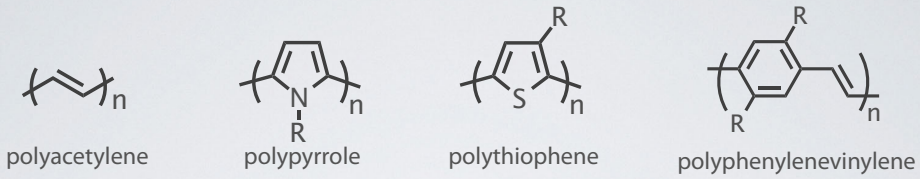
第7回SPring-8次世代先端デバイス研究会
2019年11月7日@ＡＰ品川　京急第2ビル

高分子半導体の結晶性と分子配向制御による有機太陽電池の高効率化

尾坂　格
広島大学大学院工学研究科

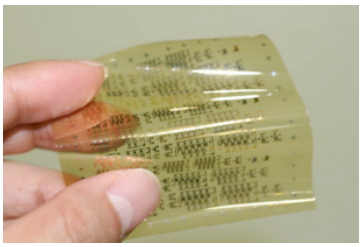
π-CONJUGATED POLYMERS



polyacetylene　polypyrrole　polythiophene　polyphenylenevinylene

- mid-1970's – mid-1990's: conducting polymers
- mid-1990's – : semiconducting polymers

OLEDs

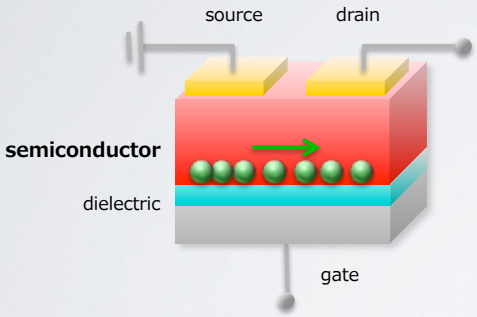


OFETs

OPVs

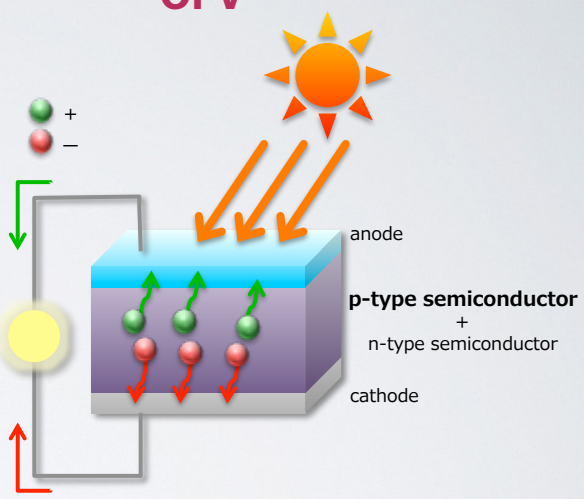
ARCHITECTURE OF OFET AND OPV

OFET



- polymer pristine film
- in-plane charge transport

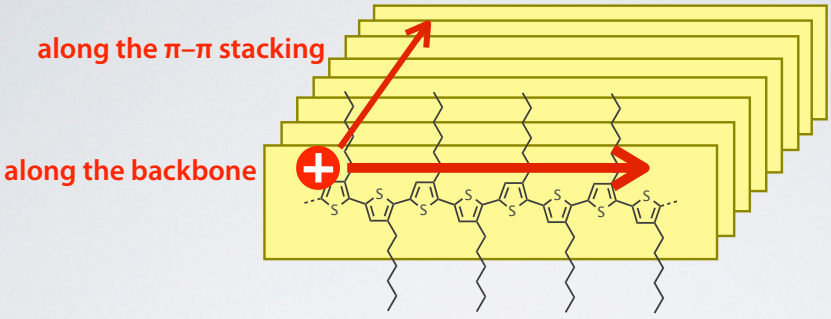
OPV



- polymer/fullerene blend film
- out-of-plane charge transport

CARRIER TRANSPORT AND POLYMER ORDER

Carrier transport in semiconducting polymers



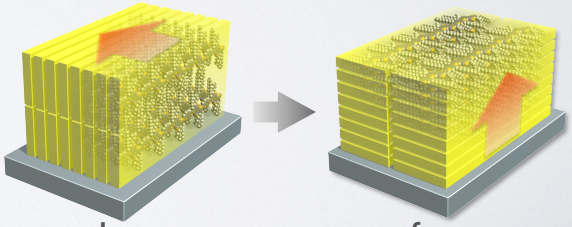
Ordering structure of semiconducting polymers

Crystallinity

amorphous → crystalline

carrier mobility

Orientation



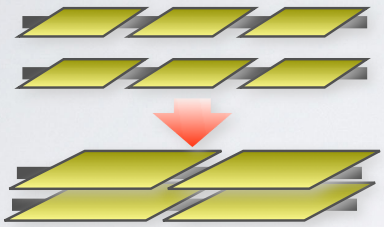
edge-on → face-on

transport direction

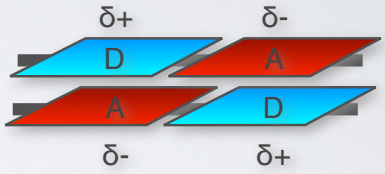
KEY TO DEVELOPING CRYSTALLINE POLYMERS

Backbones (Building units)

