

有機デバイス高性能化に向けた 高分子半導体の配向制御

尾坂 格

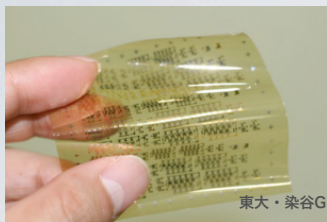
理化学研究所 創発物性科学研究センター



1

ORGANIC ELECTRONICS

有機トランジスタ（OFET）



東大・梁谷G

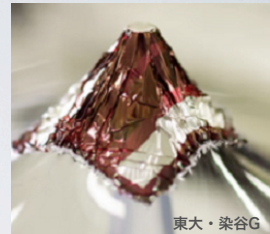


東大・梁谷G

有機薄膜太陽電池（OPV）



米・Konarka社



東大・梁谷G

有機EL（OLED）

有機ELディスプレイ



韓国・LG電子

有機EL照明



山形大・城戸G

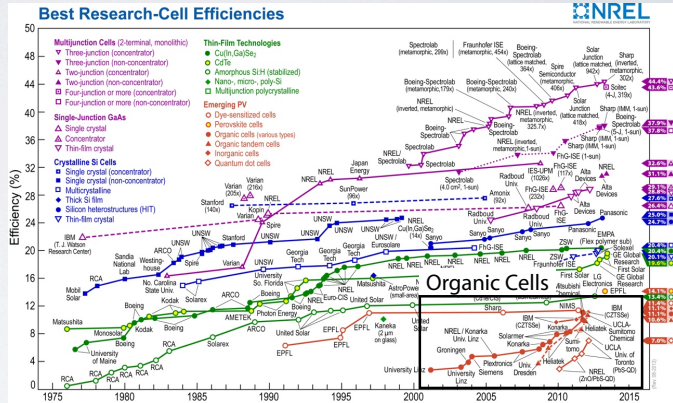
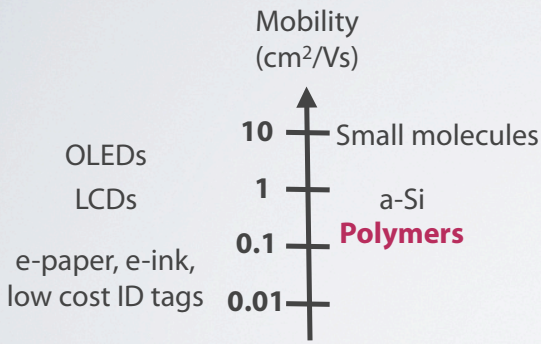
特長

- 軽量・フレキシブル
- 塗布プロセス（ロールトゥロールプロセス）
 - 高生産性・大面積化
 - 省エネルギー・省資源
 - 低コスト

CURRENT STATUS OF POLYMER-BASED DEVICES

OFETs

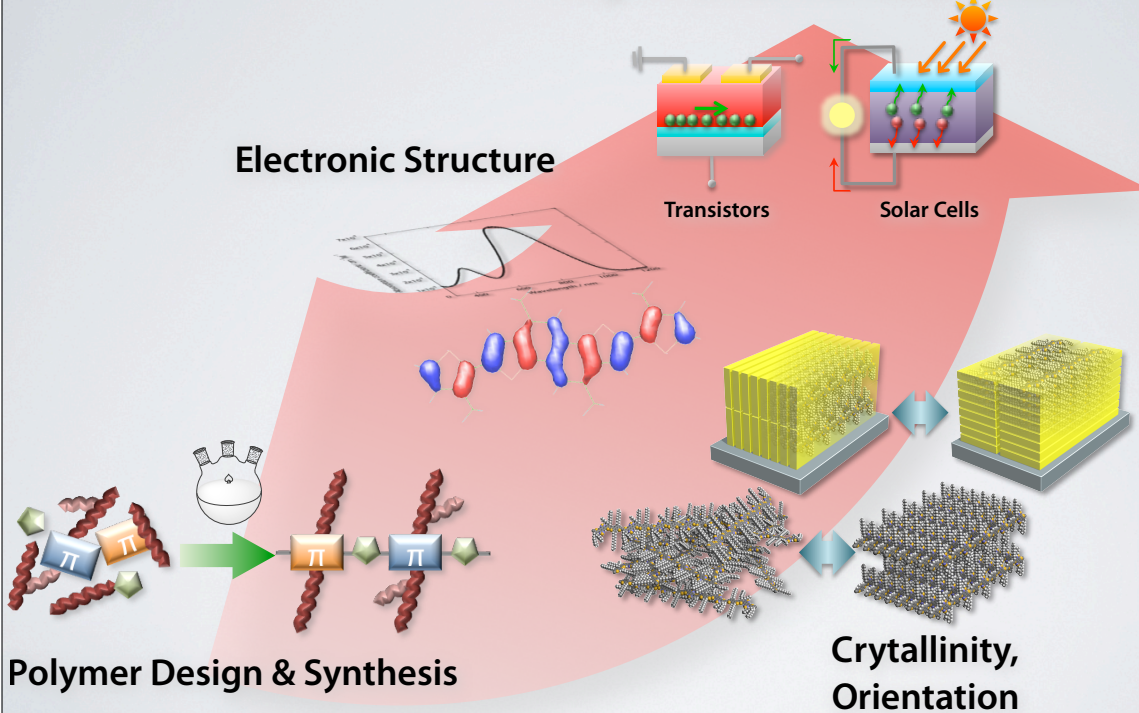
Solar cells (OPVs)



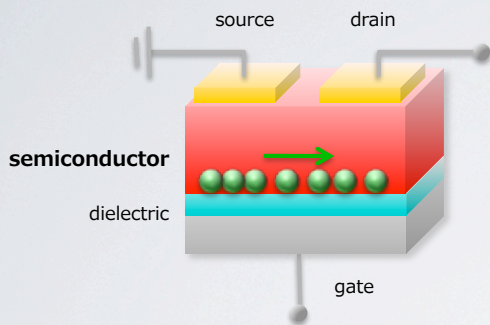
Conjugated polymer-based solar cells: typically 5–7%

