SPring-8利用推進協議会
次世代先端デバイス研究会（第1回）
2014年3月14日 @連合会館（御茶ノ水・東京）

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

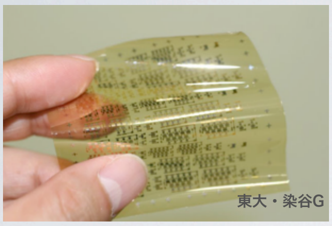
尾坂　格

理化学研究所 創発物性科学研究センター

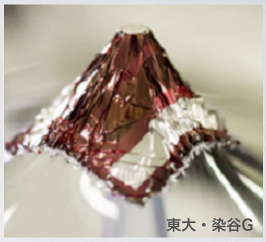
さきがけ PRESTO　RIKEN　CEMS

ORGANIC ELECTRONICS

有機トランジスタ（OFET）



有機薄膜太陽電池（OPV）



有機EL（OLED）

有機ELディスプレイ

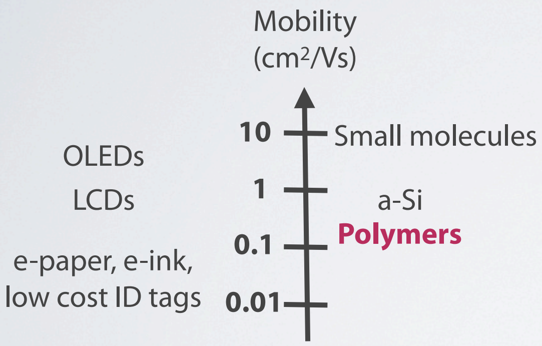
有機EL照明

特長

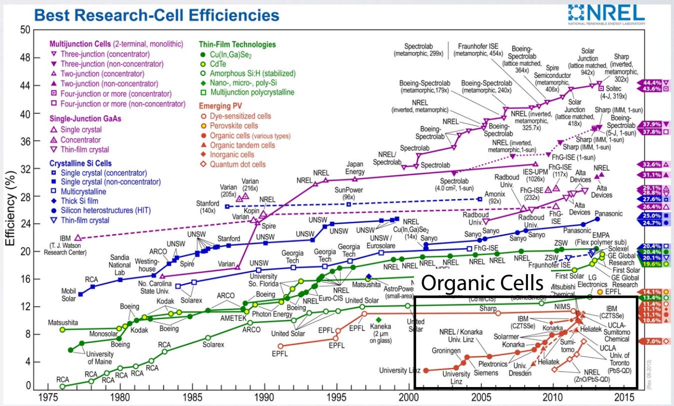
- 軽量・フレキシブル
- 塗布プロセス（ロールトゥロールプロセス）
  - 高生産性・大面積化
  - 省エネルギー・省資源
  - 低コスト

CURRENT STATUS OF POLYMER-BASED DEVICES

OFETs

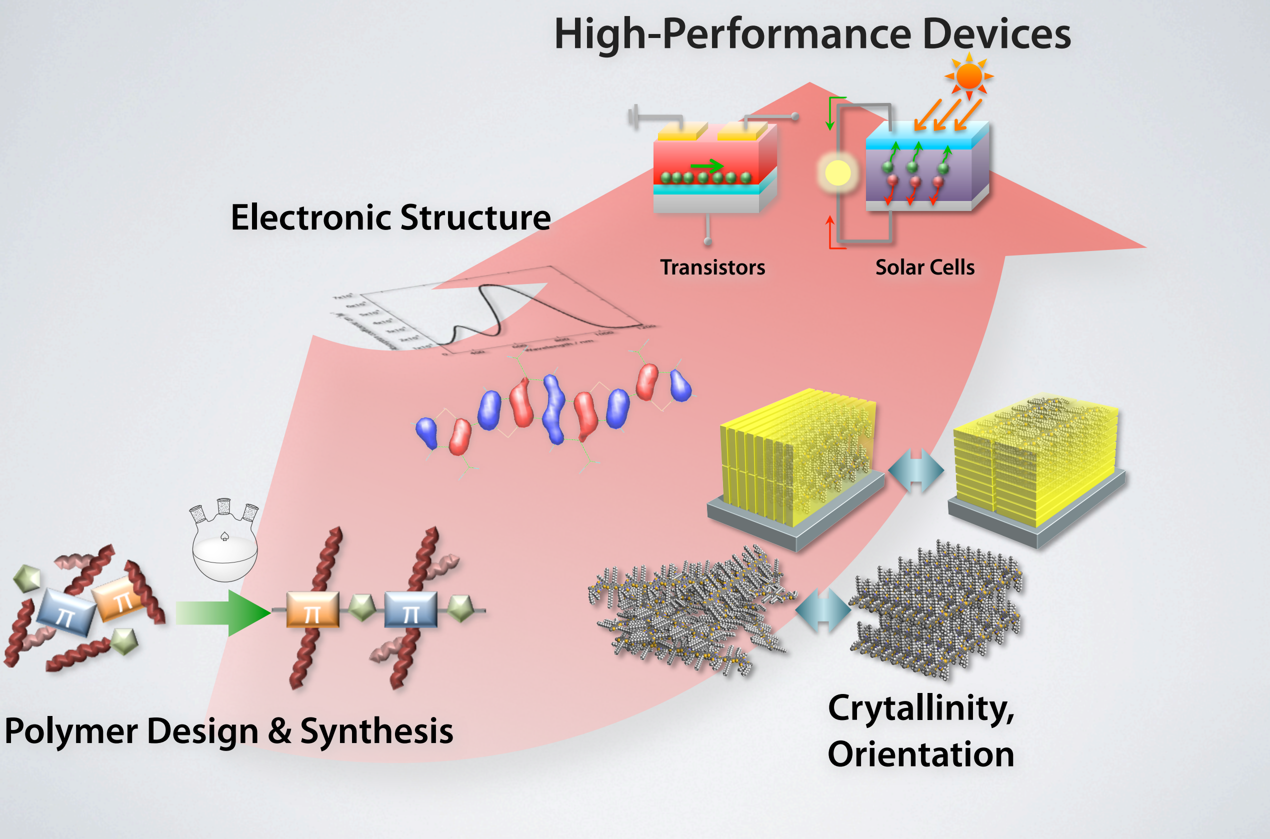


Solar cells (OPVs)

