixing donors with methanofullerene derivatives, the efficient exciton dissociation is achieved with a large interfacial area, overcoming the limited exciton diffusion length in the BHJ materials, and the high photovoltaic performance is demonstrated. However, continuous pathways for the selective transportation of both electrons and holes to electrodes are essential, and must be controlled to allow maximum absorption of thick films without significant recombination loss [45]. The optimum separation of donor and acceptor phases must have a balance between a large interfacial area and continuous pathways for carrier transportation [46]. Recently, significant progress to control the separation of donor and acceptor phases in BHJ OSCs has been made by optimization of device preparation conditions, including the application of the adjustment of the volume fractions of the components, thermal annealing treatment, and processing additives [19, 21, 47].

Postproduction heat treatment is one approach toward controlling separation of donor and acceptor phases, which resulted in improvement of both J_{sc} and FF . Recent studies have demonstrated improved PCE after thermally annealing polymer-fullerene composite OSCs at elevated temperatures [19, 48-50]. In 2003, F. Padinger et al. reported the high PCE of 3.5% for P3HT:PCBM composite OSCs after postproduction thermal annealing at 75 °C [48]. This demonstration led to extensive studies on the “thermal annealing” approach, and PCE values up to 5% were demonstrated [19]. The higher PCE was attributed to thermally induced morphology modification, thermally induced crystallization, and improved transport across the interface between the BHJ material and the Al electrode.

The thermal annealing approach has been utilized to control the nanoscale morphology of BHJ thin films made of C6PcH₂ and [60]PCBM via spin-casting for photovoltaic applications. Although the improved photovoltaic performance of C6PcH₂:[60]PCBM BHJ OSCs was observed after 10 minute postproduction thermal annealing at 60 °C, the photovoltaic performances of the OSCs were strongly degraded for all parameters after 15 minute of thermal annealing at 125 °C [51]. After thermal annealing, the surface of the thin films, which was observed by optical microscopy, revealed

the presence of defects and holes within the active layer, which might have caused the diffusion of aluminum atoms through the active layer and probably contributed to the lower performances of the OSCs.

Recently, the addition of an alkanedithiol to the main solvent has been shown to markedly improve the photovoltaic performance of BHJ OSCs [21, 52-54]. Although evidences of the formation of phase-separated BHJ materials were clearly observed from AFM images of the surface composite films, there was no alkanedithiol in the thoroughly dried films [21]. It was suggested that the alkanedithiol functioned as a processing additive that improved the nanoscale morphology of the BHJ materials. Moreover, one found that there is no indication of improving crystallization in composite thin films either with or without dithiol processing.

Herein, we clarify two effects of processing additives on BHJ thin films made of C6PcH₂ and [60]PCBM via spin-casting that are used for photovoltaic applications. By adding various solvents as processing additives to a volume of a few percent, i) nanoscale phase separation was promoted and ii) the crystallinity of the discotic C6PcH₂ molecules with the hexagonal structures was reinforced. The photovoltaic cells in the structure of indium tin oxide (ITO)/MoO_x/BHJ/LiF/Al (Fig. 2.1), with the optimum phase-separated BHJ materials and high crystallinity of the discotic C6PcH₂ molecules, had a PCE of 4.2%.

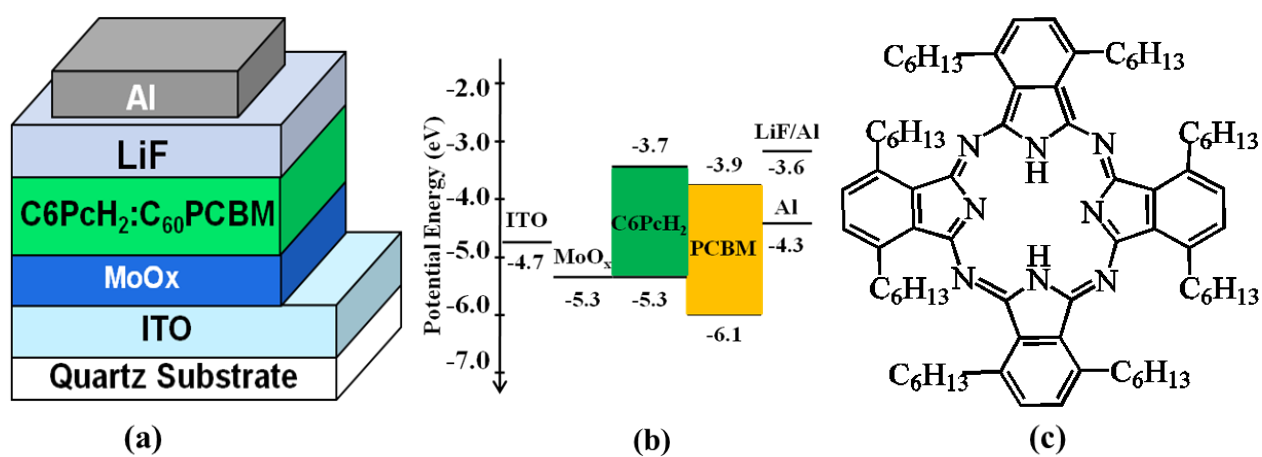


Fig. 2.1. (a) device architecture, (b) energy levels.liquid crystal classification, and (c) Chemical structure of C6PcH₂ molecule.

2.2 Experimental procedure

C6PcH₂, as shown in Fig. 2.1(c), was synthesized as described in the literature [55], with slight modifications, and fully purified by column chromatography (using silica gel with toluene as the eluent), which was followed by repeated recrystallization from toluene-methanol (1:2) solution [9]. PCBM and the solvents used as processing additives, such as 1,8-diiodooctane (DIO), 1,8-dichlorooctane (Chlor), 1,8-dibromooctane (Brom), and 1,8-octanedithiol (Oct), were purchased from Frontier Carbon and Sigma-Aldrich, respectively.

BHJ thin films were prepared under optimized conditions in accordance with the following procedure. An ITO-coated quartz substrate was cleaned with detergent, ultrasonicated in water, chloroform, acetone, and isopropyl alcohol, and subsequently dried with UV-induced ozone. 6-nm-thick MoO_x films were thermally evaporated onto ITO at a rate of 0.1 Å/s under a vacuum of about 2×10^{-5} Pa. A solution containing a mixture of C6PcH₂:[60]PCBM (2:1) in different organic solvents with or without a processing additive was stirred using an ultrasonic washer, which increased the temperature of the solution to 45 °C, and spin-cast at 2000 rpm onto a MoO_x layer. The concentration of the solution with the various primary solvents was summarized in Table 2.1 and the active layers were approximately 130 nm. Herein, the thickness of the active layers was estimated from AFM images. Finally, a 0.3-nm-thick LiF buffer layer and an 80-nm-thick aluminum layer were deposited through a shadow mask by thermal evaporation under a vacuum of about 2×10^{-5} Pa. The active area of the device was 4 mm².

Table 2.1. Solution concentrations in this study

	C6PcH ₂ (mg/ml)	[60]PCBM (mg/ml)
Chloroform	14.9	7.45
Trichloroethylene	20.4	10.2
Toluene	22	11

The device characteristic was measured under irradiation intensity of 100 mW/cm² using an XES 301 (AM 1.5 G) full spectrum solar simulator. The current density-voltage (*J-V*) characteristics were measured using a source measurement unit (Keithley 2400). Otherwise, EQE spectra were measured with a programmable electrometer using Xe lamp light passed through a monochromator as a light source. The integrated EQE values always showed good agreement with the measured valued of *J*_{sc}. The absorbance spectra, PL spectra, and surface morphology were measured by spectrophotometry (Shimadzu UV-3150), using a fluorescence spectrophotometer (F-4500), and AFM (Keyence

VN-8000), respectively. Furthermore, the crystallinity of the C6PcH₂ thin films was evaluated by XRD (Rigaku RINT 2000).

2.3 Effects of processing additive on donor-acceptor phase separation and crystallization

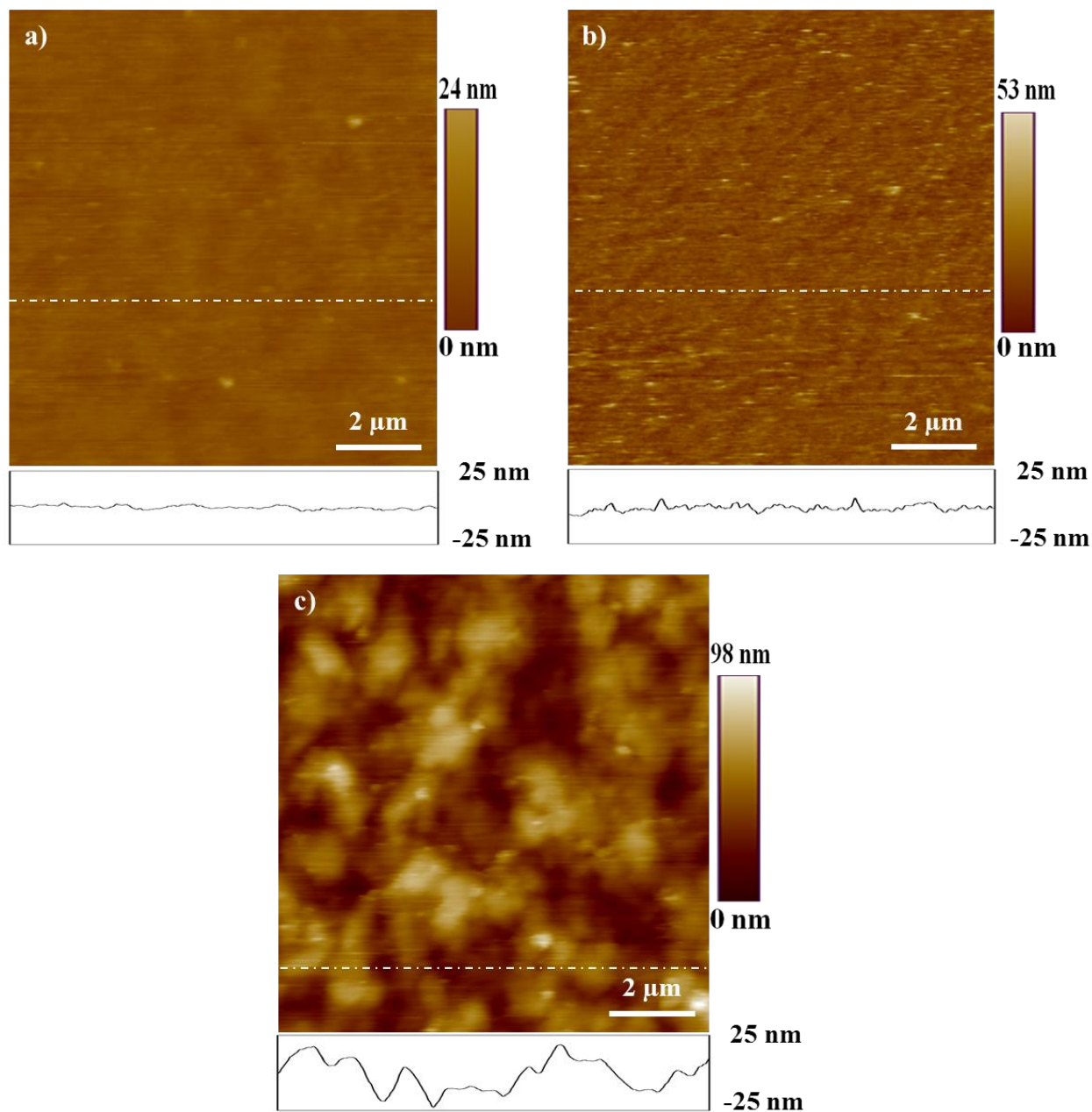


Fig. 2.2. AFM images of surface of C6PcH₂: [60]PCBM composite thin films: (a) without DIO, (b) with 0.2% v/v of DIO, and (c) with 0.8% v/v of DIO.

One found that the domains of BHJ materials, which observed from surfaces of composite thin films, were elongated and the donor and acceptor phases were separated by utilizing processing additives [21, 54]. Figure 2.2 shows the surface morphologies of C6PcH₂: [60]PCBM composite thin

films with different amounts of DIO as a processing additive in toluene solution, which were observed by AFM.

The C6PcH₂:[60]PCBM composite thin film, spin-cast from the blend solution in pure toluene, has a smooth surface with an average surface roughness of 1.4 nm. Upon adding 0.2% and 0.8% v/v of DIO as a processing additive, a number of islands, which considered to be C6PcH₂ domains and/or [60]PCBM clusters, appeared on the smooth surface of the C6PcH₂:[60]PCBM composite thin film, and the average surface roughness gradually increased to 3.2 nm and 13.1 nm, respectively. This result suggests that utilizing DIO as a processing additive caused the phase separation in BHJ films.

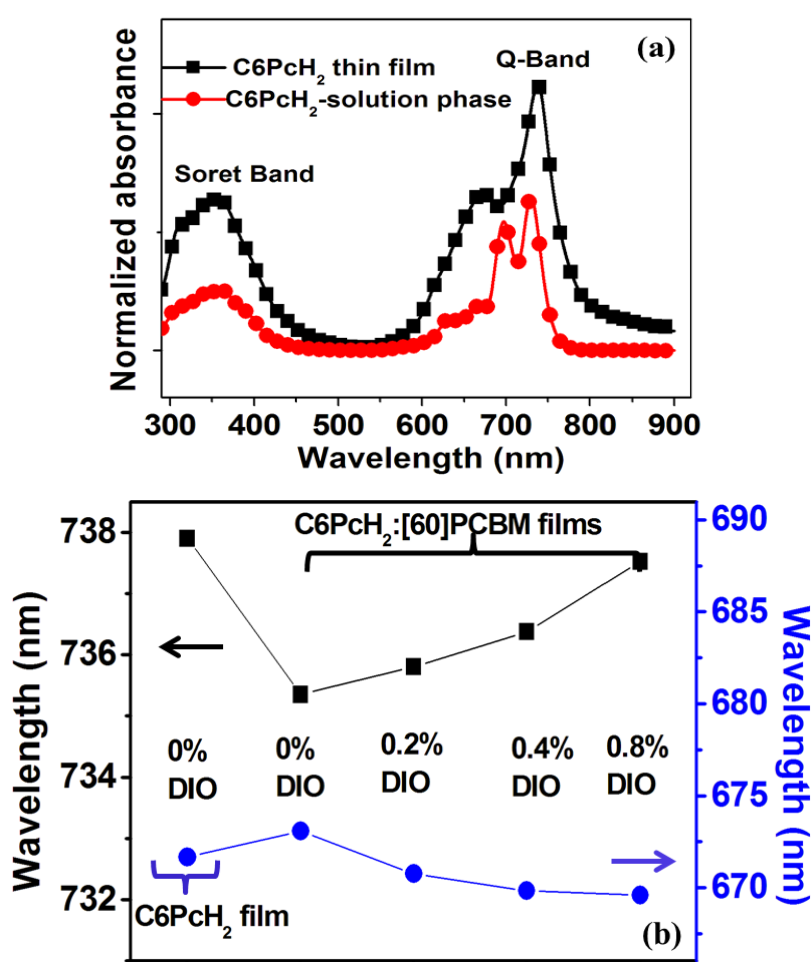


Fig. 2.3. (a) Absorbance spectra of C6PcH₂ in dried thin film and in toluene solution. Absorbance spectra of C6PcH₂ in toluene solution was normalized at 729.8 nm (b) Dependence of size of the Davydov splitting on different amounts of DIO.

Aggregates of phthalocyanine molecules generally exhibit an absorbance spectrum with a broad Q-band that is blue-shifted (H-aggregates) or red-shifted (J-aggregates) with respect to the solution

phase [56-58]. However, the C6PcH₂ spin-cast thin film, as depicted in Fig. 2.3(a), showed blue and red shifts of the Q-band relative to the solution phase from 697.4 nm to 671.8 nm and from 729.8 nm to 737.9 nm, respectively. Although more efforts should be made to understand the arrangement of discotic C6PcH₂ with hexagonal structures, it can be seen that this splitting is consistent with Davydov splitting, which occurs in a crystalline lattice containing translationally nonequivalent molecules, such as a columnar “herringbone” array [58].

Different band shapes in absorbance spectra might result from variations in the orientation and/or packing of molecules within thin films. In particular, the size of Davydov splitting in an allowed electronic transition is a direct measure of the interaction energy between molecules with differing site symmetries [59, 60]. The Davydov splittings, which are indicated by the difference of the Q-band peak wavelengths, of the absorbance spectra of C6PcH₂ and C6PcH₂:[60]PCBM spin-cast thin films fabricated on quartz substrates from toluene with and without DIO as a processing additive are shown in Fig. 2.3(b). The Davydov splitting at the Q-band of the C6PcH₂:[60]PCBM thin films increased gradually upon adding DIO. The increase in the Davydov splitting indicated that the discotic C6PcH₂ with the hexagonal structures interacted more strongly and/or that there was an improvement in the local structural order of the C6PcH₂ molecules compared with the case that the films were processed using pure toluene.

On the other hand, the decrease in the Davydov splitting with the addition of [60]PCBM to the C6PcH₂ thin films indicated that the molecular separation of the discotic C6PcH₂ with the hexagonal structures increased owing to the diffusion of [60]PCBM into the C6PcH₂ domains, which might occur in a C6PcH₂:[60]PCBM mixture. Combining all the above mentioned results, we suggest that donor and acceptor phases were separated by utilizing DIO as a processing additive.

Figure 2.4 shows XRD patterns of C6PcH₂ and C6PcH₂:[60]PCBM thin films fabricated on glass substrates with and without DIO in toluene solution as a processing additive. It can be seen that the diffraction peak of the C6PcH₂ thin film occurred at approximately 4.86°, which corresponds to the intercolumnar distance in the hexagonal structures of 18.2 Å. The increase in the full width at half maximum (FWHM) of the XRD patterns upon adding [60]PCBM, as shown in Table 2.2, indicated that the crystallinity of the discotic C6PcH₂ with the hexagonal structures was reduced owing to the dispersion of [60]PCBM into the C6PcH₂ domains. In contrast, upon incorporating DIO as a processing additive, the FWHM decreased and the crystallinity of the discotic C6PcH₂ with the hexagonal structures was markedly improved. The strong dependence of the crystallinity of C6PcH₂ molecules upon the addition of DIO is completely opposite that of low-band-gap polymers such as poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]-dithiophene)-*alt*-4,7-(2,1,3-benzothiadi

azole)], in which the absence of crystallization was reported for the both cases with and without processing additives [21].

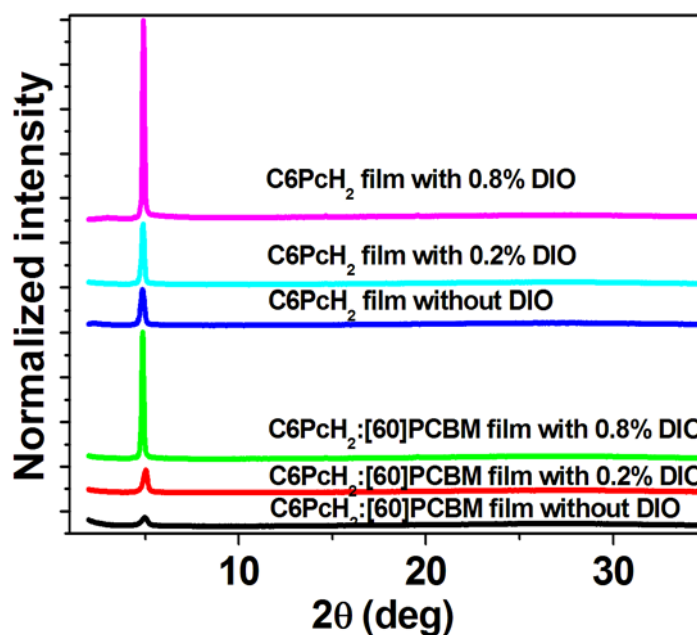


Fig. 2.4. XRD patterns of C6PcH₂ and C6PcH₂:[60]PCBM composite thin film with different amounts of DIO. All XRD patterns were normalized at 4.88°.

Table 2.2. FWHM of XRD patterns of C6PcH₂ and C6PcH₂:[60]PCBM composite thin film with and without DIO as a processing additive in toluene solution

	No DIO	0.2% DIO	0.8% DIO
C6PcH ₂ films	0.26°	0.18°	0.13°
C6PcH ₂ :[60]PCBM films	0.56°	0.29°	0.13°

Moreover, upon adding DIO, the FWHM of the XRD patterns of the C6PcH₂ thin films was gradually decreased, as shown in Table 2.2, and the crystallinity of the discotic C6PcH₂ columns in the hexagonal structures was improved. This indicated that the addition of DIO affects not only the separation of [60]PCBM and C6PcH₂ phases but also the crystallization of C6PcH₂ molecules in the hexagonal structures.

One saw that during the stirring process using ultrasonic treatment, the temperature of the solution increased and the solubility of C6PcH₂ molecules in DIO was improved. These C6PcH₂ molecules in the DIO-solution phase recrystallized during natural cooling. It is proposed that the recrystallization of the C6PcH₂ in the DIO-solution phase caused the improved crystallinity of the discotic C6PcH₂ in the dried thin films. This process is similar to the recrystallization from

toluene-methanol solution, as reported by Miyake et al. [9]. To establish the validity of the proposal, the C6PcH₂ thin films were fabricated by spin-casting from the solution while stirring using a magnetic rod. It is noted that the temperature of the BHJ blend solution was remained at room temperature during the stirring process using the magnetic rods. The XRD patterns of the thin films had an FWHM of approximately 0.22° and there was no indication of the improved crystallinity of C6PcH₂ molecules in the dried thin films either with or without the solvents as processing additives.

