Supporting Information

# Improvement in Interlayer Structure of p–i–n-Type Organic Solar Cells with Use of Fullerene-Linked Tetrabenzoporphyrin as Additive

Yuto Tamura,[a] Mitsuharu Suzuki, [a] Takaki Nakagawa,[b] Tomoyuki Koganezawa,[c] Sadahiro Masuo,[b] Hironobu Hayashi,[a] Naoki Aratani,[a] Hiroko Yamada[a]

[a]Division of Materials Science, Graduate School of Science and Technology, Nara Institute of Science and Technology, 8916-5 Takayama-cho, Ikoma, Nara 630-0192, Japan

[b]Department of Applied Chemistry and Environment, Kwansei Gakuin University, 2-1 Gakuen, Sanda, Hyogo 669-1337, Japan

[c]Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

**S1. Crystallinity of BP–$C_{60}$ after thermal annealing**

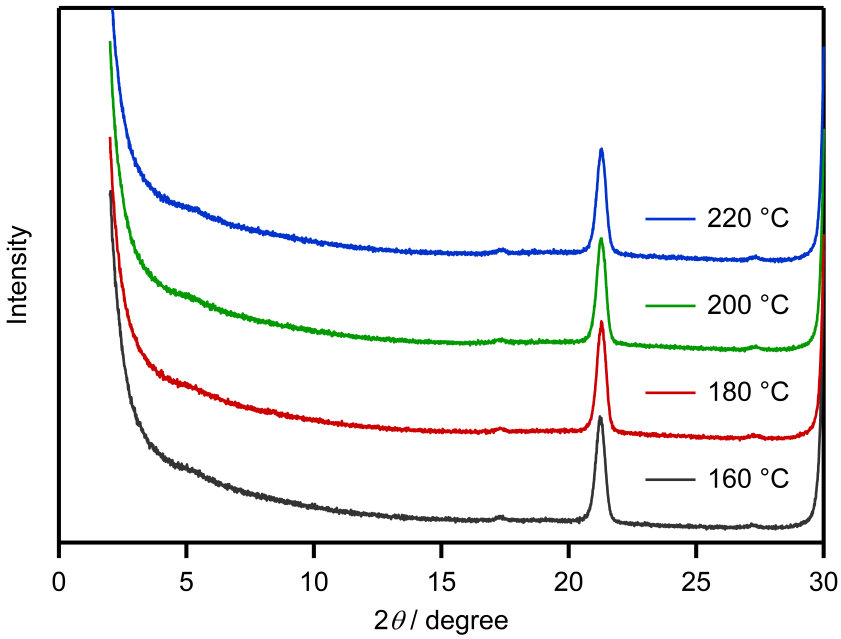



Figure S1. Out-of-plane X-ray diffraction patterns of **BP–$C_{60}$** prepared by heating of **CP–$C_{60}$** films for 20 min on the ITO/glass substrate in $N_2$-filled glove box. The characteristic peaks around 21 º and 30 º are identified as the ITO/glass substrate.