MATERIALS DEVELOPMENT TOWARD HI-PERFORMANCE DEVICES

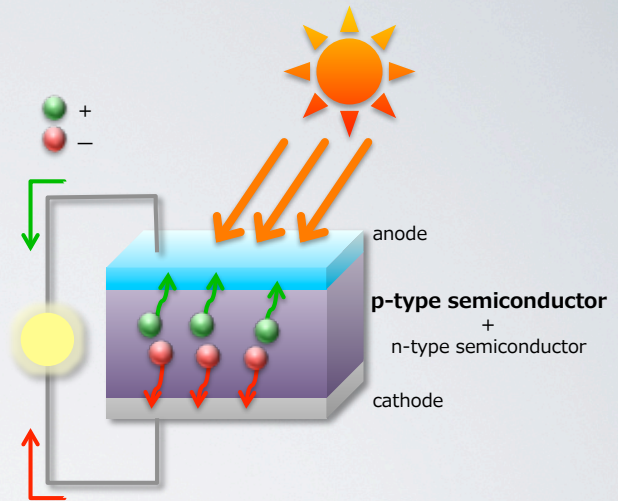
High-Performance Devices



TRANSISTOR AND SOLAR CELL



- ✓ low-lying HOMO (oxidative stability)
- ✓ in-plane charge transport
- ✓ high crystallinity
- ✓ orientation

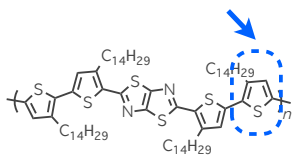


- ✓ low-lying HOMO (V_{oc})
- ✓ wide absorption (small band gap)
- ✓ out-of-plane charge transport
- ✓ high crystallinity
- ✓ orientation

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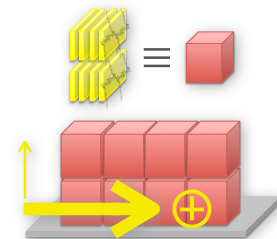
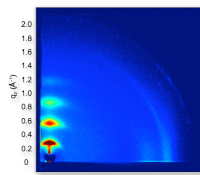
THIAZOLOTHIAZOLE-THIOPHENE COPOLYMERS

electron donating group

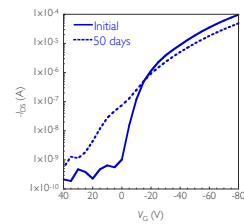


PTzQT-14

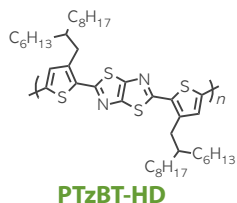
I. Osaka, R.D. McCullough, et al. *Adv. Mater.* **2007**, *19*, 4160
I. Osaka, R.D. McCullough, et al. *JACS* **2009**, *131*, 2521



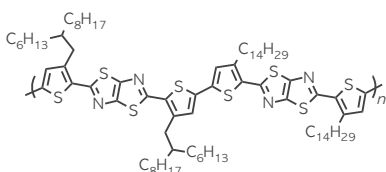
edge-on oriented; $\sim 0.3 \text{ cm}^2/\text{Vs}$



good stability;
HOMO = -5.0 eV

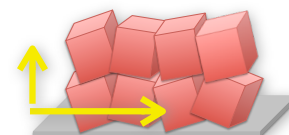
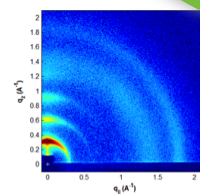


PTzBT-HD

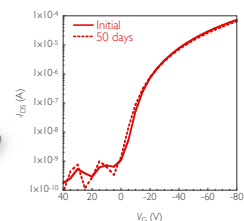


PTzBT-14HD

I. Osaka, et al., *Chem. Mater.*, **2010**, *22*, 4191.



predominantly edge-on, but partially face-on;
 $\sim 10^{-4} \text{ cm}^2/\text{Vs}$ (PTzBT-HD)
 $\sim 0.1 \text{ cm}^2/\text{Vs}$ (PTzBT-14HD)

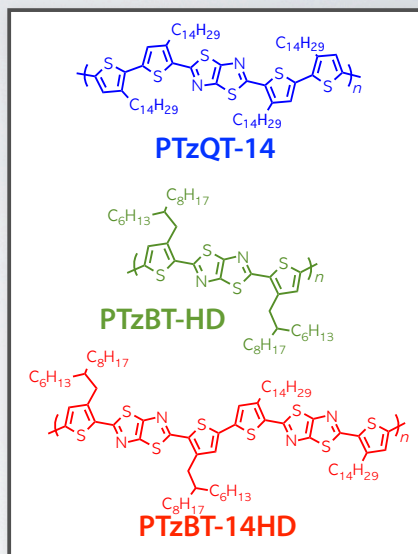
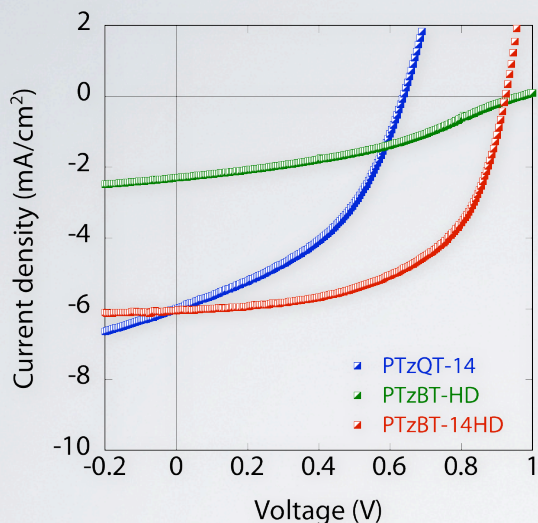


high stability;
HOMO = -5.2 eV

lower FET mobility, but better for OPVs?

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OPV PROPERTIES OF THE POLYMERS

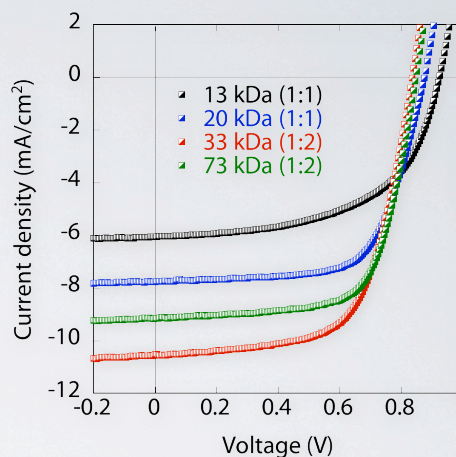
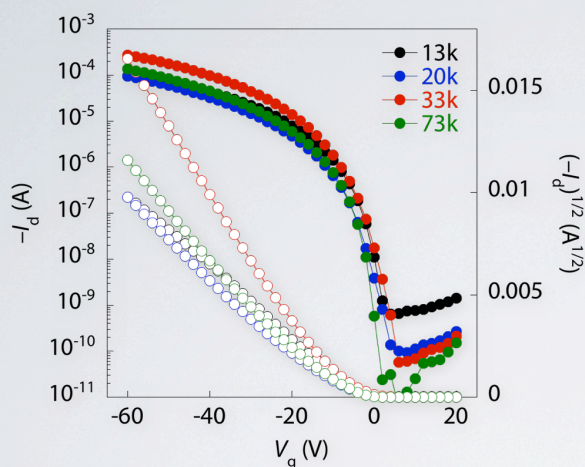


