Identifying Molecular Orientation in a Bulk Heterojunction Film by Infrared Reflection Absorption Spectroscopy

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ABSTRACT: The molecular orientation of organic molecules of zinc phthalocyanine (ZnPc) in single-component films on copper iodide (CuI) substrates can be controlled to achieve a molecular orientation lying flat on the substrate (flat-on) owing to π–d orbital interactions between the ZnPc molecules and the CuI. A 3-fold enhancement in the performance of organic photovoltaic cells has been reported by introducing a CuI interlayer between a ZnPc:fullerene (C60) bulk heterojunction (BHJ) film and the substrate. However, the mechanism underpinning the resultant solar cell performance enhancement was unclear. Herein, we report on the results of using in situ reflection absorption spectroscopy measurements during the vacuum deposition of coevaporated ZnPc:C60 BHJ films on various substrates to investigate the ZnPc molecular orientation. Our results revealed that the flat-on molecular orientation of ZnPc molecules in ZnPc:C60 BHJ films on CuI interlayers and flat-on ZnPc substrates can be successfully identified via the strong π–π interactions between the BHJ film and the substrate. The π–π interactions between individual ZnPc molecules are stronger than the π–d interactions between ZnPc molecules and CuI in coevaporated ZnPc:C60 films, as is evident from the molecular orientation of ZnPc, as determined by in situ reflection absorption spectroscopy. Our findings demonstrate that precisely controlling the molecular orientations of the films could enhance organic photovoltaic (OPV) performance. The present work provides important insights that will enable the design of higher performance OPV cells.

INTRODUCTION

In recent years, research in the field of thin-film organic photovoltaics (OPVs) toward commercialization has progressed significantly since the introduction of donor–acceptor interfaces.7–9 The bulk heterojunction (BHJ) structure that is widely used as an active layer in OPVs provides not only a large interfacial area for exciton dissociation but also an interpenetrated nanoscale network for charge carrier transport.10 A power conversion efficiency (PCE) of over 10% has been reported in solution-processed BHJ OPV cells, which use a blend of a polymer and an acceptor.4,9,10 In contrast, coevaporation methods are able to precisely control layer thicknesses in BHJ structures on the order of nanometers by controlling the evaporation rates and times.11 However, it is very difficult to control the molecular orientation, morphology, and crystallinity in coevaporated BHJ films by changing the evaporation parameters. A BHJ structure is created owing to several molecular characteristics such as the interaction forces between molecules and between molecules and substrates, molecular aggregation ability, and molecular adsorption and desorption abilities on the substrate.12–14 To further enhance OPV performance, understanding the precise control of the interactions between the molecules and between the molecules and the substrate is key as it will allow the production of the ideal BHJ structure without carrier traps, which are created by molecular aggregations, grain boundaries, and areas that deviate from the ideal donor–acceptor molecular ratio.15

By controlling the interactions between molecules and between molecules and substrates, it is already possible to control the molecular orientation in films evaporated onto a substrate.16 Small-molecular organic semiconductors, such as zinc phthalocyanine (ZnPc), adapt a standing-up (edge-on) molecular orientation on conventional substrates, that is, glass, indium-tin-oxide (ITO), and poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) substrates. On copper iodide (CuI) substrates, ZnPc molecules take on a molecular orientation lying flat on the substrate (flat-on) owing to the π–d interactions between the ZnPc molecules and CuI.17,18 Not only does the flat-on molecular orientation of the ZnPc molecules improve the light absorption coefficient, it also allows for efficient charge transfer in the BHJ film. As a result, we were previously able to obtain...
an OPV cell with the 3-fold higher PCE of 4.56% by introducing a CuI film between the coevaporated ZnPc:C60 BHJ film and the substrate.19 We assumed that the higher light absorption coefficient was obtained by controlling the molecular orientation of the ZnPc molecules to be flat-on in the coevaporated ZnPc:C60 BHJ film owing to π–d interactions. However, the study of the molecular orientation of ZnPc in coevaporated ZnPc:C60 BHJ films has not yet been demonstrated with common techniques such as X-ray diffraction (XRD) and transmission electron microscopy (TEM), owing to the low crystallinity and amorphous state of ZnPc in coevaporated ZnPc:C60 BHJ films. Yokoyama et al.20–23 measured the molecular orientation in organic amorphous films via variable angle spectroscopic ellipsometry measurements. The molecular orientations of various small-molecule organic semiconductors for organic light-emitting diodes have been successfully measured both for amorphous single-component films and in doped films. Those results highlight that it might be possible to find an efficient optical measurement method to identify molecular orientation in coevaporated BHJ films.