introduction of fused-rings

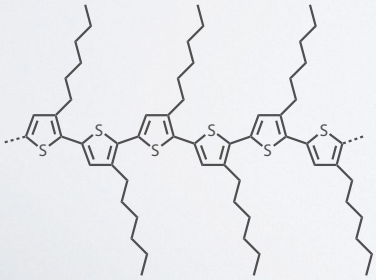


donor (D)–acceptor (A) system

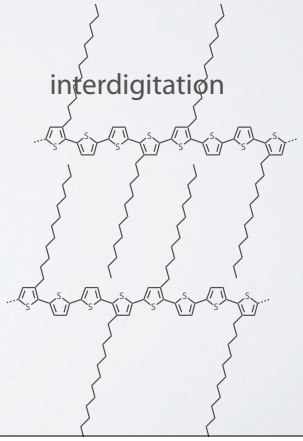


Side chains

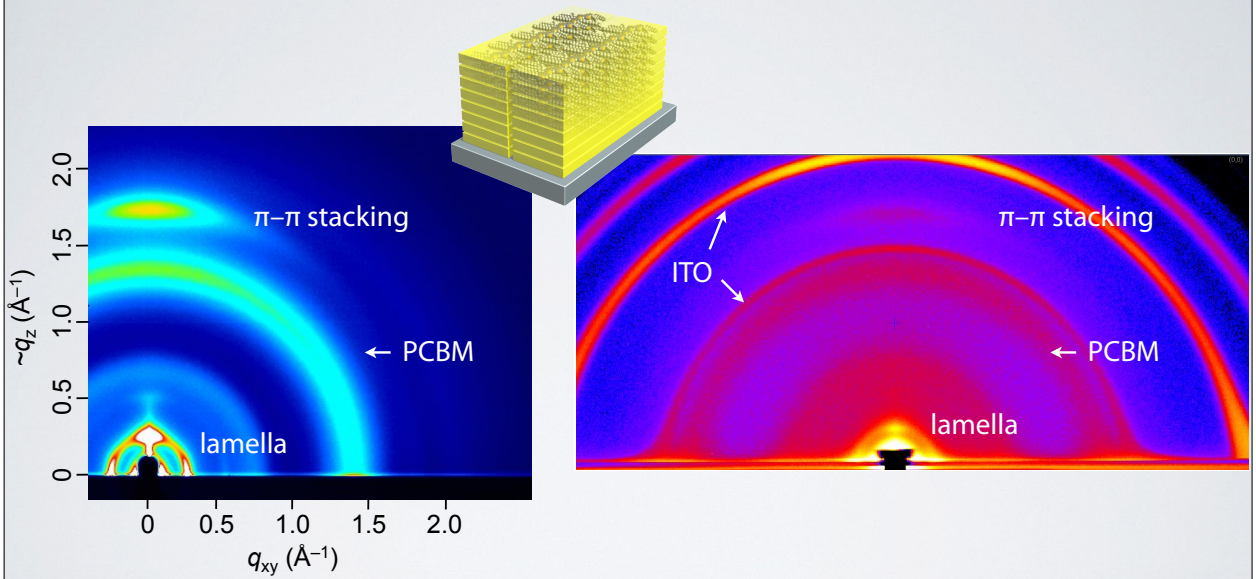
regioregularity



interdigitation



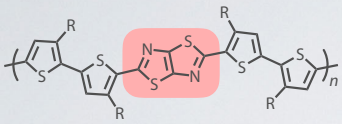
2D GIWAXS PATTERNS OF A POLYMER/FULLERENE FILM



SPring-8, BL46XU
thickness ~300 nm

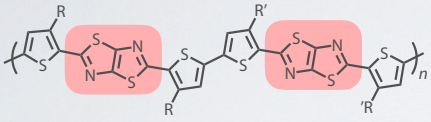
Commercial Instrument
thickness ~300 nm

THIOPHENE-THIAZOLOTHIAZOLE COPOLYMER



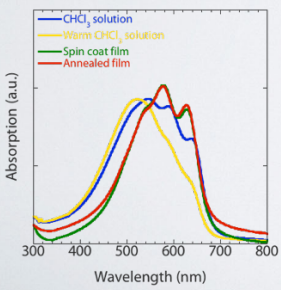
PTzQT-14 μ_h ~0.3 cm²/Vs

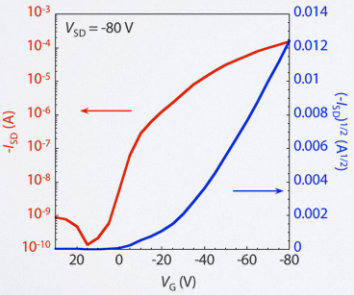
I.Osaka, R.D.McCullough, et al. *Adv.Mater.* **2007**, *19*, 4160.
I.Osaka, R.D.McCullough, et al. *JACS* **2009**, *131*, 2521.

