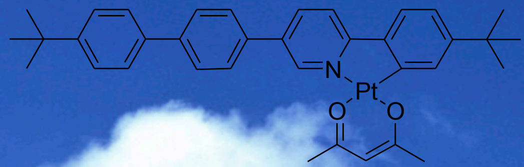
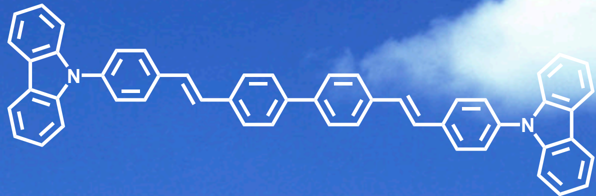
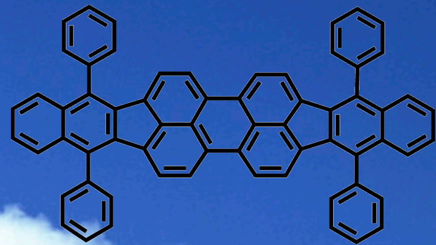
BEANS

BEANS: Bio Electoro-mechanical Autonomous Nano Systems

NEDO

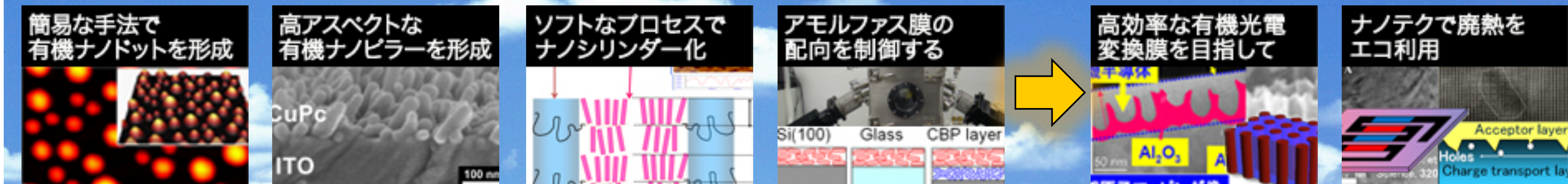






有機ナノ構造制御による飛躍的な光電子物性の発現

(I) 高効率有機EL素子
(II) 高効率有機太陽電池
(III) 高性能有機熱電素子

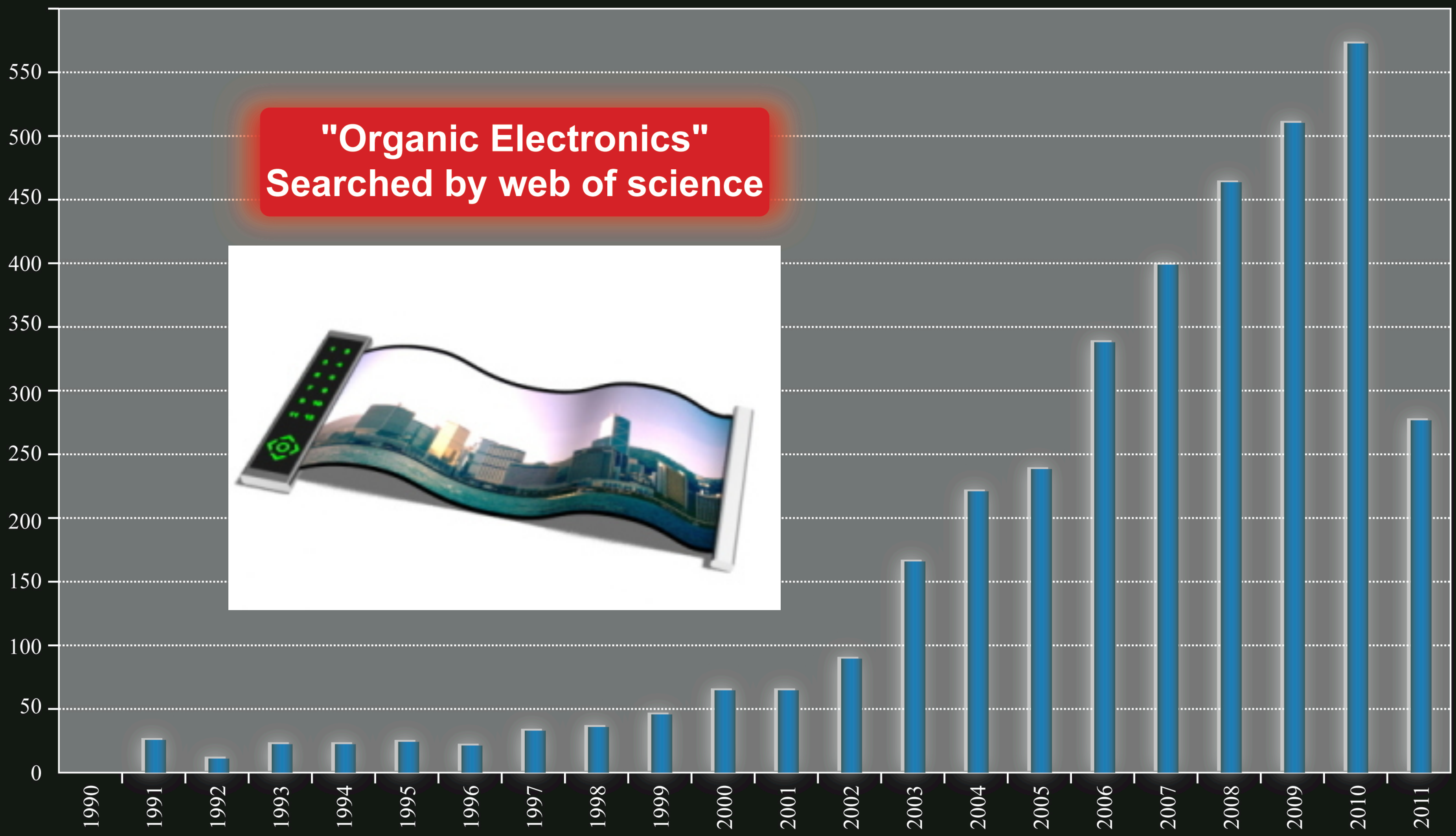


九州大学未来化学創造センター
Life Beans 九州

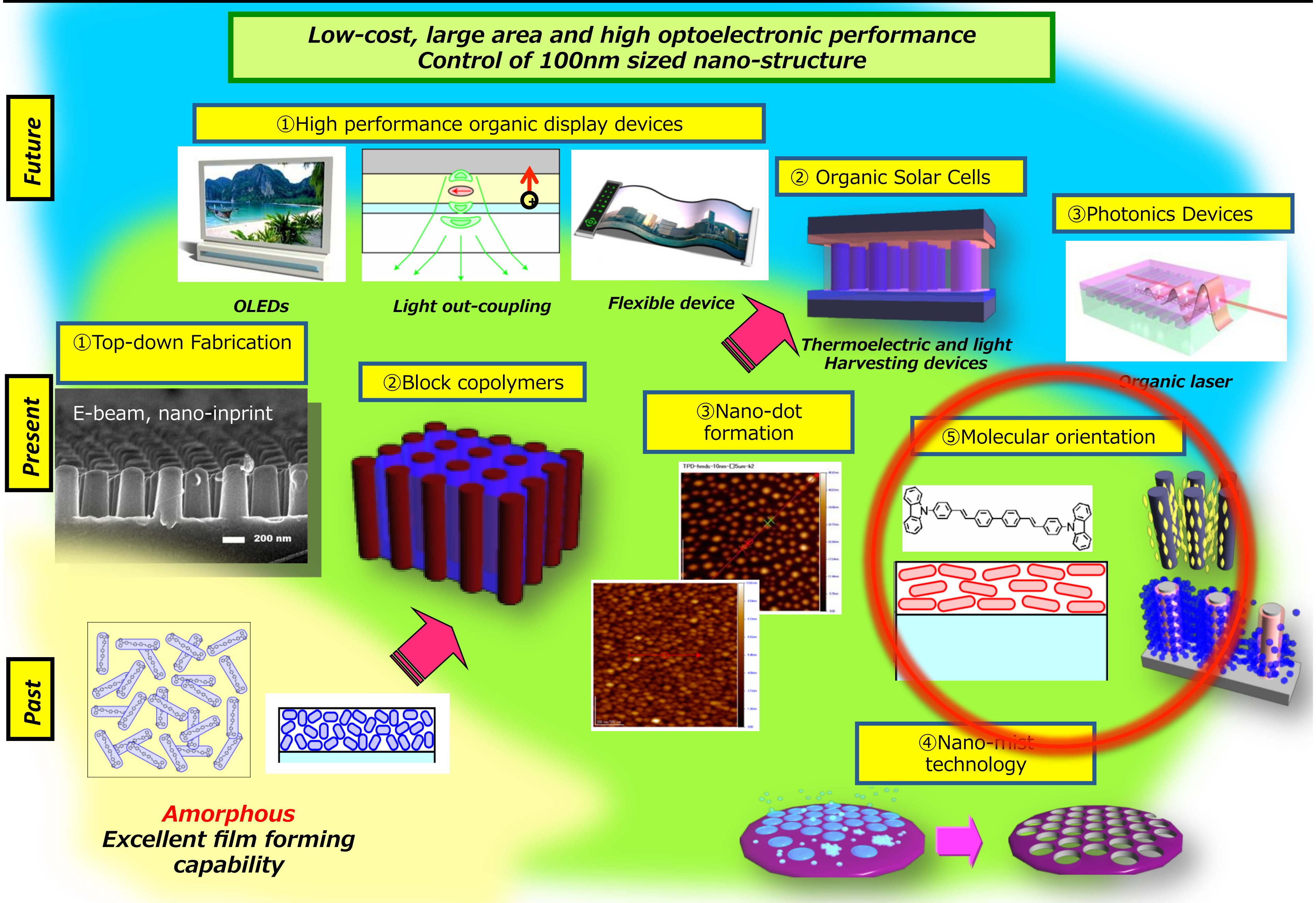
安達千波矢・種田将嗣・原田健太郎・平出雅哉


有機半導体エレクトロニクスの工業化へ向かって
Gen-1
Gen-2
Gen-3
Gen-4
OPC
Organic photo-
conductor
Organic
Semiconductor
Conducting
Polymer
OLED Mobile
Flexible
Organic TV
有機EL
有機レーザー
有機太陽電池
有機熱電素子
有機FET
有機センサー
有機メモリー
集積化
OLED
Lighting
Flexible
Display
OSC
Bio Electronics
Organics provide unique abilities; high efficiency, flexible,
low-cost, low-temp fabrication, and high compatibility with bio-applications
1960
1990
2000
2010
2020

有機半導体エレクトロニクスの拡大



有機半導体エレクトロニクスにおけるナノ構造の重要性（有機デバイスへの応用）



（I）高効率有機EL素子へ

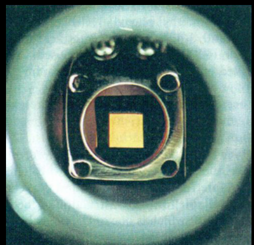
$$\eta_{ext} = \eta_{\text{int}}\eta_p = \underbrace{\gamma}_{\sim 100\%}\underbrace{\eta_r}_{\sim 100\%}\underbrace{\eta_{PL}}_{\sim 100\%}\underbrace{\eta_p}_{\sim 20\%}$$

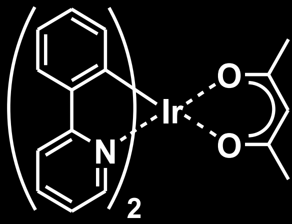
γ: e/h injection, transport and recom. eff.