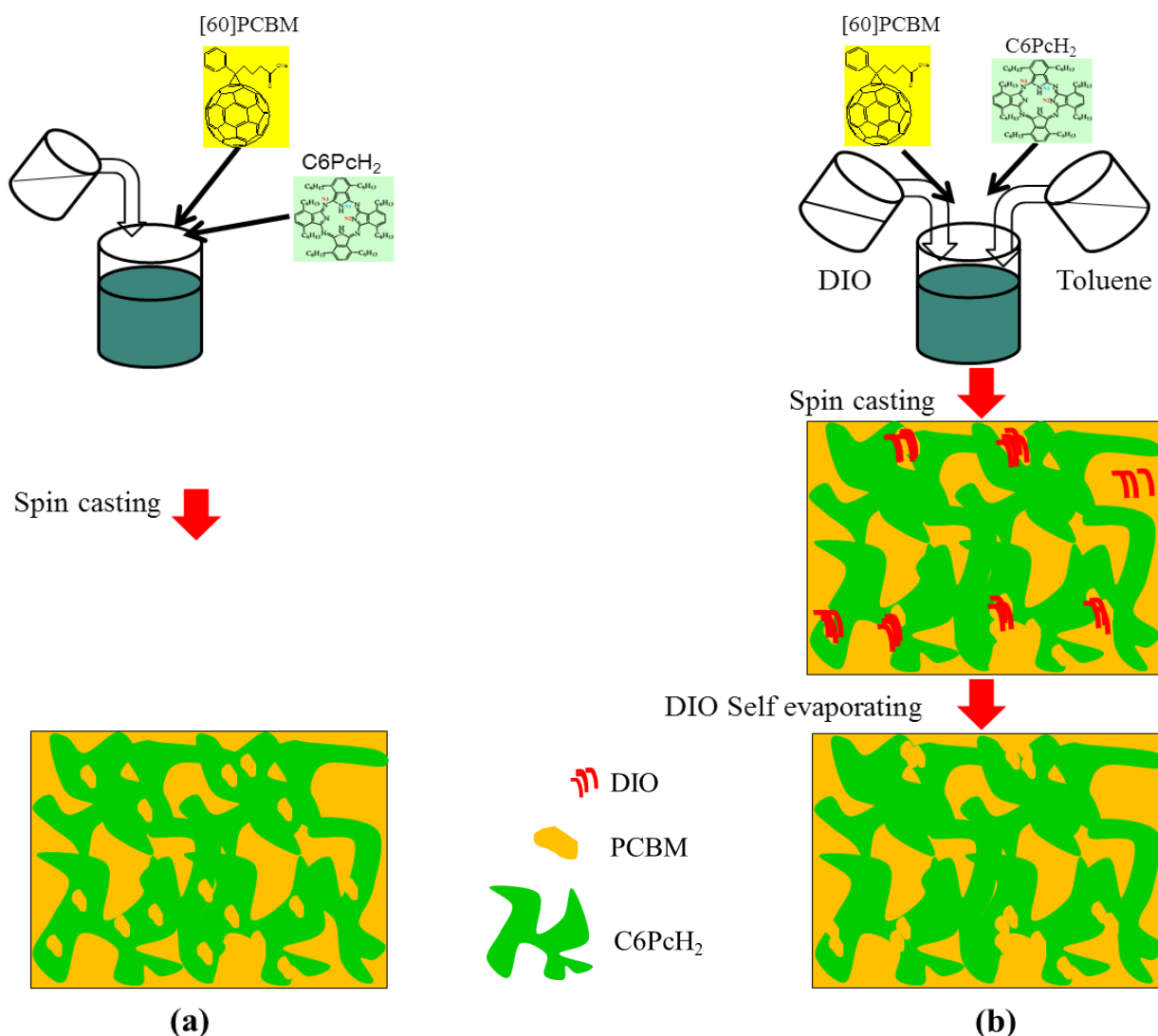


Fig. 2.5. Proposed models during spin-cast processing (a) without DIO and (b) with DIO.

Furthermore, a model described in the following is proposed and illustrated in Fig. 2.5 to explain the aforementioned effects of DIO on the separation of C6PcH₂ and [60]PCBM phases. One found that when C6PcH₂ and [60]PCBM are dissolved in toluene, C6PcH₂ domains extend freely in the solvent and probably do not interact with PCBM. During spin-coating, when toluene is extracted

rapidly, the whole system is quenched into a metastable state and [60]PCBM molecules are finely dispersed between C6PcH₂ domains, interrupting the ordering of C6PcH₂ molecules. This is supported by the decreases in Davydov splitting widths, smooth surface morphology, and low crystallization of discotic C6PcH₂ in hexagonal structures.

On the other hand, when a small amount of DIO exists in the mixture solvent, the situation is different. Because the vapor pressure of toluene (111 °C) is lower than DIO (167 °C), toluene evaporates faster than DIO during spin-cast processing, and the concentration of DIO gradually increases in the mixture. Due to the poor solubility of C6PcH₂ molecules in DIO (Fig. 2.6), [60]PCBM, which dissolved in DIO solvent, initially form clusters and precipitate. Moreover, with the smaller amount of [60]PCBM contained in toluene, the C6PcH₂ domains are able to self-organize. Finally, [60]PCBM and C6PcH₂ domains were separated. In other words, the composite active layer “intelligently” phase separates into the optimum morphology in one single step rather than two stages in “thermal annealing”, and takes less time than “solvent annealing” [19-20].

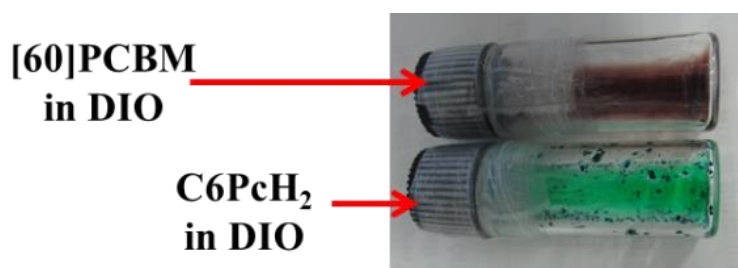


Fig. 2.6. Photos of BHJ materials in DIO solvent

2.4 Effects of processing-additive-induced donor-acceptor phase separation and crystallization on photovoltaic properties

One found that the photovoltaic performance of BHJ OSCs is strongly dependent on the donor-acceptor phase separation and crystallinity of the BHJ materials [19-21, 61, 62]. Thus, when the adding DIO to the BHJ blend solution induced the separation of C6PcH₂ and [60]PCBM and the crystallization of C6PcH₂ molecules in hexagonal structures, the improving photovoltaic performance is expected. Figure 2.7 shows the EQE and *J-V* characteristics of C6PcH₂:[60]PCBM devices with the different amounts of DIO mixed with toluene in an ITO/MoO_x/BHJ/LiF/Al structure under AM 1.5G illumination at an intensity of 100 mW/cm². The cell characteristics for all devices are summarized in Table 2.3.

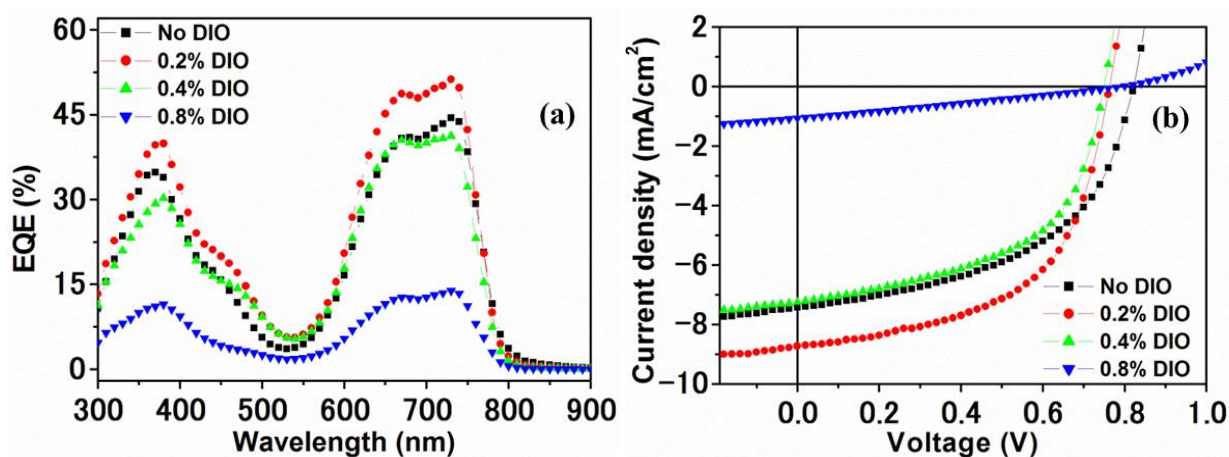


Fig. 2.7. (a) EQE spectra and (b) J - V characteristics of C6PcH₂:[60]PCBM BHJ OSCs with different amounts of DIO mixed with toluene.

Table 2.3. Cell characteristics of C6PcH₂:[60]PCBM BHJ OSCs with different amounts of DIO mixed with toluene under AM 1.5G illumination at an intensity of 100 mW/cm².

DIO	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)
No DIO	7.4	0.82	0.51	3.1
0.2 %	8.7	0.77	0.55	3.7
0.4 %	7.3	0.75	0.53	2.9
0.8 %	1.1	0.79	0.23	0.2

The devices, the active layers of which were spin-cast from C6PcH₂:[60]PCBM blends in pure toluene solution, showed the EQE of 44% at the Q-band of C6PcH₂ molecules and the PCEs of 3.1% with J_{sc} of 7.4 mA/cm², V_{oc} of 0.82 V, and FF of 0.51. By utilizing DIO as a processing additive to modify the nanoscale phase separation and the crystallinity, the performance of the BHJ OSCs was controlled. In particular, by adding 0.2% v/v of DIO in toluene solution the EQE at the Q-band increased to 51%. As a result of the increase in EQE, the J_{sc} and PCE increased to 8.7 mA/cm² and 3.7%, respectively, and the FF was improved from 0.51 to 0.55 due to the modified nanomorphology of the C6PcH₂:[60]PCBM thin films. However, the photovoltaic performance of the C6PcH₂:[60]PCBM BHJ OSCs was reduced with the low PCE of 0.23% upon adding 0.8% v/v of DIO, as shown in Table 2.3.

To explain the effects of the donor-acceptor phase separation and crystallization of C6PcH₂ molecules in hexagonal structure on the photovoltaic performance of C6PcH₂:[60]PCBM BHJ OSCs,

we proposed the schematics in the following and illustrate it in Fig. 2.8. In the cases of no DIO, [60]PCBM molecules were probably dispersed between C6PcH₂ domains during spin-cast processing. Although this resulted in the large interfacial areas of donor and acceptor and the high efficient exciton dissociation, the crystallization of C6PcH₂ domains were reduced. The deterioration of crystallization of the BHJ materials, therefore, caused the poor transportation of both electrons and holes to electrodes. As a result, the photovoltaic performance of the BHJ OSCs was poor.

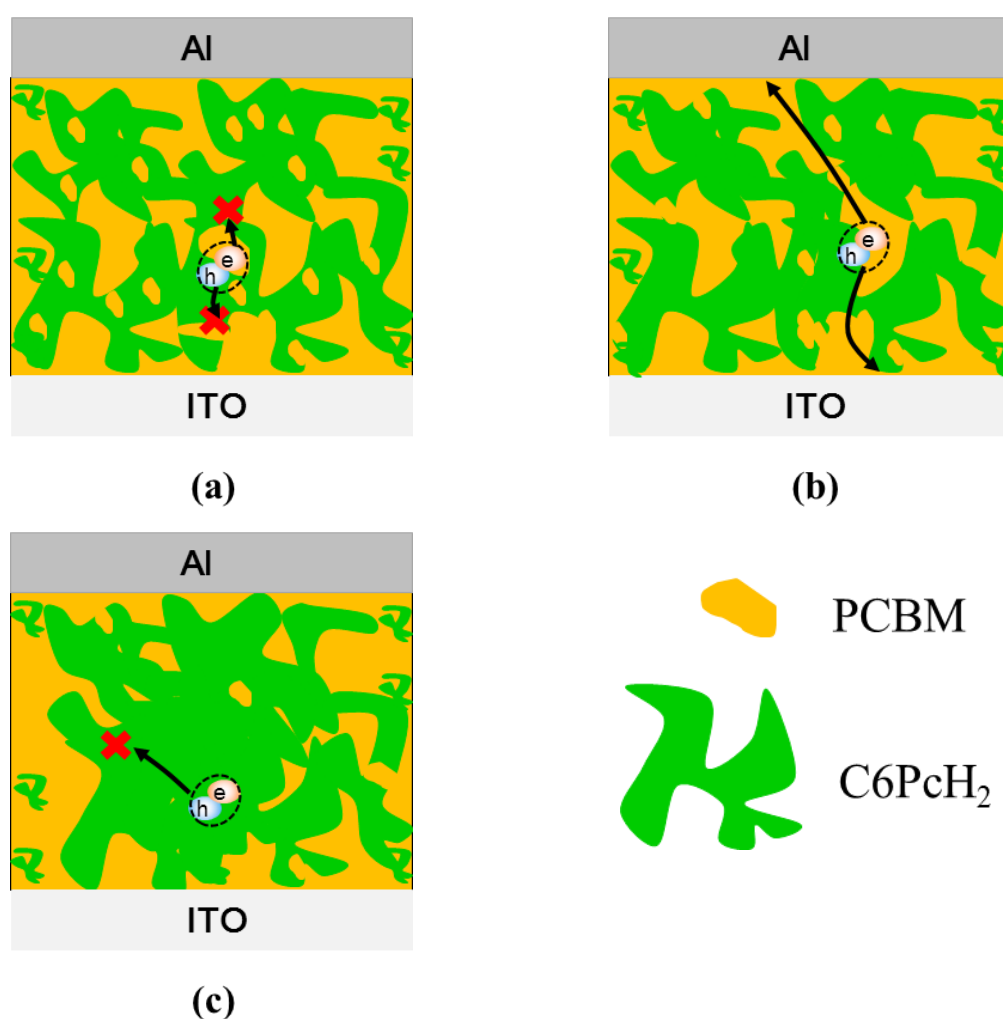


Fig. 2.8. Proposed schematics of donor-acceptor phase-separated structures of the active layers fabricated with (a) no DIO, (b) 0.2% DIO, and (c) 0.8% DIO.

By adding small amount of DIO to the BHJ blend solutions, [60]PCBM was separated from the C6PcH₂ domains and the crystallization of C6PcH₂ molecules in the hexagonal structures was improved due to the poor solubility of C6PcH₂ in DIO and the difference in boiling point between DIO and toluene. As a result, the continuous pathways for the transportation of charge carrier to

electrodes were improved. However, by adding 0.8% v/v of DIO to the BHJ blend solutions, the interfacial areas of donor and acceptor phases became smaller and the efficient exciton dissociation was low. This also resulted in the low photovoltaic performance of the BHJ OSCs. The optimum nanoscale phase separation and crystallization of the BHJ materials, and the high photovoltaic performance of the C6PcH₂:[60]PCBM BHJ OSCs was probably achieved by adding 0.2% v/v of DIO to the BHJ blend solution.

The proposed schematics was confirmed by taking the PL spectra of the C6PcH₂ C6PcH₂:[60]PCBM thin films into consideration. Figure 2.9 shows the PL spectra of the C6PcH₂ and C6PcH₂:[60]PCBM thin films fabricated on quartz substrates with the different amount of DIO and the dependence of the relative quenching efficiency (Q) on the amount of DIO. Herein, Q was calculated from the equation; $Q = 1 - (\text{total PL of BHJ sample}/\text{total PL of reference sample})$.

The PL spectra of C6PcH₂ thin films had a predominant peak at 766 nm and a shoulder around 820 nm, which relate with the Q-band of the C6PcH₂ absorption spectra [63]. The PL intensity of C6PcH₂:[60]PCBM thin films was markedly suppressed and the Q drastically increased upon adding [60]PCBM. The PL suppression and the increases in Q was due to the nonradiative decay of photogenerated-excitons through the photoinduced-electron transfer from the excited state of C6PcH₂ to [60]PCBM [1-4]. Furthermore, the increases in the Q indicated that the interfacial areas of donor and acceptor were enlarged, which caused the high efficiency of exciton dissociation. By adding small amount of DIO to the blend solutions, the Q was reduced. It is suggested that the interfacial areas of donor and acceptor phases was reduced, which was in good agreement with the schematics proposed above.

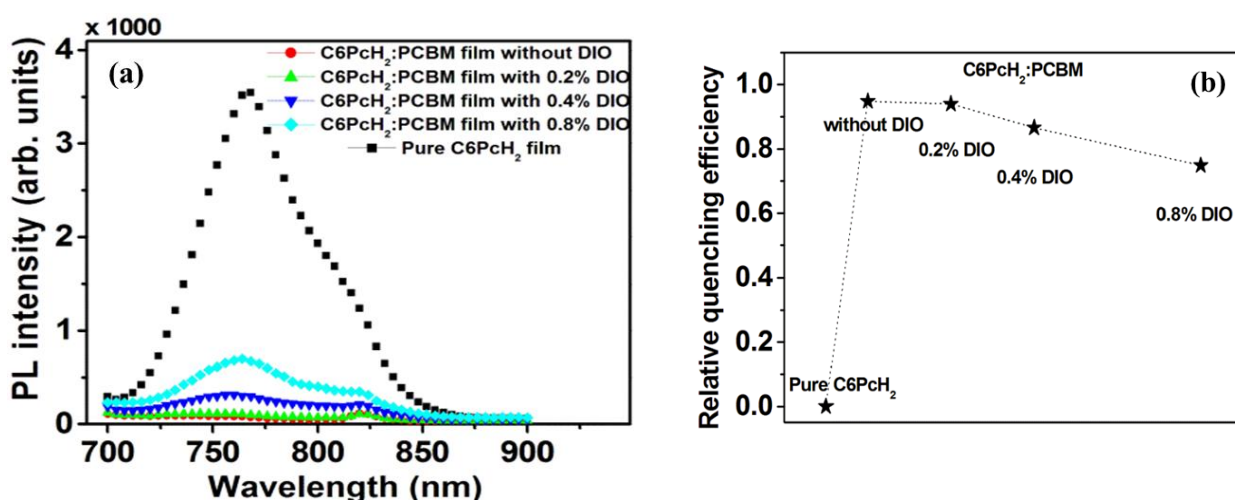


Fig. 2.9. (a) PL spectra of C6PcH₂ and C6PcH₂:[60]PCBM composite thin films with the different amount of DIO and (b) dependence of the relative quenching efficiency on the amount of DIO; the excitation wavelength is 670 nm.

2.5. Improving photovoltaic properties by optimizing donor-acceptor phase separation and crystallization

According to the proposed models, the processing additives in the mixture solvent approach should fulfill the following requirements: first, the compound must have higher boiling point than that of the primary solvent. Second, the solubility of [60]PCBM and C6PcH₂ in the compound must be different. Third, the compound must be miscible with the primary solvent. Based on these requirements, the new processing additives with the different boiling points were selected, as shown in Table 2.4. On the other hand, the various primary solvents, as shown in Table 2.5, were utilized. By using the various processing additives mixed with the different primary solvents, the optimum donor-acceptor phase separation and crystallization of discotic C6PcH₂ are expected hence the photovoltaic properties must be improved.

Table 2.4. Boiling points of the processing additives in this study.

	DIO	Oct	Brom	Chlor
Boiling point (°C)	167	269	270	116

Table 2.5. Boiling points of the primary solvent in this study.

	Chloroform	Toluene	Trichloroethylene
Boiling point (°C)	62	111	87

Figure 2.10 shows the surface morphologies of C6PcH₂: [60]PCBM composite thin films with the various primary solvents, which were observed by AFM. The C6PcH₂: [60]PCBM composite thin film without DIO exhibited a smooth surface, as shown in Fig. 2.10(a). By adding 0.2% v/v of DIO to the BHJ blend solutions, all of the C6PcH₂: [60]PCBM composite thin films showed a number of islands, which is considered to be discotic C6PcH₂ domains and/or [60]PCBM clusters. This result suggests that utilizing DIO mixed with all of primary solvents in this study caused the phase separation of the BHJ materials. However, the discotic C6PcH₂ domains and/or [60]PCBM clusters on the C6PcH₂: [60]PCBM composite thin films utilized trichloroethylene possessed higher uniformity than those of the composite thin films utilized chloroform or toluene.

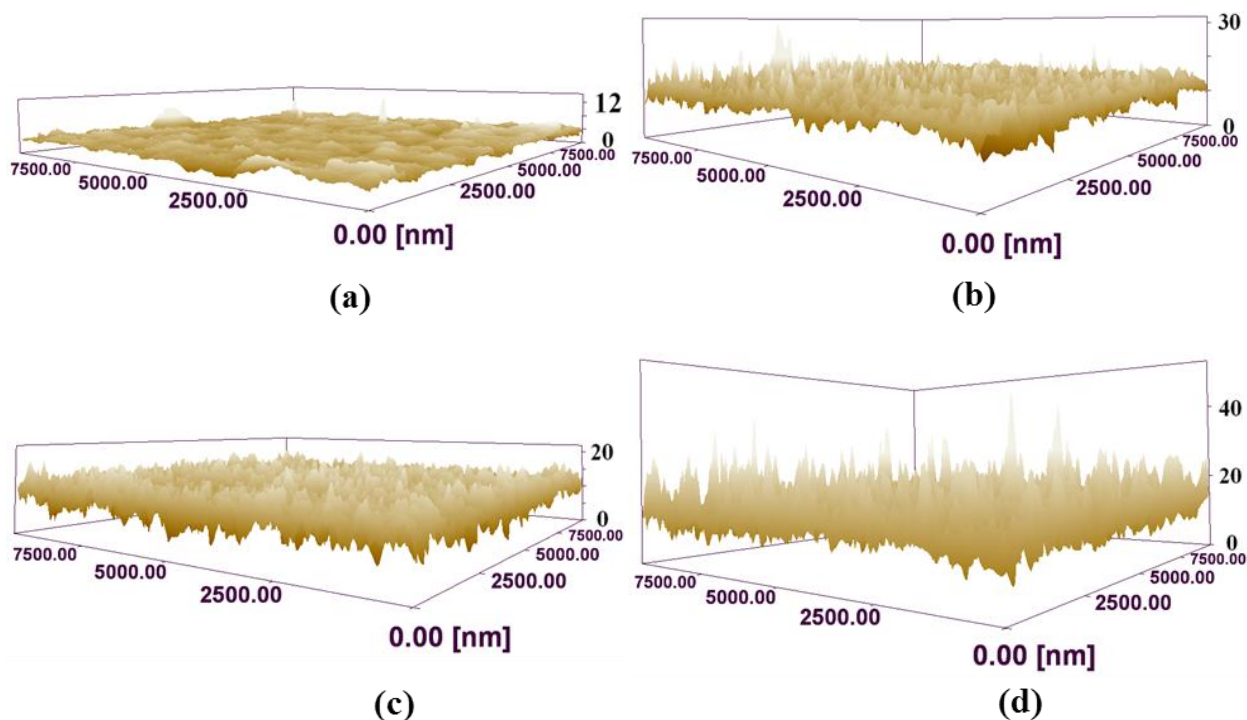


Fig. 2.10. AFM images of the C6PcH₂:[60]PCBM composite thin films without DIO (a) and with DIO (b, c, and d) in the various solvents: chloroform (a, b), TCE (c), and toluene (d).