In this study, we used a facile, in situ infrared reflection absorption spectroscopy (IR-RAS) measurement method to identify the molecular orientation of ZnPc in coevaporated ZnPc:C60 BHJ films. We also used this technique to study the difference between the strength of the π–π interactions between ZnPc molecules and the strength of π–d interactions between ZnPc molecules and CuI in coevaporated ZnPc:C60 BHJ films.

## RESULTS AND DISCUSSION

Figure 1 shows a schematic illustration of the IR-RAS measurement setup to identify the molecular orientation angle of ZnPc in ZnPc:C60 BHJ films in situ during evaporation. The chemical structures of ZnPc and C60 are shown in Figure 2a,b, respectively. ZnPc is a planar molecule with a high crystallinity, and C60 is a spherical molecule that is a good electron acceptor.

IR-RAS measurements were performed by reflecting infrared light off the substrate, exciting the aromatic C–H out-of-plane bending vibration and in-plane bending vibration of the ZnPc molecules on the substrate (as shown in Figure 3) owing to the absorption of light at a specific wavelength. Only the moment perpendicular to the substrate of those vibrations was detected by applying p-polarized light to the incident infrared light. When most ZnPc molecules are parallel to the surface, we see out-of-plane bending vibration, whereas when most ZnPc molecules are perpendicular to the surface, we see the in-plane bending vibration. From the results of the IR-RAS measurements, we can quantify the molecular orientation of the ZnPc molecules using the orientation parameter, S

$$S = \frac{1}{2} (3 \cos^2 \theta - 1) = \frac{3}{2} + \frac{R}{R_t} - \frac{1}{2}$$

where $\theta$ is the angle between the long molecular axis and the direction perpendicular to the substrate surface, $R$ is the peak intensity ratio of the aromatic C–H out-of-plane bending vibration {A(o-o-p)} and the in-plane bending vibration {A(i-p)} in the film, and $R_t$ is the value of $R$ in a KBr pellet.24,25 Yokoyama et al.26 revealed that when $S = -0.5$, the resultant molecules are completely parallel to the surface. In contrast, when $S = 1$, the molecules are completely perpendicular to the surface. They investigated the molecular orientation in organic amorphous films using the optical anisotropy of the films using variable angle spectroscopic ellipsometry.21–23 ZnPc takes on an amorphous state in coevaporated ZnPc:C60 BHJ films. Conversely, ZnPc adopts a crystal state in a single-component ZnPc film. However, its crystallinity is low because the evaporations were performed at room temperature in this work. No peak shift of the aromatic C–H bending vibration was seen in the IR-RAS spectra of the coevaporated ZnPc:C60 films compared to that for single-component ZnPc films owing to the low crystallinity of ZnPc. Thus, we analyzed the observed IR-RAS spectra assuming that the aromatic C–H out-of-plane bending vibration is perpendicular to the molecular plane. With regard to spectra fitting, the peak position and intensity were calculated on the basis of observed raw spectral data using a graphing and data analysis software package (Origin).