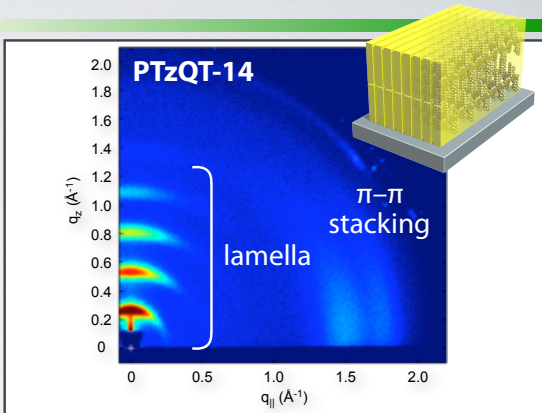


PTzBT-14HD μ_h ~0.4 cm²/Vs, PCE ~5.7%

I. Osaka, et al., *Chem. Mater.*, **2010**, *22*, 4191.
I. Osaka, et al. *Adv. Mater.* **2012**, *24*, 425.

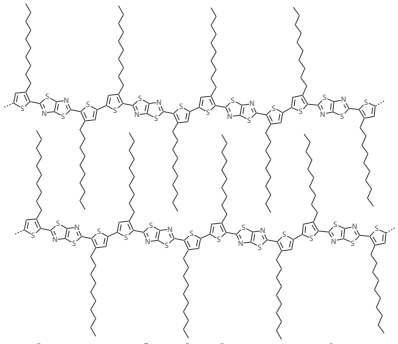






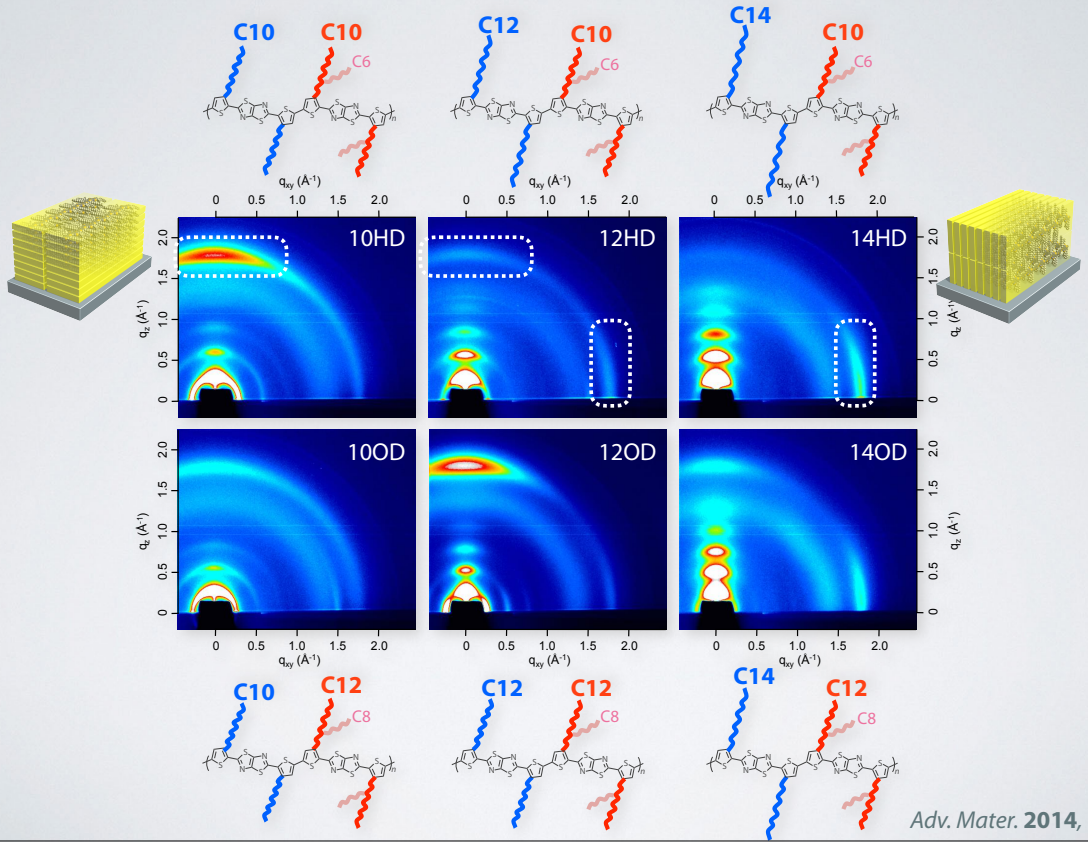
2D pattern of grazing incidence X-ray diffraction

@Cornell High Energy Synchrotron Source



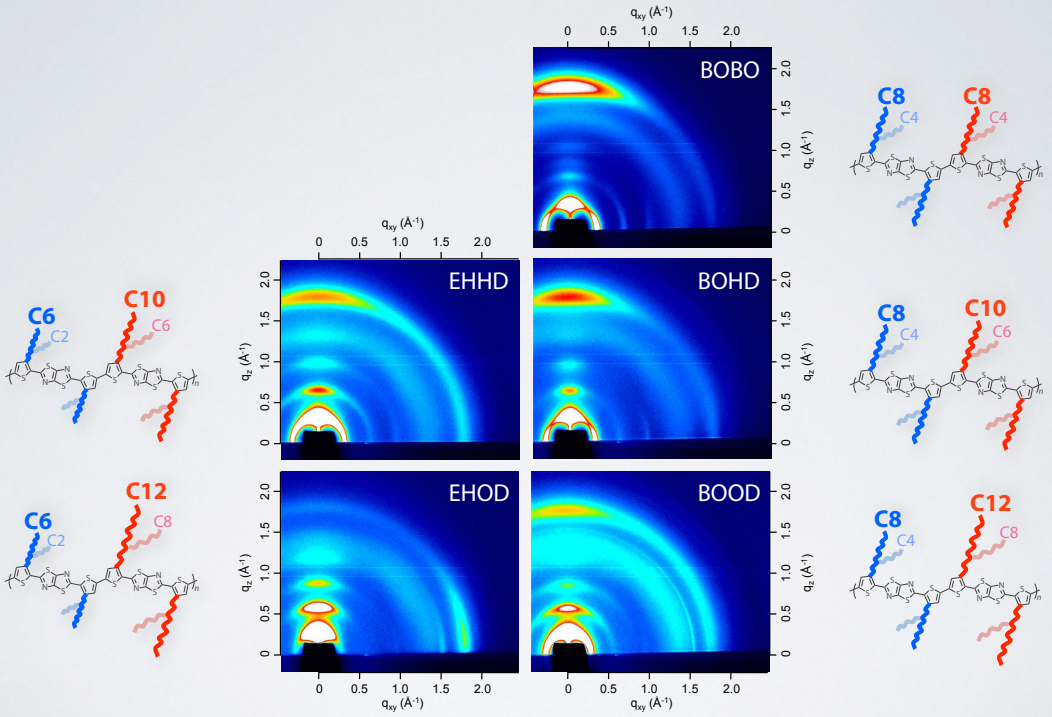
Schematic of "side chain interdigitation"