ITO/ PEDOT-PSS/ polymer:PC₆₁BM (1:1)/ LiF/ Al

Polymer	M_n / M_w	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
PTzQT-14	15k / 27k	6.0	0.64	0.43	1.6
PTzBT-HD	8.7k / 16k	2.3	0.96	0.37	0.8
PTzBT-14HD	13k / 18k	6.1	0.92	0.56	3.2

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OFET AND OPV PROPERTIES OF PTzBT-14HD DEVICES



Si/ SiO₂ / FDTs (SAM)/ polymer/ Au

ITO/ PEDOT-PSS/ polymer:PC₆₁BM/ LiF/ Al

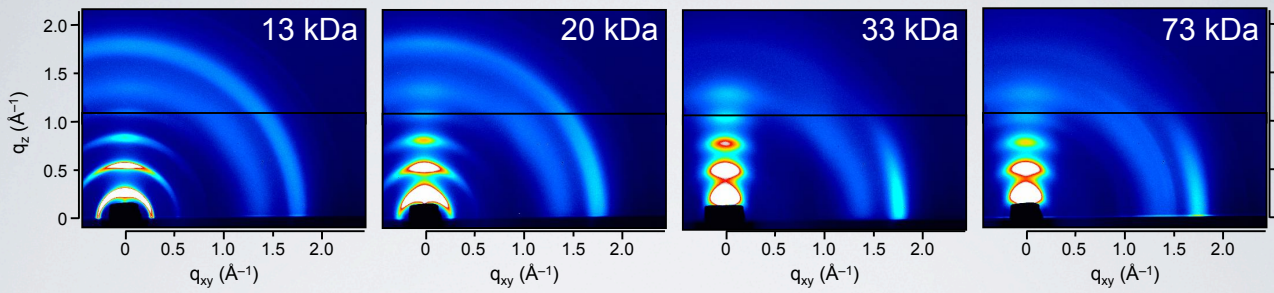
M_n	OFET		p:n	OPV			
	μ (cm ² /Vs)	I_{on}/I_{off}		J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
13 kDa	~0.1	~10 ⁵	1:1	6.1	0.92	0.56	3.2 (3.0)
20 kDa	~0.16	~10 ⁶	1:1	7.8	0.88	0.67	4.6 (4.3)
33 kDa	~0.42	~10 ⁷	1:2	10.5	0.84	0.64	5.7 (5.3)
73 kDa	~0.23	~10 ⁷	1:2	9.2	0.85	0.68	5.3 (4.8)

I. Osaka, M. Saito, H. Mori, T. Koganezawa, K. Takimiya, *Adv. Mater.* **2012**, 24, 425.

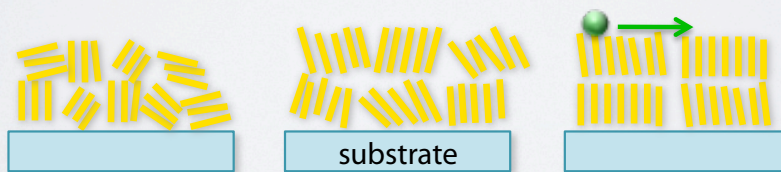
8

POLYMER STRUCTURE IN THE THIN FILM

2D-GIXD patterns of the polymer-only films (measured at SPring 8, BL19B2)



molecular weight

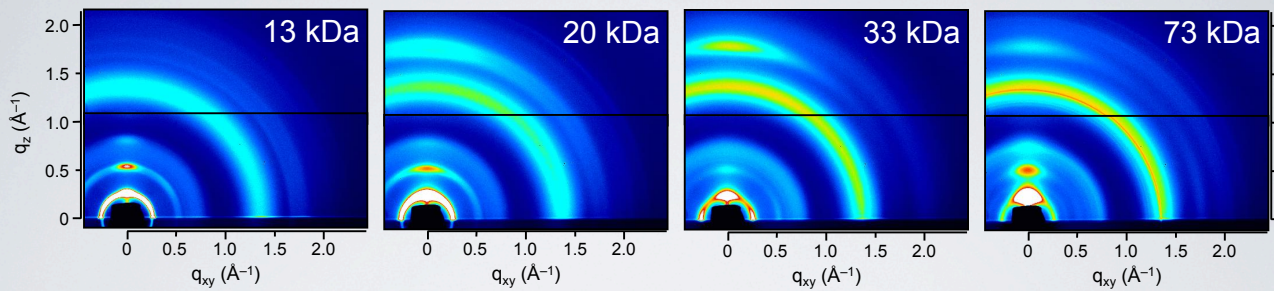


higher crystallinity, enhanced edge-on orientation in the high MW polymer

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POLYMER STRUCTURE IN THE BLEND FILM