Figure 2.11 shows the Davydov splitting at the Q-band of the absorbance spectra of C6PcH₂:[60]PCBM composite thin films utilizing 0.2% v/v of various processing additives, such as DIO, Chlor, Brom, and Oct. Herein, the C6PcH₂:[60]PCBM composite thin films was spin-cast on quartz substrates from the solutions containing a mixture of C6PcH₂:[60]PCBM in chloroform mixed with various processing additives. Although Davydov splitting at the Q-band occurred for all process additives, the addition of Oct induced less Davydov splitting than those of the other solvents.

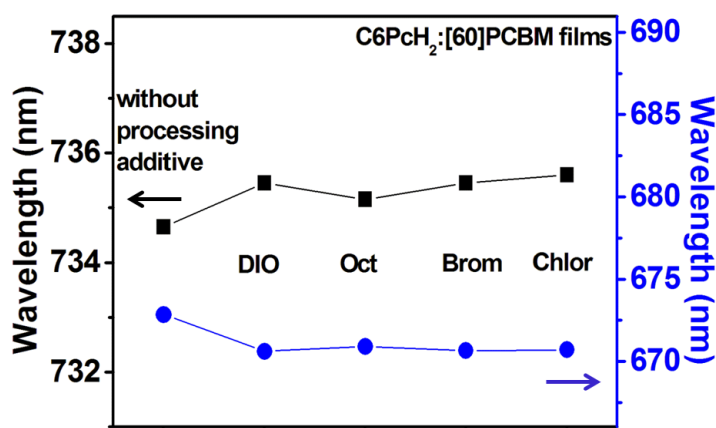


Fig. 2.11. Dependence of size of the Davydov splitting on 0.2% v/v of various processing additives.

Figure 2.12 shows XRD patterns of C6PcH₂:[60]PCBM thin films with 0.2% v/v of various solvents as processing additives, such as DIO, Chlor, Brom, and Oct, in chloroform solution. All the XRD patterns exhibited the similar shapes and consisted of the only diffraction peak appeared at approximately 4.88°, corresponding to Miller indices of (200)/(110) (using indices based on a rectangular cell). Furthermore, the FWHM of all XRD patterns are summarized in Table 2.6. Although decreases in the FWHM of the XRD patterns or the improved crystallinity of the discotic C6PcH₂ columns in the hexagonal structures occurred for all the processing-additive solvents, the addition of Oct as a processing additive resulted in the lowest crystallinity.

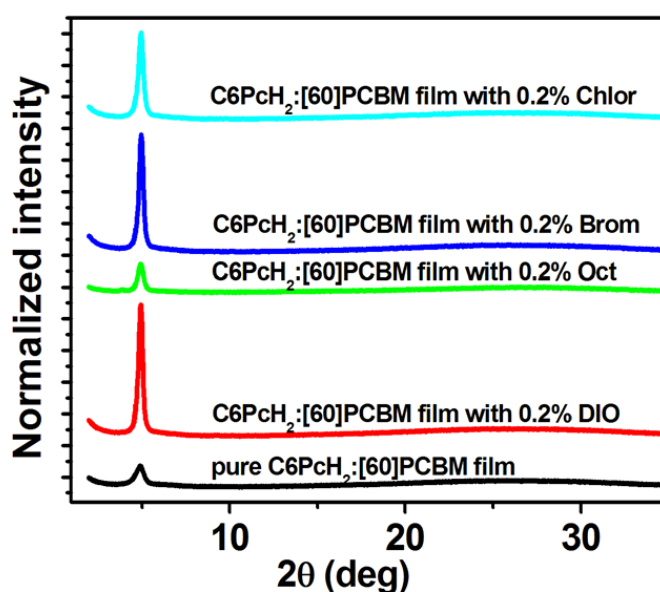


Fig. 2.12. XRD patterns of C6PcH₂:[60]PCBM composite thin film with 0.2% v/v of various processing additives. All XRD patterns were normalized at 4.88°.

Table 2.6. FWHM of XRD patterns of C6PcH₂:[60]PCBM composite thin film with and without different processing additives mixed with chloroform

	No processing additives	0.2% DIO	0.2% Oct	0.2% Brom	0.2% Chlor
C6PcH ₂ :[60]PCBM films	0.92 °	0.31 °	0.49 °	0.3 °	0.36 °

Figure 2.13 shows the EQE and J-V characteristics of C6PcH₂:[60]PCBM devices with the various primary solvents mixed with 0.2% v/v of DIO in an ITO/MoO_x/BHJ/LiF/Al structure under AM 1.5G illumination at an intensity of 100 mW/cm². The cell characteristics for all devices are summarized in Table 2.7.

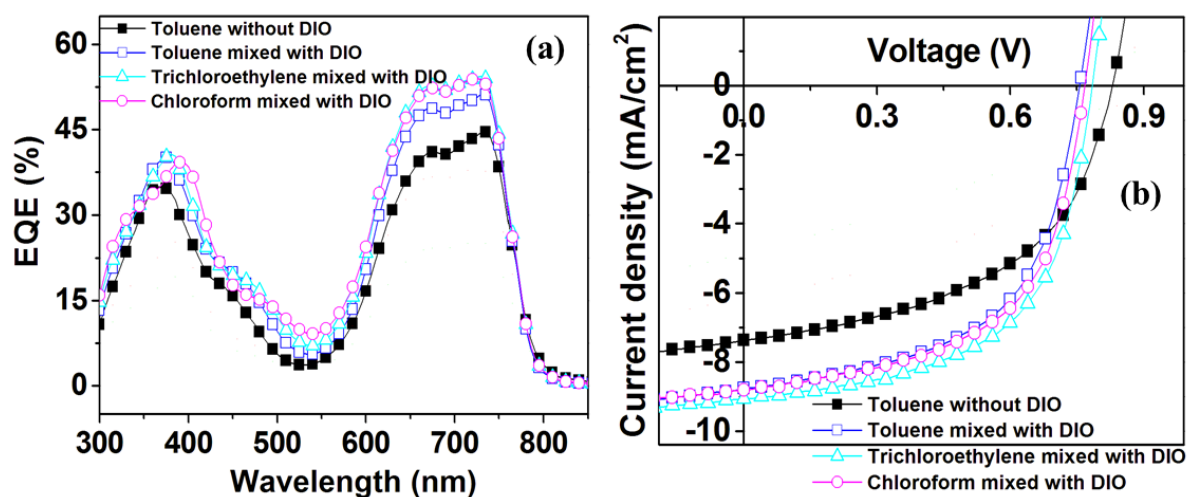


Fig. 2.13. (a) EQE spectra and (b) J-V characteristics of C6PcH₂:[60]PCBM BHJ OSCs with various primary solvents.

Table 2.7. Cell characteristics of the C6PcH₂:[60]PCBM BHJ OSCs with the different primary solvent mixed with 0.2% v/v of DIO under AM 1.5G illumination at an intensity of 100 mW/cm².

Primary solvents	Processing additives	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)
Toluene	None	7.4	0.83	0.50	3.1
Toluene	0.2% DIO	8.8	0.75	0.56	3.7
Trichloroethylene	0.2% DIO	9.1	0.78	0.58	4.1
Chloroform	0.2% DIO	8.8	0.77	0.58	3.9

The C6PcH₂:[60]PCBM devices without DIO in toluene showed the EQE of 44% at the Q-band of C6PcH₂ and the PCEs of 3.1% with J_{sc} of 7.4 mA/cm², V_{oc} of 0.83 V, and FF of 0.50. The devices utilizing toluene as the primary solvents showed the higher photovoltaic performance, compared with the devices using chloroform or trichloroethylene as primary solvents (not shown here) due to the high toluene-solvent-induced crystallization of discotic C6PcH₂ [64]. By utilizing DIO as a processing additive to modify the nanoscale phase separation and crystallinity, the photovoltaic performance of all devices was improved. Particularly, by utilizing trichloroethylene mixed with 0.2% v/v DIO, the EQE was improved from 38% to 54% at the Q-band and the PCE increased to 4.1% with the J_{sc} of 9.1 mA/cm², V_{oc} of 0.78 V, and FF of 0.58. Although more efforts should be made to understand the roles of primary solvents on improvement of the photovoltaic properties, it is suggested that the higher photovoltaic performance of devices utilizing trichloroethylene mixed with 0.2% v/v DIO, compared with the devices utilizing chloroform or toluene mixed with 0.2% v/v DIO was probably due to the high uniformity of surface morphology as the aforementioned describe in the AFM images of surface of composite thin films [65, 66].

Figure 2.14 shows the EQE and J-V characteristics of C6PcH₂:[60]PCBM devices with the various processing additives in an ITO/MoO_x/BHJ/LiF/Al structure under AM 1.5G illumination at an intensity of 100 mW/cm². The cell characteristics for all devices are summarized in Table 2.8. Herein, chloroform was utilized as the primary solvent.

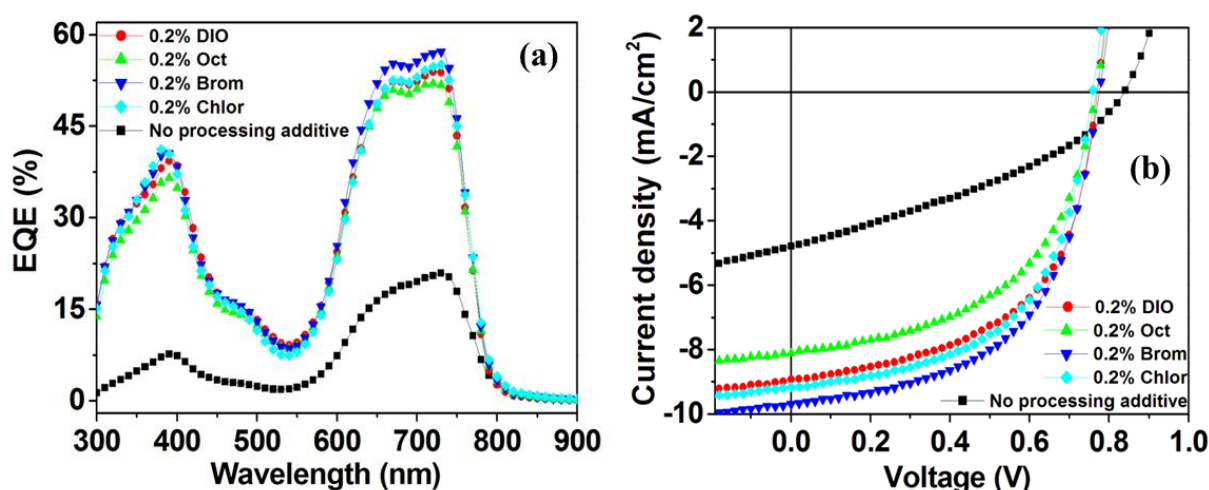


Fig. 2.14. (a) EQE spectra and (b) J-V characteristics of C6PcH₂:[60]PCBM BHJ OSCs with various processing additives.

Table 2.8. Cell characteristics of the C6PcH₂:[60]PCBM BHJ OSCs with different processing additives mixed with chloroform under AM 1.5G illumination at an intensity of 100 mW/cm².

Processing additives	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)
None	4.8	0.84	0.35	1.4
0.2% DIO	8.9	0.77	0.55	3.8
0.2% Oct	8.1	0.77	0.53	3.3
0.2% Brom	9.7	0.78	0.56	4.2
0.2% Chlor	9.2	0.76	0.56	3.9

It is found that except for the Oct-containing solution, by incorporating a processing additive up to a volume of a few volume percent, the performance of the BHJ OSCs was markedly improved. In particular, by adding 0.2% v/v Brom to chloroform solution, the EQE at the Q-band was improved from 21% to 57%, and J_{sc} and PCE increased to 9.7 mA/cm² and 4.2%, respectively. The relatively low performance of the cell utilizing Oct solvent as a processing additive might have resulted from the slight decrease in the Davydov splitting at the Q-band of the absorbance spectrum and the low crystallinity, as shown in the XRD patterns. Obviously, the nanoscale phase separation and the crystallization of the BHJ materials were clearly optimized and the performance of the BHJ OSCs was markedly improved by utilizing various processing additives [67].

2.6 Conclusions

The effects of processing additives on the nanoscale phase separation, crystallization, and photovoltaic performance of the BHJ OSCs utilized discotic C6PcH₂ mixed with [60]PCBM were studied. By incorporating processing additives to a volume of a few percent, the separation of donor and acceptor phases in C6PcH₂:PCBM thin films, which was discussed by taking the Davydov splitting at the Q-band of the absorbance spectra and the surface nanomorphology into consideration, was improved. It was proposed that the separation of donor and acceptor phases was promoted due to the higher boiling point of the processing additives, compared with that of the primary solvents and the different solubility of [60]PCBM and C6PcH₂ in processing additives. Furthermore, the crystallization of discotic C6PcH₂ in hexagonal structures has been improved by using processing additives. It was suggested that the improved crystallization was probably due to increases in the solubility of C6PcH₂ in processing additives.

Moreover, the effects of the processing-additive induced donor-acceptor phase separation and the

processing-additive induced crystallization of the BHJ materials on the photovoltaic properties of the BHJ OSCs utilized discotic C6PcH₂ mixed with [60]PCBM were reported. Particularly, without DIO [60]PCBM molecules were dispersed between C6PcH₂ domains during spin-cast processing, resulted in deteriorating the crystallization of C6PcH₂ domains. As a result, the transportation of both electrons and holes to electrodes were degraded and the photovoltaic performance of the BHJ OSCs was poor.

By adding small amount of DIO to the BHJ blend solutions, [60]PCBM was separated from the C6PcH₂ domains and the crystallization of C6PcH₂ molecules in the hexagonal structures was improved. As a result, the continuous pathways for the transportation of charge carrier to electrodes were extended and the photovoltaic performance of the BHJ OSCs was improved. However, by adding 0.8% v/v of DIO to the BHJ blend solutions, the interfacial areas of donor and acceptor phases became smaller and the efficient exciton dissociation was low. This also resulted in the low photovoltaic performance of the BHJ OSCs. The optimum nanoscale phase separation and crystallization of the BHJ materials was probably achieved by adding 0.2% v/v of DIO to the BHJ blend solution.

Although more efforts should be made to understand the roles of primary solvents as well processing additives on the improvement of the photovoltaic properties of the BHJ OSCs utilized discotic C6PcH₂ mixed with [60]PCBM, the nanoscale phase separation and the crystallization of the BHJ materials were clearly optimized and the performance of the BHJ OSCs was markedly improved by utilizing various processing additives mixed with the different primary solvents. In particular, by adding 0.2% v/v of Brom to the solution containing BHJ blends in trichloroethylene, the EQE at the Q-band was improved to 57%, and the PCE increased to 4.2%, with a J_{sc} of 9.7 mA/cm², a V_{oc} of 0.76 V, and an FF of 0.56.

Chapter 3

Roles of fullerene derivatives in photovoltaic properties of solar cells

3.1 Introduction

As described in Chapter 2, by utilizing processing additives, the C6PcH₂:[60]PCBM based BHJ OSCs showed the relatively high PCE of 4.2% and EQE at Q band of phthalocyanine close to 60% with the optimum donor-acceptor phase separation and crystallization of the BHJ materials. However, the EQE at around 500 nm was limited due to the low absorption of both C6PcH₂ molecules and [60]PCBM. When J_{sc} can be estimated from the EQE, as shown in equation (1.4), the low EQE at around 500 nm will reduce the PCE. Thus, the improvement of the EQE at around 500 nm becomes one major challenge for the BHJ OSCs utilizing C6PcH₂.

Moreover, one found that during spin-cast processing, [60]PCBM molecules were dispersed between C6PcH₂ domains, resulted in the deterioration of crystallization of discotic C6PcH₂ in the hexagonal structures. The deterioration of crystallization of the BHJ materials caused the poor transportation of both electrons and holes to electrodes and the poor photovoltaic performance of the BHJ OSCs. In terms of BHJ OSCs, One found that the balance between a large interfacial area and continuous pathways for carrier transportation and/or the optimum nanoscale morphology are necessary for the high photovoltaic performance [46]. Recent significant progresses to control nanoscale morphology in BHJ OSCs have been made by optimization of the device preparation conditions, including the adjustment of the volume fractions of the components, thermal annealing treatment, and processing additives [19, 21, 47]. Although the application of thermal annealing treatment and processing additives to optimize the donor-acceptor phase separation and crystallization of the C6PcH₂:[60]PCBM BHJ materials have been described in the previous chapters, the effects of the BHJ blend ratios on photovoltaic properties of BHJ OSCs utilizing C6PcH₂ were not yet concerned.

In this chapter, the roles of fullerene derivatives in the photovoltaic properties of the BHJ OSCs utilizing C6PcH₂ were studied. By using various fullerene derivatives, the EQE at around 500 nm and the photovoltaic performance was improved. Furthermore, the effects of blend ratios on the photovoltaic properties of BHJ OSCs utilizing C6PcH₂ were also discussed.

3.2 Experimental Procedure

C6PcH₂ was synthesized as described in the literature [55], with slight modifications, and fully purified by column chromatography (using silica gel with toluene as the eluent), which was followed by repeated recrystallization from toluene-methanol (1:2) solution [9]. The fullerene derivatives, such as [60]PCBM, [70]PCBM, and bis-adduct of [60]PCBM (Bis[60]PCBM), as shown in Fig. 3.1, were purchased from Frontier Carbon Ltd.

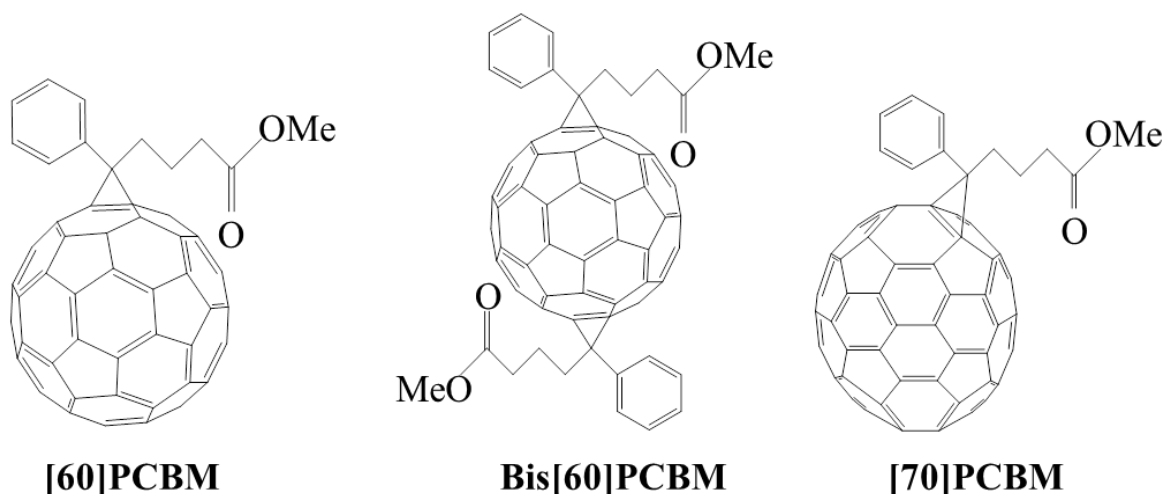


Fig. 3.1. Chemical structure of fullerene derivatives in this study.

BHJ thin films were prepared under optimized conditions in accordance with the following procedure. An ITO-coated quartz substrate was cleaned with detergent, ultrasonicated in water, chloroform, acetone, and isopropyl alcohol, and subsequently dried with UV-induced ozone. 6-nm-thick MoO_x films were thermally evaporated onto ITO at a rate of 0.1 Å/s under a vacuum of about 2×10^{-5} Pa. After transferring the films to a N₂-filled glove box, a solution containing a mixture of C6PcH₂ and various fullerene derivatives (3:2) in chloroform mixed with DIO was stirred using an ultrasonic washer and spin-cast at 2000 rpm onto a MoO_x layer. Herein, DIO plays a key role as a processing-additive solvent to control nanoscale morphology of BHJ active layer. Otherwise, C6PcH₂:[70]PCBM BHJ thin films with various blend ratios have been fabricated. The concentration of the BHJ solution was 22.35 mg/ml, and the active layer thickness was approximately 130 nm. Finally, a 0.3-nm-thick LiF buffer layer and an 80-nm-thick aluminum layer were deposited through a shadow mask by thermal evaporation under a vacuum of about 2×10^{-5} Pa. The active area of the device was 4 mm².

The device characteristic was measured under irradiation intensity of 100 mW/cm² using an XES 301 (AM 1.5 G) full spectrum solar simulator. The *J-V* characteristics were measured using a source

measurement unit (Keithley 2400). Otherwise, EQE spectra were measured with a programmable electrometer using Xe lamp light passed through a monochromator as a light source. The integrated EQE values always showed good agreement with the measured value of J_{sc} . The absorbance spectra, PL spectra were measured by spectrophotometry (Shimadzu UV-3150), using a fluorescence spectrophotometer (F-4500). Furthermore, the crystallinity of the C6PcH₂ molecules in thin films was evaluated by XRD (Rigaku RINT 2000).

3.3 Improving the photovoltaic performance using various fullerene derivatives

The absorption spectra of the [70]PCBM and C6PcH₂: [70]PCBM composite thin films fabricated on quartz substrates are shown in Fig. 3.2, along with those of [60]PCBM. Although [60]PCBM accounts for 40% of the weight of the photoactive layers, the absorption spectrum of the C6PcH₂: [60]PCBM composite thin film showed strong peaks at the Q-band and B-band of C6PcH₂ molecules and weak absorption at around 500 nm. The low absorption of C₆₀ fullerene derivatives is attributed to their high degree of symmetry, making the lowest-energy transitions formally dipole forbidden [68]. Therefore, when the C₆₀ moiety of [60]PCBM is replaced by a less symmetrical fullerene, these transitions become allowed and the absorption dramatically increases [68-71]. By employing asymmetric [70]PCBM fullerene derivatives with C6PcH₂ instead of [60]PCBM, the absorption of the composite thin films at around 500 nm markedly increased due to the optical transitions in the visible region of C₇₀ molecules.