**S2. Photoabsorption capability of the fabricated p–i–n devices**

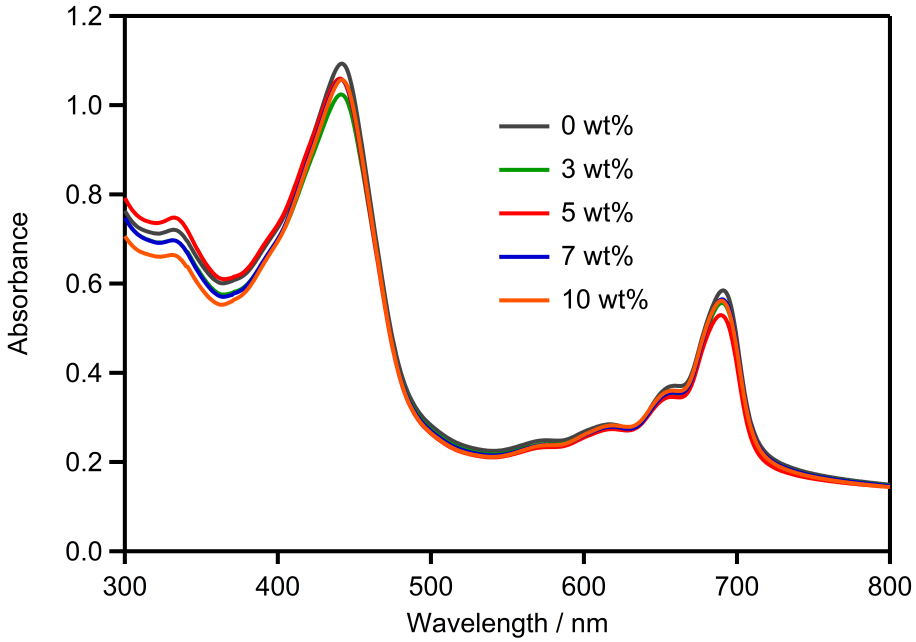



Figure S2. UV-vis absorption spectra of actual p–i–n devices in this study.

**S3. Additional AMF images**

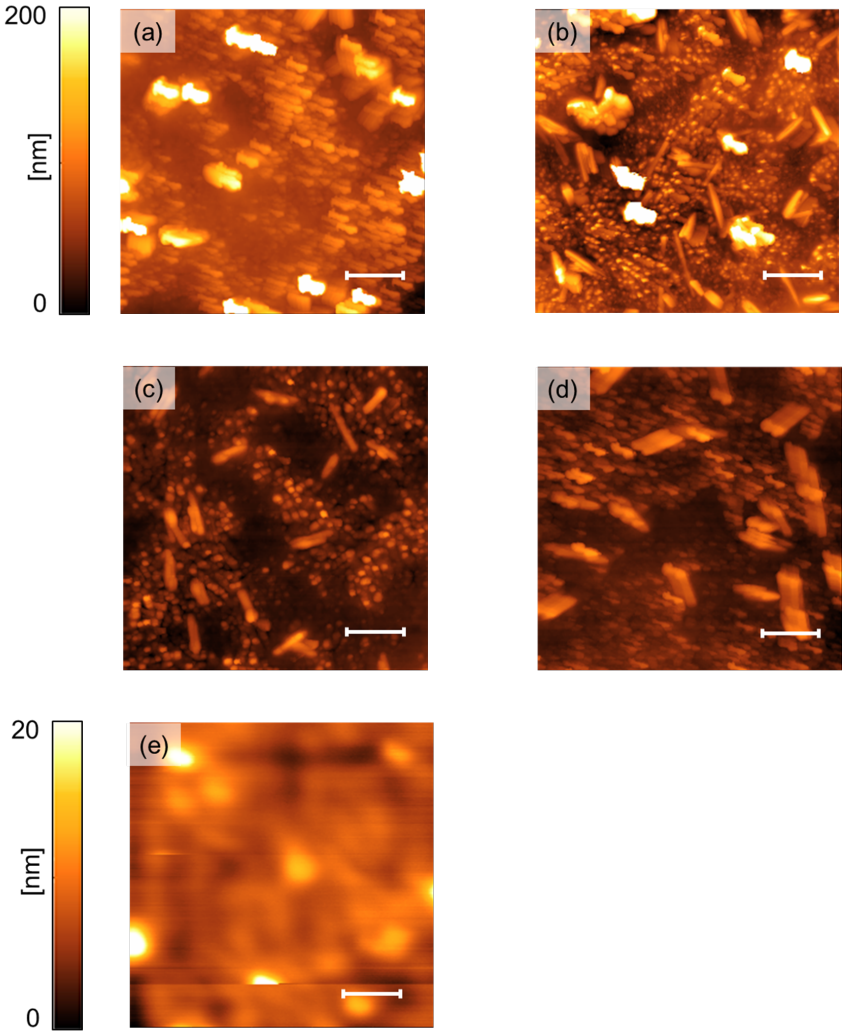
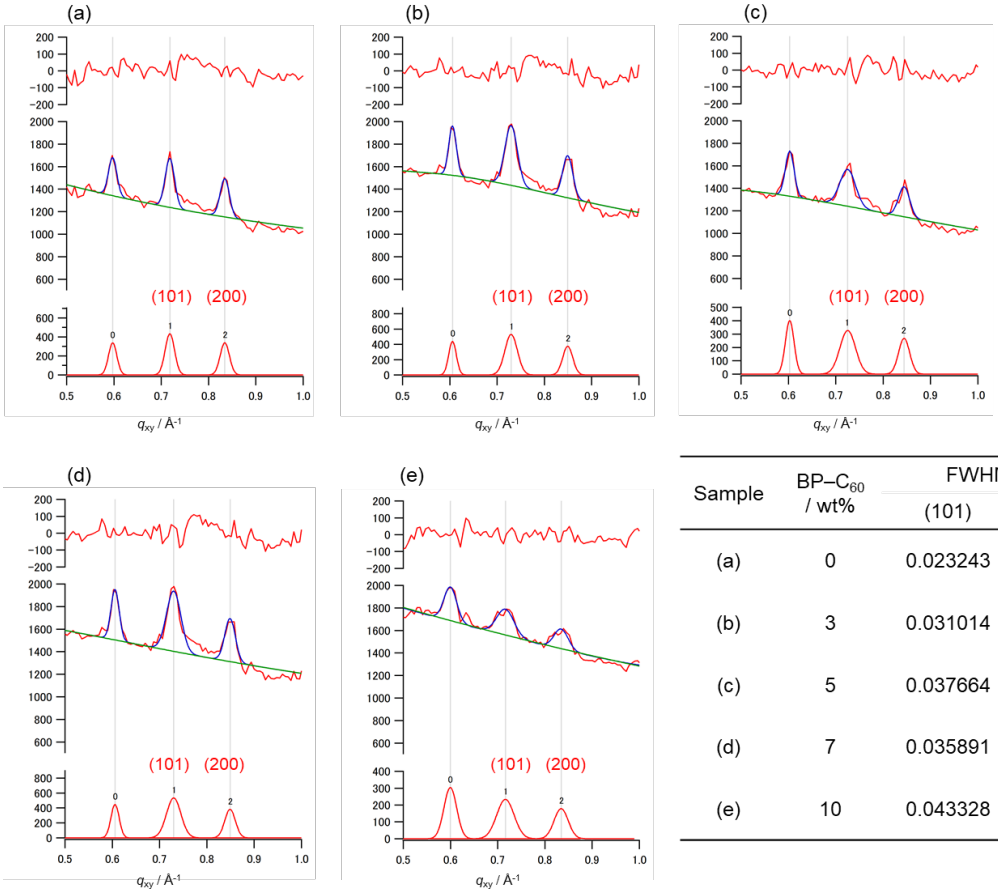