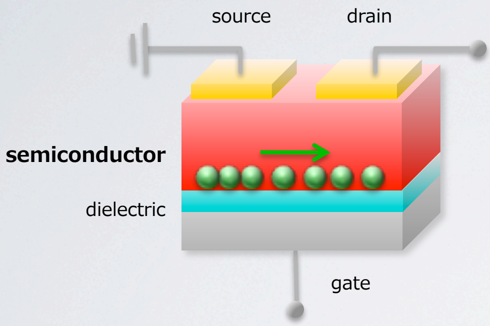


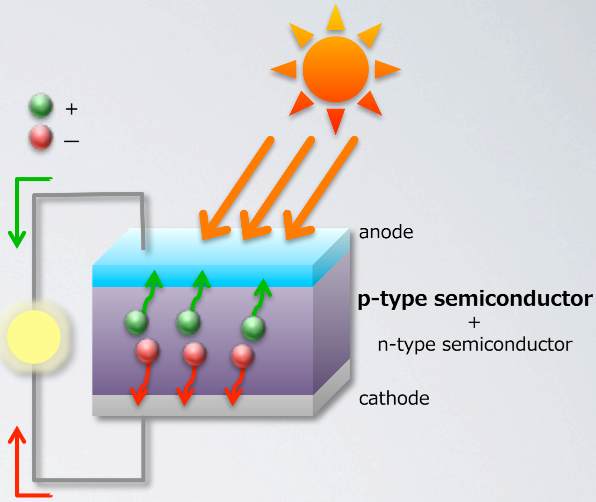
Conjugated polymer-based solar cells: typically 5–7%

MATERIALS DEVELOPMENT TOWARD HI-PERFORMANCE DEVICES



TRANSISTOR AND SOLAR CELL



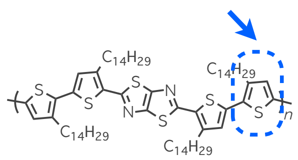


- ✓ low-lying HOMO (oxidative stability)
- ✓ in-plane charge transport
  - ✓ high crystallinity
  - ✓ orientation

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

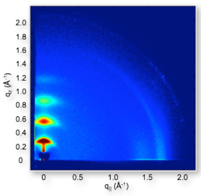
THIAZOLOTHIAZOLE-THIOPHENE COPOLYMERS

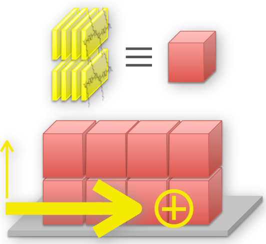
electron donating group



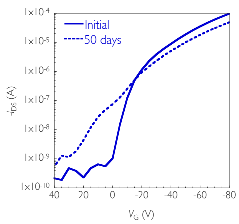
PTzQT-14

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

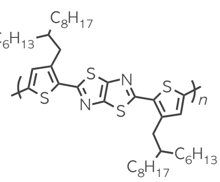




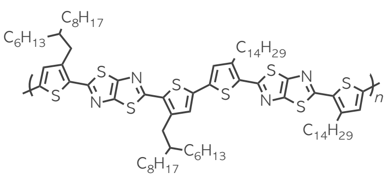
edge-on oriented; **~0.3 cm²/Vs**



good stability;
HOMO=–5.0 eV

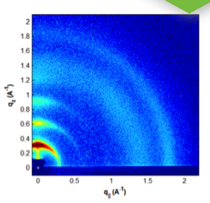


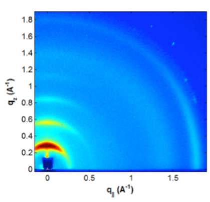
PTzBT-HD

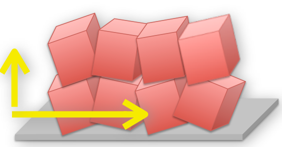


PTzBT-14HD

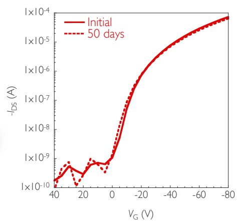
I. Osaka, et al., *Chem. Mater.*, **2010**, *22*, 4191.







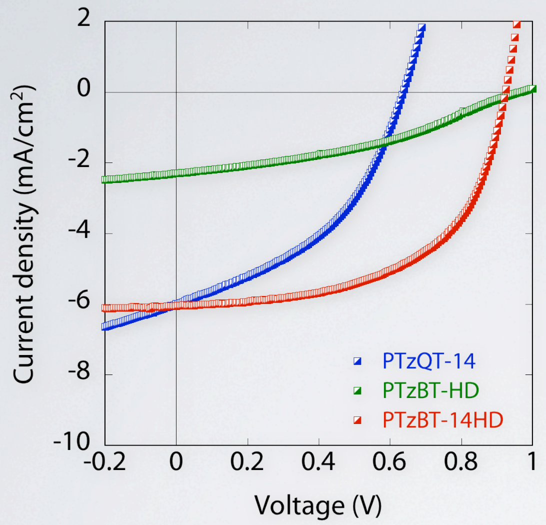
predominantly edge-on, but partially face-on;
~10^{-4} cm²/Vs (PTzBT-HD)
~0.1 cm²/Vs (PTzBT-14HD)

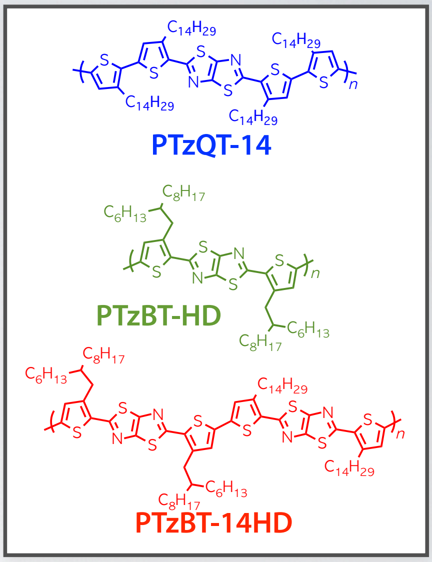


high stability;
HOMO=–5.2 eV

lower FET mobility, but better for OPVs?