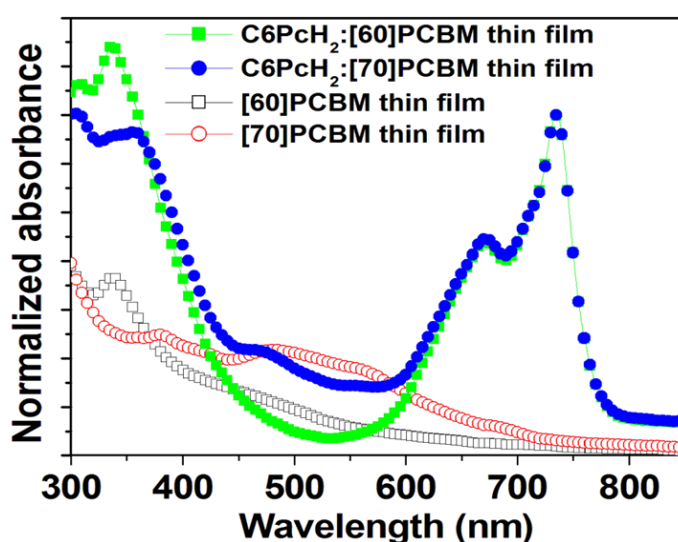


Fig. 3.2. Absorbance spectra of the C6PcH₂: [70]PCBM and C6PcH₂: [60]PCBM composite thin films. Absorbance spectra were normalized at 730 nm.

Figure 3.3 shows the XRD patterns of composite thin films with various fullerene derivatives fabricated on glass substrates. It can be seen that the diffraction peak of C6PcH₂ thin film appeared at approximately 4.86°, which corresponds to the intercolumnar distance in a hexagonal structure of 18.2 Å. The dependences of the FWHM of XRD peaks upon adding fullerenes are shown in Table 3.1. An increase in the FWHM upon adding fullerenes indicated that the crystallinity of the discotic C6PcH₂ columns in hexagonal structures was lowered owing to the dispersion of the fullerene molecules into the C6PcH₂ domains, which were in good agreement with the proposed models in the chapter 2 [66, 67]. Although increases in the FWHM of the XRD peaks or decreases in the crystallinity of the discotic C6PcH₂ columns in hexagonal structures occurred in all of the composite thin films, the addition of [70]PCBM and Bis[60]PCBM to the composite thin films resulted in the lower crystallinity than those of the [60]PCBM acceptors.

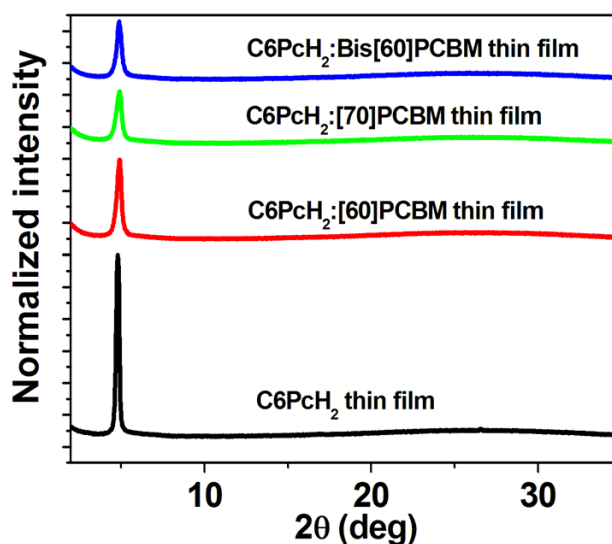


Fig. 3.3. XRD patterns of the composite thin films with various fullerene derivatives. All XRD patterns were normalized at 4.88°.

Table 3.1. FWHMs of XRD peaks of composite thin films with various fullerene derivatives.

	C6PcH ₂ thin films	C6PcH ₂ :[60]PCBM thin films	C6PcH ₂ :[70]PCBM thin films	C6PcH ₂ :Bis[60]PCBM thin films
FWHM	0.23°	0.36°	0.45°	0.40°

Figure 3.4 shows the EQE and J-V characteristics of the BHJ OSCs utilizing C6PcH₂ mixed with the various fullerene derivatives in an ITO/MoO_x/BHJ/LiF/Al structure under AM 1.5G illumination at an intensity of 100 mW/cm². The cell characteristics for all devices are summarized in Table 3.2. The C6PcH₂:[60]PCBM devices showed the EQE of 53% and 8% at the Q-band and around 500 nm,

respectively. As a result of the high EQE, the J_{sc} , as shown in Fig. 3.4(b), was measured to be 8.1 mA/cm². The V_{oc} was 0.76 V, and the PCE was estimated to be 3.7%. By employing an asymmetric [70]PCBM fullerene derivative with C6PcH₂ instead of [60]PCBM, the EQE at around 500 nm was improved from 8% to 24%, which was in good agreement with the absorption spectra. Although the EQE at the Q-band was slightly decreased, which can be attributed to the relatively low crystallinity of C6PcH₂ in the C6PcH₂: [70]PCBM composite thin films, J_{sc} and the PCE were markedly improved to 10.2 mA/cm² and 3.9%, respectively.

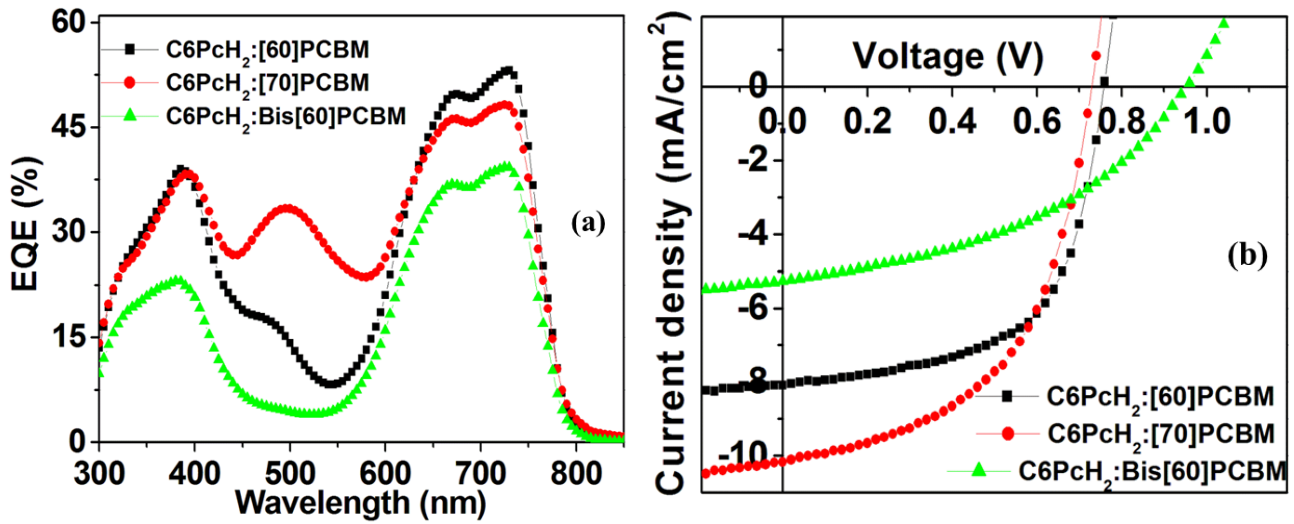


Fig. 3.4. (a) EQE spectra and (b) J-V characteristics of the BHJ OSCs with various fullerene derivatives.

Table 3.2. Cell characteristics of the BHJ OSCs utilizing C6PcH₂ mixed with various fullerene derivatives under AM 1.5G illumination at an intensity of 100 mW/cm².

	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)
C6PcH ₂ : [60]PCBM BHJ OSCs	8.1	0.76	0.60	3.7
C6PcH ₂ : [70]PCBM BHJ OSCs	10.2	0.73	0.53	3.9
C6PcH ₂ : Bis[60]PCBM BHJ OSCs	5.3	0.96	0.42	2.1

The essential parameters that determine the PCE of BHJ OSCs are V_{oc} , FF , and J_{sc} . The maximum V_{oc} is considered to be limited by the work function of the metal electrodes and the energy

gap between the HOMO of the donor materials and the lowest unoccupied molecular orbital (LUMO) of the acceptor fullerenes (ΔE_{DA}) [70-73]. Although the difference between V_{oc} and ΔE_{DA} is still subject to debate, a linear relationship between V_{oc} and ΔE_{DA} has been experimentally confirmed [73]. By employing Bis[60]PCBM, the LUMO level of which is 0.1-0.2 eV higher than that of [60]PCBM, instead of [60]PCBM, V_{oc} was markedly improved from 0.76 to 0.96 V, as shown in Table 3.2 [74]. However, the Bis[60]PCBM:C6PcH₂ solar cells had a relatively low J_{sc} of 5.27 mA/cm². It was suggested that this result is attributed to the decrease in the energy gap between the LUMO levels of the donor and acceptor, which directly corresponds to the efficiency of the photoinduced charge separation [75].

Figure 3.5 shows the PL spectra of composite thin films with various fullerene derivatives fabricated on quartz substrates. The PL spectra of C6PcH₂ thin films exhibited a predominant peak at 766 nm and a shoulder at around 820 nm, which is related to the Q-band of the C6PcH₂ absorption spectrum [63]. The PL intensity was drastically suppressed upon adding fullerene derivatives, such as Bis[60]PCBM, [70]PCBM, and [60]PCBM, owing to photoinduced electron transfer from the excited state of C6PcH₂ to the fullerene derivative acceptor [1-4]. It was found that the PL quenching of C6PcH₂:[60]PCBM or C6PcH₂:[70]PCBM composite thin films was more marked than that of C6PcH₂:Bis[60]PCBM composite thin films. This result suggested that the energy gap between the LUMO levels of the donor and acceptor was reduced by employing Bis[60]PCBM with C6PcH₂ instead of [60]PCBM or [70]PCBM, which is consistent with the J - V characteristics.

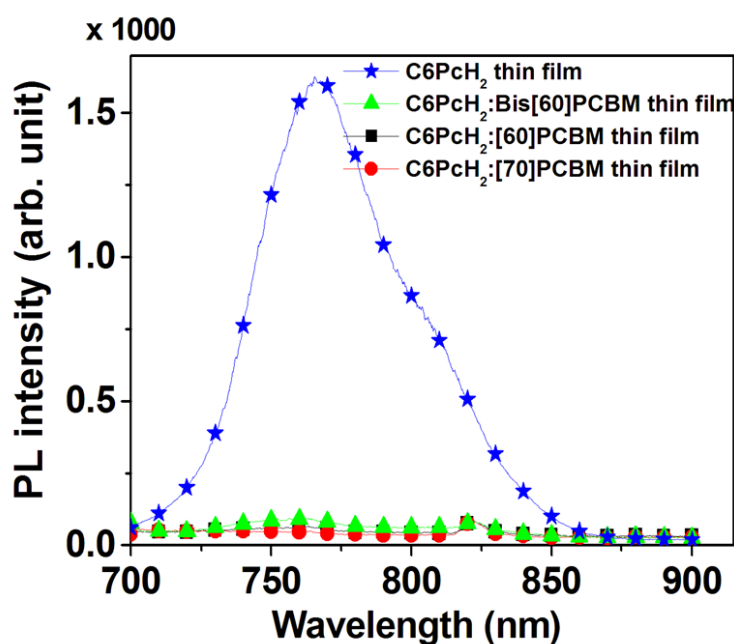


Fig. 3.5. PL spectra of the composite thin films; the excitation wavelength is 670 nm.

3.4 Blend ratio dependences of photovoltaic properties

Figure 3.6 shows the absorbance spectra of the C6PcH₂:[70]PCBM composite thin films with the various blend ratios fabricated on quartz substrates. Obviously, the visible-region absorption spectra consisted of a strong Q-band and a B-band of C6PcH₂ molecules, and a shoulder around 500 nm of [70]PCBM. By increasing the [70]PCBM volume fractions, the absorbance around 500 nm was improved, but the absorbance at the Q band of C6PcH₂ molecules was reduced.

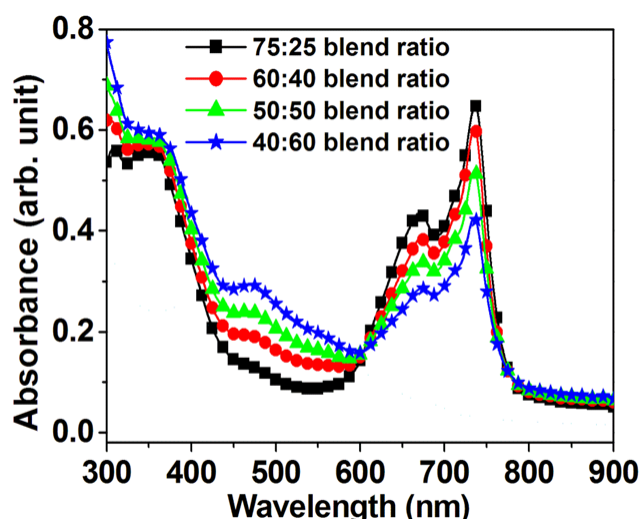


Fig. 3.6. absorbance spectra of the C6PcH₂:[70]PCBM composite thin films with the various blend ratios.

One found that the increases in [70]PCBM volume fractions did not only affect to the absorption intensities but also the Davydov splitting at Q-band of C6PcH₂ molecules and/or the molecular interaction of discotic C6PcH₂ in the hexagonal structures. The dependence of the Davydov splitting at Q-band of C6PcH₂ molecules on the blend ratios is shown in Fig. 3.7. It exhibited that the width of Davydov splitting was drastically reduced upon increasing the [70]PCBM volume fractions. When the width of Davydov splitting in an allowed electronic transition is corresponding to the interaction energy between molecules with different site symmetries [59, 60], the decreases in Davydov splitting indicated that the molecular interaction of discotic C6PcH₂ with the hexagonal structures was weakened owing to the dispersion of [70]PCBM into the C6PcH₂ domains during the spin-cast processing, which were in good agreement with the proposed models in the chapter 2.

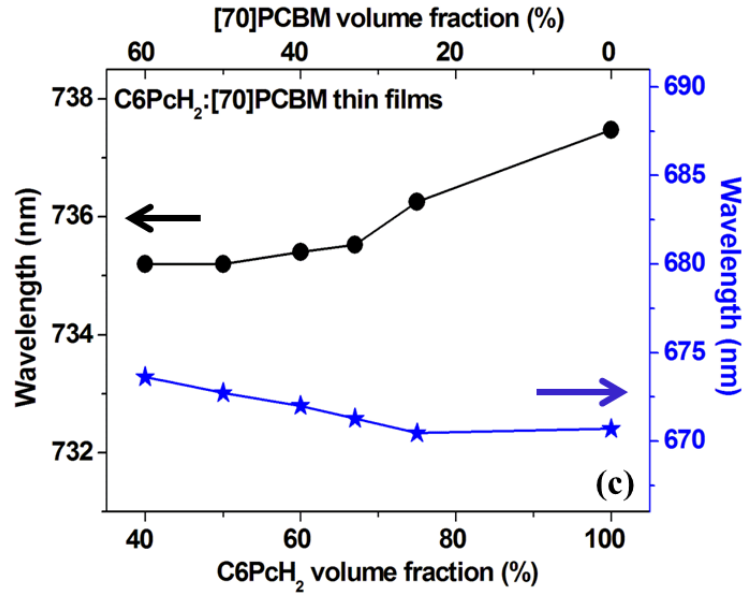


Fig. 3.7. Blend ratio dependences of the Davydov splitting at Q-band.

Figure 3.8 shows the XRD patterns of C6PcH₂ and C6PcH₂:[70]PCBM composite thin films spin-cast on glass substrates. All the XRD patterns exhibited the similar shapes and consisted of the only diffraction peak at approximately 4.88°, corresponding to Miller indices of (200)/(110) (using indices based on a rectangular cell). Moreover, the intercolumnar distance of discotic C6PcH₂ in the hexagonal structures was estimated to be 18.1 Å.

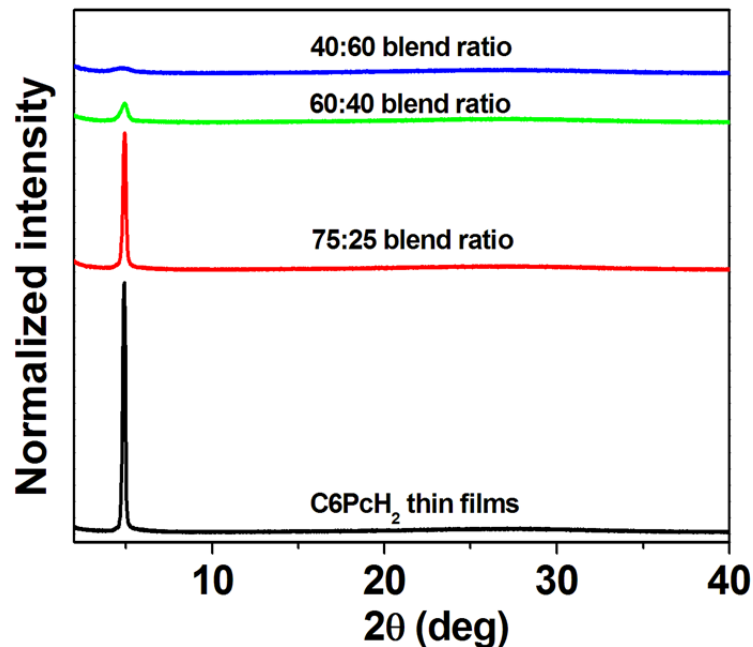


Fig. 3.8 XRD patterns of C6PcH₂ and C6PcH₂:[70]PCBM composite thin films with various the blend ratios. All XRD patterns were normalized at 4.88°.

Table 3.3. FWHM of XRD pattern of C6PcH₂ and C6PcH₂:[70]PCBM composite thin film with the various blend ratios.

	C6PcH ₂	C6PcH ₂ :[70]PCBM thin films with various blend ratios			
	thin films	75:25	67:33	60:40	50:50
FWHM	0.18°	0.2°	0.3°	0.54°	1.16°

Furthermore, the FWHM of the XRD patterns with the different [70]PCBM volume fraction are summarized in Table 3.3. One found that the FWHM was drastically enlarged upon increasing the [70]PCBM volume fractions. Particularly, by increasing the [70]PCBM volume fraction to 50%, the FWHM of the XRD patterns were extended from 0.2 to 1.16°. When FWHM of XRD pattern is directly corresponding to crystallization of molecules, increases in the FWHM of thin film XRD patterns upon adding [70]PCBM indicated that the crystallization of discotic C6PcH₂ with hexagonal structures was reduced owing to the dispersion of PCBM into the C6PcH₂ domains, which was in good agreement with the aforementioned decreases in Davydov splitting.

Although by employing an asymmetric [70]PCBM fullerene derivative instead of [60]PCBM, EQE at around 500 nm was improved due to the strong absorption of [70]PCBM [68], the clear peaks of EQE at around 500 nm, corresponding to [70]PCBM was not yet observed. Figure 3.9 shows the EQE spectra and the J-V characteristics under AM 1.5G illumination at an intensity of 100 mW/cm² of C6PcH₂:[70]PCBM BHJ OSCs with the various blend ratios in an ITO/MoO_x/BHJ/LiF/Al structure. The cell characteristics for all devices are summarized in Table 3.4. The EQE spectra exhibited the peaks corresponding to strong Q-band and B-band of C6PcH₂, and a clear peak around 500 nm of [70]PCBM. The clear peak at around 500 nm, furthermore, indicated that the photogenerated excitons of both the donor materials and the acceptor materials attributed to the photovoltaic performance.

Moreover, by increasing [70]PCBM volume fraction, the EQE at Q-band was improved to be around 53%. As a result, the J_{sc} increased to 10.2 mA/cm², when the ratio of C6PcH₂ to [70]PCBM was 60 to 40. With the V_{oc} of 0.73 V, the PCE was estimated to be 3.9%. We suggested that the interfacial areas between donor and acceptor was enlarged by increasing volume fraction of [70]PCBM in composite thin films, resulting in the improved photovoltaic performance.

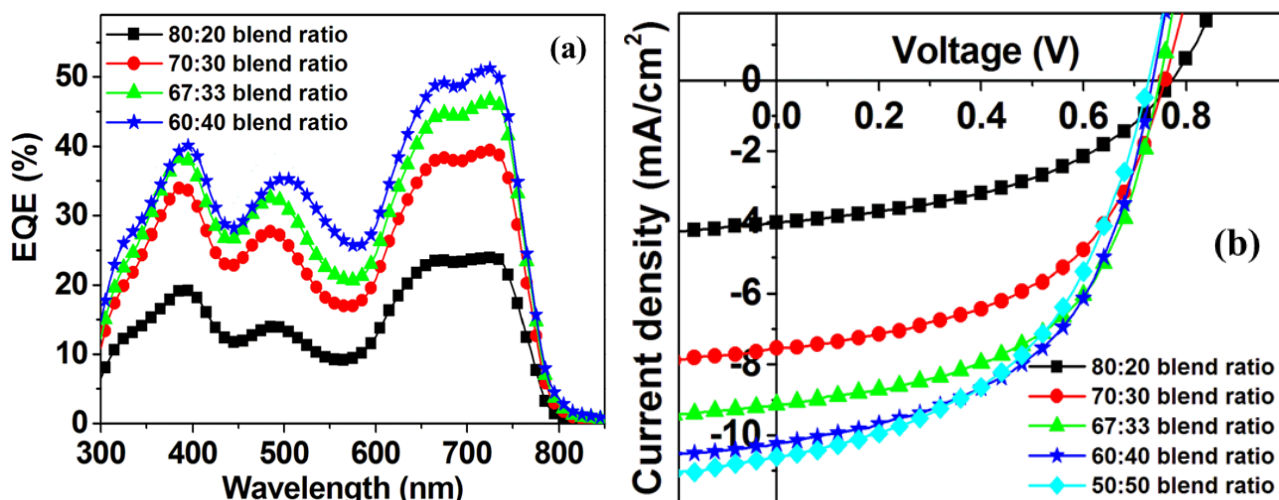


Fig. 3.9. (a) EQE spectra and (b) J-V characteristics of the C6PcH₂:[70]PCBM BHJ OSCs with various blend ratios.

Table 3.4. Cell characteristics of the C6PcH₂:[70]PCBM BHJ OSCs with various blend ratios under AM 1.5G illumination at an intensity of 100 mW/cm².