2D-GIXD patterns of the polymer/ $PC_{61}BM$ films



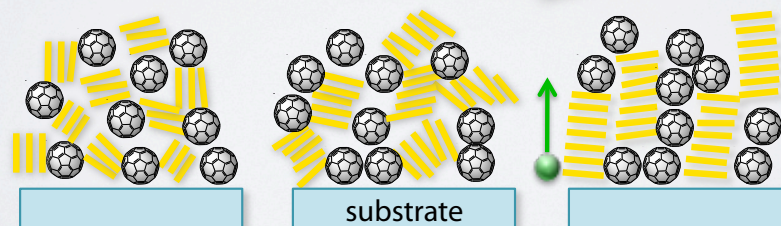
p:n = 1:1

1:1

1:2

1:2

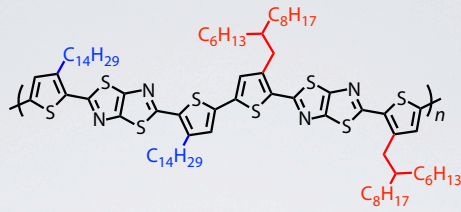
molecular weight



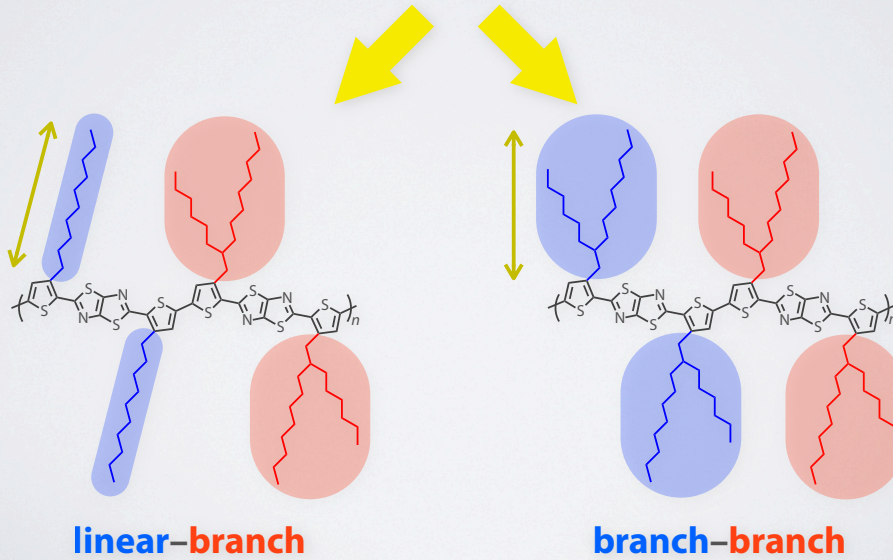
polymer tends to face-on orient by blending with $PC_{61}BM$
better out-of-plane charge transport in the high-MW polymer

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SIDE CHAIN TUNING

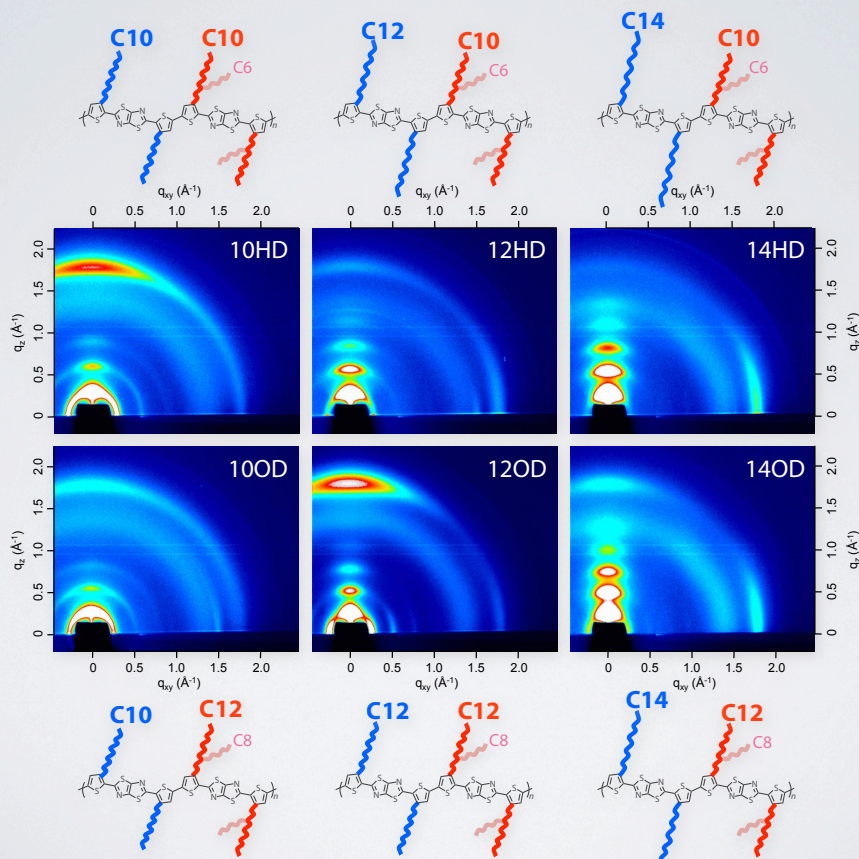


Can we control the polymer orientation by tuning the composition of side chains?



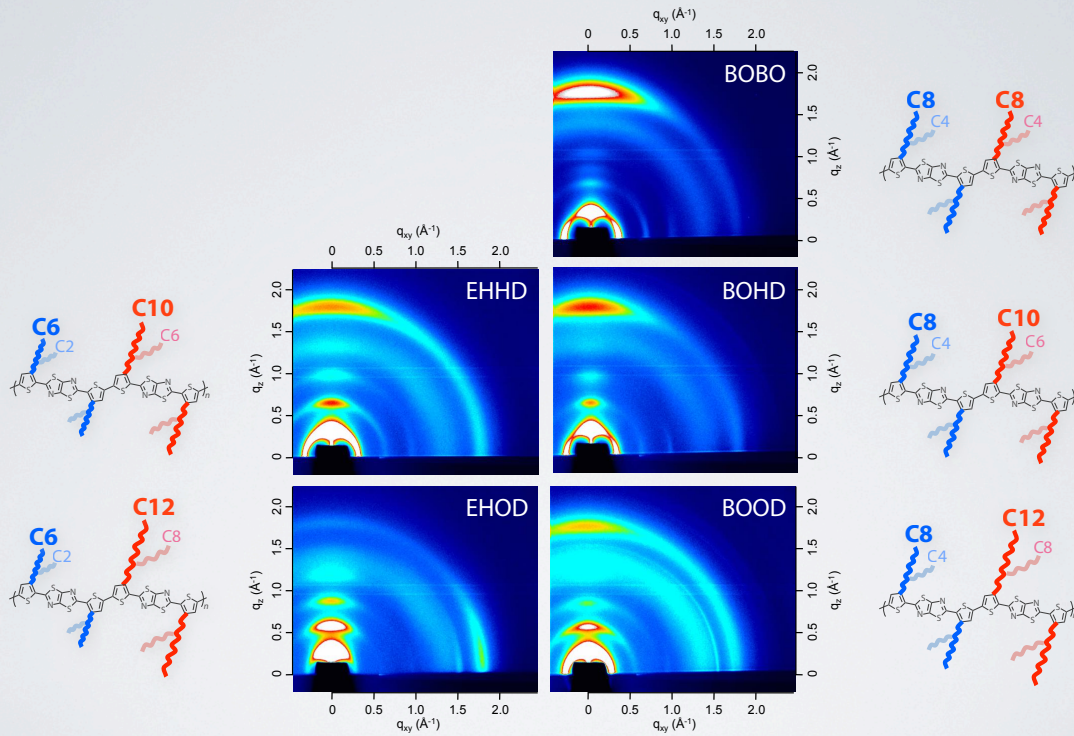
11

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



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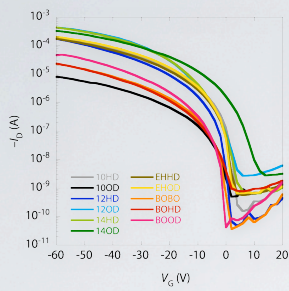
2D-GIXD OF PTzBT WITH ALL-BRANCHED SIDE CHAIN



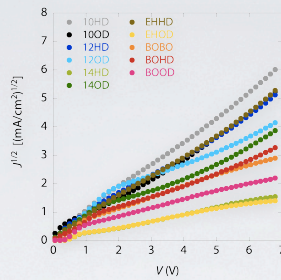
I. Osaka, M. Saito, H. Mori, T. Koganezawa, K. Takimiya, *Adv. Mater.* **2014**, *26*, 331–338.