η_r: exciton production efficiency

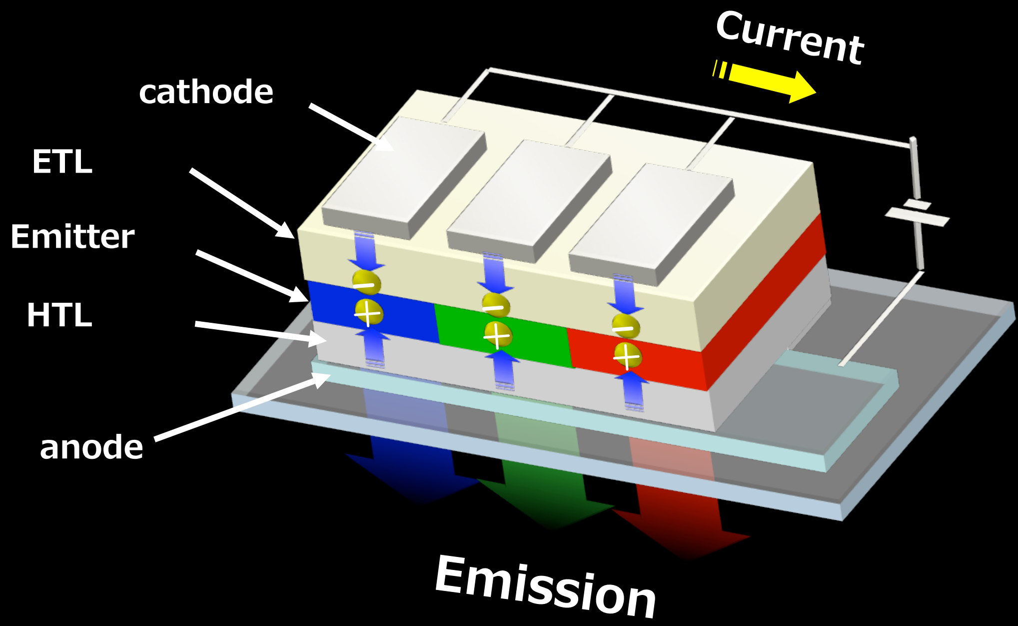
η_{PL}: PL quantum efficiency

η_p: light out-coupling efficiency





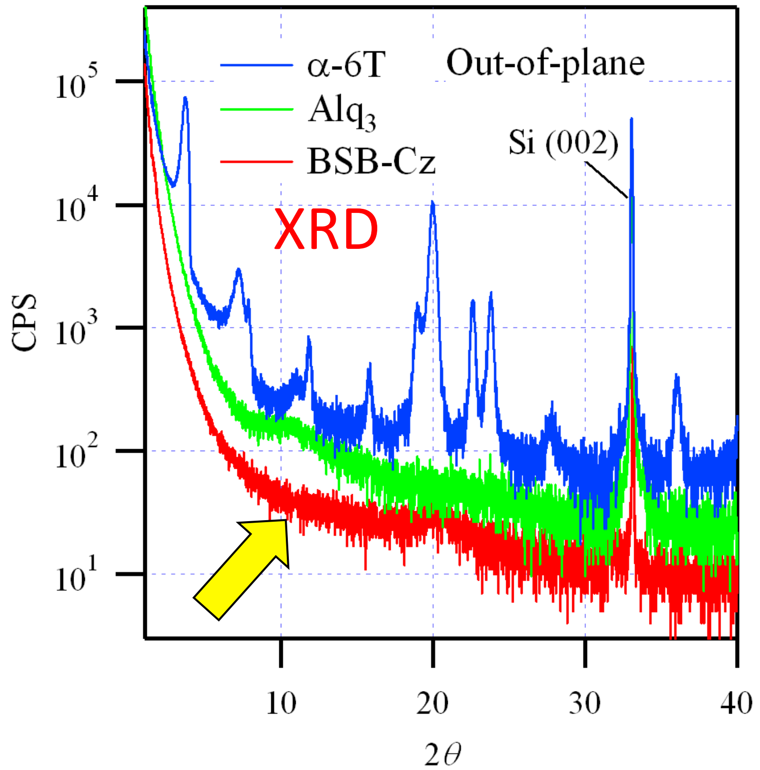
Internal EL efficiency
~100%

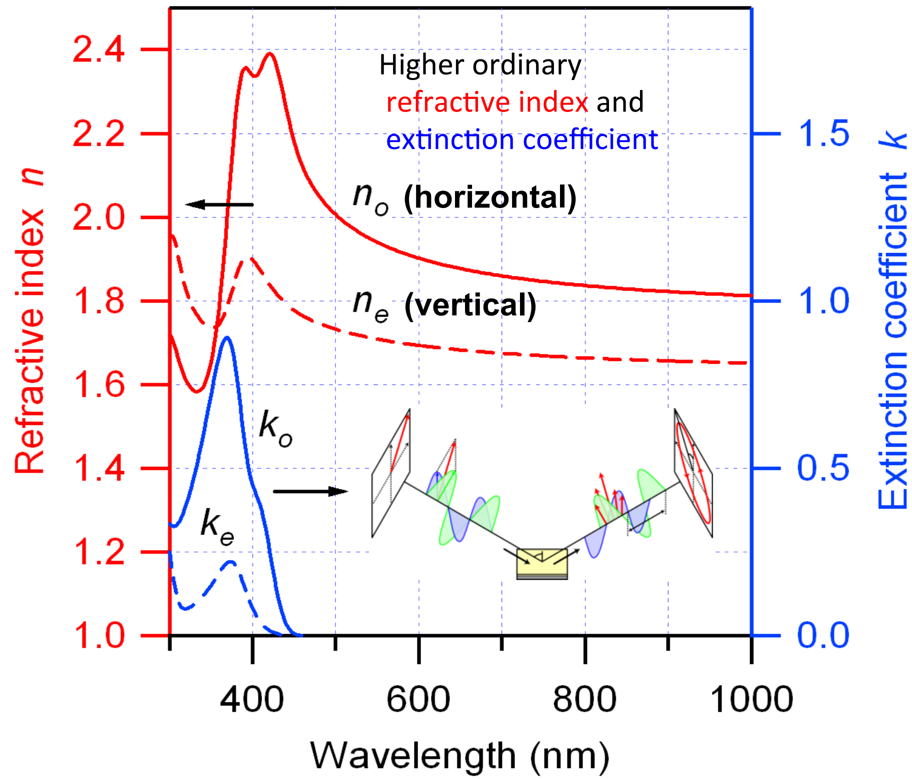


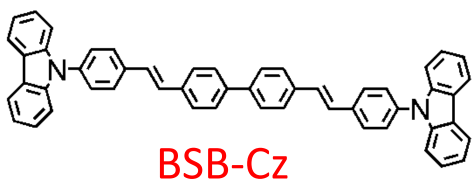
究極の高性能化へ

- ✓ 分子配向による光取り出し効率の向上
- ✓ 駆動電圧の低下

分光エリプソメーターによる分子配向評価

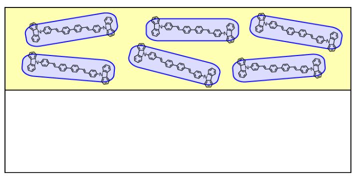


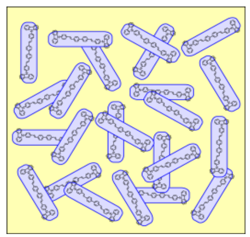


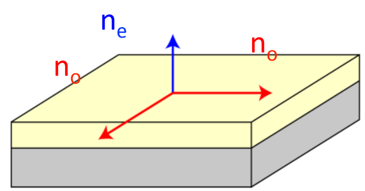


BSB-Cz

Lateral orientation
(Random in plane)