Figure S3. AFM height images of the surface of n-layer of p–i–n devices which composed different amounts of BP–$C_{60}$: (a) 0 wt%; (b) 3 wt%; (c) 5 wt%; (d) 7 wt%; (e) 10 wt%. RMS values of these films are (a) 44.7 nm, (b) 33.5 nm, (c) 19.0 nm, (d) 16.5 nm, and (e) 2.33 nm, respectively. The image (e) is attached different height scale bar because of the very smooth surface. The scale bars correspond to 2 μm.

## S4. 1D vertical line cuts from 2D-GIWAXD data in the in-plane direction and their line fittings




| Sample | BP–$C_{60}$ / wt% | FWHM value | |
|---|---|---|---|
| | | (101) | (200) |
| (a) | 0 | 0.023243 | 0.022902 |
| (b) | 3 | 0.031014 | 0.025147 |
| (c) | 5 | 0.037664 | 0.027209 |
| (d) | 7 | 0.035891 | 0.026315 |
| (e) | 10 | 0.043328 | 0.035057 |

Figure S4. The fitting patterns of 1D vertical line cuts from 2D GIWAXD data in the in-plane direction in the Structure I. Amounts of BP–$C_{60}$ in the Structure I are (a) 0 wt%, (b) 3 wt%, (c) 5 wt%, (d) 7 wt%, and (e) 10 wt%, respectively. (101) and (200) planes of crystalline BP are observed at $q_{xy}$ = 0.71 and 0.82 Å$^{-1}$ in all of films. The Gaussian function is used for these fitting to estimate full width at half maximum (FWHM) values of (101) and (200) planes. Estimated FWHM values were summarized in the table.