2D-GIXD OF PTzBT WITH LINEAR-BRANCHED SIDE CHAIN



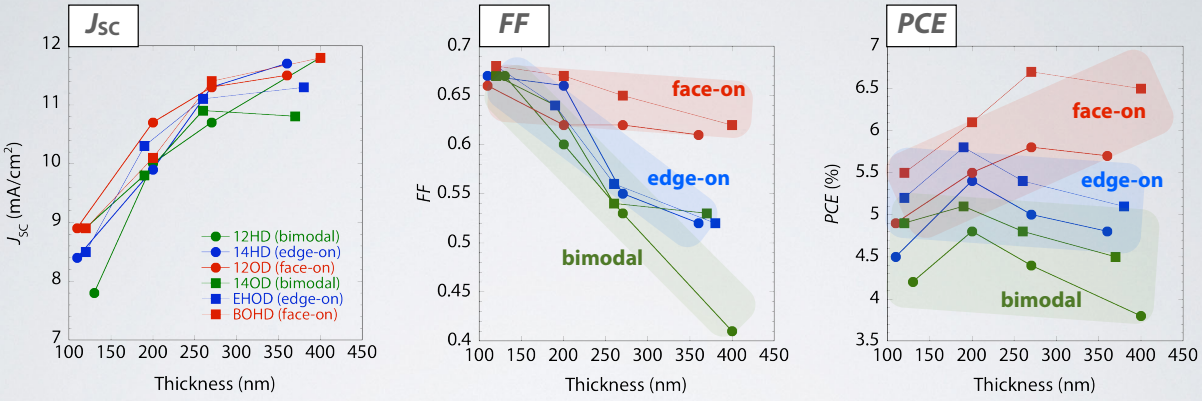
Adv. Mater. **2014**, *26*, 331.

2D-GIXD OF PTzBT WITH ALL-BRANCHED SIDE CHAIN



I. Osaka, M. Saito, T. Koganezawa, K. Takimiya, *Adv. Mater.* **2014**, *26*, 331–338.

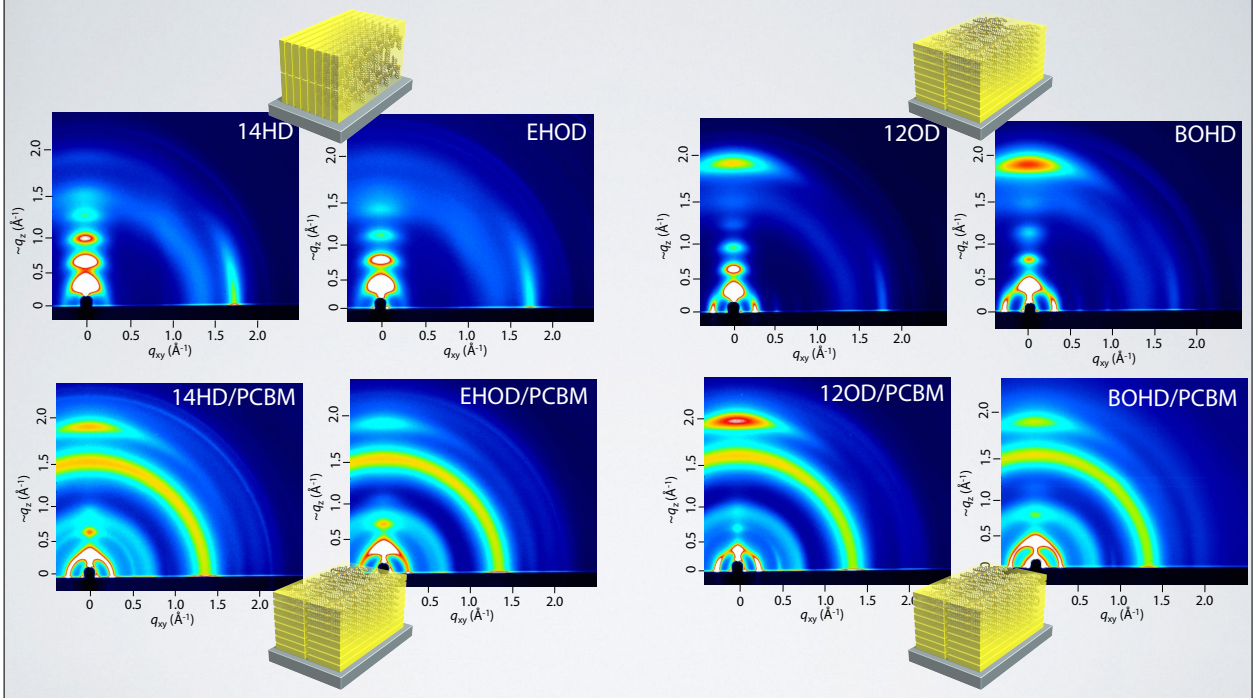
DIFFERENCE IN THICKNESS DEPENDENCE BY ORIENTATION



Control of crystallinity/orientation leads to an increase of J_{SC} without a loss of *FF* and V_{OC}, resulting in the improvement of efficiency.