The IR-RAS spectra of single-component ZnPc films formed on PEDOT:PSS or CuI substrates are shown in Figure 4a,b. Seoudi et al.26 revealed that the bands centered at 730 and 1120 cm$^{-1}$ are assigned to the out-of-plane and in-plane bending vibrations of the aromatic C–H bond, respectively. The values of $S$ determined from the IR-RAS measurements were 0.73 on the PEDOT:PSS substrate and 0.13 on the CuI substrate (Figure 4c). In the single-component ZnPc film on the PEDOT:PSS substrate, the ZnPc film displays a high crystallinity with molecules stacked in the edge-on orientation because of the weak interactions between the ZnPc molecules.
and the substrate. Conversely, the single-component ZnPc film on the CuI substrate shows a large out-of-plane bending vibration peak (730 cm$^{-1}$) for the aromatic C–H unit, which suggests that the number of flat-on ZnPc molecules was larger owing to π–d interactions. The XRD spectra of single-component ZnPc films show that the diffraction peaks correspond to the edge-on ZnPc crystalline order ($2\theta = 6.9$, $d = 12.8$ Å) and the flat-on ZnPc crystalline order ($2\theta = 27.9$, $d = 3.2$ Å) (Figure S1).27 The ZnPc grown on the PEDOT:PSS substrate exhibits edge-on ZnPc peaks, whereas the ZnPc grown on the CuI substrate shows face-on ZnPc peaks. Thus, detecting molecular orientation with IR-RAS measurements is viable as the XRD results agree with the orientation states determined via IR-RAS.

Our results demonstrate that IR-RAS can be used to investigate the molecular orientation in coevaporated...
ZnPc:C60 BHJ films on PEDOT:PSS and CuI substrates. However, no useful signal could be detected using XRD for the coevaporated ZnPc:C60 BHJ film as the crystallinity of ZnPc was lowered by blending it with C60, and the resultant BHJ film possesses an amorphous structure. According to the IR-RAS spectra shown in Figure 5a, the changes in the peak intensities of the out-of-plane and in-plane vibrations by inserting CuI into a coevaporated ZnPc:C60 BHJ stack are smaller than those for single-component ZnPc films. The S values for four different film thicknesses (Figure 5c) indicate that the ZnPc molecular orientation differs slightly from that of a coevaporated ZnPc:C60 BHJ film. However, on the surface of the substrate, the value of S decreased from 0.57 to 0.25 by inserting the CuI film (thickness of 5 nm) into the layer stack. This clearly shows that orientation control via π–π interactions was successful and that the number of face-on ZnPc molecules could be increased, particularly at the surface of the substrate, even in coevaporated ZnPc:C60 BHJ films.

To further investigate the precise control of the molecular orientation via π–π interactions between ZnPc molecules at the interface, coevaporation was performed on a ZnPc/PEDOT:PSS/ITO layer stack (edge-on ZnPc substrate) and a ZnPc/CuI/PEDOT:PSS/ITO layer stack (face-on ZnPc substrate). Figure 6a,b shows that the IR-RAS spectral peak of the out-of-plane bending vibration (730 cm⁻¹) is larger when inserting a CuI layer, which increases the amount of face-on ZnPc. The value of S on the surface of the substrate (CuI thickness of 5 nm) decreased from 0.60 on the edge-on ZnPc substrate to 0.07 on the face-on ZnPc substrate, as shown in Figure 6c. The single-component ZnPc film on CuI was highly oriented (S = −0.13) owing to π–d interactions. The ZnPc molecules in the coevaporated ZnPc:C60 BHJ film, meanwhile, interacted via π–π bonds with the face-on ZnPc molecules on the surface of the face-on ZnPc substrate, resulting in a face-on molecular orientation of ZnPc. Consequently, we compared the strength of the molecular orientation control via the orientation parameter, S, as shown in Figure 7. The values of S in the single-component ZnPc films on the PEDOT:PSS and CuI substrates were 0.73 and −0.13, respectively. Conversely, the values of S in 5 nm-thick films of coevaporated ZnPc:C60 on PEDOT:PSS, CuI, and the face-on ZnPc substrates were 0.57, 0.25, and 0.07, respectively. The coevaporated ZnPc:C60 BHJ film is less influenced by molecular orientation control than the single-component ZnPc film. However, the ZnPc molecules in the coevaporated ZnPc:C60 BHJ films are influenced by the molecular orientation control and are more strongly controlled to the face-on molecular orientation on the face-on ZnPc substrate than on the CuI substrate. These results indicate that the π–π interactions between the ZnPc molecules are stronger than the π–d interactions between the ZnPc molecules and CuI in the coevaporated ZnPc:C60 BHJ film. The results also suggest that the thicker the coevaporated ZnPc:C60 BHJ film is, the weaker the molecular orientation control is, as demonstrated by comparing the orientation parameter S for each film thickness. The value of S in the single-component ZnPc films is almost constant regardless of the film thickness. In contrast, the value of S in the coevaporated ZnPc:C60 BHJ film on all substrates increases as the film thickness increases. The values of S in 5–40 nm-thick BHJ films on the PEDOT:PSS, CuI, and face-on ZnPc substrates were increased from 0.57 to 0.77, 0.25 to 0.73, and 0.07 to 0.67, respectively. The increase of S mainly continues until the coevaporated ZnPc:C60 BHJ film thickness is increased to 20 nm or more, and thereafter the value of S approaches a constant value as the thickness is increased up to 40 nm. These results reveal that the ZnPc molecules in coevaporated ZnPc:C60 BHJ films are randomly oriented or mainly adopt the face-on orientation in films with thicknesses of 10 nm or lower because of π–d or π–π interactions; the number of edge-on ZnPc molecules increases along with film thickness as those interactions weaken, the thicker the film is (Table 1).