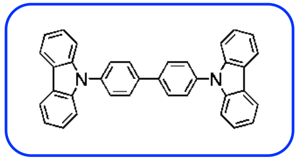


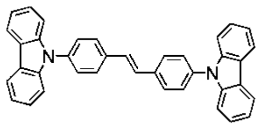


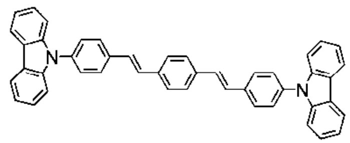


配向性を目指した分子設計

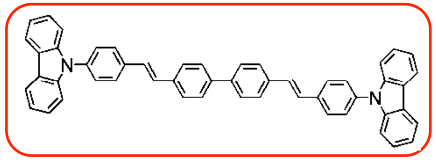
CBP



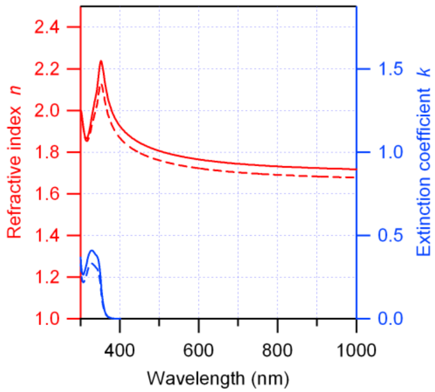


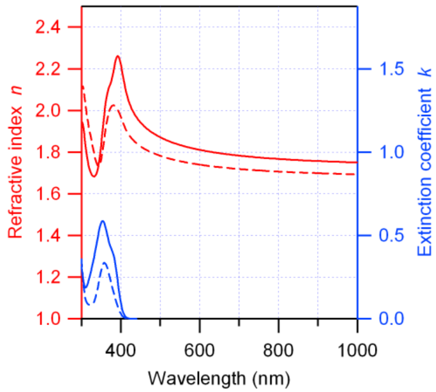


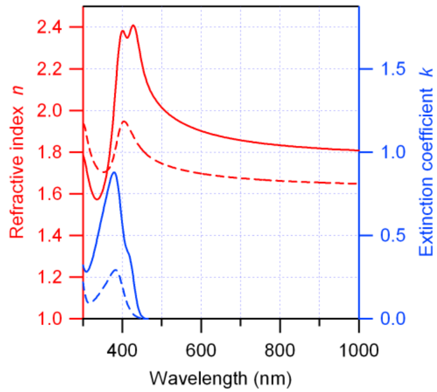
BSB-Cz

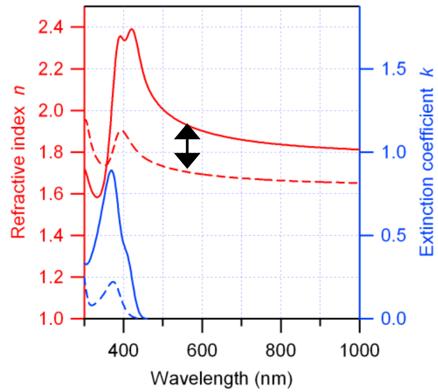


Length ~18Å | ~21Å | ~27Å | ~32Å









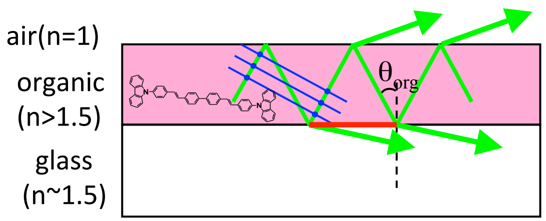
$\Delta n = 0.04$ | $\Delta n = 0.08$ | $\Delta n = 0.23$ | $\Delta n = 0.23$

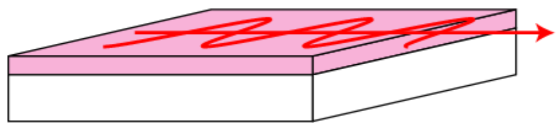
$\Delta n = n_0 - n_e$

Isotropic ——— Laterally oriented

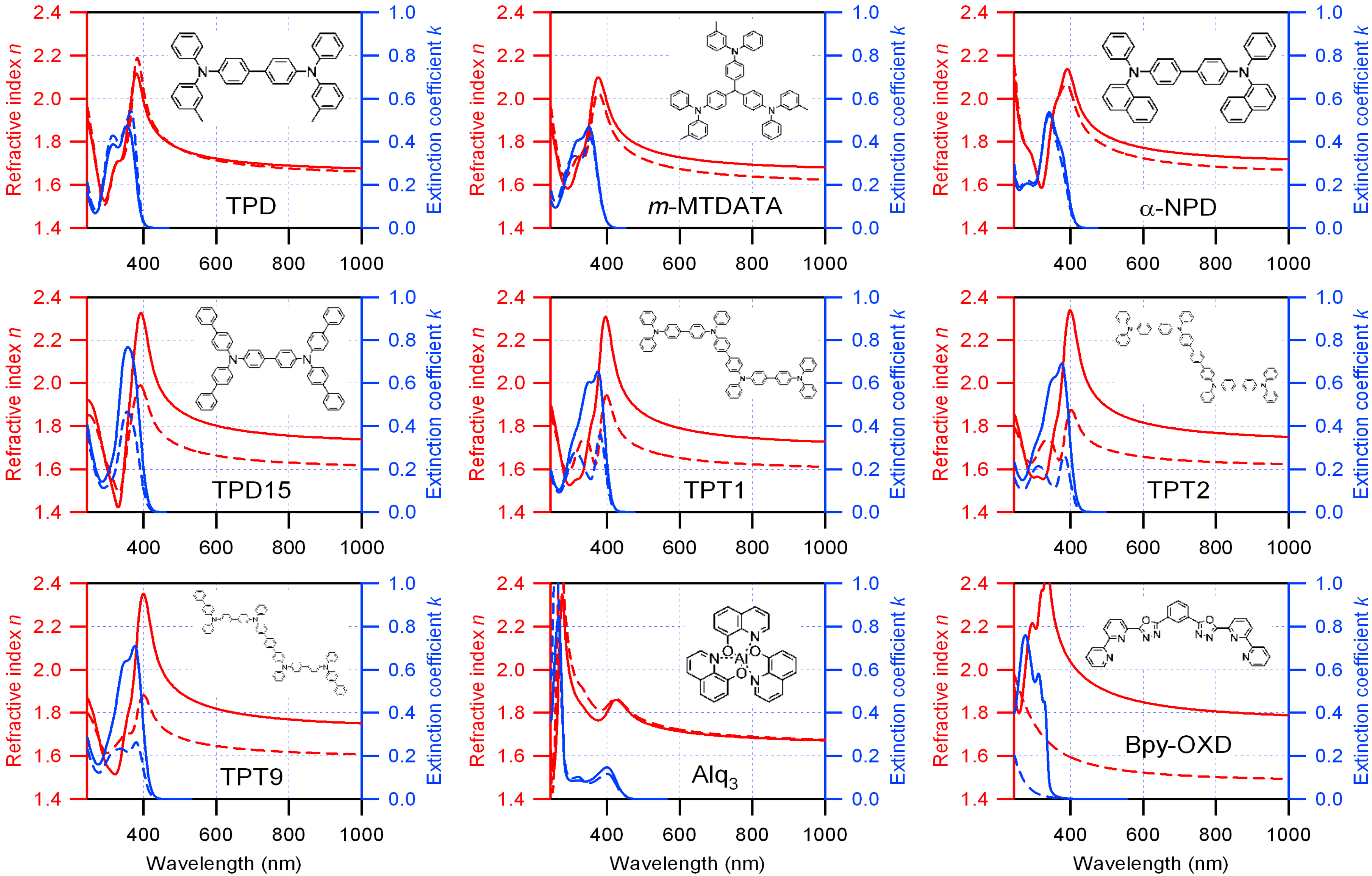
The longer molecular length, the larger optical anisotropy