C6PcH ₂ :[70]PCBM blend ratios	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)
80:20	4.0	0.77	0.45	1.4
70:30	7.5	0.76	0.51	3.0
67:33	9.1	0.75	0.54	3.7
60:40	10.2	0.73	0.52	3.9
50:50	10.6	0.73	0.48	3.7

The PL spectra of C6PcH₂ and C6PcH₂:[70]PCBM thin films fabricated on quartz substrates with the various blend ratios are shown in Fig. 3.10(a). The PL spectra of C6PcH₂ thin films had a predominant peak at 766 nm and a shoulder around 820 nm, which relate with the Q-band of the C6PcH₂ absorption spectra [63]. The PL intensity of C6PcH₂:[70]PCBM thin films was markedly suppressed depending on [70]PCBM blend ratio. This suppression was due to the nonradiative decay of photogenerated-excitons through the photoinduced-electron transfer from the excited state of C6PcH₂ to [70]PCBM [1-4]. Moreover, Q was strong dependent on the [70]PCBM volume fraction, as shown in Fig. 3.10(b). The increases in Q indicated that the interfacial areas between donor and acceptor was enlarged by increasing the [70]PCBM volume fraction, which was in good agreement with the aforementioned increases in the J_{sc} and PCE.

Although the J_{sc} and PCE of the OSCs utilizing C6PcH₂ mixed with [70]PCBM was improved with increasing the volume fraction of [70]PCBM, the FF was reduced when the [70]PCBM volume fraction was higher than 33%. As shown in Table 3.4, the FF decreased to 0.48, which caused the relatively low PCE of 3.7%, when the ratio of C6PcH₂ to [70]PCBM was 50 to 50. It was supposed that with the high volume fraction of [70]PCBM, crystallinity of C6PcH₂ molecules was reduced and the continuous pathways for the transportation of charge carriers to electrodes were deteriorated.

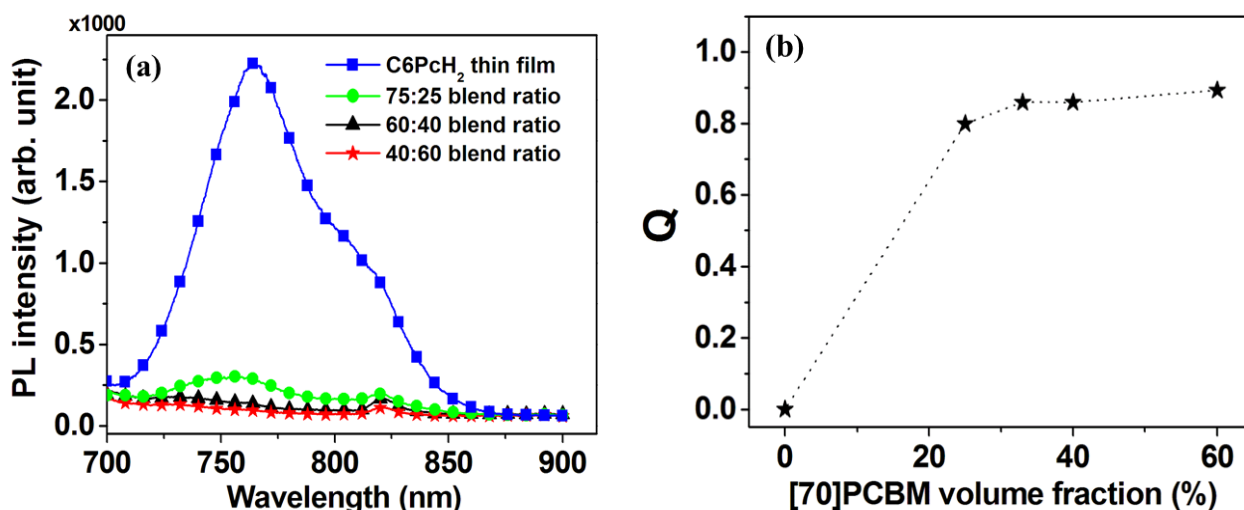


Fig. 3.10. (a) PL spectra of C6PcH₂ and C6PcH₂: [70]PCBM composite thin films with the various blend ratios and (b) Dependence of the relative quenching efficiency on the blend ratios; the excitation wavelength is 670 nm;

3.4 Conclusions

In this chapter, the roles of fullerene derivatives in the photovoltaic properties of the BHJ OSCs utilizing C6PcH₂ were studied. The photovoltaic performance of C6PcH₂-based BHJ OSCs was improved by using various fullerene derivatives, such as [60]PCBM, [70]PCBM, and Bis[60]PCBM. Particularly, by replacing the C₆₀ moiety of [60]PCBM with the asymmetric C₇₀, the absorption of composite thin films at around 500 nm increased, the EQE of the solar cells at around 500 nm was improved from 8% to 24%, and J_{sc} increased to 10.2 mA/cm². On the other hand, a high V_{oc} of 0.96 V was attained using Bis[60]PCBM with a higher LUMO level. Although the addition of [70]PCBM or Bis[60]PCBM to the composite thin films resulted in a lower crystallinity than that in case of the [60]PCBM, the photovoltaic performance of the BHJ OSCs utilizing [70]PCBM and Bis[60]PCBM fullerene derivatives was markedly improved.

Moreover, the blend ratio dependence of the photovoltaic properties in BHJ OSCs utilizing

C6PcH₂ mixed with [70]PCBM was reported. With increasing the volume fraction of [70]PCBM, the J_{sc} was improved to 10.6 mA/cm² due to enlarging the donor and acceptor interfacial areas. On the other hand, when the [70]PCBM volume fraction was higher than 33%, the FF was reduced owing to deteriorating crystallization of discotic C6PcH₂ molecules with hexagonal structures, which was in good agreement with the results of absorption spectra and XRD patterns. The OSCs with the optimum blend ratio showed the high PCE of 3.9%.

Chapter 4

Alkyl substituent length dependence of photovoltaic performance of solar cells

4.1 Introduction

During the recent interest in organic electronic devices such as organic thin-film transistors, organic light emitting diodes and OSCs, liquid crystals have attracted much attention as a novel type of molecular semiconductors [8, 76]. Indeed, high carrier mobilities have been realized even in mesophases where the mesogenic molecules are fluctuating with orientational or/and positional order. Typical structures of mesogenic molecules are of “rod-like” and “disk-like” types which are known as calamitic and discotic liquid crystals, respectively [77].

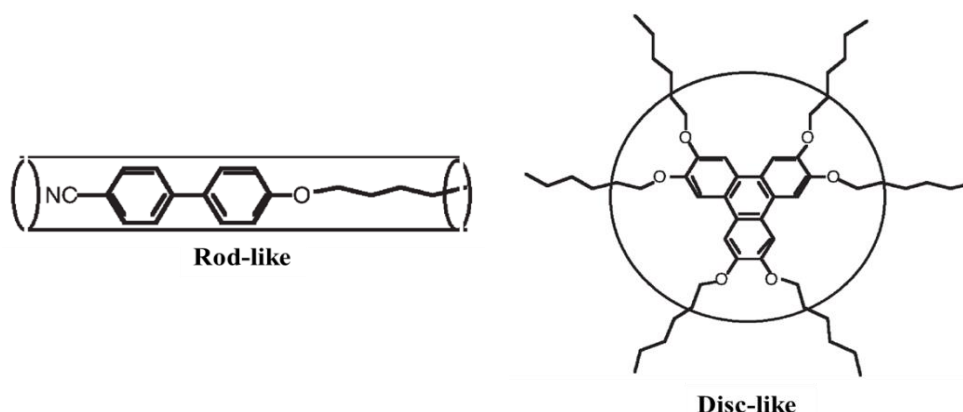


Fig. 4.1. Typical shapes of molecules for calamitic and discotic liquid crystals.

The mesogenic molecule consists of a rigid core with, in most cases, a π -electronic conjugation system and alkyl tails/substituents in the terminal/peripheral positions for calamitic/discotic liquid crystals, respectively, as illustrated in Fig. 4.1. The π -electronic systems being core parts of the mesogenic molecules play an important role for electronic conduction. On the other hand, the flexible parts of molecules definitively play an important role for the self-assembling nature. The self-organization is reasonably expected to facilitate the easy formation of a large-area mono-domain film with uniform alignment of molecules through their characteristic orientational order. In addition, on the basis of the requirement for “wet processing” in thin film device fabrication, the flexible parts of molecules have made such alkylated π -electronic conjugation systems much more attractive

due to their good solubility in common organic solvents [77].

On the history of liquid crystalline semiconductors, discotic liquid crystals opened up the doors to the present status of research, and this was initiated by the collaborative works between Bayreuth and Mainz in Germany. They found that typical discotic mesogens, hexaalkylthio and hexaalkoxy-triphenylenes, show fast mobilities of charge carriers in the columnar mesophases of 10^{-1} and 10^{-3} cm^2/Vs , respectively [78]. In particular, the former reaches the mobility range exhibited by a-silicon. Nevertheless, it is surprising to see that such a high mobility of charge carriers could be realized in a medium in which the molecules are likely to fluctuate within a limited framework (orientational/positional order). This fast mobility in mesophases is interpreted as an electronic process of charge transport by carrier hopping among the molecules and the disordered model proposed by Bassler is often used for understanding the characteristic properties observed so far [79]. Although, many reports have been published on liquid crystalline semiconductors in recent years, not so many compounds have been investigated so far as BHJ OSCs for example, and most did not exhibit the expected properties resulting from drift mobility measurements [80, 81].

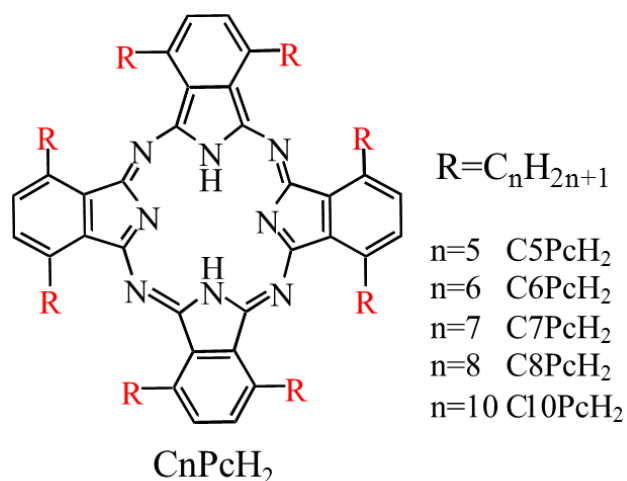


Fig. 4.2. Molecular structure of C_nPcH_2 in this study.

As we described in the previous chapters, C_6PcH_2 exhibits the high hole and electron drift mobilities in the crystalline phase at room temperature and the BHJ OSCs based on C_6PcH_2 mixed in various fullerene derivatives exhibited the relatively high PCEs [67, 70]. Although, the octaalkylphthalocyanine (C_nPcH_2) with different alkyl substituents were described as potential donors for BHJ OSCs, roles of the alkyl substituents in the self-assembling, optical and electronic properties of C_nPcH_2 were not fully understood yet [82]. In this study, the dependences of optical and electronic properties, structures, and photovoltaic performance of BHJ OSCs utilizing C_nPcH_2 (with n are 5, 6, 7, 8 and 10), as shown in Fig. 4.2, mixed with [70]PCBM on the length of alkyl

substituents were reported.

4.2 Experimental Procedure

CnPcH₂ was synthesized as described in the literature [55], with slight modifications, and fully purified by column chromatography (using silica gel with toluene as the eluent), which was followed by repeated recrystallization from toluene-methanol (1:2) solution [9]. The fullerene derivatives, [70]PCBM were purchased from Frontier Carbon Ltd.

BHJ thin films were prepared under optimized conditions in accordance with the following procedure. An ITO-coated glass substrate was cleaned with detergent, ultrasonicated in water, chloroform, acetone, and isopropyl alcohol, and subsequently dried with UV-induced ozone. 6-nm-thick MoO_x films were thermally evaporated onto ITO substrates at a rate of 0.1 Å/s under a vacuum of about 2×10^{-5} Pa. After transferring the films to a N₂-filled glove box, a solution containing a mixture of CnPcH₂ and [70]PCBM (3:2) in chloroform with the addition of 0.2% v/v of DIO was spin-cast onto a MoO_x layer. Herein, DIO plays a key role as a processing-additive solvent to control nanoscale morphology of BHJ active layer. The concentration of the BHJ solution was 22.35 mg/ml and the thickness of the active layers was estimated approximately to be 100 ~ 150 nm using AFM. Finally, a 0.3-nm-thick LiF buffer layers and 80-nm-thick aluminum films were deposited through a shadow mask by thermal evaporation under a vacuum of about 2×10^{-5} Pa. The active area of the device was 4 mm².

The *J-V* characteristics were measured using a source measurement unit (Keithley; 2400) and an XES 301 (AM 1.5 G) full spectrum solar simulator at an irradiation intensity of 100 mW/cm². EQE spectra were measured with a programmable electrometer using xenon lamp light passed through a monochromator as a light source. The integrated EQE values show good agreement with the measured *J_{sc}*.

The absorption spectra and the XRD patterns of the BHJ thin films were measured using a spectrophotometer (Shimadzu, UV-3150) and an X-ray diffractometer (Rigaku, RINT 2000), respectively. The ionization potentials of CnPcH₂ were measured using a photoelectron spectroscopy in air (Riken Keiki, AC-2).

The drift mobility of charge carriers of CnPcH₂ was determined under low vacuum by time-of-flight (TOF) technique, as shown in Fig. 4.3 [9]. A sandwich cell, consisting of two ITO-coated glass substrates and a polyimide spacer with thicknesses of a dozen of micrometers, was fabricated. The actual cell gaps were evaluated by an interference technique of light transmittance. Subsequently, CnPcH₂ was injected into the sandwich cell in the isotropic phase and naturally cooled

down to room temperature. A DC bias was applied between the electrodes using batteries connected in series, and the sample was irradiated using a Nd:YAG laser (λ : 355 nm, pulse width: 1 ns). Finally, the generated current transients were detected by an oscilloscope (Teledyne LeCroy, HDO4054), and the mobility was calculated according to the equation, $\mu = d^2/tE$, where d , t , and E are the sample thickness, transit time and applied field, respectively.

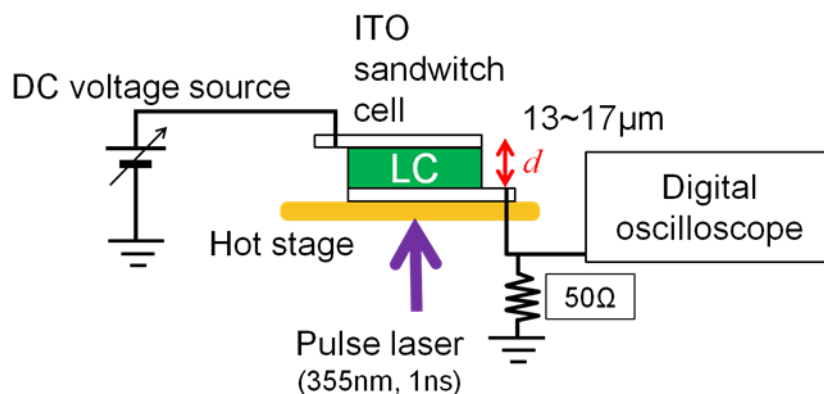


Fig. 4.3. TOF measurement diagram.

4.3 Dependence of optical and electronic properties and structures of C_nPcH₂ on alkyl substituent length

Figure 4.4 shows absorption spectra at Q-band of C_nPcH₂ in both solution and solid phases. The absorption spectra of solution of C_nPcH₂ exhibited intense Q-band absorption arising from the $a_{1u}-e_g$ ($\pi-\pi^*$) transition around 700 and 730 nm and the low intensity transitions to shorter wavelength arising from vibrational fine structure. The dependence of absorption in solution phase of C_nPcH₂ on the length of alkyl substituents is insignificant due to the isolated states of the C_nPcH₂-discotic molecules in solution phases.

In contrast to the solution-phase absorption spectra, the absorption spectra of C_nPcH₂ thin films were strongly dependent on the alkyl substituent length. Although the Q band of all C_nPcH₂ thin films was both blue- and red-shifted relative to their solution-phase absorption spectrum with clear Davydov splitting due to the exciton splitting arising from non-equivalent molecules, as in a columnar “herringbone” array of metal-free mesogenic phthalocyanines, the shape of Q-band was markedly modified by controlling the length of alkyl substituents [58]. Particularly, by lengthening the alkyl substituents, the Q-band was enlarged. Moreover, positions of the absorption peaks corresponding to Q-band of C_nPcH₂ are summarized in Table 4.1. It indicated that by lengthening the alkyl substituents from 5 to 9, the positions of Q_x and Q_y were shifted from 671 and 744 nm to 652 and 781 nm, respectively, and the Davydov splitting increased. When the size of Davydov splitting in

an allowed electronic transition is a direct measure of the interaction energy between molecules with differing site symmetries, one indicated that the alkyl substituents affected the alignment of phthalocyanine-discotic columns in hexagonal structures.

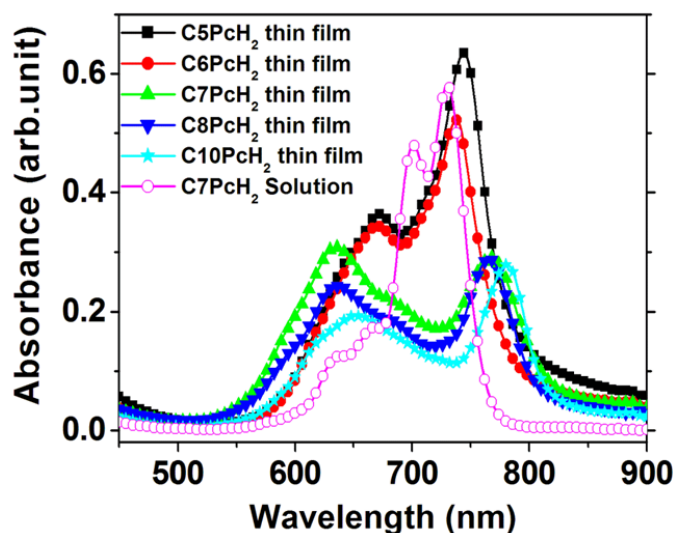


Fig. 4.4. Absorption spectra at Q-band of C7PcH₂ in solution phase and CnPcH₂ (with n being 5, 6, 7, 8 and 10) in solid.

Table 4.1. Positions of the absorption peaks corresponding to the Q-band of CnPcH₂.

	Q _x (nm)	Q _y (nm)
C7PcH ₂ in solution phase	700	730
C5PcH ₂ in solid phase	671	744
C6PcH ₂ in solid phase	670	738
C7PcH ₂ in solid phase	635	767
C8PcH ₂ in solid phase	636	765
C10PcH ₂ in solid phase	652	781

In terms of CnPcH₂, the ligands play an important role for electronic conduction and the alkyl substituents definitively attribute to the self-assembling nature [77]. However, when the absorptions of CnPcH₂ are strongly dependent on the alkyl substituent length, the electronic band structures of CnPcH₂ should be modified by changing the length of alkyl substituents. The photoelectron spectra of CnPcH₂ thin films spin-cast on ITO-coated glass substrates are shown in Fig. 4.5 and the HOMO levels of CnPcH₂ were estimated and summarized in Table 4.2. Herein, the photoelectron spectra of all CnPcH₂ thin films were measured under air ambient. It exhibited that the HOMO levels of CnPcH₂ drastically increased by lengthening the alkyl substituents, which was in good agreement

with the aforementioned increases in Davydov splitting. Particularly, while the HOMO levels of C5PcH₂ and C6PcH₂ were around -5.22 eV, by lengthening the alkyl substituents the HOMO levels of C7PcH₂ and C8PcH₂ increased to -5.05 and -5.08 eV, respectively.

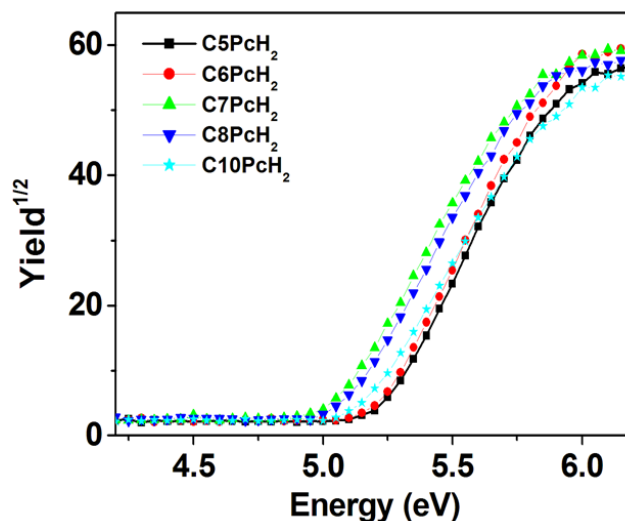


Fig. 4.5. Photoelectron spectrum of C_nPcH₂.

Table 4.2. HOMO levels of C_nPcH₂.

	HOMO (eV)
C5PcH ₂	-5.22
C6PcH ₂	-5.22
C7PcH ₂	-5.05
C8PcH ₂	-5.08
C10PcH ₂	-5.15

Table 4.3. Intercolumnar distance, D of C_nPcH₂-discotic columns.

	C5PcH ₂	C6PcH ₂	C7PcH ₂	C8PcH ₂
D (Å)	17.0	18.1	18.6	19.0

Analysis of structures of C_nPcH₂, furthermore, was performed using X-ray diffractometer. Figure 4.6 shows the XRD patterns of C_nPcH₂ thin films spin-cast on glass substrates. The XRD patterns of all C_nPcH₂ exhibited only the reflections in the small angle regions from 3° to 6°, corresponding to Miller indices of (200)/(110) (using indices based on a rectangular cell). The absence of reflections in the wide-angle region indicates that stacking period of discotic C_nPcH₂ along columnar axis is

disordered [82]. Moreover, the intercolumnar distance between the axes of neighboring C_nPcH_2 -discotic columns, D was estimated, as shown in Table 4.3. It indicated that D gradually increased from 17.0 to 19.0 Å on changing from C_5PcH_2 to C_8PcH_2 .

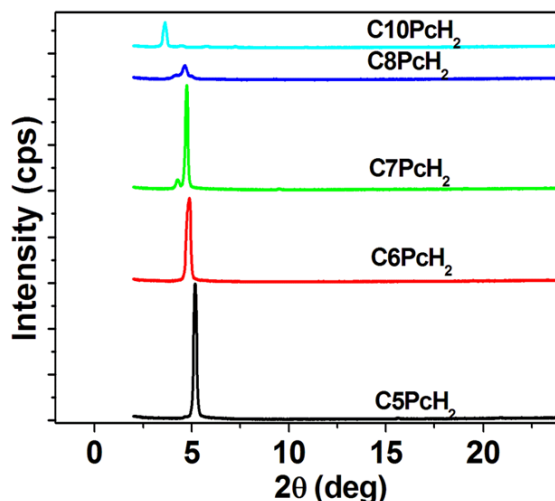


Fig. 4.6. XRD patterns of C_nPcH_2 thin films spin-cast on glass substrates.

