Research Center for Photovoltaics

赤外反射吸収分光法によるバルクヘテロ膜中での分子配向の同定

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Introduction

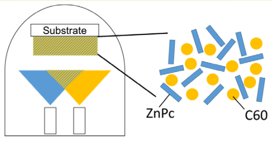


Fig. The image of co-evaporation film

Co-evaporated BHJ film

Merit: High charge separation efficiency
Demerit: Low charge transport efficiency

It is important to control the morphology and crystalline order of co-evaporated BHJ film

CuI molecular orientation control layer

It is well-known that molecular orientation of ZnPc molecules in single film on CuI substrate are controlled to lying-down orientation due to π-d interaction between ZnPc molecules and CuI.[1]

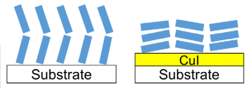


Fig. (L) standing-up orientation ZnPc (R) lying-down orientation ZnPc

We have already reported the three-fold improvement of OPVs performance by introducing the CuI interlayer between co-evaporated ZnPc:C60 BHJ film and substrate.[2]

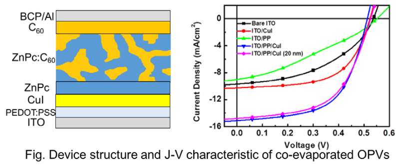


Fig. Device structure and J-V characteristic of co-evaporated OPVs

Table Summary of solar cells performances.

	PCE (%)	V_{OC} (V)	J_{SC} (mA/cm^2)	FF
Bare ITO	2.38	0.54	9.68	0.46
ITO/CuI	3.19	0.52	10.3	0.59
ITO/PEDOT:PSS	1.55	0.55	9.01	0.32
ITO/PEDOT:PSS/CuI	4.56	0.51	15.1	0.59
ITO/PEDOT:PSS/CuI[a]	4.37	0.53	14.8	0.56

We estimated that the higher light absorption coefficient was obtained by lying-down molecular orientation control of ZnPc molecules in ZnPc:C60 film.

However, information of the ZnPc molecular orientation in ZnPc:C60 films has not been obtained by XRD and TEM measurements owing to its low crystallinity.

This work

Infrared reflection absorption spectroscopy (IR-RAS) is enabled to measure the molecular orientation (parameter:S[3]) in amorphous ZnPc:C60 film.

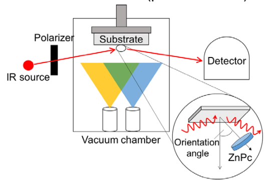
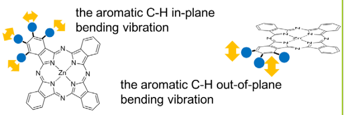


Fig. The image of IR-RAS measurement



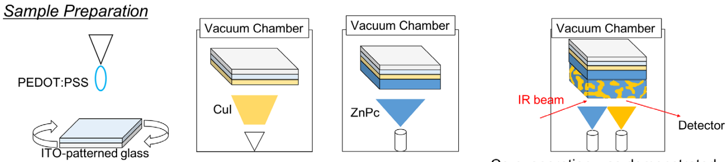
$$S = \frac{1}{2}\langle 3cos^2\theta - 1\rangle = \frac{3}{2 + \frac{R}{R_r}} - \frac{1}{2}$$

R: out-of-plane/in-plane intensity ratio

Rr: out-of-plane/in-plane ratio in KBr pellet [4]

Experiment

Sample Preparation



Prepared substrates

- PEDOT:PSS/ITO (PEDOT:PSS substrate)
- CuI (5 nm)/PEDOT:PSS/ITO (CuI substrate)
- ZnPc (20 nm)/CuI/PEDOT:PSS/ITO (ZnPc substrate)

Co-evaporation was demonstrated on various substrate and IR-RAS was performed under in-situ conditions during evaporation.

Molecular orientation in single ZnPc film

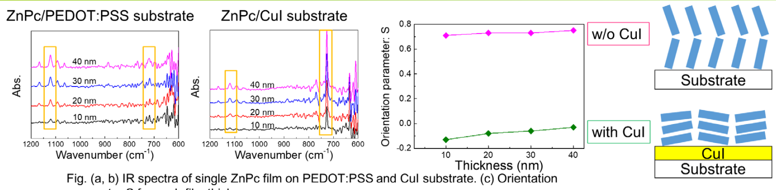


Fig. (a, b) IR spectra of single ZnPc film on PEDOT:PSS and CuI substrate. (c) Orientation parameter S for each film thickness

The value of S

- 0.73 on PEDOT:PSS substrate
- -0.13 on CuI substrate

S = -0.5 if the molecules are completely parallel
S = 1 if they are completely perpendicular

On PEDOT:PSS substrate, ZnPc molecules with high crystallinity stacks molecules each other and formed standing-up orientation because of weak interaction between ZnPc molecules and substrate.
On CuI substrate, ZnPc molecules are formed lying-down orientation due to π-d interaction between ZnPc molecules and CuI.