TE mode



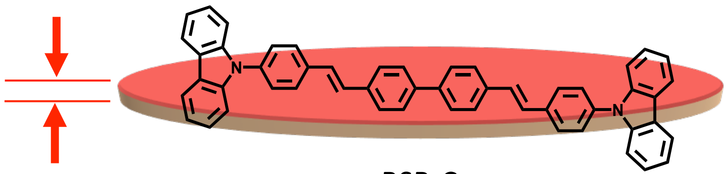


様々な分子の配向性



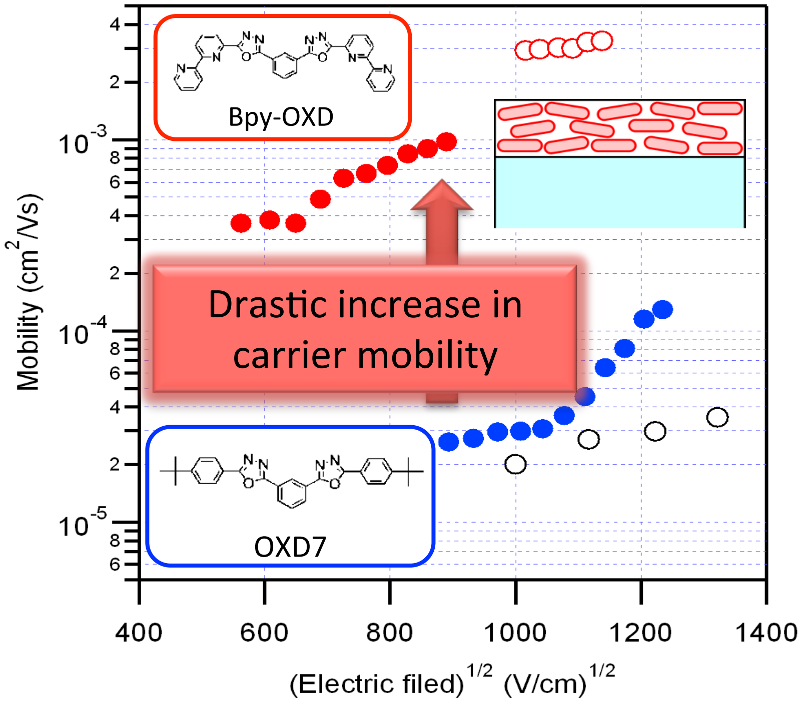
Large optical anisotropies were observed
in amorphous films of long or planar molecules.