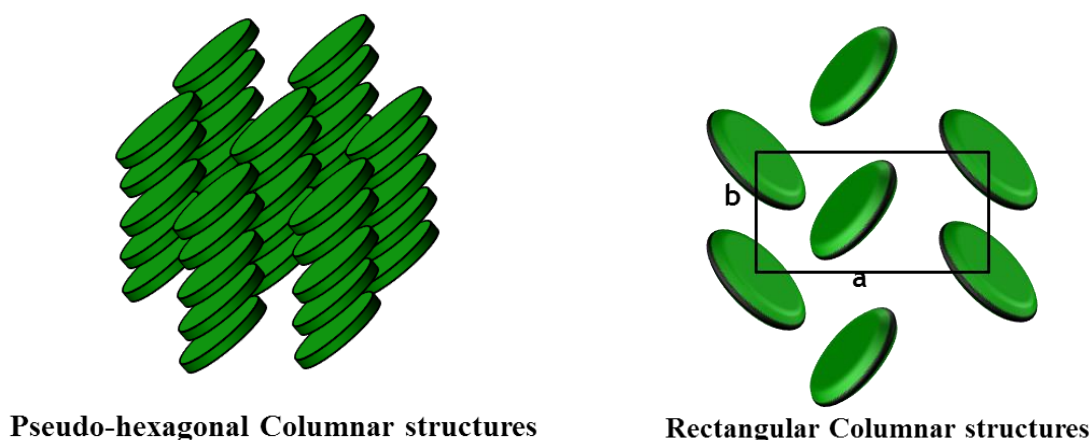


Fig. 4.7. C_nPcH_2 structures in this study.

From a geometrical point of view, besides stacking period of molecules along columnar axis, columnar structures are also characterized by intercolumnar stacking, which was experimentally determined by small angle X-ray diffraction. In 1991, Cherodian et al. reported the structures of C_nPcH_2 at the mesophases by using X-ray diffractometer [83]. One found that absence of a peak corresponding to the (210) plane suggests the lattice is “ c ” centered. Coincidence of (200) and (110) peaks, and absence of (210) peak further implies that the lattice constant $a = 3^{1/2} \times b$, and that the

mesogenic phthalocyanine comprises columnar stacks of co-facial molecules arranged within a classical two dimensional hexagonal lattice symmetry, which is denoted as pseudo-hexagonal structures [83]. On the other hand, symmetry of columns is likely to be 2-D rectangular lattice if diffraction arising from (210) plane and splitting of (200)/(110) or (310/020) (because $a \neq 3^{1/2} \times b$) are apparent, as shown in Fig. 4.7 [83].

As shown in Fig. 4.6, the peaks, corresponding to (200)/(110) planes, were coincident in the case of C5PcH₂ and C6PcH₂, and split when alkyl substituent was lengthened to 7, 8, or 10. Although other peaks in the small region of all C_nPcH₂ XRD patterns in this study were absent possibly because of the finite resolution of the diffractometer and/or slenderness of spin-cast films, it was suggested that symmetry of C5PcH₂ and C6PcH₂ columns was probably pseudohexagonal structures, and that the symmetry of the long-alkyl-substituent C_nPcH₂ (with n is 7, 8 and 10) columns was likely to be 2-D rectangular lattices.

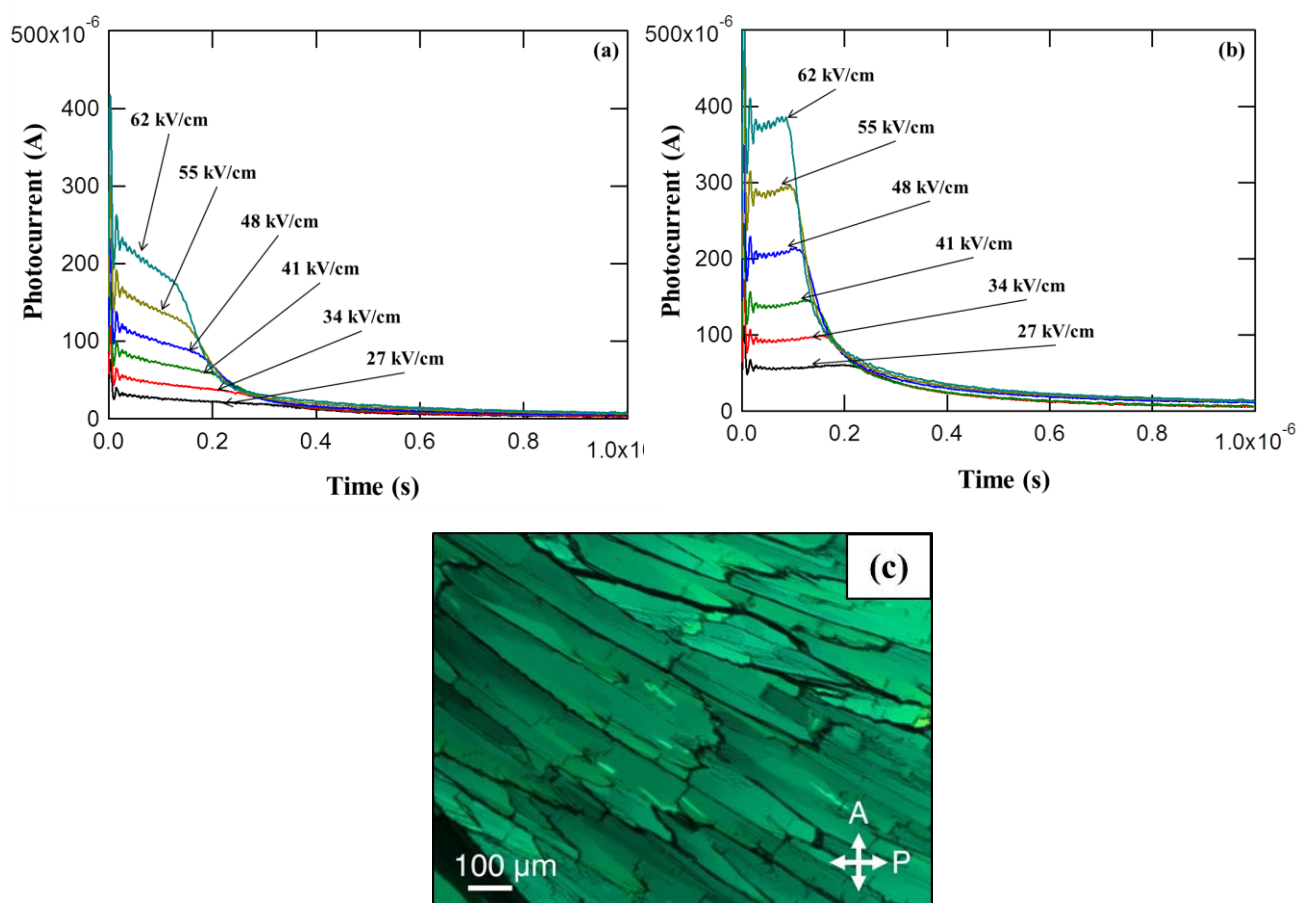


Fig. 4.8. Transient photocurrent decay curves for (a) hole and (b) electron, and (c) polarizing photomicrograph of C5PcH₂, in the crystal phase at 25 °C.

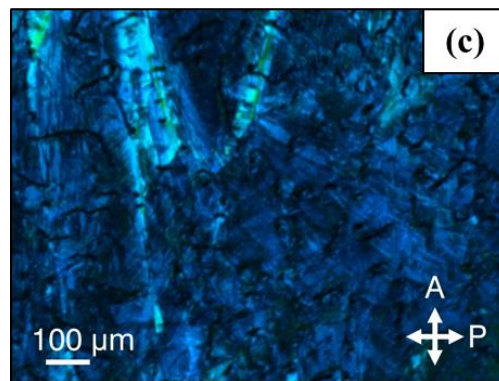
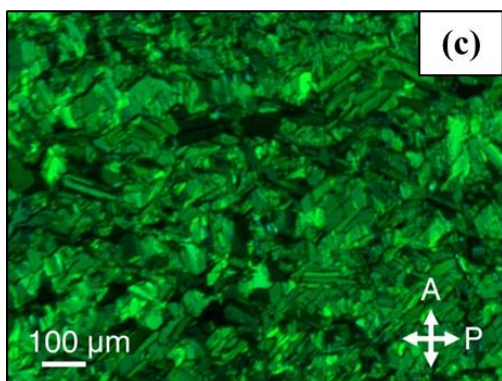
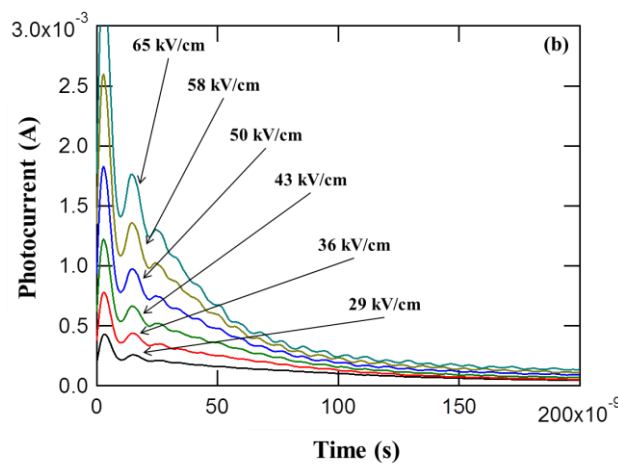
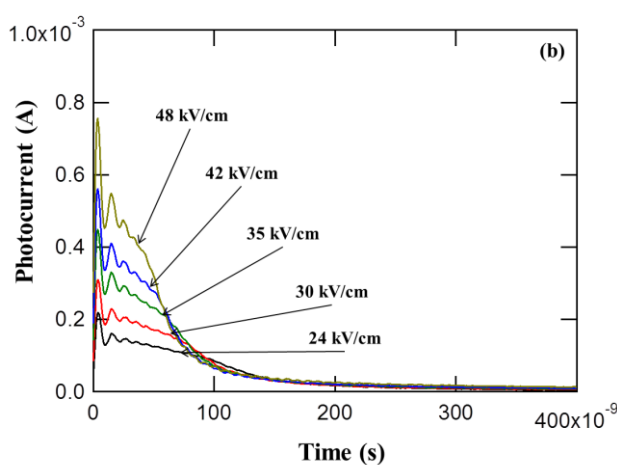
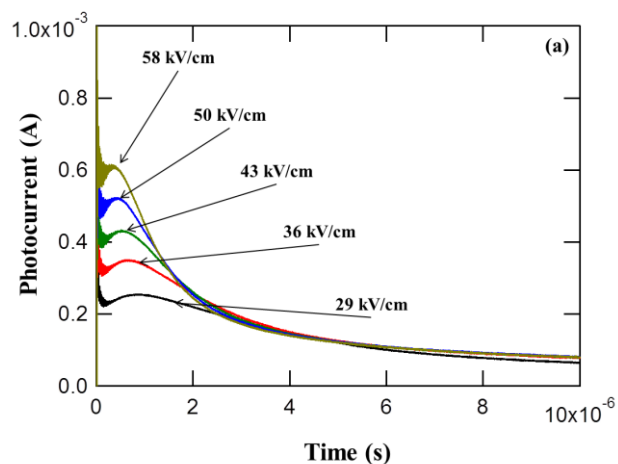
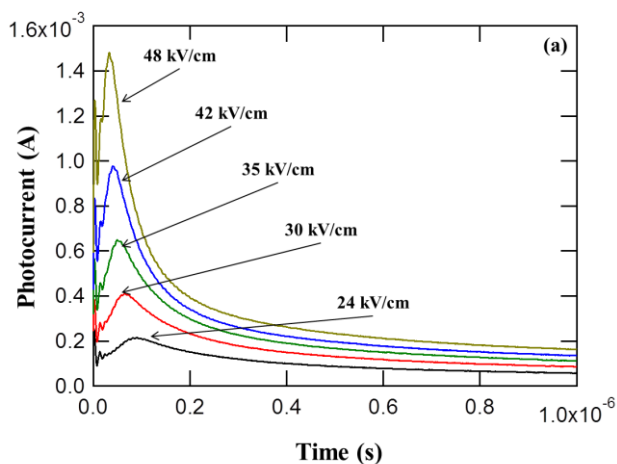


Fig. 4.9. Transient photocurrent decay curves for (a) hole and (b) electron, and (c) polarizing photomicrograph of C6PcH₂, in the crystal phase at 25 °C.

Fig. 4.10. Transient photocurrent decay curves for (a) hole and (b) electron, and (c) polarizing photomicrograph of C8PcH₂, in the crystal phase at 25 °C.

When the structures of C_nPcH₂ are modified by lengthening the alkyl substituents, the strong dependence of the charge carrier mobilities of C_nPcH₂ on the alkyl substituents length should be expected. Figure 4.8, 4.9, and 4.10 shows the transient photocurrent decay curves for hole and

electron and the polarizing photomicrograph of C5PcH₂, C6PcH₂, and C8PcH₂, respectively, in the crystal phase at 25 °C. The hole and electron mobilities of all C_nPcH₂ were estimated and summarized in Table 4.4.

Table 4.4. Hole and electron mobilities in the crystal phase at 25 °C of C5PcH₂, C6PcH₂, and C8PcH₂, measured by using TOF.

	Hole mobility (cm ² /Vs)	Electron mobility (cm ² /Vs)
C5PcH ₂ in solid phase	0.15	0.23
C6PcH ₂ in solid phase	0.81	0.70
C8PcH ₂ in solid phase	0.03	0.51
C10PcH ₂ in solid phase	0.02	---

One found that the hole mobilities of C_nPcH₂ was strongly dependent on the length of alkyl substituents, which contributed to the crystallinity and the molecular packing. While C5PcH₂ and C6PcH₂ in the pseudohexagonal structure exhibited the high hole mobilities of 0.15 and 0.81 cm²/Vs, the hole mobilities of C8PcH₂ and C10PcH₂ in the 2-D rectangular lattice were reduced to 0.03 and 0.02 cm²/Vs, respectively. In contrast, the dependence of the electron mobility on the alkyl substituent length was minimal. Particularly, C5PcH₂, C6PcH₂, and C8PcH₂ showed the electron mobilities of 0.23, 0.70, and 0.51 cm²/Vs, respectively. This surprisingly resulted in the balance of the electron and hole mobilities in the short-alkyl-substituent C_nPcH₂ (C5PcH₂ and C6PcH₂), and the imbalance of the electron and hole mobilities in the long-alkyl-substituent C_nPcH₂ (C8PcH₂) [84].

4.4 Dependence of photovoltaic performance on alkyl substituent length

Figure 4.11 shows the EQE and *J-V* characteristics of C_nPcH₂: [70]PCBM devices in an ITO/MoO_x/BHJ/LiF/Al structure under AM 1.5G illumination at an intensity of 100 mW/cm². The cell characteristics for all devices are summarized in Table 4.5. All the EQE spectra showed the strong Q-band and B-band of C_nPcH₂, and a shoulder around 500 nm of [70]PCBM. It is noted that the peak at around 500 nm corresponding to the absorption of [70]PCBM did not clearly appeared, which were different from the EQE of C6PcH₂: [70]PCBM devices in the chapter 3. This result was probably due to the absorption of glass substrates used in this experiment. Moreover, the EQE was strongly dependent on the length of alkyl substituents. Particularly, by shortening the alkyl substituents, the EQE at Q-band was improved from 22 to 49%.

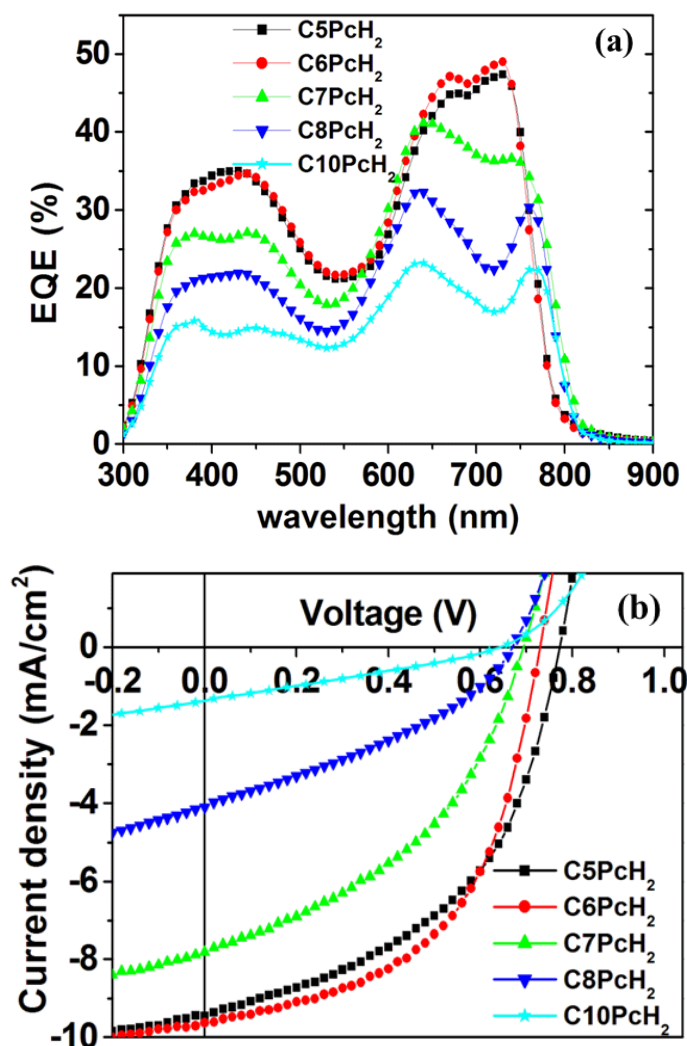


Fig. 4.11. (a) EQE spectra and (b) J - V characteristics of the C_nPcH_2 : $[70]PCBM$ BHJ OSCs.

Table 4.5. Characteristics of C_nPcH_2 -based BHJ OSCs, measured under 100 mW/cm^2 light illumination.

BHJ OSCs	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	Efficiency (%)
C5PcH ₂	0.77	9.5	0.48	3.5
C6PcH ₂	0.73	9.6	0.53	3.7
C7PcH ₂	0.69	7.8	0.42	2.6
C8PcH ₂	0.67	4.1	0.35	1.0
C10PcH ₂	0.65	1.4	0.28	0.3

One found that J_{sc} is directly corresponding to the value of EQE, as shown in equation (1.4) and the improved EQE often causes the high J_{sc} and PCEs. As a result of the EQE, the J_{sc} of

CnPcH₂:[70]PCBM devices was strongly dependent on the length of alkyl substituents, as shown in Table 4.5. In particular, the J_{sc} of the BHJ OSCs utilizing C8PcH₂ and C10PcH₂ were 1.4 and 4.1 mA/cm², respectively. By shortening the alkyl substituent length, the J_{sc} increased to 9.5 and 9.6 mA/cm² for the BHJ OSCs utilizing C5PcH₂ and C6PcH₂, respectively. Furthermore, the BHJ OSCs utilizing C5PcH₂ and C6PcH₂ exhibited the higher FF of 0.48 and 0.53, respectively, compared with those of the devices fabricated from the long-alkyl-substituent CnPcH₂ (C7PcH₂, C8PcH₂, or C10PcH₂). It was suggested that the aforementioned balance of the hole and electron mobility of probably induced the high FF of the devices utilizing C5PcH₂ and C6PcH₂ [85].

One found that the maximum V_{oc} otherwise is considered to be limited by the work function of the metal electrodes and the energy gap between the HOMO of the donor materials and the LUMO of the acceptor fullerenes, ΔE_{DA} [70-73]. Although the difference between V_{oc} and ΔE_{DA} is still subject to debate, a linear relationship between V_{oc} and ΔE_{DA} has been experimentally confirmed [73]. Hence, with the aforementioned increases in HOMO levels, the V_{oc} of CnPcH₂-based BHJ OSCs exhibited the strong dependence on the length of alkyl substituents. Particularly, by shortening the alkyl substituents, the V_{oc} was improved from 0.65 to 0.77 V and the PCE of devices increased to 3.7% [84].

4.6 Conclusions

In summary, the strong dependences of optical and electronic properties, structures, and photovoltaic performance of BHJ OSCs utilizing CnPcH₂ mixed [70]PCBM on the length of alkyl substituents were studied. By decreasing the length of alkyl substituents, stacking of the discotic CnPcH₂ columns was probably changed from 2-D rectangular lattices to pseudohexagonal structures, and Davydov splitting at the Q-band of CnPcH₂ absorbance spectra decreased. As a result, the short-alkyl-substituent CnPcH₂ (C5PcH₂ and C6PcH₂) exhibited the deeper HOMO energy levels and the balance of hole and electron mobility. Furthermore, the EQE at Q-band of CnPcH₂-based BHJ OSCs was improved from 22 to 49%, the PCE increased to 3.7% by altering the length of alkyl substituents.

Chapter 5

Mechanism of degradation and improvement of stability on mesogenic-phthalocyanine-based solar cells

5.1 Introduction

Research in the field of OSCs is still in an exciting phase with a rapid progression of improvements in the technique as detailed in a series of reviews [86-92]. Although, the researches were carried out with the many research areas from field of polymer to low band-gap materials, and small-molecule OSCs, from planar-heterojunction OSCs to BHJ OSCs, and from single layer OSCs to tandem OSCs, the main direction has been only towards the achievements of as the high PCEs as possible under simulated sunlight.

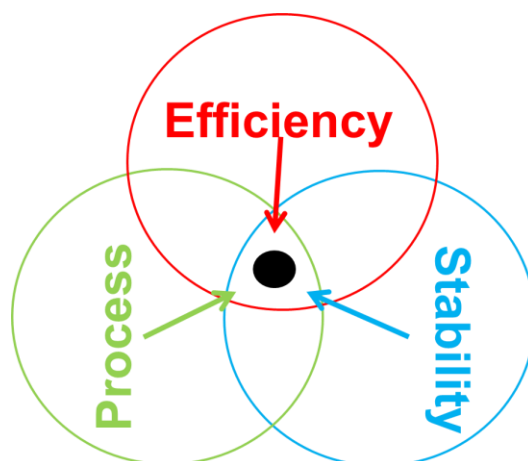


Fig. 5.1. Challenges of unifying efficiency, stability and process for BHJ OSCs.

The important aspects other than the PCEs that have been identified are the stability and the processing, as shown in Fig. 5.1 [93, 94]. However, these individual areas, especially the poor stability of OSCs, have been given relatively little consideration. Moreover, when inorganic silicon-based solar cells may last on the order of 25 years, organic devices must be improved tremendously to become technologically interesting. A number of studies have been carried out and they exhibited that the stability/degradation issue is rather complicated and certainly not yet fully understood, though progress has been made.