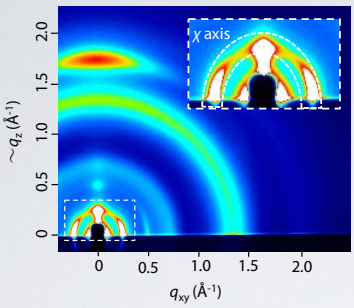
I. Osaka, M. Saito, T. Koganezawa, K. Takimiya, *Adv. Mater.* **2014**, *26*, 331–338.

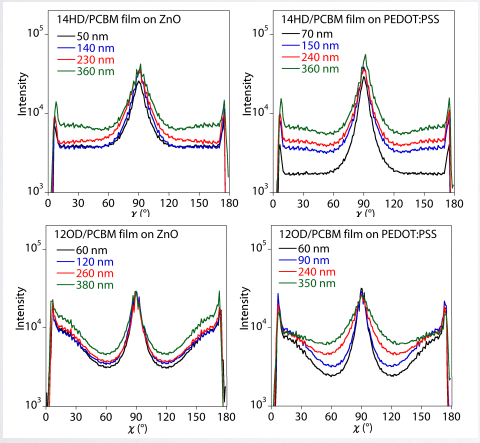
ORIENTATION IN NEAT VS BLEND FILMS

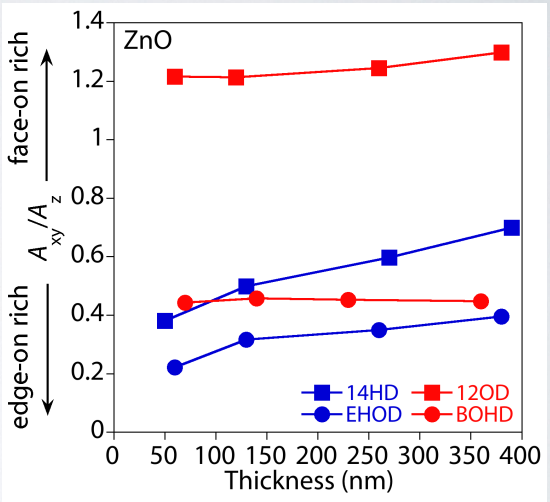


M. Saito, T. Koganezawa, I. Osaka, *ACS Appl. Mater. Interfaces*, **2018**, *10*, 32420–32425.

POLE FIGURE ANALYSIS

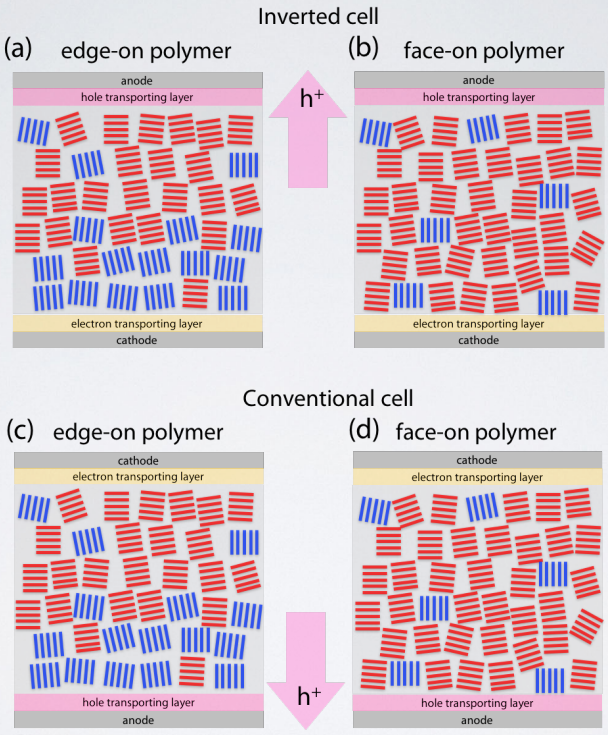






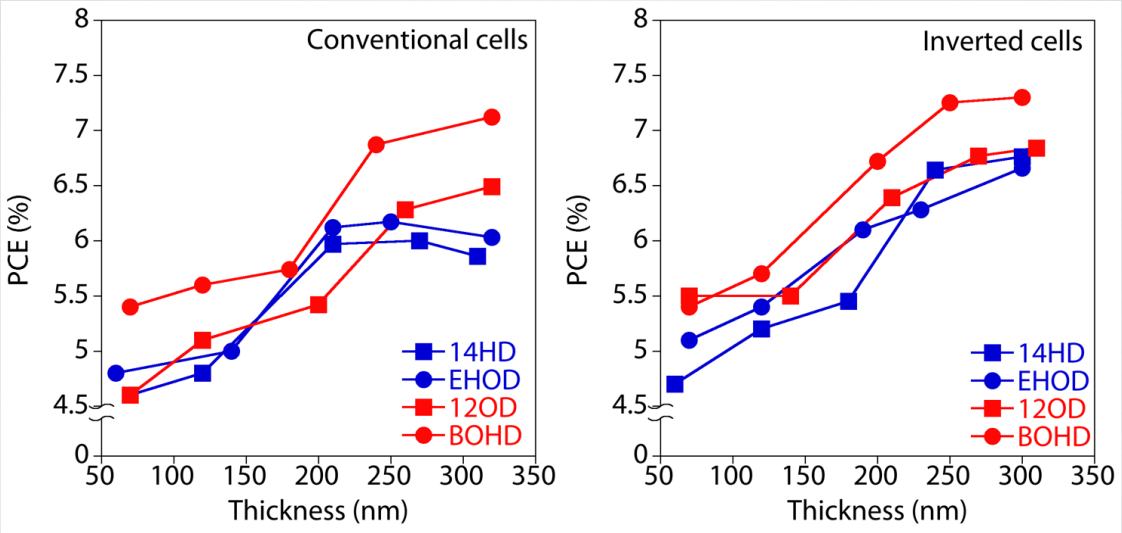
ACS Appl. Mater. Interfaces, **2018**, *10*, 32420.