分子配向性によるデバイス特性の向上



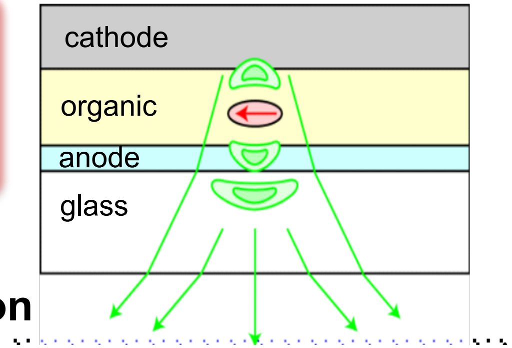
BSB-Cz

Flat and rod-like shaped molecule

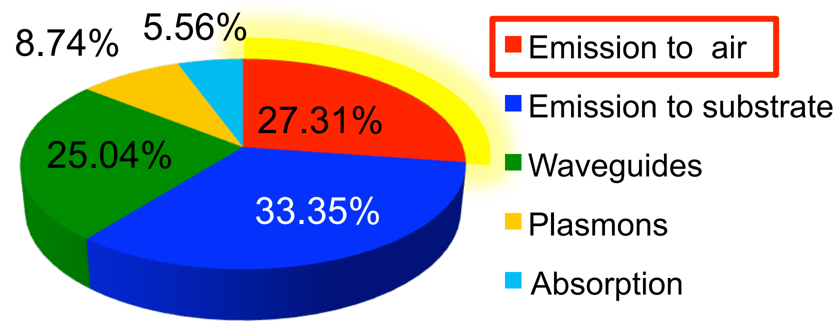


30% のエネルギー変換効率の向上

Couple-out efficiency
Random orientation : 17%
Parallel orientation : 27%

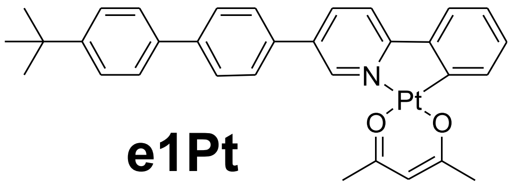


Parallel dipole orientation

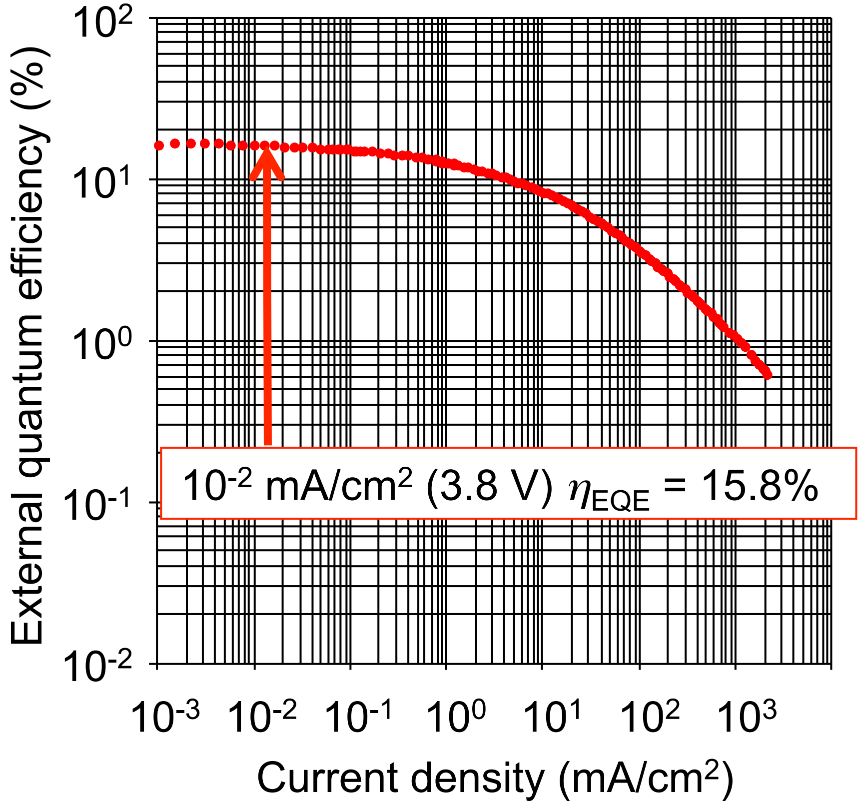


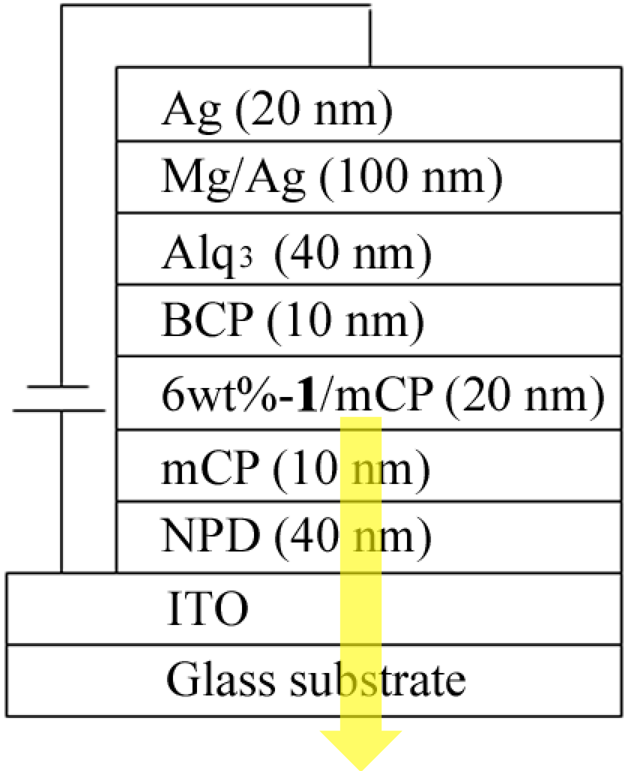
50%の光取り出し効率の向上

リン光デバイスによる高効率化へ　(APEX in press)



e1Pt





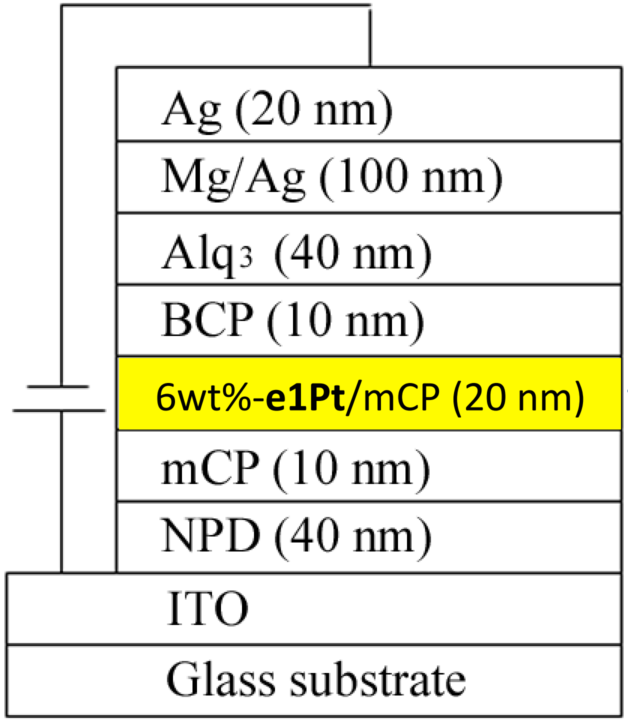
$$\eta_{EQE} = \Phi_{out} \times \eta_{\phi(int)}$$
$$= \gamma \times \eta_{ST} \times \Phi_{PL} \times \Phi_{out}$$

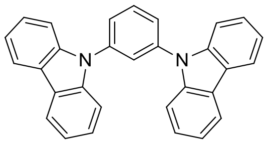
Φ_{out} = 32 %!

(Φ_{PL} = 50%, γ=100%, η_{ST} =100%)

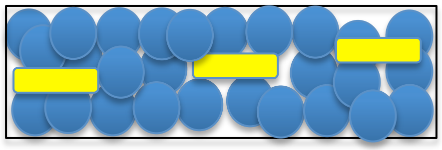
Horizontal Orientation of Linear-Shaped Platinum(II) Complex and Demonstrations of High Light Out-Coupling Efficiency in Organic Light Emitting Diodes
Appl. Phys. Exp. 4, 071602 (2010)
<u>Masatsugu Taneda</u>, Takuma Yasuda, and Chihaya Adachi