OPV PROPERTIES OF THE POLYMERS

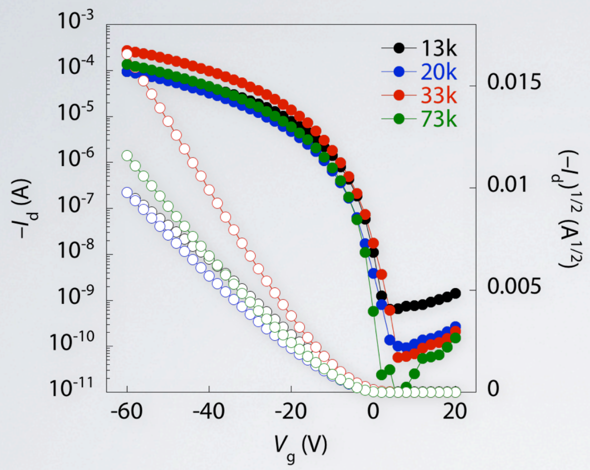


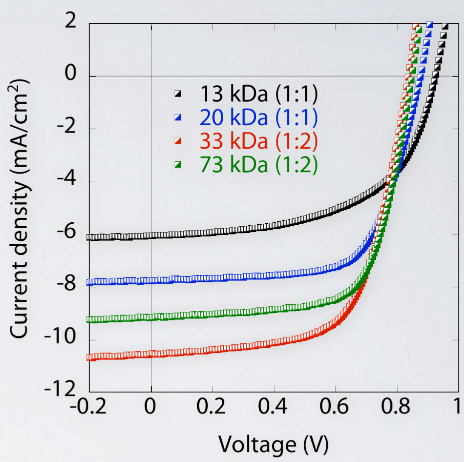


ITO/ PEDOT-PSS/ **polymer:$PC_{61}BM$ (1:1)**/ LiF/ Al

Polymer	M_n / M_w	J_{SC} (mA/cm²)	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**

OFET AND OPV PROPERTIES OF PTzBT-14HD DEVICES





Si/ SiO_2 / FDTS (SAM)/ **polymer**/ Au

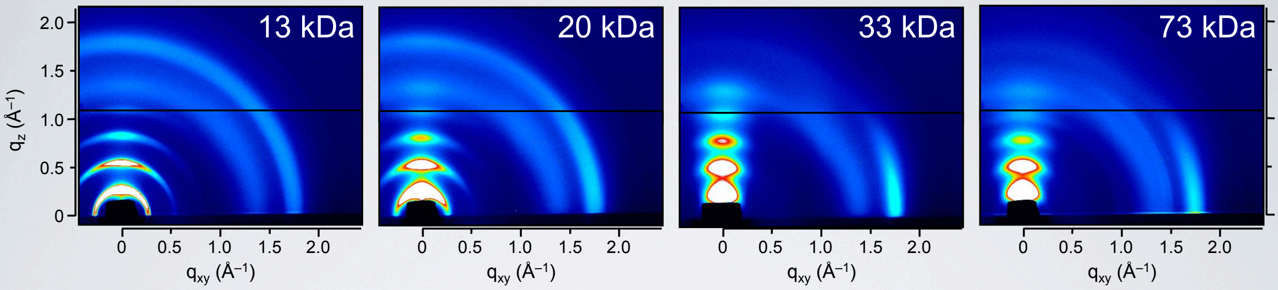
ITO/ PEDOT-PSS/ **polymer:$PC_{61}BM$**/ LiF/ Al

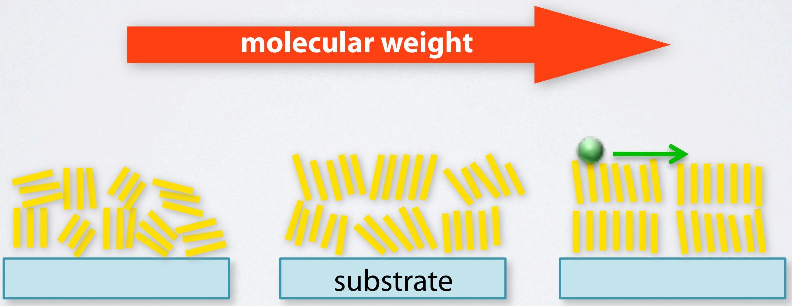
M_n	OFET		OPV				
	μ (cm²/Vs)	I_{on}/I_{off}	p:n	J_{SC} (mA/cm²)	V_{OC} (V)	*FF*	PCE (%)
13 kDa	~0.1	~10^5	1:1	6.1	0.92	0.56	3.2 (3.0)
20 kDa	~0.16	~10^6	1:1	7.8	0.88	0.67	4.6 (4.3)
33 kDa	~0.42	~10^7	1:2	10.5	0.84	0.64	5.7 (5.3)
73 kDa	~0.23	~10^7	1:2	9.2	0.85	0.68	5.3 (4.8)

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

POLYMER STRUCTURE IN THE THIN FILM

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

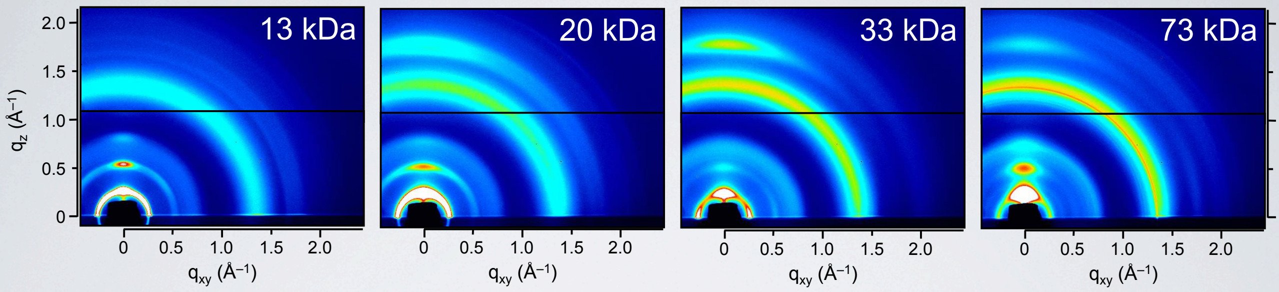




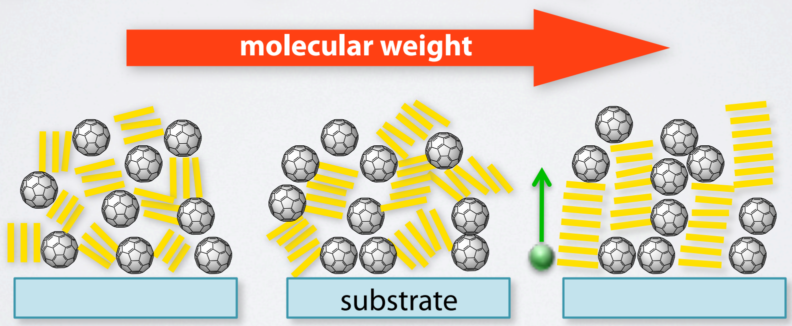
higher crystallinity, enhanced edge-on orientation in the high MW polymer