![Figure 7. Orientation parameter S for four different film thicknesses, where noninteractions are black, π–d interactions are blue, and π–π interactions are red.](image)

To investigate the correlation between the ZnPc molecular orientations and the surface morphologies in coevaporated ZnPc:C60 BHJ films, we observed the surface morphologies by atomic force microscopy (AFM), as shown in Figure 8. The AFM image of the surface of the ZnPc:C60 BHJ film on the PEDOT:PSS substrate shows a smooth surface (Figure 8a), which indicates that no phase separation occurred during the coevaporation step. The AFM image of the surface of the ZnPc:C60 BHJ film on the CuI substrate in Figure 8b shows the growth of large domains on the surface and the increase in the root-mean-square (RMS) roughness values from 1.39 to 1.69, which indicates that phase separation of the ZnPc and C60 molecules occurred during the coevaporation step owing to the π–d interactions at the interfaces between the CuI substrate and the ZnPc molecules. The strong π–π interactions between the face-on ZnPc substrate and the ZnPc molecules and the strong aggregation and phase separation in the ZnPc:C60 BHJ film on the face-on ZnPc substrate are shown in Figure 8c; the RMS roughness values increased to 3.69, double those for the PEDOT:PSS substrate. Three-dimensional AFM images of ZnPc films on (a) PEDOT:PSS/ITO and (b) CuI/PEDOT:PSS/ITO substrates are shown in the Supporting Information in Figure S2. We have already reported the investigation of the phase separation in ZnPc:C60 BHJ films on CuI and PEDOT:PSS substrates conducted using cross-sectional energy filtered TEM and cross-sectional bright field TEM. The most ideal interpenetrating network in a ZnPc:C60 BHJ layer was observed when using the CuI substrate owing to the strong π–π interactions between the

| Films          | Interaction | θ     | Orientation parameter: S |
|---------------|-------------|-------|--------------------------|
| ZnPc/PEDOT:PSS | π–d         | 25    | 0.73                     |
| ZnPc:C60/PEDOT:PSS | π–d     | 33    | 0.57                     |
| ZnPc:C60/CuI   | π–d         | 45    | 0.25                     |
| ZnPc:C60/ZnPc/CuI | π–π     | 52    | 0.07                     |
| ZnPc/CuI       | π–d         | 60    | −0.13                    |

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face-on ZnPc substrate and the ZnPc molecules in the ZnPc:C60 BHJ layer. The results of previous TEM observations and our AFM investigation here strongly support our IR-RAS measurement results that demonstrate that the high S value in the coevaporated ZnPc:C60 BHJ film on the face-on ZnPc substrate origins from the signals of face-on ZnPc molecules inside of the aggregated ZnPc domains in the ideal interpenetrating network.