"DISTRIBUTION" OF ORIENTATION THROUGH THICKNESS



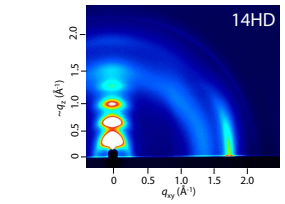
M. Saito, T. Koganezawa, I. Osaka, *ACS Appl. Mater. Interfaces,* **2018**, *10,* 32420.

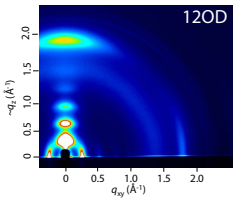
CORRELATION BETWEEN ORIENTATION AND CELL STACKS

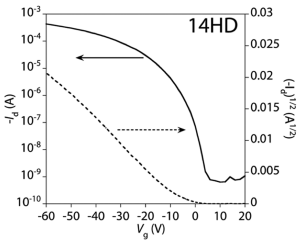


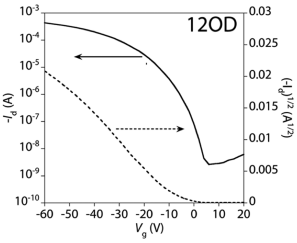
M. Saito, T. Koganezawa, I. Osaka, *ACS. Appl. Mater. Interfaces* **2018**, *10,* 32420–32425.

ORIENTATION AT THE SUBSTRATE INTERFACE



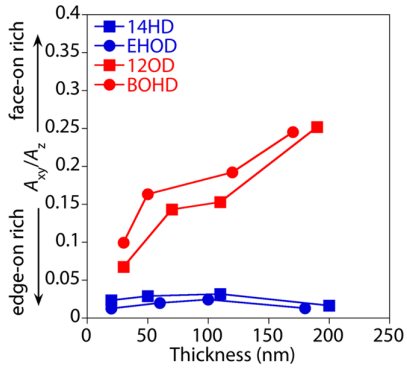




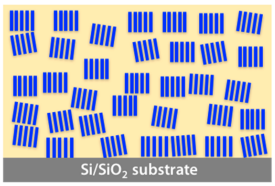


μ = ~0.2 cm² V⁻¹ s⁻¹

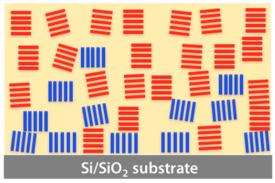
μ = ~0.2 cm² V⁻¹ s⁻¹



a edge-on polymers (14HD, EHOD)



b face-on polymers (12OD, BOHD)



M. Saito, T. Koganezawa, I. Osaka, *ACS Appl. Polym. Mater.* **2019**, *1*, 1257.

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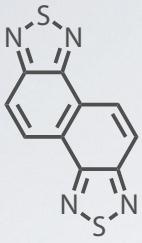
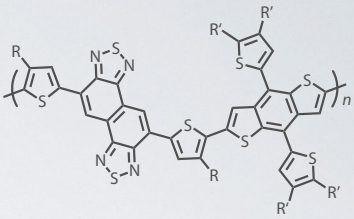
NAPHTHOBISTHIADIAZOLE



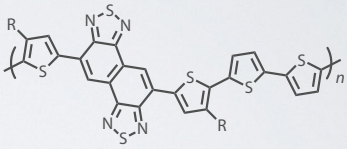
Naphthobisthiadiazole (NTz)

- rigid, π-extended system
- strong electron acceptor

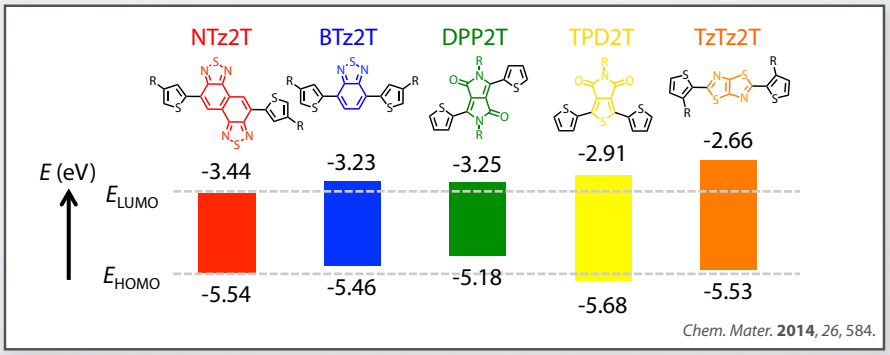
S. Mataka, et al. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 68.