POLYMER STRUCTURE IN THE BLEND FILM

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



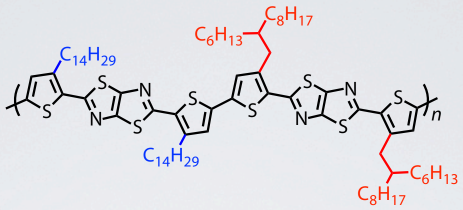
p:n = 1:1 | 1:1 | 1:2 | 1:2



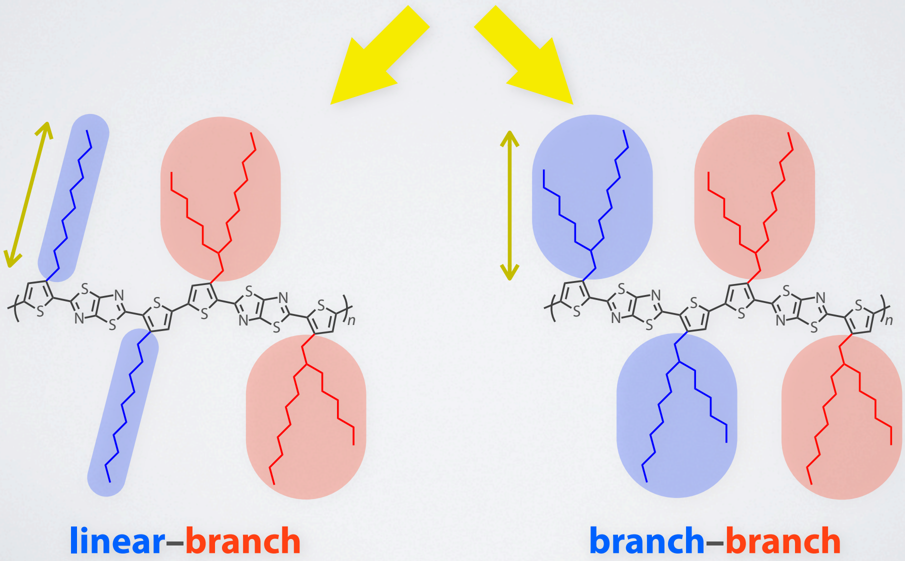
polymer tends to face-on orient by blending with $PC_{61}BM$