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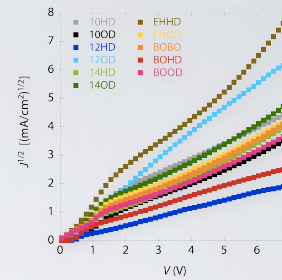
MOBILITIES OF THE POLYMERS



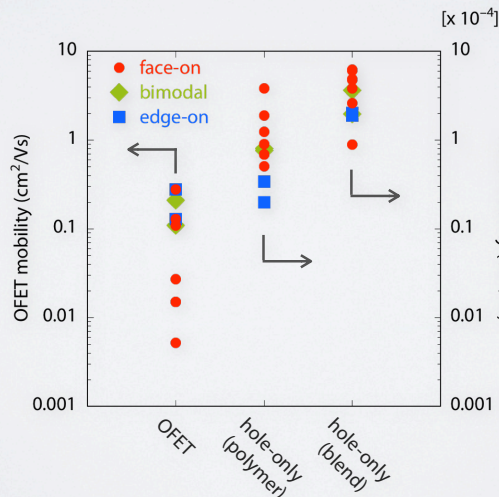
Si/SiO₂ (F-DTS)/polymer/Au
OFET



ITO/PEDOT-PSS/polymer/MoO₃/Al
hole-only device (polymer)

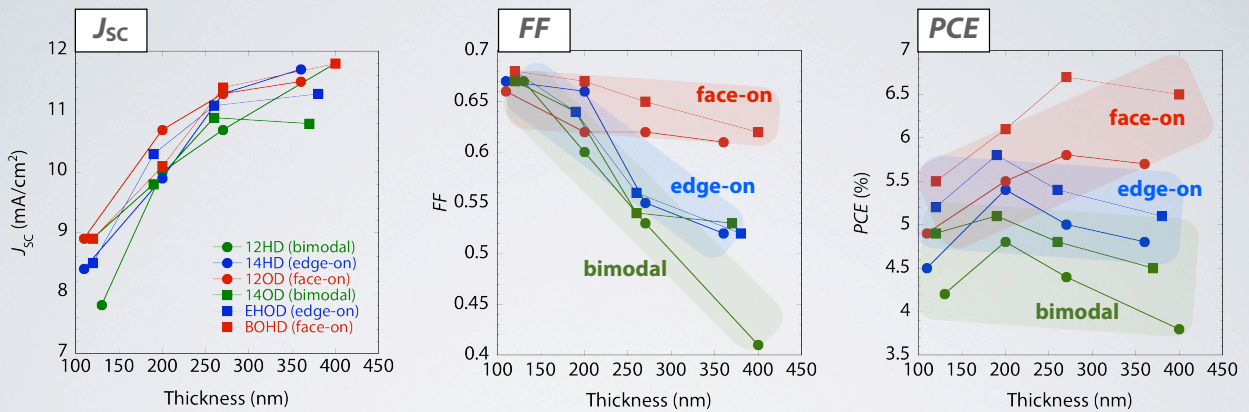


ITO/PEDOT-PSS/polymer:PC₆₁BM/MoO₃/Al
hole-only device (blend)



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OPV PROPERTIES: THICKNESS DEPENDENCE

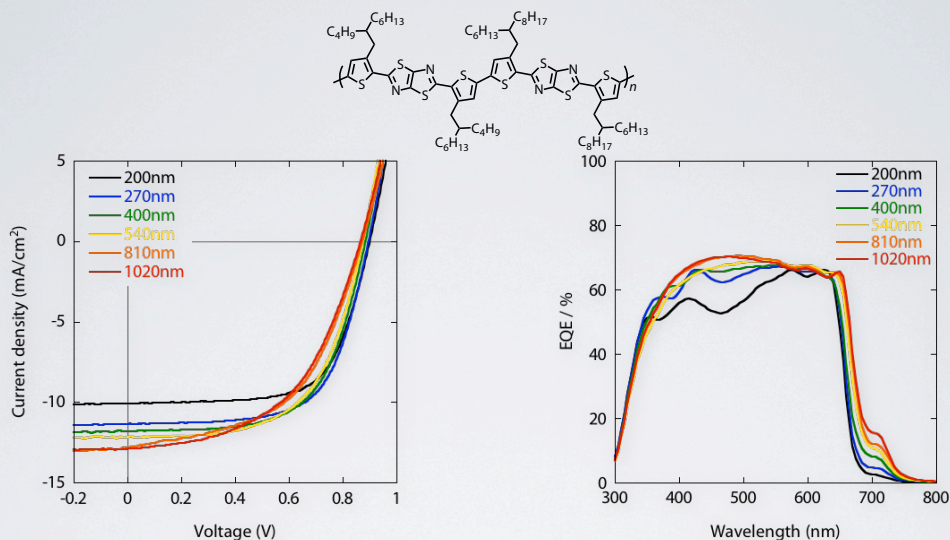


Control of crystallinity/orientation leads to an increase of J_{sc} without a loss of FF and V_{oc} , resulting in the improvement of efficiency.