OSC degradation generally could be clarified from the chemical, structural, and electrical viewpoints, as illustrated in Fig. 5.2. It has been reported that environmental conditions, such as oxygen and moisture dramatically degrade the lifetime of OSCs, whereas buffer layers on the active layer play an important role in improving the stability [95, 96]. However, further detailed studies are required to allow comprehensive understanding of the degradation mechanism and hence to extend the device lifetime.

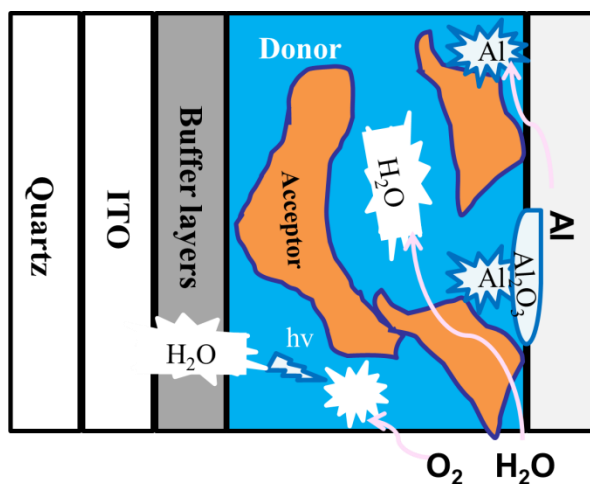


Fig. 5.2. Cross section view of OSCs with the many processes that conspire to degrade BHJ OSCs.

As described in Chapter 2, by utilizing processing additives, the $C6PcH_2$:[60]PCBM based BHJ OSCs showed the relatively high PCE of 4.2% and EQE at Q band of phthalocyanine close to 60% with the optimum donor-acceptor phase separation and crystallization of the BHJ materials. Furthermore, the structures, optical and electronic properties of C_nPcH_2 were studied in Chapter 4. However, the stability and the mechanism of degradation of the OSCs utilizing $C6PcH_2$ were not yet concerned. In this chapter, the high stability as well as the mechanism of degradation of $C6PcH_2$ -based BHJ OSCs was reported. The operation time dependence of the cell characteristics of $C6PcH_2$ -based cells have been compared with those of the cells with a conventional donor material, P3HT, in the different ambient. Furthermore, the degradation mechanisms of the OSCs have been investigated. To improve the stability, various buffer layers have been introduced between the counter electrode and the active layer.

5.2 Experimental Procedure

C6PcH₂ was synthesized as described in the literature [55], with slight modifications, and fully purified by column chromatography (silica-gel with toluene as eluent) followed by repeated recrystallization from toluene–methanol (1:2) solution [9]. Regioregular P3HT and [60]PCBM were purchased from Merck and Frontier Carbon, respectively.

BHJ films were prepared under optimized conditions in accordance with the following procedures. The ITO-coated quartz substrate was cleaned with detergent, ultrasonicated in water, chloroform, acetone, and isopropyl alcohol, and subsequently dried with UV-induced ozone. 6-nm-thick MoO_x films were thermally evaporated onto ITO substrates at a rate of 0.1 Å/s under a vacuum of about 2×10^{-5} Pa. After transferring the films to a N₂-filled glove box, a solution containing a mixture of C6PcH₂:[60]PCBM (2:1) in toluene or chloroform was spin-cast at 500 rpm onto a MoO_x layer. The concentration of the solution with the various solvents for C6PcH₂:[60]PCBM BHJ OSCs was summarized in Table 5.1 and the thickness of the active layers was approximately 180 nm. Herein, the thickness of the active layers was measured using AFM. On the other hand, a similar process with the blend solution, as summarized in Table 5.2, was performed to fabricate the P3HT-based devices. Herein, the PCE of each device were optimized by adjusting the ratios of donor and acceptor. Finally, a 0.3-nm-thick LiF buffer layer and a 80-nm-thick aluminum or silver cathode were deposited through a shadow mask by thermal evaporation under a vacuum of about 2×10^{-5} Pa. In the case of the cells with a low-work-function cathode, a 25-nm-thick Ca layer was fabricated and then covered with an Al layer to protect it from oxidization. The active area of the device was 4 mm².

Table 5.1. Solution concentrations for C6PcH₂: [60]PCBM BHJ OSCs in this study

	C6PcH ₂ (mg/ml)	[60]PCBM (mg/ml)
Chloroform	8	4
Toluene	14.2	7.1

Table 5.2. Solution concentrations for P3HT: [60]PCBM BHJ OSCs in this study

	P3HT (mg/ml)	[60]PCBM (mg/ml)
Chloroform	5	5

The devices characteristics were measured using a XES 301 (AM 1.5 G) full spectrum solar simulator at an irradiation intensity of 100 mW/cm^2 , which increased the temperature of the environment of the device up to $45 \text{ }^\circ\text{C}$. The J-V characteristics were measured using a source measure unit (Keithley, 236). Otherwise, EQE spectra were measured with a programmable electrometer using xenon lamp light passing through a monochromator as a light source. The integrated EQE values always show good agreement with the measured J_{sc} . The absorbance spectra were measured by spectrophotometry (Shimadzu UV-3150). Furthermore, the chemical characteristics and crystallinity of the C6PcH₂ molecule in thin films were also evaluated by X-ray diffraction (Rigaku RINT 2000) and X-ray photoelectron spectroscopy (XPS; Shimadzu ESCA 850).

5.3 High stability of BHJ OSCs utilizing C6PcH₂

Figure 5.3 shows the cell characteristics of the P3HT:[60]PCBM BHJ OSCs and C6PcH₂:[60]PCBM BHJ OSCs without packaging or encapsulation as a function of time under light illumination at 100 mW/cm^2 . Herein, the P3HT-based solar cells in the simple structure of ITO/MoO_x/BHJ/Al showed an initial PCE of 1.8%, with a J_{sc} of 7.2 mA/cm^2 , an V_{oc} of 0.55 V, and a FF of 0.46, each of which was normalized by its initial value. The results indicated that the PCE of the devices fabricated using P3HT decreased by approximately 38% after 9 h of continuous illumination in air ambient owing to the rapid degradation of J_{sc} . Otherwise, V_{oc} and FF seem to be slightly degraded. This result was comparable to those in a previous report by Kawano and Adachi [96].

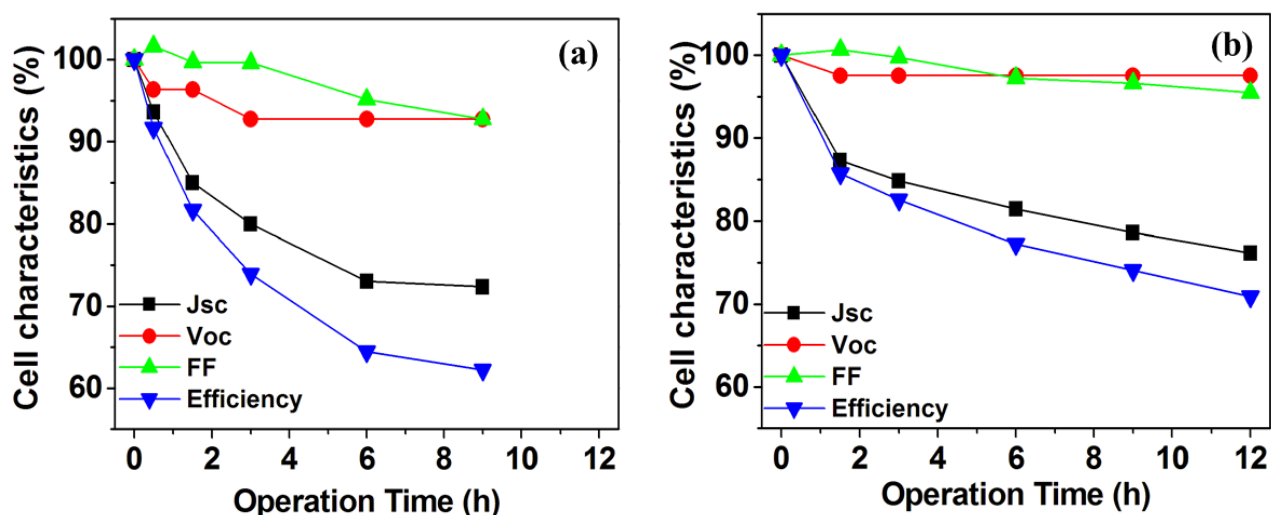


Fig. 5.3. Cell characteristics, normalized by their initial values, as a function of illumination time under 100 mW/cm^2 light illumination, of the OSCs fabricated utilizing (a) P3HT and (b) C6PcH₂.

On the other hand, the C6PcH₂:[60]PCBM BHJ OSCs in the structure of ITO/MoO_x/BHJ/Al were fabricated and the photovoltaic performances and stability of devices were measured under the similar ambient conditions. It exhibited that the stability of the devices fabricated using C6PcH₂ was higher than that of the devices fabricated using P3HT. In particular, the PCEs of the devices fabricated using C6PcH₂ remained at about 71% after 12 h illumination, as shown in Fig. 5.3(b). Herein, the initial PCEs of the BHJ OSCs utilizing C6PcH₂ were estimated to be 1.89% with a J_{sc} of 5.28 mA/cm², a V_{oc} of 0.81 V, and a FF of 0.44.

Furthermore, the device lifetime was evaluated under various conditions, such as air or nitrogen atmosphere, without illumination by a solar simulator, as shown in Fig. 5.4. The device lifetime was totally improved by utilizing C6PcH₂ in the simple structure of ITO/MoO_x/BHJ/Al without the any ambient-condition dependence.

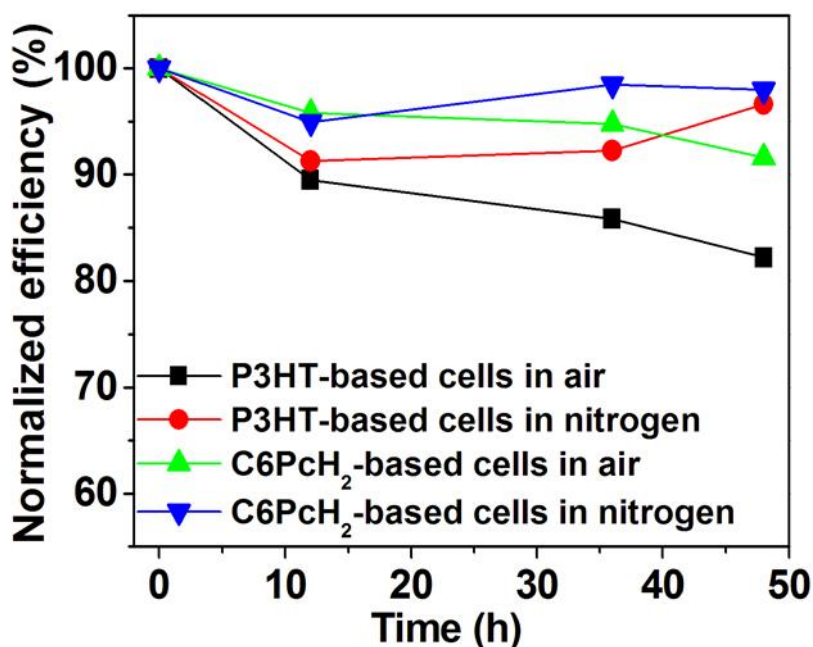


Fig. 5.4. Normalized efficiency as a function of time of the C6PcH₂:[60]PCBM BHJ OSCs and P3HT:[60]PCBM BHJ OSCs, stored in a dark environment.

5.4 Mechanism of degradation of BHJ OSCs utilizing C6PcH₂

To investigate the degradation mechanism of BHJ OSCs fabricated utilizing C6PcH₂, the active layers were spin-cast from the C6PcH₂:[60]PCBM blend solutions onto glass substrates and then illuminated by the solar simulator. The properties of the solar-simulator illuminated thin films were characterized from the viewpoints of the XRD patterns, XPS spectra, and absorption spectra.

Figure 5.5 shows the absorption spectra of the C6PcH₂:[60]PCBM composite thin films with

and without illumination. It is seen that the absorption spectra of C6PcH₂: [60]PCBM composite thin films without illumination exhibited the strong Q-band and B-band at around 700 and 350 nm, respectively. However, after 100 h of illumination in air environment, the absorption peak that originated from the Q band at approximately 700 nm in wavelength disappeared, and the pristine green color of C6PcH₂ also disappeared, as shown in Fig. 5.6. On the other hand, the absorption spectra of the C6PcH₂: [60]PCBM composited thin films and the pristine green color of C6PcH₂ seemed to be unchanged while the thin film was illuminated in vacuum by the solar simulator. It is hypothesized that photooxidation is one of the main mechanisms of the degradation of the devices utilizing C6PcH₂.

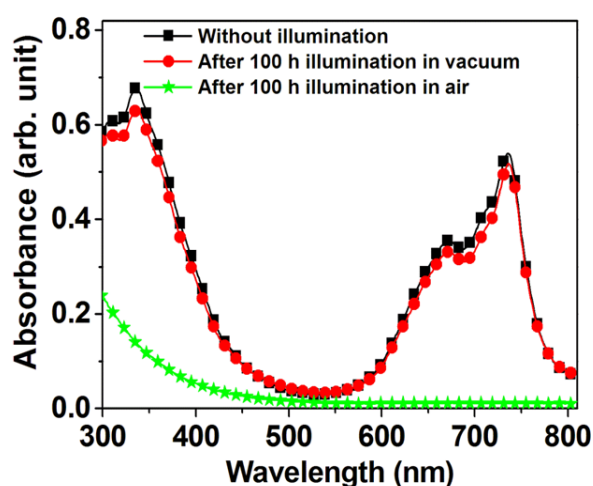


Fig. 5.5. Absorption spectra of the C6PcH₂: [60]PCBM composite thin films with and without illumination.

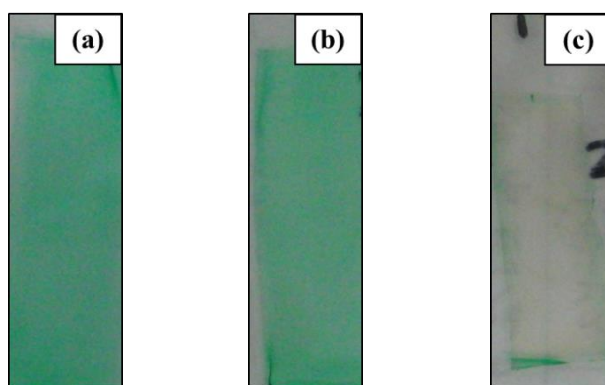


Fig. 5.6. Images of the C6PcH₂: [60]PCBM composite thin films (a) before illumination, and after 100 hour illumination in (b) vacuum and (c) air.

Figure 5.7 shows the XRD patterns of the C6PcH₂: [60]PCBM composite thin films with and without illumination in air environment. The XRD patterns of all composite thin films exhibited only

the reflections in the small angle regions at approximately 5° , corresponding to the intercolumnar distance between the axes of neighboring C6PcH₂-discotic columns, D. Moreover, the D was estimated and summarized in Table 5.3. The intercolumnar distance D of hexagonal columns in the C6PcH₂:[60]PCBM composite thin film, measured immediately after spin-casting, was estimated to be 17.66 Å. However, after illuminating under solar simulator in air, the distance D was enlarged. In particular, the distances between two columns in the hexagonal structure of the C6PcH₂ molecule became 17.95 and 18.03 Å after 50 and 100 h of illumination in air, respectively.

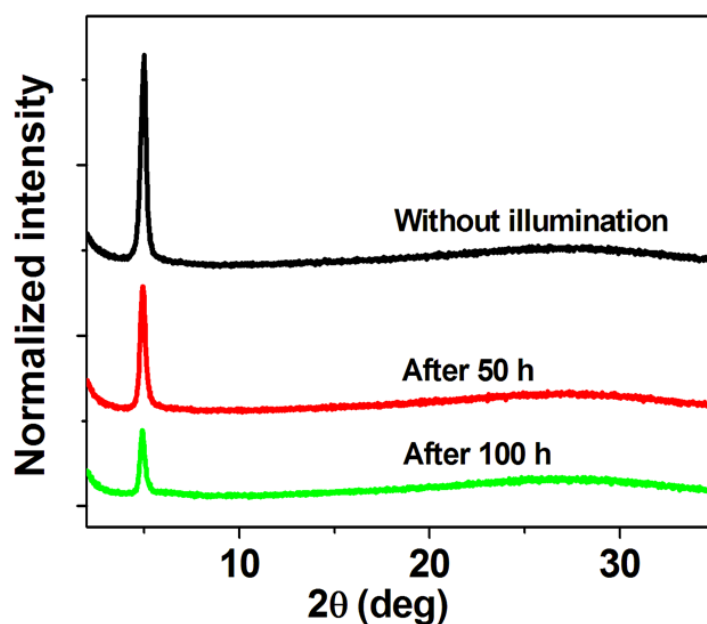


Fig. 5.7. XRD patterns of C6PcH₂:[60]PCBM composite thin films with and without illumination in air. All XRD patterns were normalized at 4.88° .

Table 5.3. Intercolumnar distance of the hexagonal columns in the C6PcH₂:[60]PCBM composite thin films with and without illumination.

	D (Å)
Origin	17.66
After 50 h	17.95
After 100 h	18.03

The C6PcH₂:[60]PCBM composite thin films with and without illumination were characterized by XPS, as shown in Fig. 5.8(a). It exhibited that the N1s core-level spectra consisted of three components of binding energies: 398.9, 400.4, and 402.7 eV. It was reported that the peak at 398.9 eV is associated with twofold-coordinated nitrogens: the two pyrrole aza nitrogens and the four

meso-bridging aza nitrogens, denoted as N2 and N3 in Fig. 5.8(b), respectively [97]. Otherwise, the peak at 400.4 eV is associated with the two threefold-coordinated pyrrole nitrogens bonded to hydrogen atoms in the central ring of the molecule, denoted as N1 in Fig. 5.8(b) [97]. The weak peak at 402.7 eV is due to shake-up transitions [98]. Obviously, after the illumination period, the ratio of the intensity at 398.9 eV to that at 400.4 eV rapidly decreased. This meant that the bonds of nitrogen atoms at N3 and N2 with neighboring carbons were broken, or the C6PcH₂ rings were opened. Furthermore, the increase in the concentrations of oxygen atoms in the C6PcH₂ and [60]PCBM composite thin films with illumination in air (Table 5.4) also must be the evidence of the photochemical reaction between oxygen atoms and organic active layer materials.

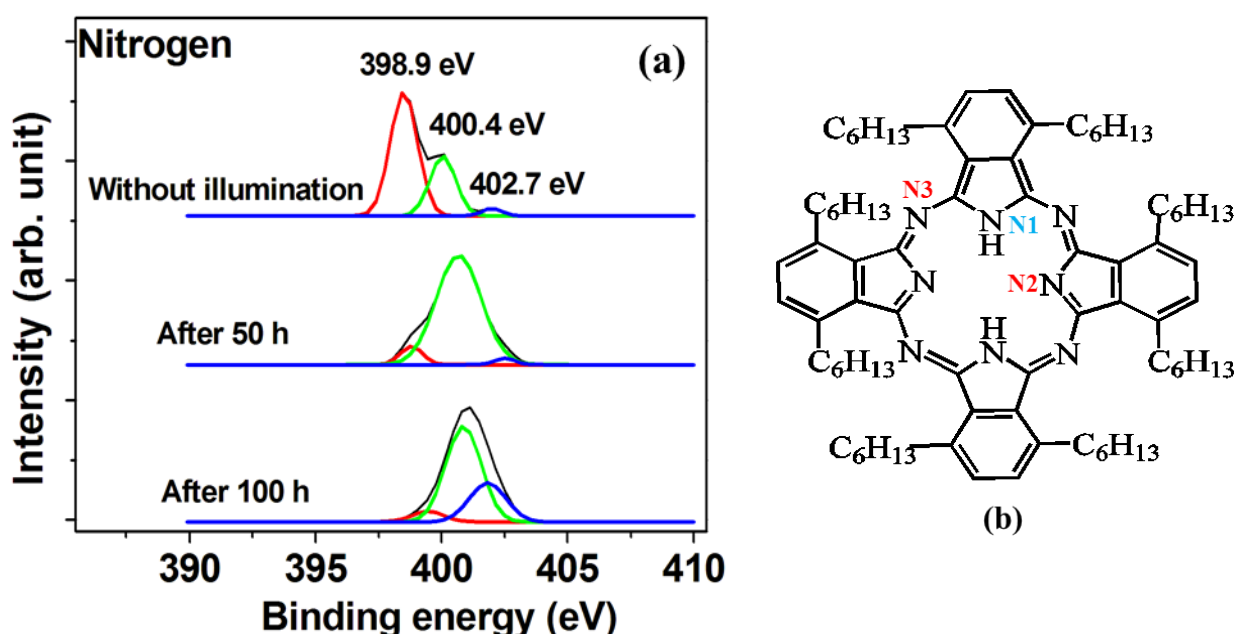


Fig. 5.8. (a) XPS spectra of C6PcH₂:[60]PCBM composite thin films with and without illumination in air and (b) Molecular structure of C6PcH₂.

Table 5.4. Concentration of oxygen atoms (%) in the C6PcH₂:[60]PCBM composite thin films with and without illumination.

	No etching	3s etching	6s etching
Origin	0.59	0	0
After 50 h	18.49	3.26	2.40
After 100 h	27.21	14.08	9.58

5.5 Effects of counter electrodes and buffer layers at top of cell on stability

The stability of OSCs, however, depends not only on the photooxidation of the organic BHJ materials, but also on the oxidation of metal at counterelectrodes and the reaction between the metal and the organic material. In the terms of OSCs, Al with a low work function is commonly deposited as a top electrode by thermal evaporation and plays an important role in efficient electron extraction. However, during thermal evaporation processes, the hot metal atoms might react with oxygen species remaining in the vacuum chamber and diffuse into the organic layers, which would affect the OSC lifetime [99, 100]. Herein, the effects of the counter electrodes and buffer layers at the top of cells on the stability of C6PcH₂:[60]PCBM BHJ OSCs were studied.