better out-of-plane charge transport in the high-MW polymer

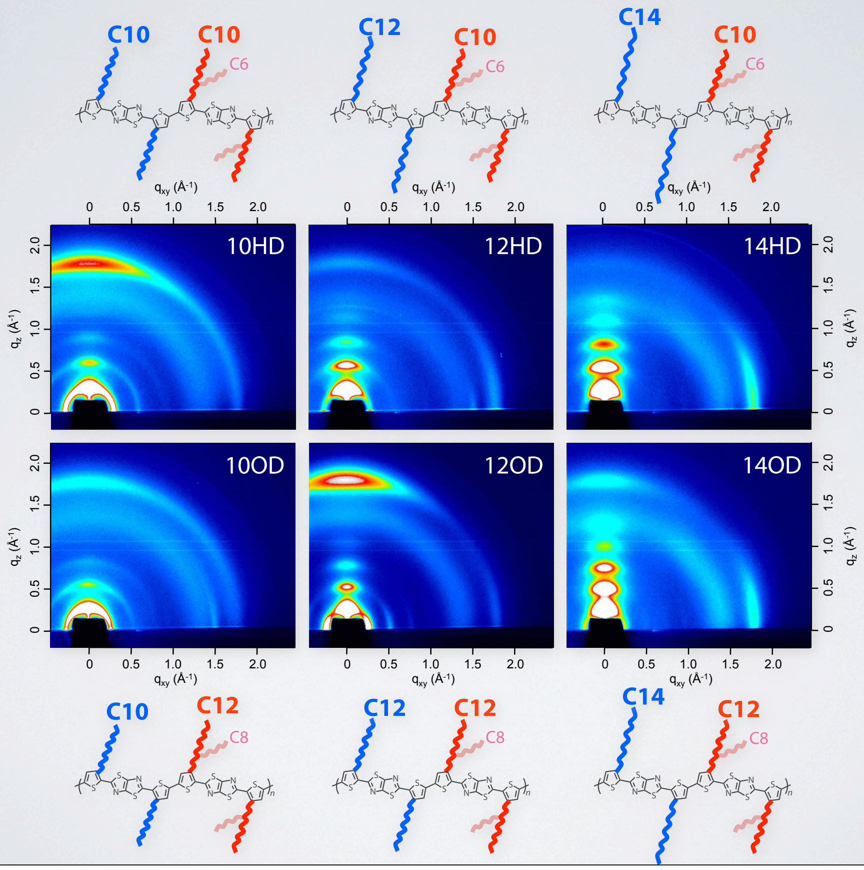
SIDE CHAIN TUNING



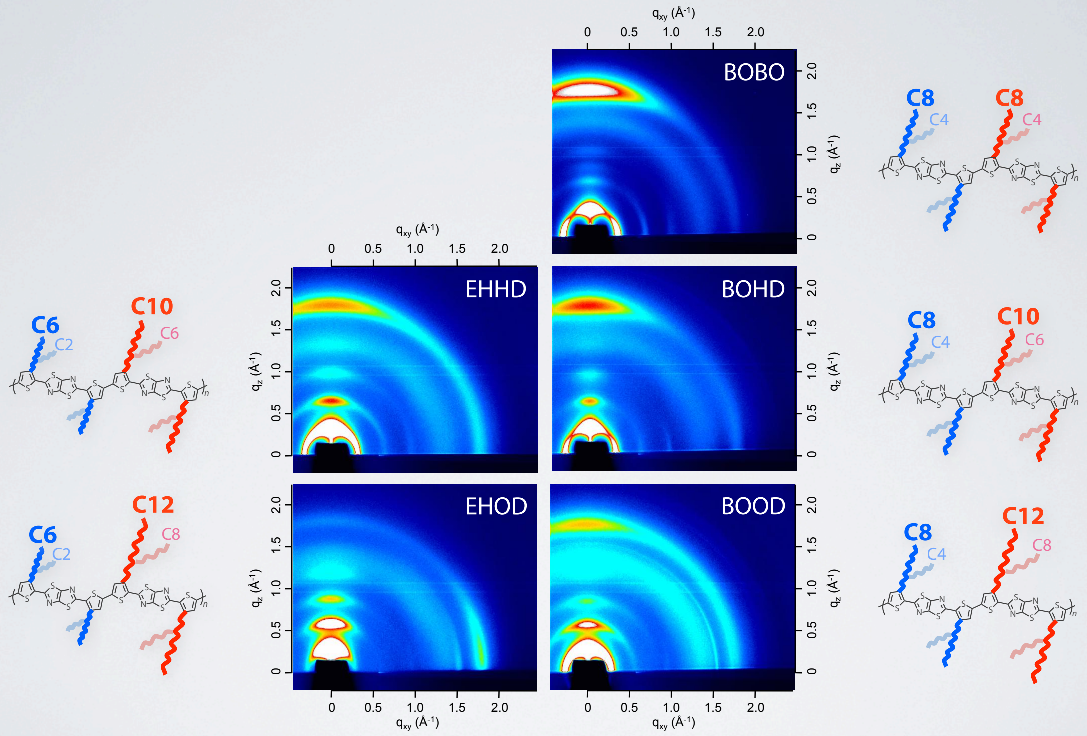
Can we control the polymer orientation by tuning the composition of side chains?



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

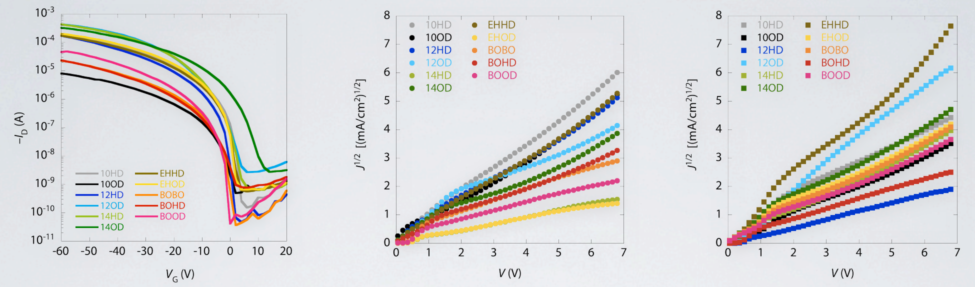


2D-GIXD OF PTzBT WITH ALL-BRANCHED SIDE CHAIN



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

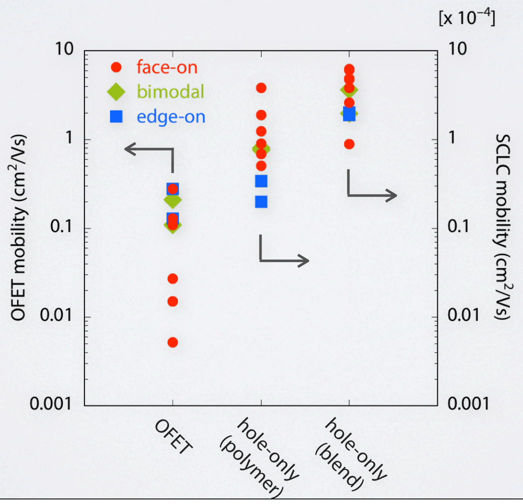
MOBILITIES OF THE POLYMERS



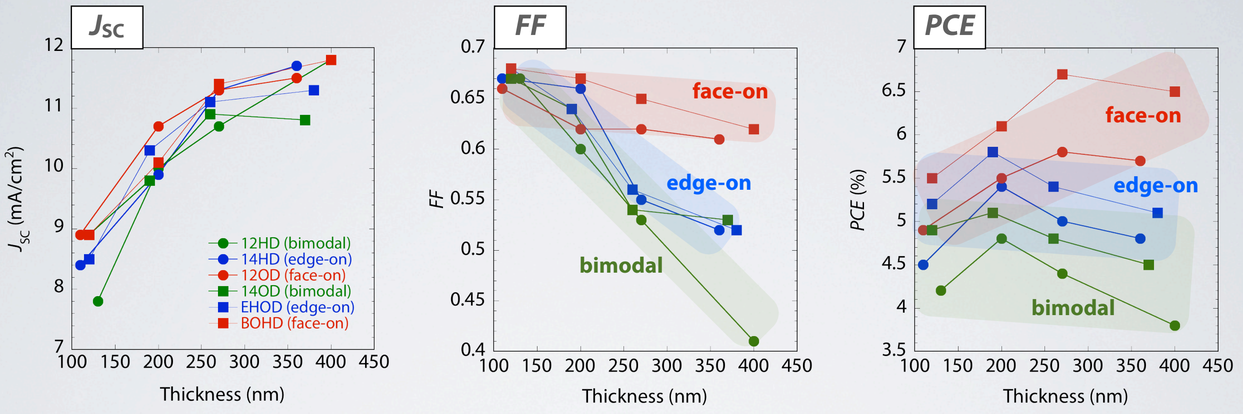
Si/ SiO_2 (F-DTS)/ polymer/ Au — **OFET**