Herein, we have discussed the mechanism underpinning the growth of an ideal interpenetrating donor–acceptor network on a face-on ZnPc substrate. The initially evaporated ZnPc molecules land on the face-on ZnPc substrate. The ZnPc molecules are stacked in the face-on orientation via strong π–π interactions between the face-on ZnPc substrate and the ZnPc molecules. The stacked ZnPc molecules easily interact with the second layer of evaporated ZnPc molecules via strong π–π interactions, which initiates the creation of the ZnPc aggregated domains. We assumed that the face-on ZnPc molecules selectively interact with other ZnPc molecules, not the C60 molecules, owing to strong π–π interactions, as shown in Figure 9a. The initially evaporated ZnPc layer is also stacked in on the PEDOT:PSS substrate does not interact with the second layer of evaporated ZnPc molecules. Therefore, ZnPc does not aggregate or phase separate during coevaporation, as shown in Figure 9c. We also observed a decrease of S in the coevaporated ZnPc:C60 BHJ film during evaporation via IR-RAS measurements. Initially, the ZnPc aggregate domains on the surface of the face-on ZnPc substrate display face-on ZnPc molecular orientation owing to strong π–π interactions. The deposition of subsequent ZnPc aggregate domains on top of these shows a reduced degree of face-on molecular orientation owing to weak π–π interactions because of the increased distance from the substrate and because of the breakup of the aggregate domain network, which inhibits the molecular orientation control of the ZnPc molecules. Finally, we conclude that to create the perfect interpenetrating network with a face-on molecular orientation, the ZnPc aggregated domains must be grown as large as possible by controlling the substrate temperature and evaporation speed.

By performing a versatile technique, namely, IR-RAS measurements, in situ we were able to precisely investigate the ZnPc molecular orientation in coevaporated ZnPc:C60 BHJ films. Our results reveal that the ZnPc molecules in coevaporated ZnPc:C60 BHJ films could be precisely controlled to adopt the face-on orientation on CuI and ZnPc substrates, whereas they adopted an edge-on orientation on PEDOT:PSS substrates. In addition, ZnPc molecules in the ZnPc:C60 films on face-on ZnPc substrates could be controlled to adopt a more face-on orientation compared to that on a CuI substrate. These results demonstrate that the π–π interactions between the ZnPc molecules are stronger than the π–d interactions between ZnPc molecules and CuI. Our results also suggested that those interactions could be used to control the molecular orientation of ZnPc molecules in the first few deposited nanometers in coevaporated ZnPc:C60 BHJ films. Thicker coevaporated ZnPc:C60 BHJ films showed weaker molecular orientation control, however.

#### EXPERIMENTAL SECTION

ZnPc and C60 were purchased from Sigma-Aldrich (Tokyo, Japan) and Frontier Carbon Corporation (Tokyo, Japan), respectively, and ZnPc was further purified three times prior to use. The samples were fabricated on ITO-patterned glass substrates, which were pretreated by oxygen plasma for 20 min prior to use. PEDOT:PSS films were spin-coated onto ITO and annealed at 135 °C for 10 min on a hot plate. Then, CuI (5 nm) and ZnPc (20 nm) films were evaporated onto the samples. Finally, a ZnPc:C60 coevaporated film (40 nm) was deposited via vacuum evaporation. Coevaporation was conducted on a PEDOT:PSS/ITO (PEDOT:PSS substrate), CuI/PEDOT:PSS/ITO (CuI substrate), and ZnPc/CuI/
PEDOT:PSS/ITO (ZnPc substrate) layer stack to precisely investigate the control of the molecular orientation by π–d interactions and π–π interactions. As reference, single-component ZnPc films on PEDOT:PSS and CuI substrates were also measured. XRD (Rigaku Co.) and atomic force microscopy (AFM; SPM-9600 apparatus, Shimadzu) were used to investigate the molecular orientation and morphology, respectively.

The ZnPc molecular orientation was measured in situ via IR-RAS measurements using an Fourier transform infrared (FT-IR) device (FT/IR 6300, JASCO). The FT-IR device was p-polarized and re-direction perpendicular to the substrate surface. All spectra were also measured. XRD (Rigaku Co.) and atomic force microscopy (AFM; SPM-9600 apparatus, Shimadzu) were used to investigate the control of the molecular orientation by π–d interactions and π–π interactions. As reference, single-component ZnPc films on PEDOT:PSS and CuI substrates were also measured.

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