F. Huang, Y. Cao, et al. *JACS* **2011**, *133*, 9638.



I. Osaka, K. Takimiya, et al. *JACS* **2012**, *134*, 3498.



Chem. Mater. **2014**, *26*, 584.

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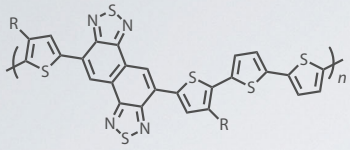
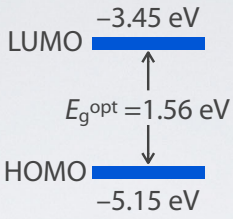
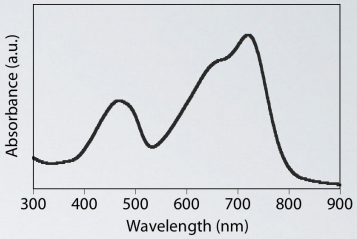
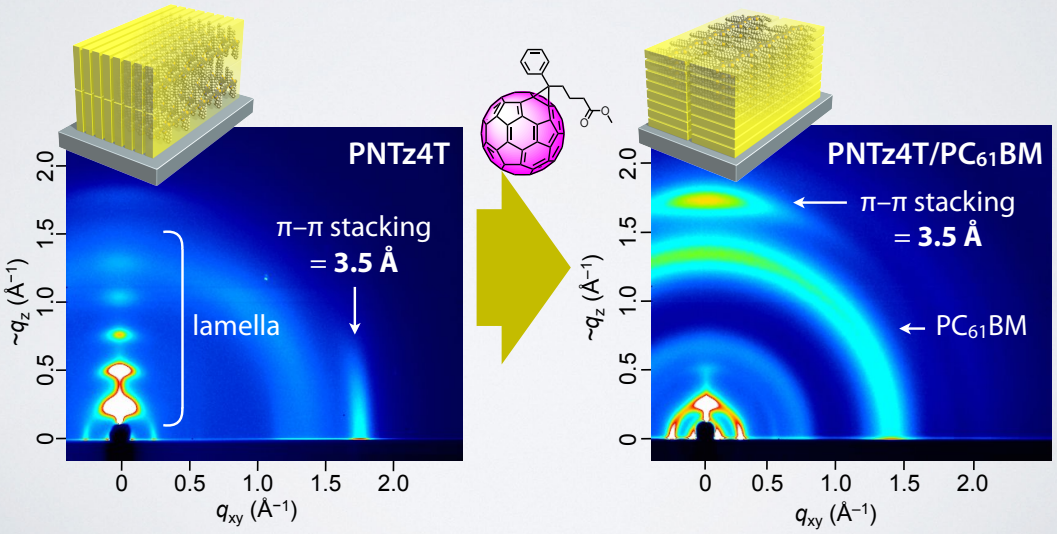
NTz-QUATERTHIOPHENE POLYMER (PNTz4T)



PNTz4T

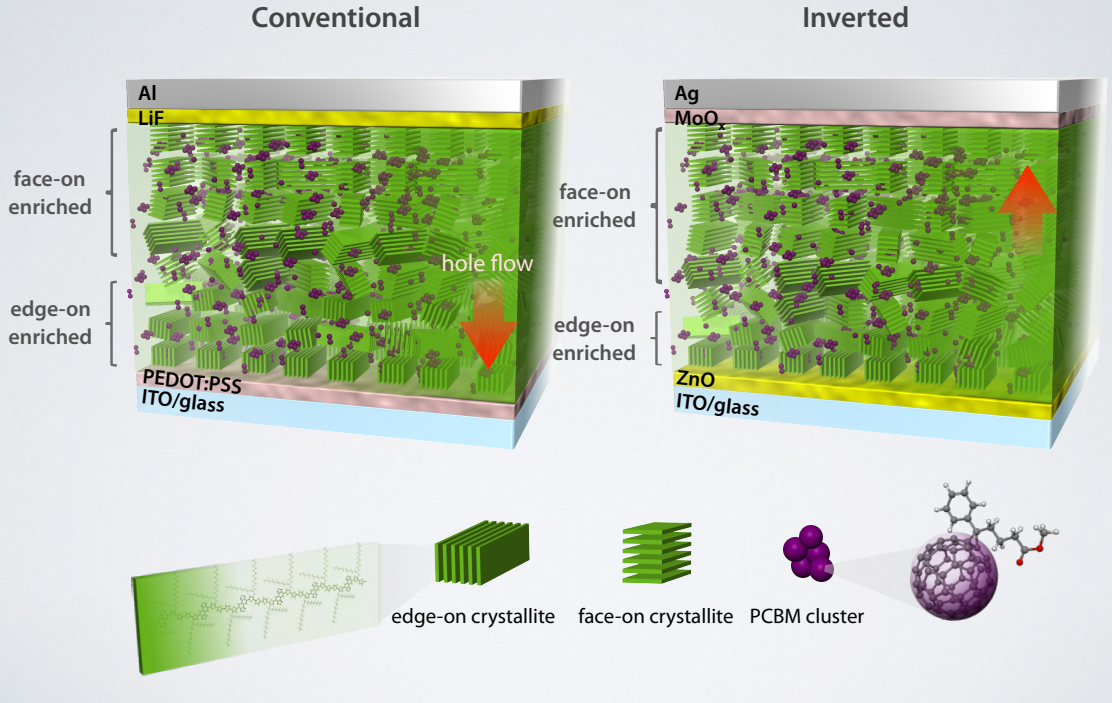






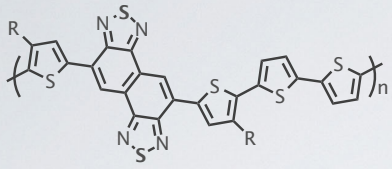
I. Osaka, M. Shimawaki, H. Mori, I. Doi, E. Miyazaki, T. Koganezawa, K. Takimiya, *JACS*, **2012**, *134*, *3498*.