ITO/ PEDOT-PSS/ polymer/ MoO_3/ Al — **hole-only device (polymer)**

ITO/ PEDOT-PSS/ polymer:$PC_{61}BM$/ MoO_3/ Al — **hole-only device (blend)**



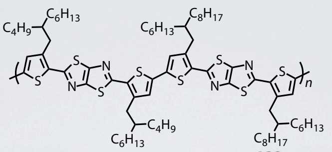
OPV PROPERTIES: THICKNESS DEPENDENCE

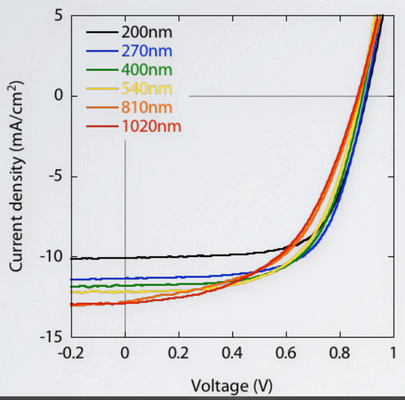


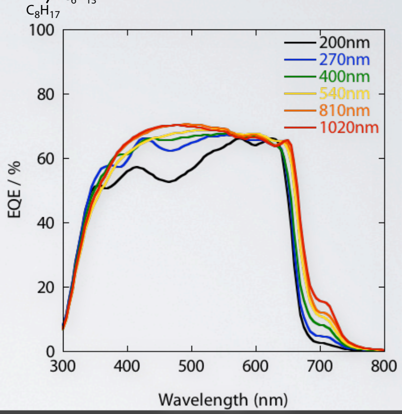
Control of crystallinity/orientation leads to an increase of J_{SC} without a loss of *FF* and V_{OC}, resulting in the improvement of efficiency.

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

PTzBT-BOHD /PC$_{61}$BM CELLS WITH THICKER LAYERS

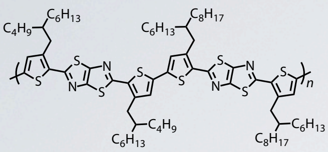




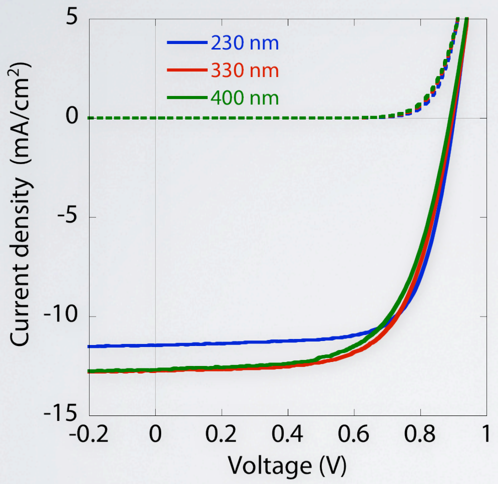


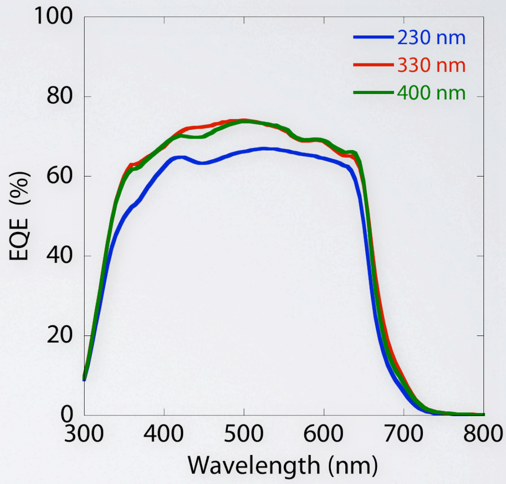
Film thickness (nm)	p:n	J_{SC} (mA/cm²)	V_{OC} (V)	FF	PCE (%)
200	1:2	10.1	0.90	0.67	6.1
270	1:2	11.4	0.89	0.65	6.7
400	1:2	11.8	0.89	0.62	6.5
540	1:2	12.2	0.88	0.60	6.4
810	1:2	12.8	0.87	0.53	5.9
1020	1:2	12.9	0.87	0.51	5.8

OPV PROPERTIES OF PTzBT-BOHD CELLS (w/PC$_{71}$BM)



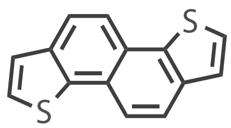
ITO/ PEDOT-PSS/ **PTzBT-BOHD:PC$_{71}$BM**/ Ca / Al



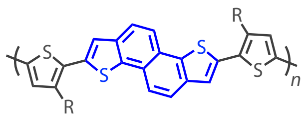


Film thickness (nm)	p:n	J_{SC} (mA/cm²)	V_{OC} (V)	FF	PCE (%)
230	1:2	11.5	0.90	0.70	7.3
330	1:2	12.7	0.90	0.65	7.5
400	1:2	12.7	0.89	0.63	7.2

NAPHTHODITHIOPHENE & NAPHTHOBISTHIADIAZOLE



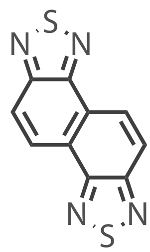
Naphtho[1,2-*b*:5,6-*b*′]dithiophene (NDT)