**S5. Molecular orientation of tetrabenzoporphyrin observed by 2D-GIWAXD.**

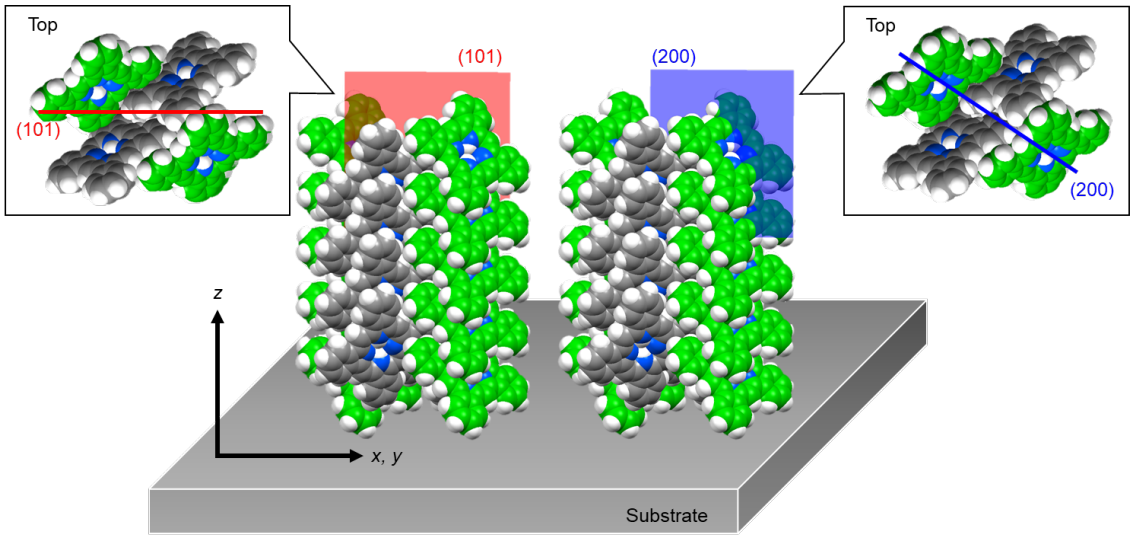



**Figure S5.** Crystal structure of BP with (101) and (200) plane observed on the substrate in this study. The single-crystal data was obtained from the literature.[1]

**S6. Additional SEM image**

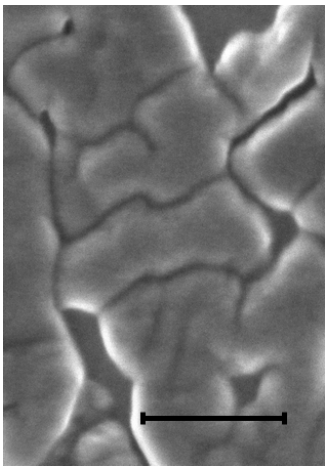


Figure S6. SEM images of BP film. The scale bars correspond to 200 nm.