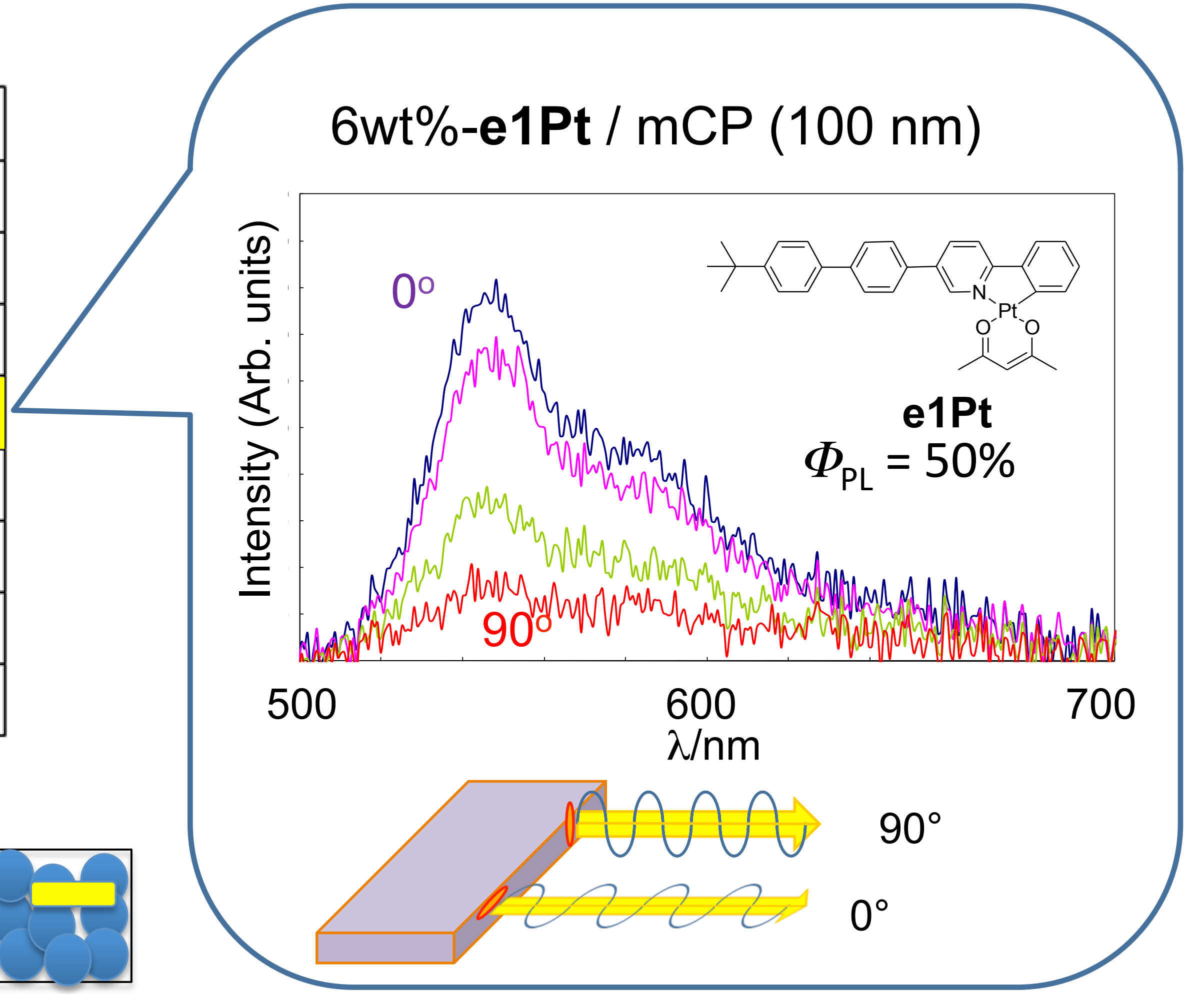
リン光デバイスによる高効率化の実現





mCP

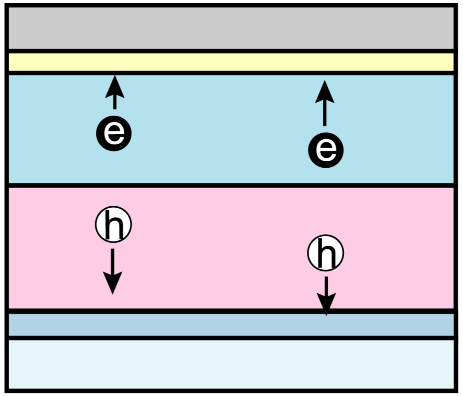
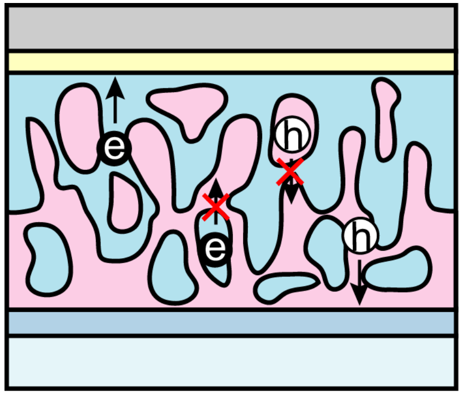
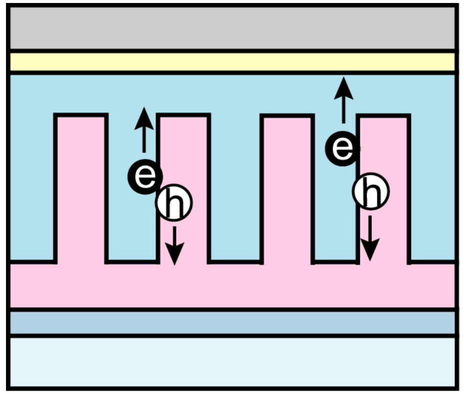




<u>ゲスト−ホスト系</u>

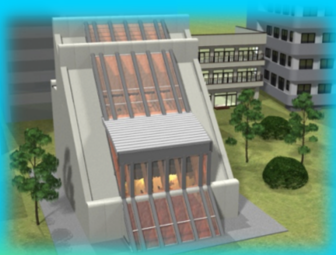
ゲスト分子は、ホストマトリックス中でも分子配向を示す

（II）有機太陽電池の高性能化へ

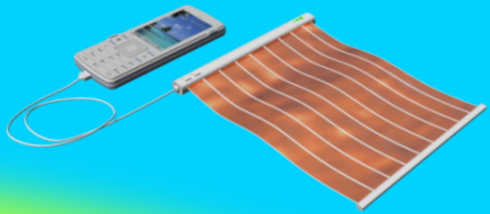
	Planer hetero structures	Bulk hetero structures	Nano-Pillar structures
	 [2] C. W. Tang *Appl. Phys. Lett.*, **48**, 183 (1986)	 [3] J. Xue et al., *Adv. Mater.* **17**, 66 (2005)	 [4] J. S. Kim et al., *Adv. Funct. Mater.* **20**, 1 (2010)
η_{A}	△	△	◎
η_{ED}	△	◎	◎
η_{CT}	◎	◎	◎
η_{CC}	◎	△	◎

Nano-pillar structures are ideal structure

有機ナノ構造体による有機太陽電池の高性能化へ



High performance Organic Solar Cells

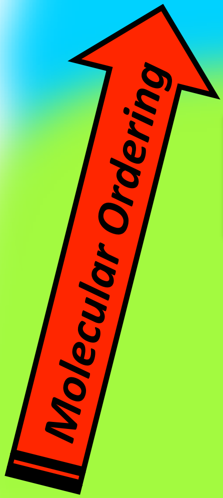


Advantage of Organic Solar Cells

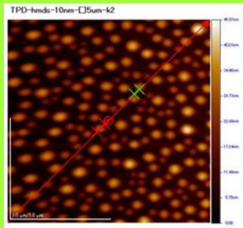
1) Low-cost: Organic Materials
2) Large Area and Flexible
3) Energy Saving for Production
3) Large Absorption Coefficient
4) Unlimited Molecular Design

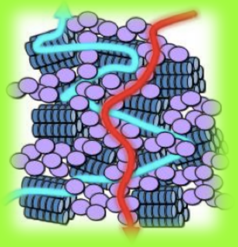
Disadvantage

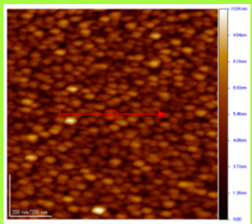
- Power Conversion Efficiency is limited. (Si based device >20%)



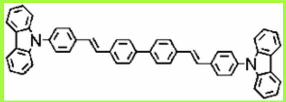
I) Control of Nano-sized morphology

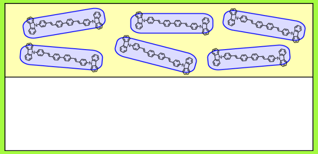


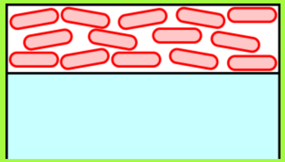




II) Control of Molecular orientation

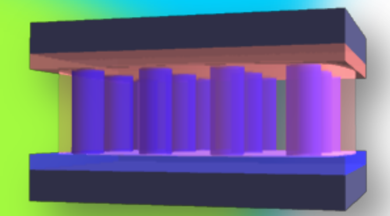




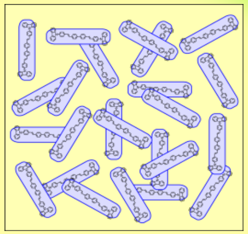


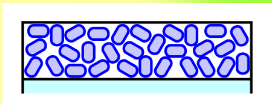
Control of amorphous morphology
Molecular orientation in amorphous films