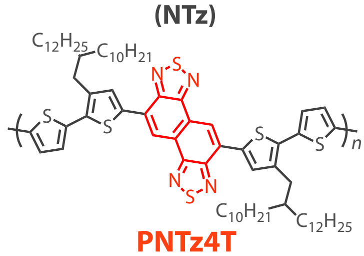
PNDTBT

***μ* = ~0.77 cm²/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)

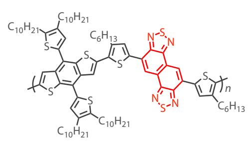


PNTz4T

***μ* = ~0.6 cm²/Vs**

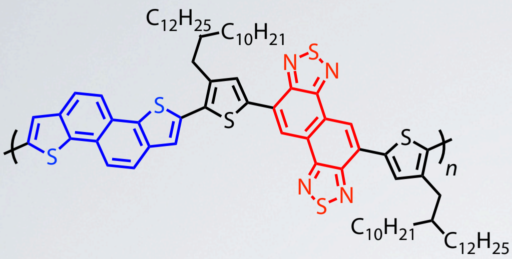
***PCE* = 6.3% (~8%)**

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



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

COPOLYMER OF NDT & NTz

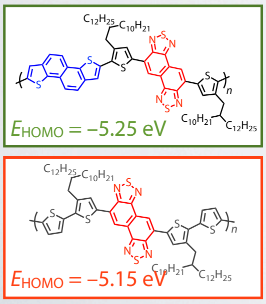


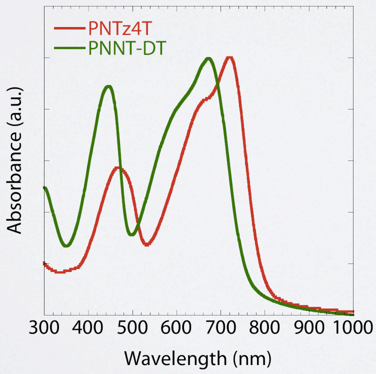
PNNT-DT
μ = ~0.54 cm²/Vs
PCE = ~4.9%

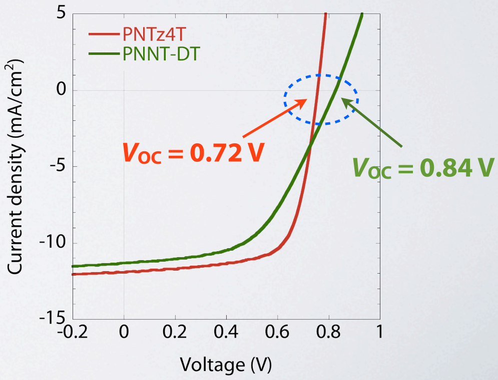
I. Osaka, K. Takimiya, et al. *ACS Macro Lett.* **2012**, *1*, 437.

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

improvement of solubility is needed

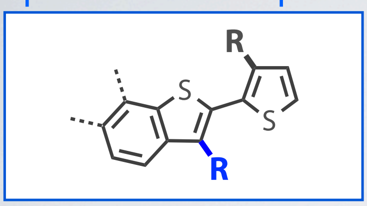






FUNCTIONALIZATION OF THE NDT CORE

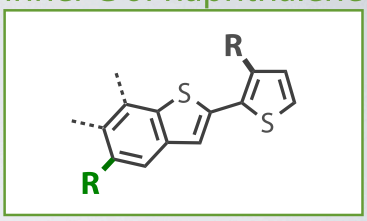
β-positions of thiophene



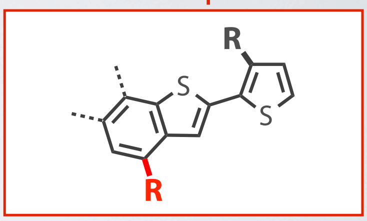
H-H coupling
steric hindrance

possible functionalization positions

inner C of naphthalene



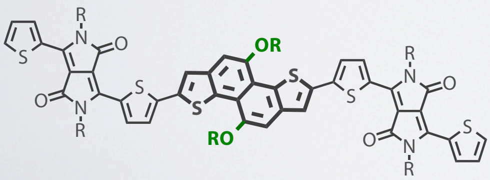
outer C of naphthalene



no steric hindrance

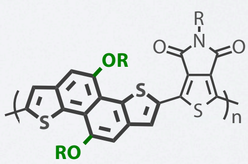
Oligomer and polymers with 4,9-functionalized NDT

4,9-Positions allow introduction of only alkoxy groups



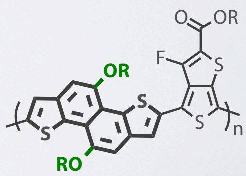
PCE = 4.4%

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



PCE = 5.3%

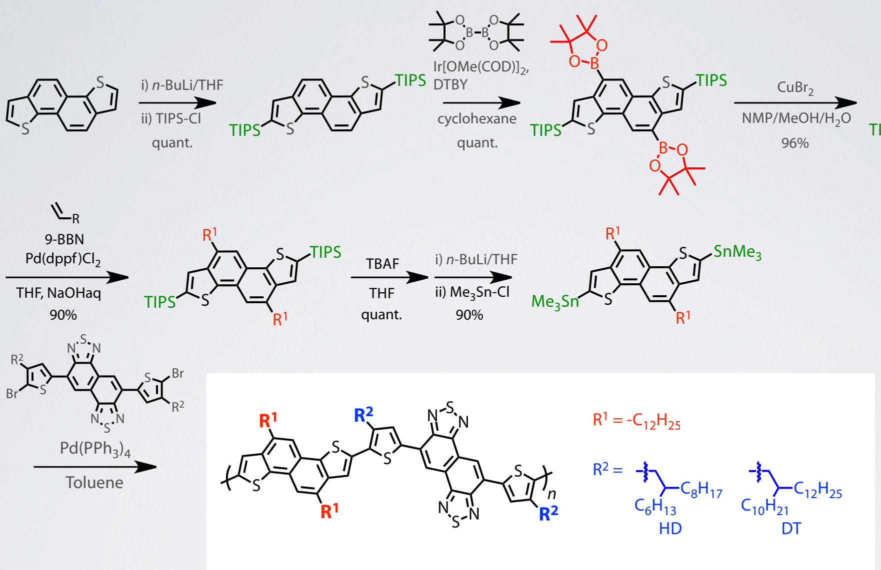
H. Wang, Y. Li, X. Li, et al. *J. Mater. Chem. A.* **2013**, *4*, 2132.



PCE = 4.9%

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

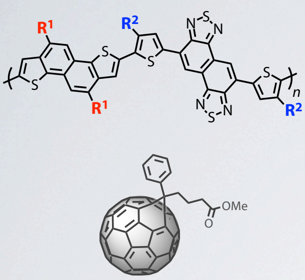
SYNTHESIS OF PNNTs WITH ALKYLATED NDT

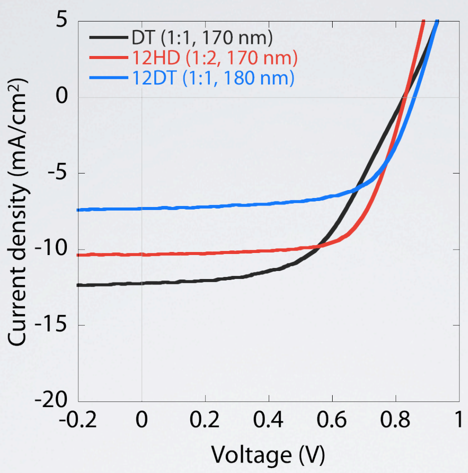


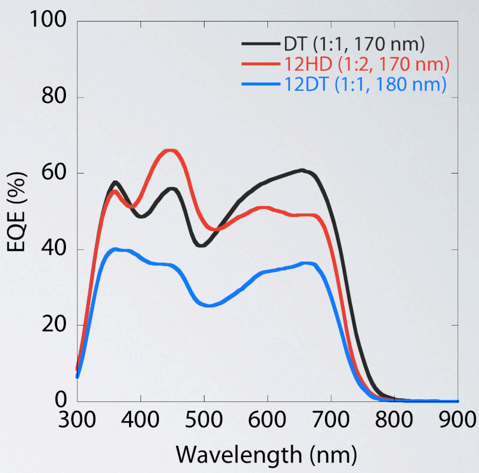
Polymer	Side chains (R^1R^2)	M_n (kDa)	PDI	solubility
PNNT-12HD	C12, HD	36.0	2.5	$CHCl_3$, ~40ºC
PNNT-12DT	C12, DT	46.1	3.0	$CHCl_3$, rt
PNNT-DT	H, DT	31.0	10	CB, DCB ~120ºC