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

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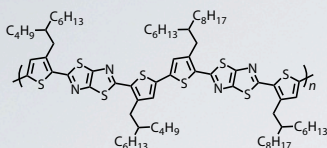
PTzBT-BOHD /PC₆₁BM CELLS WITH THICKER LAYERS



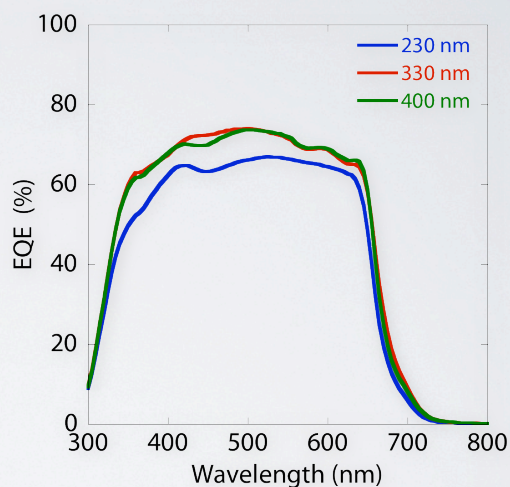
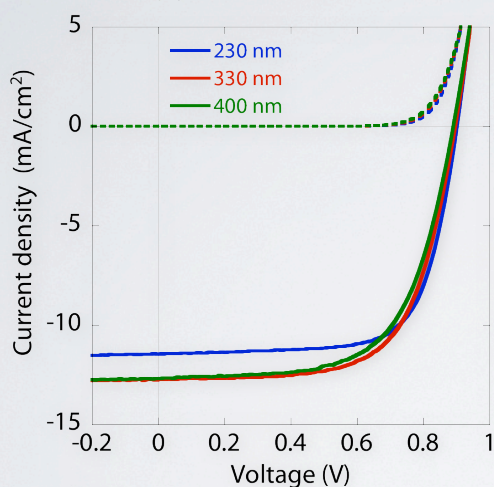
Film thickness (nm)	p:n	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
200	1:2	10.1	0.90	0.67	6.1
270	1:2	11.4	0.89	0.65	6.7
400	1:2	11.8	0.89	0.62	6.5
540	1:2	12.2	0.88	0.60	6.4
810	1:2	12.8	0.87	0.53	5.9
1020	1:2	12.9	0.87	0.51	5.8

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OPV PROPERTIES OF PTzBT-BOHD CELLS (w/PC₇₁BM)



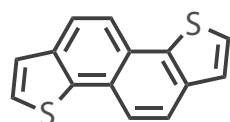
ITO/ PEDOT-PSS/ PTzBT-BOHD:PC₇₁BM/ Ca / Al



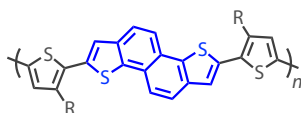
Film thickness (nm)	p:n	J _{SC} (mA/cm ²)	V _{OC} (V)	FF	PCE (%)
230	1:2	11.5	0.90	0.70	7.3
330	1:2	12.7	0.90	0.65	7.5
400	1:2	12.7	0.89	0.63	7.2

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NAPHTHODITHIOPHENE & NAPHTHOBISTHIADIAZOLE

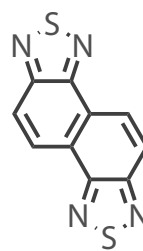


Naphtho[1,2-*b*:5,6-*b'*]dithiophene (NDT)

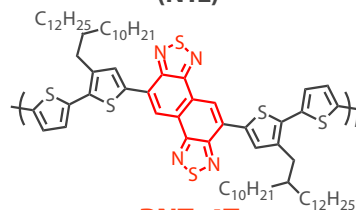


PNDBT
 $\mu = \sim 0.77 \text{ cm}^2/\text{Vs}$

I. Osaka, K. Takimiya, et al. *JACS*. **2010**, *132*, 5000.
I. Osaka, K. Takimiya, et al. *JACS*. **2011**, *133*, 6852.
I. Osaka, K. Takimiya, et al. *J. Mater. Chem. C*. **2013**, *1*, 1297.

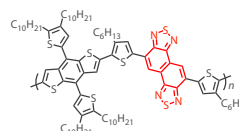


Naphtho[1,2-*c*:5,6-*c'*]bis[1,2,5]thiadiazole (NTz)



PNTz4T
 $\mu = \sim 0.6 \text{ cm}^2/\text{Vs}$
PCE = 6.3% (~8%)

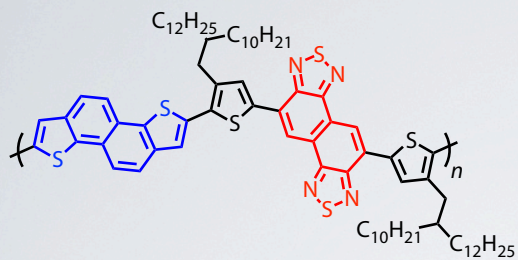
I. Osaka, K. Takimiya, et al. *JACS*, **2012**, *134*, 3498.



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

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COPOLYMER OF NDT & NTz



PNNT-DT

$\mu = \sim 0.54 \text{ cm}^2/\text{Vs}$

PCE $\sim 4.9\%$

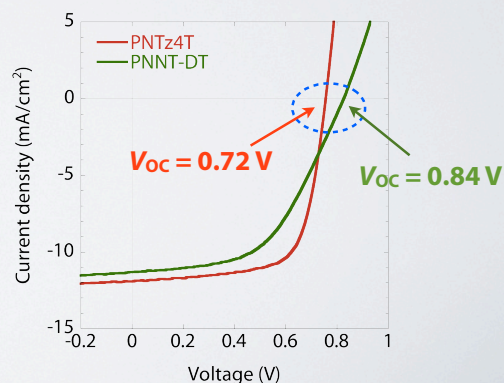
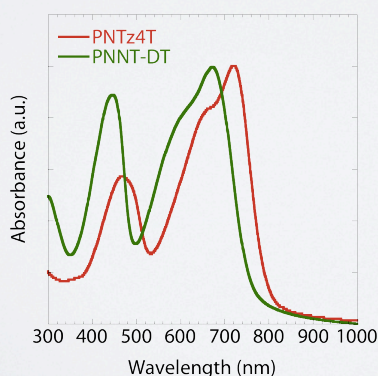
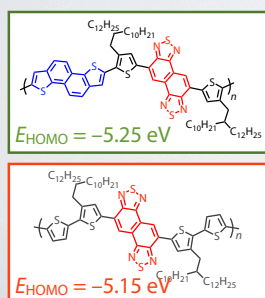
I. Osaka, K. Takimiya, et al. *ACS Macro Lett.* **2012**, 1, 437.

low solubility (soluble in CB or DCB @120°C)

low processability



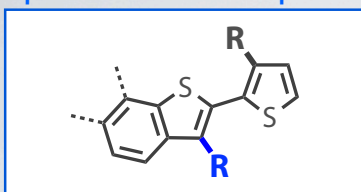
improvement of solubility is needed



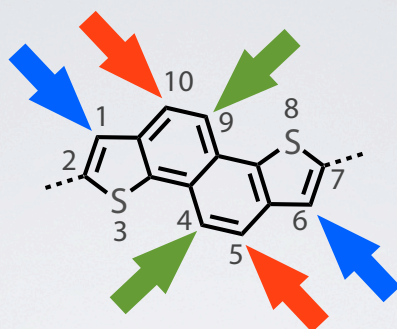
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FUNCTIONALIZATION OF THE NDT CORE