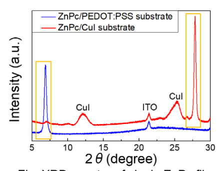


Fig. XRD spectra of single ZnPc films

with CuI: lying-down ZnPc diffraction peak (2θ = 27.8)

w/o CuI: standing-up ZnPc diffraction peak (2θ = 6.9)

Orientation identification by IR-RAS measurements is considered to be useful since XRD results agree with the orientation state evaluated by IR-RAS.

Molecular orientation in co-evaporated ZnPc:C60 BHJ film

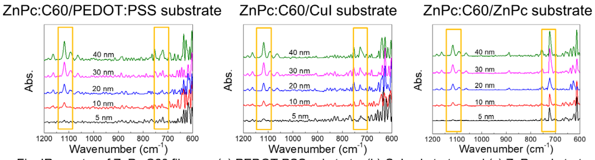


Fig. IR spectra of ZnPc:C60 films on (a) PEDOT:PSS substrate, (b) CuI substrate, and (c) ZnPc substrate

The IR-RAS spectra peak of out-of-plane bending vibration (730 cm⁻¹) turns out to be larger.

Lying-down ZnPc molecules increase.

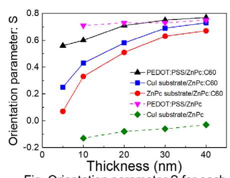


Fig. Orientation parameter S for each film thickness

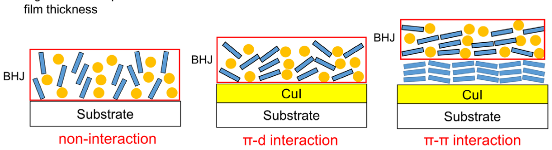
Table Orientation parameter S of films on various substrates

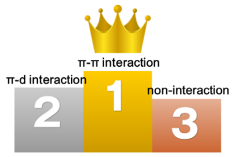
Film	interaction	S
ZnPc/PEDOT:PSS	-	0.73
ZnPc:C60/PEDOT:PSS	-	0.57
ZnPc:C60/CuI sub	π-d	0.25
ZnPc:C60/ZnPc sub	π-π	0.07
ZnPc/CuI sub	π-d	-0.13

The thicker ZnPc:C60 film is, the more relaxation of molecular orientation control occurs.

~10 nm: mainly controlled to lying-down orientation

20 nm~: standing-up orientation increase





The co-evaporated ZnPc:C60 film is influenced more weakly by molecular orientation control than single ZnPc film. However, ZnPc molecules in co-evaporated ZnPc:C60 BHJ films are also influenced by molecular orientation control, and more strongly controlled to lying-down molecular orientation on ZnPc substrate than on CuI substrate.
π-π interaction between ZnPc-ZnPc molecules is stronger than π-d interaction between ZnPc molecules and CuI.

Solar cells performance

ITO/PEDOT:PSS/CuI/ZnPc/ZnPc:C60/BCP/Al

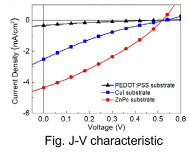


Fig. J-V characteristic

Table Summary of Solar cells performances

Substrate	Jsc (mAcm⁻²)	Voc (V)	FF	PCE (%)
PEDOT:PSS	0.33	0.49	0.18	0.03
CuI	2.51	0.53	0.19	0.25
ZnPc	4.34	0.52	0.31	0.70

The controlled lying-down orientation of ZnPc molecules in the co-evaporated ZnPc:C60 films leads to higher Jsc and PCE of solar cells.

Conclusions

- We precisely investigated the ZnPc molecular orientation in the co-evaporated ZnPc:C60 BHJ films by performing in-situ IR-RAS measurements.
- ZnPc molecules were precisely controlled to lying-down orientation onto CuI and ZnPc substrates.
- ZnPc molecules in the co-evaporated ZnPc:C60 BHJ film on lying-down ZnPc substrates were controlled to be more lying-down orientation than those on CuI substrate.
  ➡ π-π interaction between ZnPc-ZnPc molecules is stronger than π-d interaction between ZnPc molecules and CuI.
- π-π interaction and π-d interaction could be able to control the molecular orientation of ZnPc molecules at a few nanometer thickness in co-evaporated ZnPc:C60 BHJ films.
  ➡ The thicker co-evaporated ZnPc:C60 BHJ film is facilitated to weaker molecular orientation control.

Reference

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Acknowledgement

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