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

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



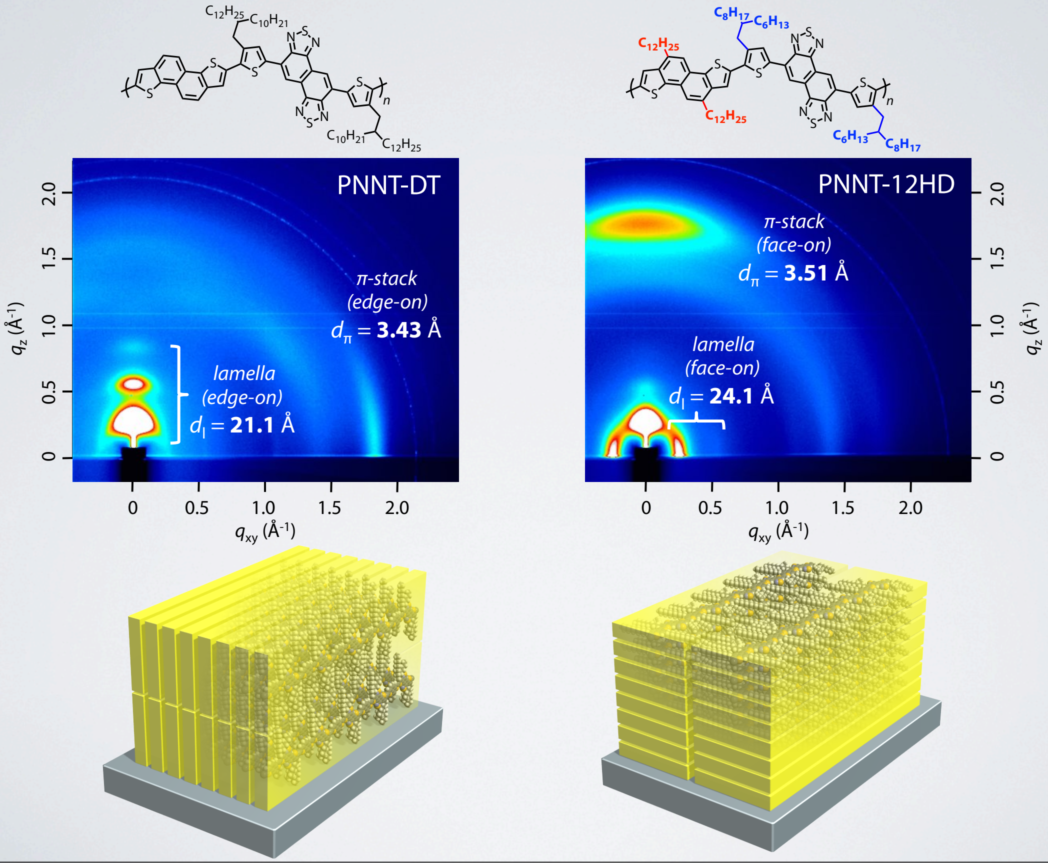




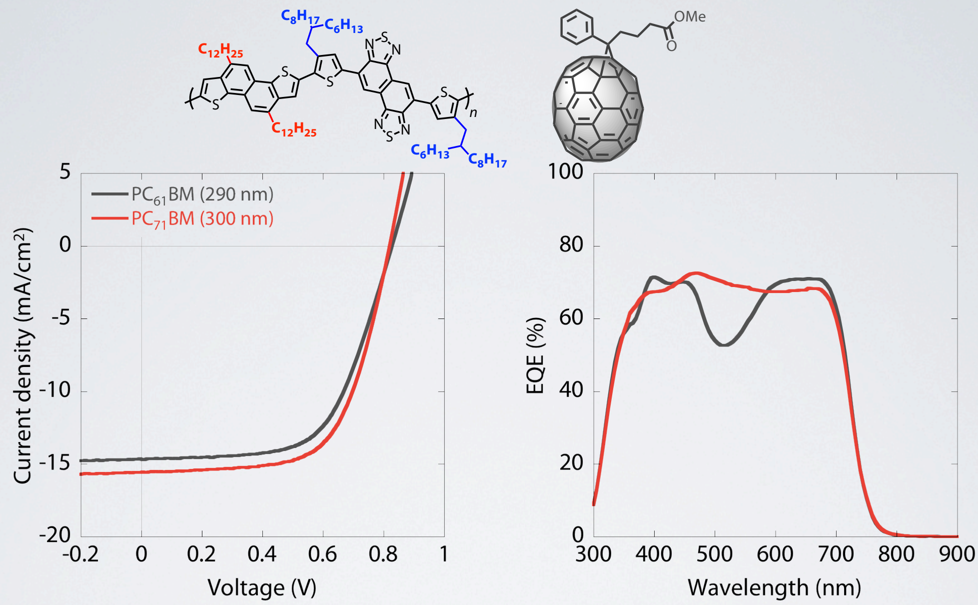
ITO/ PEDOT-PSS/ Polymer:$PC_{61}BM$ / LiF / Al

Polymer	p:n	thickness (nm)	J_{SC} (mA/cm²)	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

2D-GIXD PATTERNS



OPTIMIZED OPV PROPERTIES OF PNNT-12HD CELLS



ITO/ PEDOT-PSS/ <u>PNNT-12HD:PCBM (1:2)</u> / LiF / Al

PCBM	p:n	thickness (nm)	J_{SC} (mA/cm²)	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.

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.