SCHEMATIC ILLUSTRATIONS OF PNTz4T/PCBM BLEND FILMS



V. Vohra, K. Kawashima, T. Kakara, T. Koganezawa, I. Osaka, K. Takimiya, H. Murata, *Nat. Photon.* ***2015***, *9*, 403.

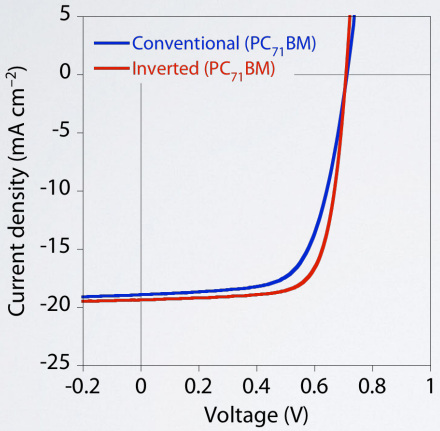
OPV PROPERTIES OF PNTz4T CELLS

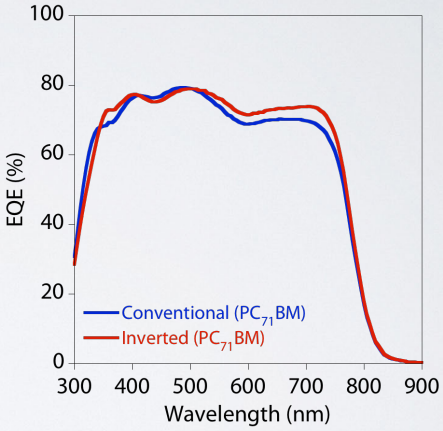


PNTz4T

Conventional cell
Al (–)
LiF
PNTz4T/$PC_{71}BM$
PEDOT:PSS
ITO (+)

Inverted cell
Ag (+)
MoO_x
PNTz4T/$PC_{71}BM$
ZnO
ITO (–)

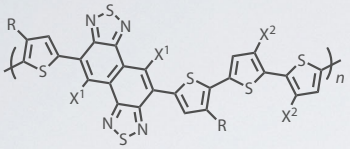




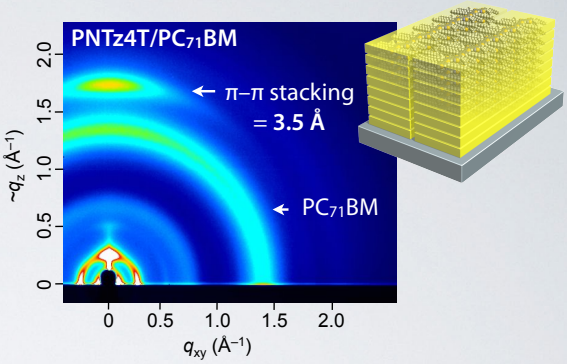
cell	thickness (nm)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
Conventional	290	18.9	0.71	0.66	8.92 [8.65]
Inverted	290	19.4	0.71	0.73	10.1 [9.77]

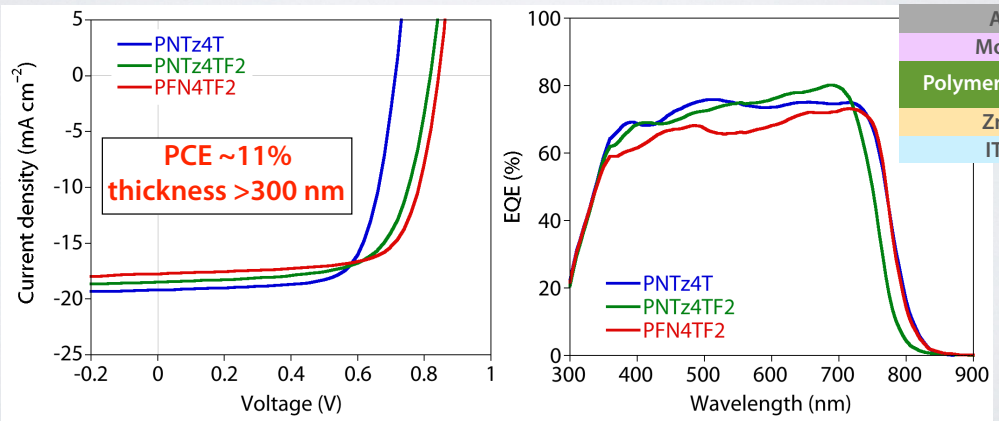
V. Vohra, K. Kawashima, T. Kakara, T. Koganezawa, I. Osaka, K. Takimiya, H. Murata, *Nat. Photon.* ***2015***, *9*, 403.

HIGH-PERFORMANCE CRYSTALLINE POLYMERS



PNTz4T ($X^1 = X^2 = H$)
PNTz4TF2 ($X^1 = H, X^2 = F$)
PFN4TF2 ($X^1 = X^2 = H$)





Ag
MoO_x
Polymer/$PC_{71}BM$
ZnO
ITO

JACS **2012**, *134*, 3498.; *Nat. Photon.* **2015**, *9*, 403.; *JACS* **2016**, *138*, 10265.