## S7. Cross-sectional STEM images and elemental mapping.

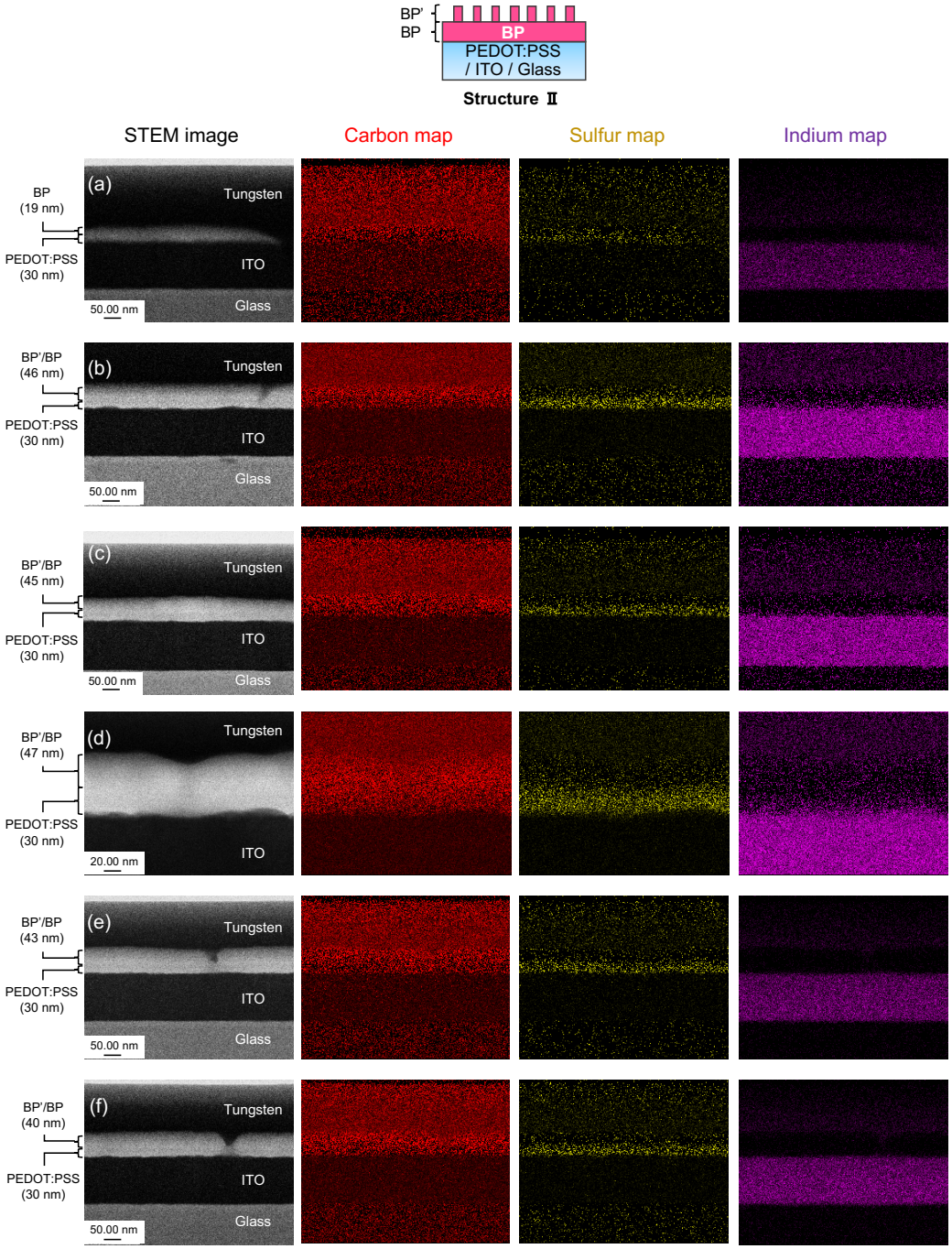



Figure S7. Cross-sectional STEM images of (a) BP film and (b–f) the Structure II with the elemental mapping. The Structure II was prepared from the Structure I which had been composed different amounts of BP–$C_{60}$: (b) 0 wt%; (c) 3 wt%; (d) 5 wt%; (e) 7 wt%; (f) 10 wt%. All of films were deposited tungsten layer on the top for preparations of the cross-sectional samples suitable for STEM analysis using the micro sampling technique.[2]

**References**

(1) Aramaki, S.; Mizuguchi, J. 29*H*,31*H*-Tetrabenzo[*b*,*g*,*l*,*q*]Porphin. *Acta Crystallographica Section E Structure Reports Online* **2003**, *59*, o1556–o1558.

(2) Young, R. J.; Moore, M. V. *Dual-Beam (FIB-SEM) Systems Techniques and Automated Applications*; 2005.