β -positions of thiophene

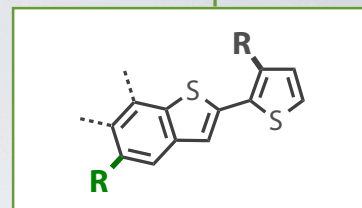


H-H coupling
steric hindrance

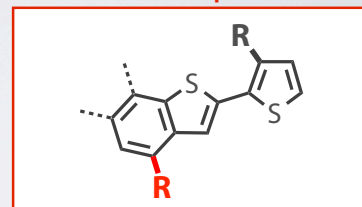


possible functionalization positions

inner C of naphthalene



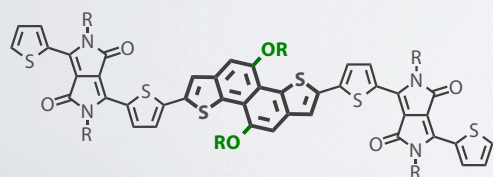
outer C of naphthalene



no steric hindrance

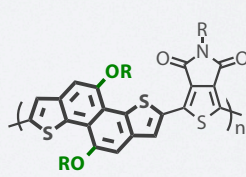
Oligomer and polymers with 4,9-functionalized NDT

4,9-Positions allow introduction of only alkoxy groups



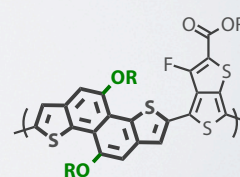
PCE = 4.4%

A. Facchetti, T. Marks, et al.
Chem. Commun. **2012**, 48, 8511.



PCE = 5.3%

H. Wang, Y. Li, X. Li, et al.
J. Mater. Chem. A. **2013**, 4, 2132.

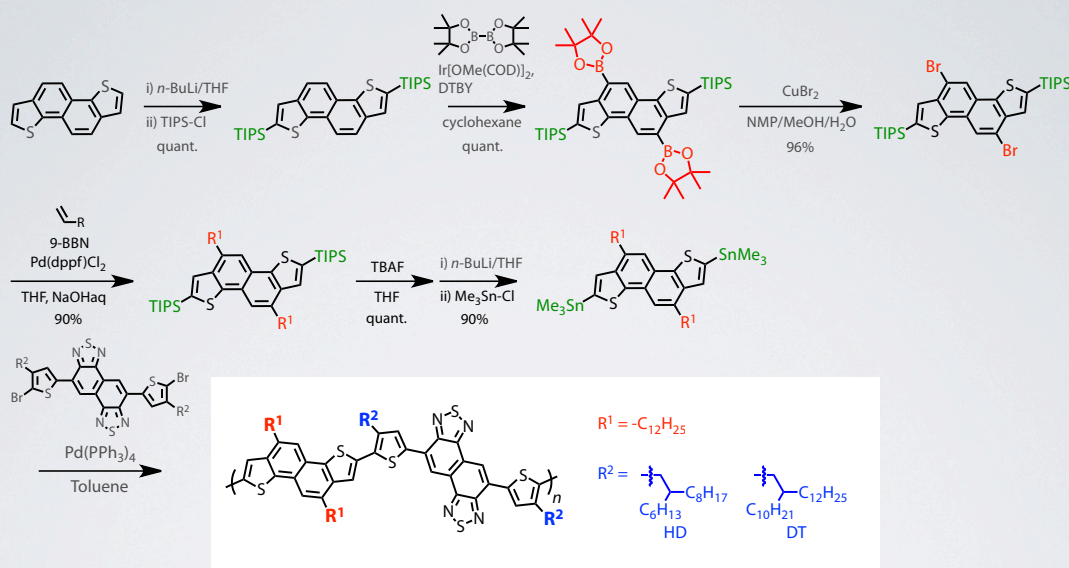


PCE = 4.9%

S.-J. Moon, S.-K. Lee, et al.
Polym. Chem. **2013**, 4, 2132.

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SYNTHESIS OF PNNTs WITH ALKYLATED NDT

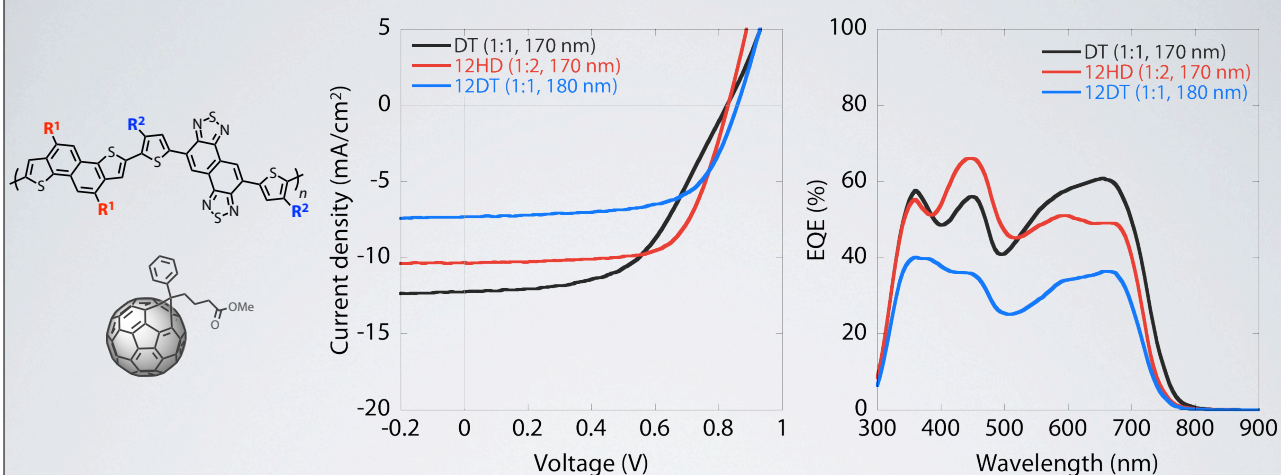


Polymer	Side chains (R^1R^2)	M_n (kDa)	PDI	solubility
PNNT-12HD	C12, HD	36.0	2.5	CHCl_3 , $\sim 40^\circ\text{C}$
PNNT-12DT	C12, DT	46.1	3.0	CHCl_3 , rt
PNNT-DT	H, DT	31.0	10	CB, DCB $\sim 120^\circ\text{C}$