Figure 5.9 shows the EQE spectra and *J-V* characteristics of the C6PcH₂:[60]PCBM BHJ OSCs with the various counter electrodes under AM 1.5G illumination at an intensity of 100 mW/cm². The cell characteristics for all devices are summarized in Table 5.5. The EQE of all C6PcH₂:[60]PCBM BHJ OSCs exhibited the strong peaks at the Q-band and B-band of the C6PcH₂. However, the EQE of the devices utilizing the Ca/Al counter electrodes was lower than that of the devices utilizing Ag or Al counter electrodes. As a result of EQE, the *J_{sc}* decreased to be 6.5 mA/cm² after adding Ca between the active layers and Al counter electrodes. On the other hand, a slight variation of the *V_{oc}* being only 40 mV was observed when changing the work function of the negative electrode from 4.8 (Ag) to 2.9 eV (Ca).

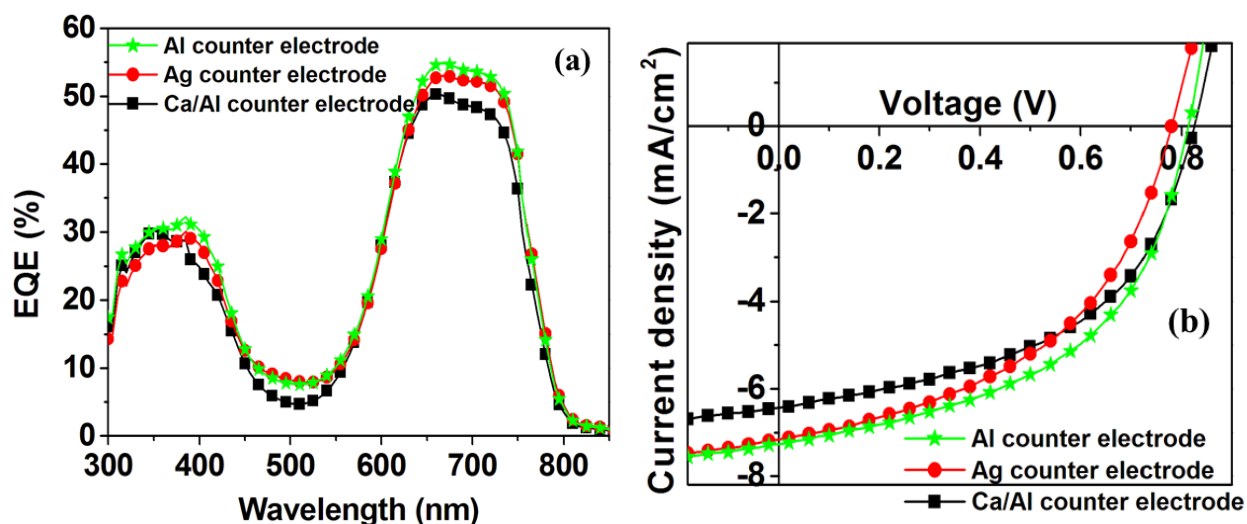


Fig. 5.9. (a) EQE spectra and (b) *J-V* characteristics of the C6PcH₂:[60]PCBM BHJ OSCs with various counter electrodes.

Table 5.5. Cell characteristics of C6PcH₂:[60]PCBM BHJ OSCs with various counter electrodes, measured under 100 mW/cm² light illumination.

Counter electrode	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	Efficiency (%)
Al	0.81	7.3	0.51	2.7
Ag	0.79	7.2	0.47	2.7
Ca/Al	0.83	6.5	0.51	3.0

Figure 5.10 shows the efficiency of the C6PcH₂:[60]PCBM BHJ OSCs with various counterelectrodes as a function of the duration of continuous illumination by the solar simulator. Note that each value is normalized by their initial values.

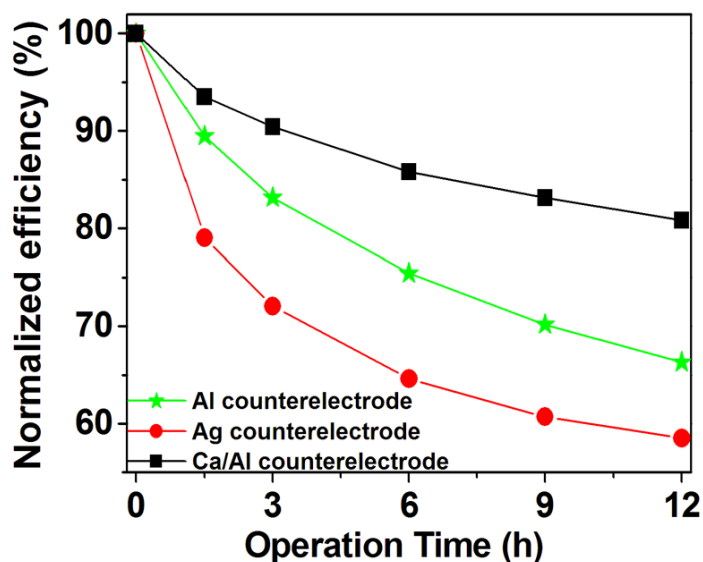


Fig. 5.10. Normalized efficiency as a function of illumination time under 100 mW/cm² light illumination in air, of the C6PcH₂:[60]PCBM BHJ OSCs with the various counter electrodes.

One found that a decrease of approximately 34% in the PCEs of the Al-based device was improved to a 19% loss in PCE upon the insertion of Ca. Utilizing Ag electrodes instead of Al electrodes, otherwise, resulted in the degradation of approximately 42% in the PCE after 12 h of illumination in air. It was assumed that the oxidized layers, which were unexpectedly created during thermal evaporation, prevent the diffusion of metal electrodes into the organic active layers and hence affect the OSC lifetime. During thermal evaporation processes, the hot metal atoms might react with oxygen species remaining in the vacuum chamber and create the oxidized metal/organic interfacial area. For the Ca electrode, which oxidizes more easily, the oxidized Ca/organic interfacial

layers were probably thicker than the oxidized Al/organic interfacial layers; hence, the cells with Ca counterelectrodes were more stable than those with Al counterelectrodes. In contrast, because of the high resistance of Ag to oxidation, the oxidized Ag/organic interfacial layers were probably thinner than the oxidized Al/organic interfacial layers; hence, the cells with Ag counterelectrodes were markedly degraded. It was considered that these oxidized layers could improve the stability of the devices. On the other hand, the oxidized Ca/organic interfacial layers probably resulted in the relatively low J_{sc} of the C6PcH₂:[60]PCBM BHJ OSCs utilizing Ca/Al counter electrodes, as described above.

LiF, reported widely to be an ideal electron injection layer with many advantages, such as ohmic-like behavior at the cathode interface and protection of the organic layer from hot Al atoms, was introduced to improve the device performance [96, 101]. The EQE spectra and J-V characteristics of the C6PcH₂:[60]PCBM BHJ OSCs with the LiF and/or C₆₀ buffer layers at the top under AM 1.5G illumination at an intensity of 100 mW/cm² are shown in Fig. 5.11. The cell characteristics for all devices are summarized in Table 5.6.

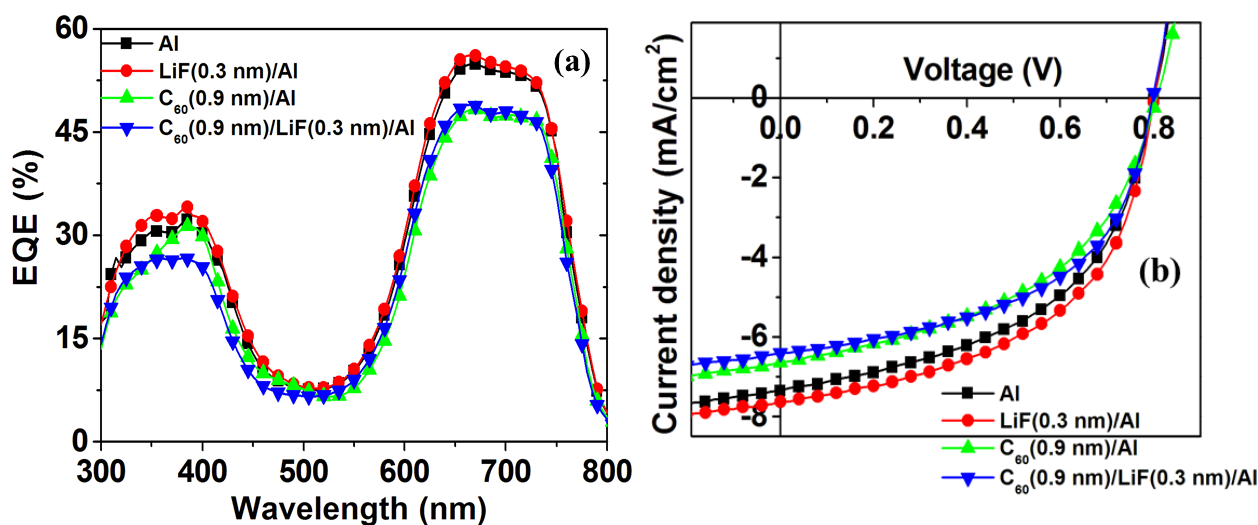


Fig. 5.11. (a) EQE spectra and (b) J - V characteristics of the C6PcH₂:[60]PCBM BHJ OSCs with various buffer layers at the top of cells.

Table 5.6. Cell characteristics of C6PcH₂:[60]PCBM BHJ OSCs with various buffer layers at the top of cells, measured under 100 mW/cm² light illumination.

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	Efficiency (%)
Al	0.80	7.4	0.51	3.0
LiF(0.3 nm)/Al	0.80	7.6	0.52	3.2
LiF(0.5 nm)/Al	0.79	7.4	0.53	3.1
LiF(0.7 nm)/Al	0.81	7.4	0.51	3.1
LiF(0.9 nm)/Al	0.80	7.4	0.48	2.8
C ₆₀ (0.9 nm)/Al	0.81	6.6	0.48	2.6
C ₆₀ (0.3 nm)/ LiF(0.3 nm)/Al	0.79	7.7	0.50	3.1
C ₆₀ (0.9 nm)/ LiF(0.3 nm)/Al	0.79	6.4	0.53	2.7

One found that increases in J_{sc} and FF were observed for the C6PcH₂-based devices upon the insertion of a thin layer of LiF between the organic layer and the Al electrode. In particular, by introducing a 0.3-nm-thick LiF layer, the FF increased from 0.51 to 0.53. Together with J_{sc} of 7.63 mA/cm², the PCE was calculated to be 3.2%. Even though the variations of the FF and PCE of devices with LiF were slight, this finding indicated that LiF lowered the effective work function of Al as well as provides ohmic-like behavior at the cathode interface.

However, after 12 h of illumination in air, the decrease of approximately 34% in the PCE of the devices with a pristine Al electrode was reduced to a 43% loss in the PCE upon the insertion of the LiF layer, as shown in Fig. 5.12. The degradation of the devices utilizing the LiF buffer layers at the top was totally opposite to the stability improvement of the P3HT-based device with inserted LiF [96]. For the clear understanding of the interaction between LiF and active layers, 0.9-nm-thick C₆₀ films have been introduced between LiF and the C6PcH₂:[60]PCBM active layers. It exhibited that the decrease of approximately 43% in the PCE was improved to a 20% loss in the PCE upon the insertion of the C₆₀ layer. On the other hand, the C6PcH₂:[60]PCBM BHJ OSCs with the 0.3-nm-thick C₆₀ layer showed the relatively low J_{sc} and the PCE of 7.71 mA/cm² and 3.09%, respectively, as summarized in Table 5.6. It was suggested that the diffusion of LiF inside the active layer, which causes the degradation of the OSC lifetime, exists; however, the C₆₀ layer plays the important role of a blocking layer that prevents the diffusion of metal atoms into the active layer, and therefore, reinforces stability.

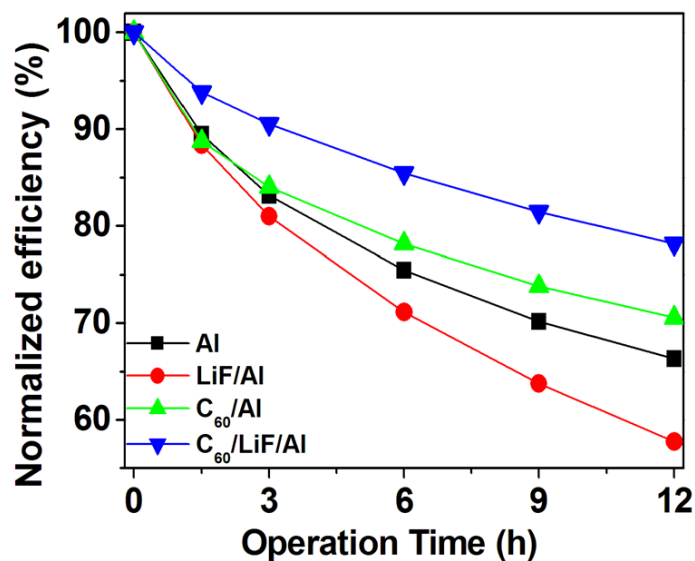


Fig. 5.12. Normalized efficiency as a function of illumination time under 100 mW/cm^2 light illumination in air, of the C6PcH_2 : $[60]\text{PCBM}$ BHJ OSCs with the various buffer layers at the top of cells.

5.6 Conclusions

The high stability as well as the mechanism of degradation of C6PcH_2 : $[60]\text{PCBM}$ BHJ OSCs was reported. The mesogenic phthalocyanine derivative C6PcH_2 -based BHJ-OSCs showed a higher stability than the cells with the conventional donor material P3HT. By studying the C6PcH_2 : $[60]\text{PCBM}$ composite thin films with and without illumination in various environments, it was clarified that the chemical bonds of two pyrrole aza nitrogens as well as the four mesobridging aza nitrogens with neighboring carbons in the C6PcH_2 molecules were broken after illumination by the solar simulator. Photooxidation of active layers could be detected from the increase in oxygen concentration in C6PcH_2 and $[60]\text{PCBM}$ composite thin films as well as from the disappearance of absorbance at the Q band of C6PcH_2 . To improve the stability, various buffer layers were introduced between the counter electrode and the active layer. Obviously, the C_{60} thin film and oxidized layer of the counter electrode increased the device lifetime.

Chapter 6

Conclusions

In this dissertation, a series of experiments were conducted in an aim to investigate and improve the photovoltaic performance of the BHJ OSCs utilizing the octaalkylphthalocyanine derivatives with the donor and acceptor phase separation. The PCEs of the BHJ OSCs utilizing C6PcH₂ were improved to 4.2% with the optimum separation of donor and acceptor phases, and the optical and electronic properties, structures, and stability of the BHJ materials were also characterized. We summarized the important achievements from each chapter as follows.

In chapter 2, the effects of processing additives on the nanoscale phase separation, crystallization, and photovoltaic performance of the BHJ OSCs utilized discotic C6PcH₂ mixed with [60]PCBM were studied. By incorporating processing additives to a volume of a few percent, the separation of donor and acceptor phases in C6PcH₂:PCBM thin films, which was discussed by taking the Davydov splitting at the Q-band of the absorbance spectra and the surface nanomorphology into consideration, was improved. It was proposed that the separation of donor and acceptor phases was promoted due to the higher boiling point of the processing additives, compared with that of the primary solvents and the different solubility of [60]PCBM and C6PcH₂ in processing additives. Furthermore, the crystallization of discotic C6PcH₂ in hexagonal structures has been improved by using processing additives. It was suggested that the improved crystallization was probably due to increases in the solubility of C6PcH₂ in processing additives.

Although more efforts should be made to understand the roles of primary solvents as well processing additives on the improvement of the photovoltaic properties of the BHJ OSCs utilized discotic C6PcH₂ mixed with [60]PCBM, the nanoscale phase separation and the crystallization of the BHJ materials were clearly optimized and the performance of the BHJ OSCs was markedly improved by utilizing various processing additives mixed with the different primary solvents. In particular, by adding 0.2% v/v of Brom to the solution containing BHJ blends in trichloroethylene, the EQE at the Q-band was improved to 57%, and the PCE increased to 4.2%, with a J_{sc} of 9.7 mA/cm², a V_{oc} of 0.76 V, and an FF of 0.56.

In chapter 3, the roles of fullerene derivatives in the photovoltaic properties of the BHJ OSCs utilizing C6PcH₂ were studied. By replacing the C₆₀ moiety of [60]PCBM with the asymmetric C₇₀, the absorption of composite thin films at around 500 nm increased, the EQE of the solar cells at

around 500 nm was improved from 8% to 24%, and J_{sc} increased to 10.2 mA/cm². On the other hand, a high V_{oc} of 0.96 V was attained using Bis[60]PCBM with a higher LUMO level. Moreover, the blend ratio dependence of the photovoltaic properties in BHJ OSCs utilizing C6PcH₂ mixed with [70]PCBM was reported. With increasing the volume fraction of [70]PCBM, the J_{sc} was improved to 10.6 mA/cm² due to enlarging the donor and acceptor interfacial areas. On the other hand, when the [70]PCBM volume fraction was higher than 33%, the FF was reduced owing to deteriorating crystallization of discotic C6PcH₂ molecules with hexagonal structures.

In chapter 4, the strong dependences of optical and electronic properties, structures, and photovoltaic performance of BHJ OSCs utilizing C_nPcH₂ mixed [70]PCBM on the length of alkyl substituents were studied. By decreasing the length of alkyl substituents, stacking of the discotic C_nPcH₂ columns was probably changed from 2-D rectangular lattices to pseudohexagonal structures, and Davydov splitting at the Q-band of C_nPcH₂ absorbance spectra decreased. As a result, the short-alkyl-substituent C_nPcH₂ (C5PcH₂ and C6PcH₂) exhibited the deeper HOMO energy levels and the balance of hole and electron mobility.

In chapter 5, the high stability as well as the mechanism of degradation of C6PcH₂: [60]PCBM BHJ OSCs was reported. The mesogenic phthalocyanine derivative C6PcH₂-based BHJ-OSCs showed a higher stability than the cells with the conventional donor material P3HT. By studying the C6PcH₂: [60]PCBM composite thin films with and without illumination in various environments, it was clarified that the chemical bonds of two pyrrole aza nitrogens as well as the four mesobridging aza nitrogens with neighboring carbons in the C6PcH₂ molecules were broken after illumination by the solar simulator. Photooxidation of active layers could be detected from the increase in oxygen concentration in C6PcH₂ and [60]PCBM composite thin films as well as from the disappearance of absorbance at the Q band of C6PcH₂. To improve the stability, various buffer layers were introduced between the counter electrode and the active layer. Obviously, the C₆₀ thin film and oxidized layer of the counter electrode increased the device lifetime.

All the described results suggested that the C_nPcH₂ is one potential donor for BHJ OSCs and the high photovoltaic performances of BHJ OSCs utilizing C_nPcH₂ are expected. To improve the PCEs of the C_nPcH₂-based BHJ OSCs, the FFs, which exhibited the low values of 0.58, must be investigated and promoted by adding the various buffer layers at the top of cells. Furthermore, the thermal annealing must be concerned when the alignment of discotic C_nPcH₂ molecules in the hexagonal structures were strongly dependent on the temperatures.

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Achievement

I. Publications

1. T. Masuda, T. Hori, K. Fukumura, T. Hayashi, **Q.-D. Dao**, H. Yoshida, A. Fujii, Y. Shimizu, and M. Ozaki, “Acceptor material dependence of photovoltaic properties in bulk heterojunction organic thin film solar cell utilizing soluble octahexylphthalocyanine”, IEEJ Trans. EIS, **132**, 1727-1732 (2012).
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8. **Q.-D. Dao**, Takashi Saito, Shohei Nakano, Hitoshi Fukui, Toshiya Kamikado, Akihiko Fujii,

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 10. M. Ohmori, H. Fukui, **Q.-D. Dao**, T. Kumada, A. Fujii, Y. Shimizu, and M. Ozaki, “Annealing Effect in Bulk Heterojunction Organic Solar Cells Utilizing Liquid Crystalline Phthalocyanine”, **To be published in *Jpn. J. Appl. Phys.***
 11. H. Fukui, S. Nakano, T. Uno, **Q.-D. Dao**, T. Saito, A. Fujii, Y. Shimizu, and M. Ozaki, “Miscibility in Binary Blends of Non-Peripheral Alkylphthalocyanines and Their Application for Bulk-Heterojunction Solar Cells”, **To be published in *Org. Electron.***

II. International Conferences

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8. K. Fukumura, T. Hori, T. Masuda, **Q.-D. Dao**, T. Hayashi, T. Kamikado, F. Nekelson, H. Yoshida, A. Fujii, Y. Shimizu, and M. Ozaki, “Photovoltaic Properties of Organic Solar Cells Utilizing Liquid Crystalline Phthalocyanine Derivative and Its Application for Tandem Solar Cell”, 2012 Taiwan-Japan Nanophotonics and Plasmonic Metamaterials Workshop, National Taiwan University, Taipei, Taiwan, January 11-12, 2012.
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 17. **Q.-D. Dao**, T. Hori, T. Masuda, K. Fukumura, T. Hayashi, T. Kamikado, H. Yoshida, A. Fujii, Y. Shimizu, and M. Ozaki, "High efficient solution processable bulk heterojunction solar cells based on mesogenic phthalocyanine", The 6th international workshop on Advanced materials science and nanotechnology (IWAMSN 2012) Halong, Vietnam 30, Oct. - 02, Nov. 2012 (Oral).
 18. **Q.-D. Dao**, T. Hori, T. Masuda, K. Fukumura, T. Hayashi, T. Kamikado, A. Fujii, Y. Shimizu, and M. Ozaki, "Effects of Processing-additive Solvents on Photovoltaic Efficiency of Mesogenic-phthalocyanine Solar Cells", 7th international conference on molecular electronics and bioelectronics (M&BE7) Fukuoka, Japan 17-19. Mar., 2013. (**Outstanding Student Poster Award**)
 19. **Q.-D. Dao**, H. Fukui, S. H. Lee, M. Ohmori, T. Kumada, A. Fujii, Y. Shimizu, and M. Ozaki, "Improvement of Photovoltaic Performance of Octahexylphthalocyanine Based Bulk

Heterojunction Solar Cells Using Processing Additives”, JSAP-MRS Joint Symposia, Doshisha University, Japan, 16-20. Sep., 2013.

III. Domestic Conferences

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2. **Q.-D. Dao**, T. Hori, T. Masuda, K. Fukumura, T. Kamikado, A. Fujii, Y. Shimuzu, and M. Ozaki, “Effects of Solvent Mixtures on Nanoscale Phase Separation and Photovoltaic Efficiency of Mesogenic - Phthalocyanine - Based Bulk Heterojunction Solar Cell”, 応用物理学会春季学術講演会, Kanagawa institute of technology, 27-30. Mar., 2013.
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