I. Osaka, T. Kakara, N. Takemura, T. Koganezawa, K. Takimiya, *JACS*, **2013**, *135*, 8834.

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OPV PROPERTIES OF PNNT-CELLS (w/ PC_{61}BM)

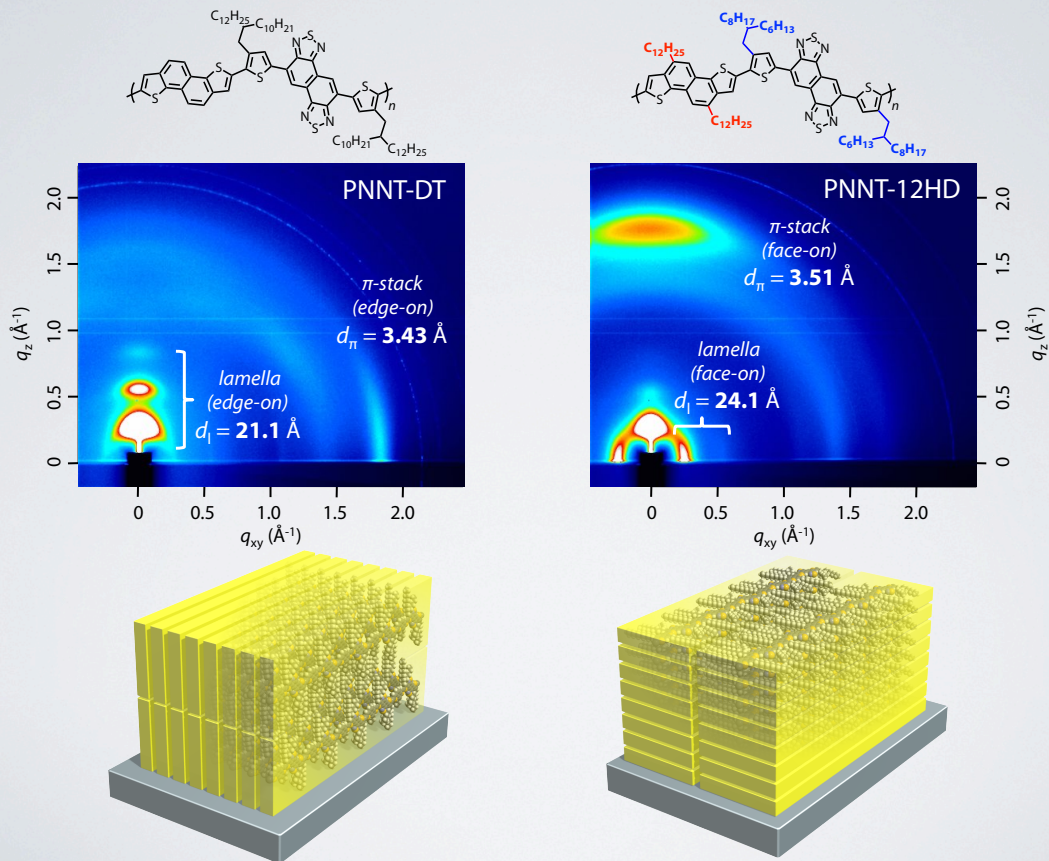


ITO/ PEDOT-PSS/ Polymer:PC₆₁BM / LiF / Al

Polymer	p:n	thickness (nm)	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
PNNT-12HD	1:2	170	10.3	0.83	0.68	5.9
PNNT-12DT	1:1	180	7.3	0.86	0.65	4.1
PNNT-DT	1:1	170	12.3	0.83	0.54	5.5

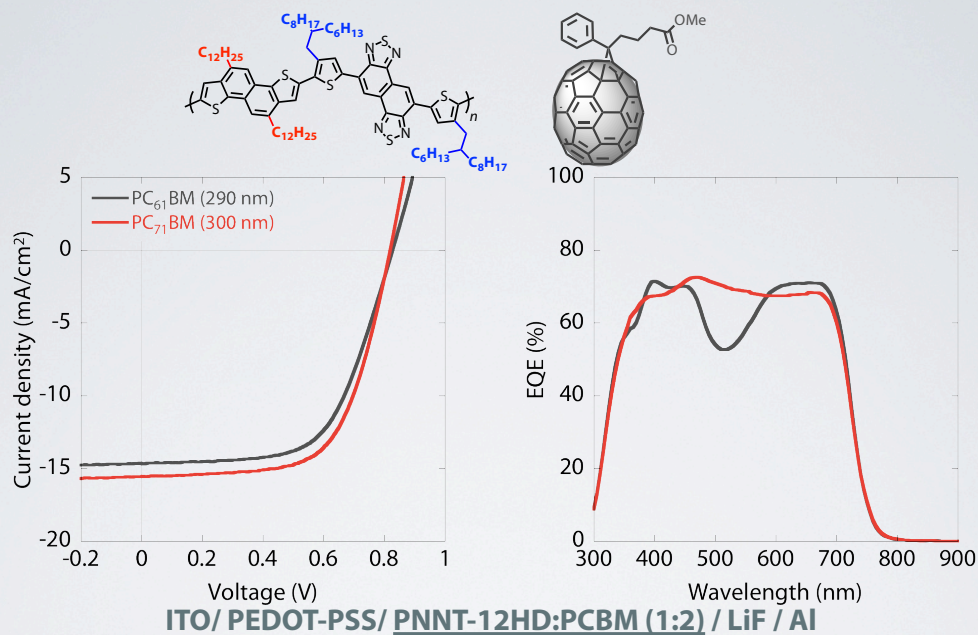
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2D-GIXD PATTERNS



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OPTIMIZED OPV PROPERTIES OF PNNT-12HD CELLS



PCBM	p:n	thickness (nm)	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
PC ₆₁ BM	1:2	290	14.7	0.83	0.61	7.5
PC ₇₁ BM	1:2	300	15.6	0.82	0.64	8.2

I. Osaka, T. Kakara, N. Takemura, T. Koganezawa, K. Takimiya, *JACS*, **2013**, *135*, 8834.

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SUMMARY

- Donor-Acceptor polymers with **thiazolothiazole** and **naphthobisthiadiazole** as the acceptor unit are presented.
- Increase of the molecular weight significantly improved the ordering structure of the polymer and the device performances.
- Blending with PCBM drastically changed the polymer orientation.
- **Orientation can be controlled by carefully tuning the side chain composition**, which allowed the **use of thick active layers without a loss of FF**, in turn leading to the efficiency improvement.
- High power conversion efficiencies of **~8.2%**, one of the highest values for conventional single junction cells, have been obtained.
- These results would be important guidelines for the design of further high-performance polymers.