III) Accurate preparation of nano-pillars



20nm sized diameter



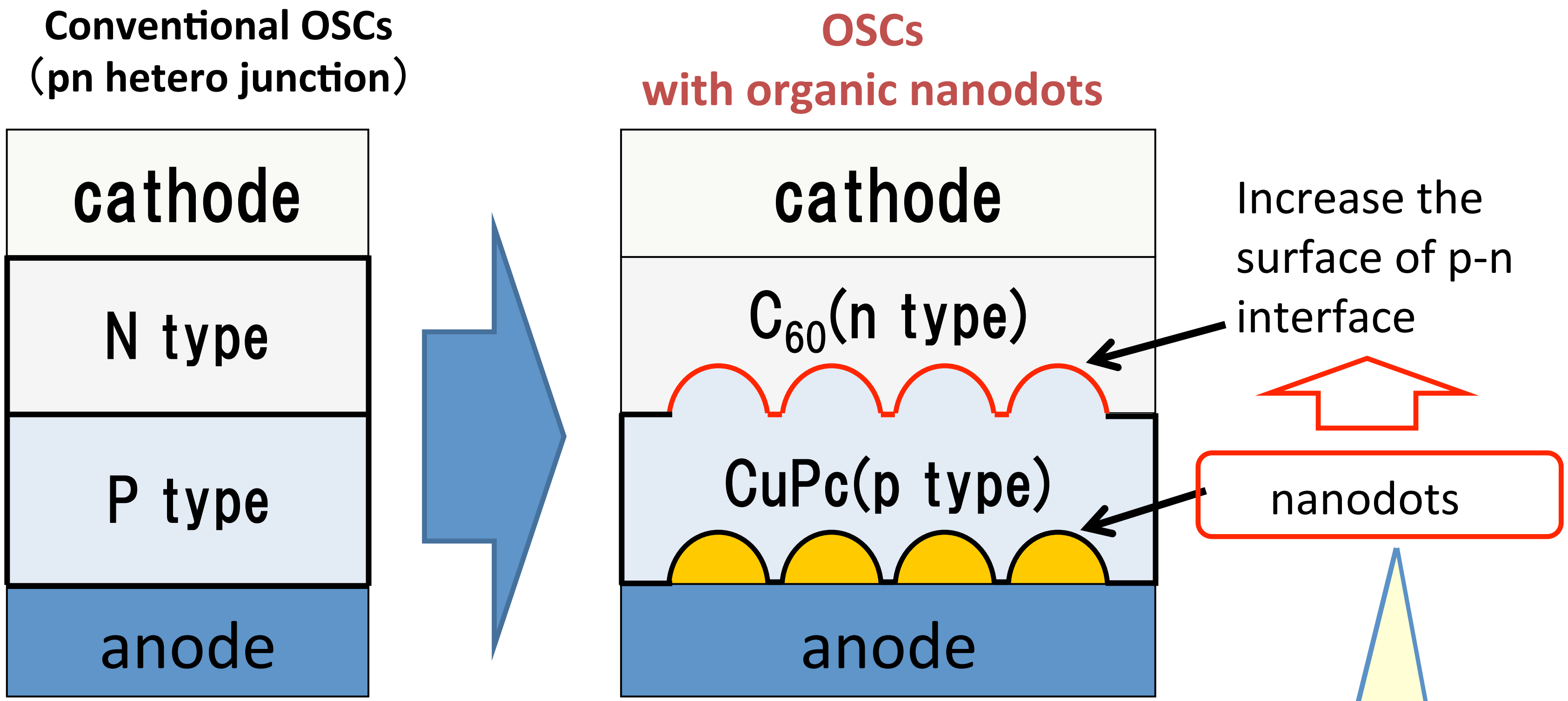


Amorphous

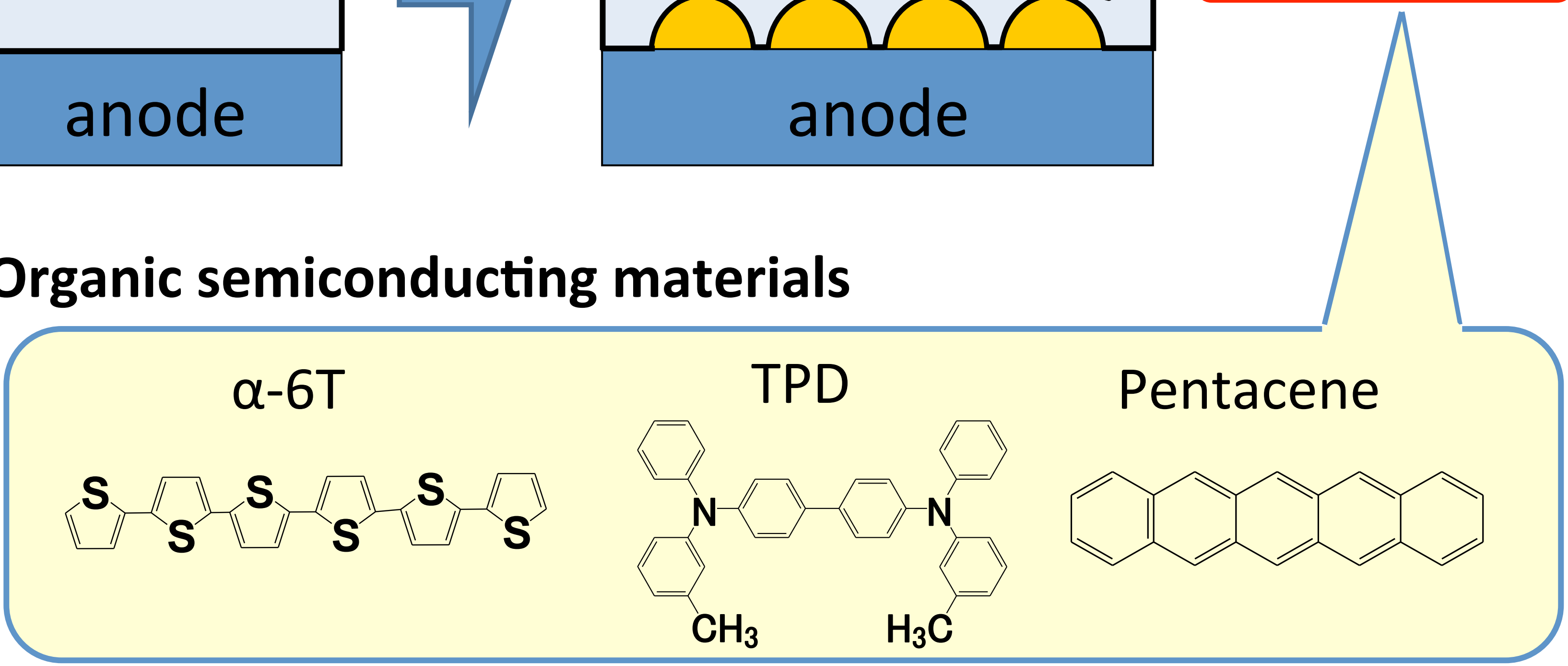
For realizing formation of pin-hole free thin films,
amorphous morphologies with multi-layer structures
with 100nm thick layers have been widely used.

(1) 有機ナノドット構造の導入
(2) 有機ナノピラー構造の導入
(3) 有機ナノグレイン制御
(4) 分子配向性によるOSC特性の向上

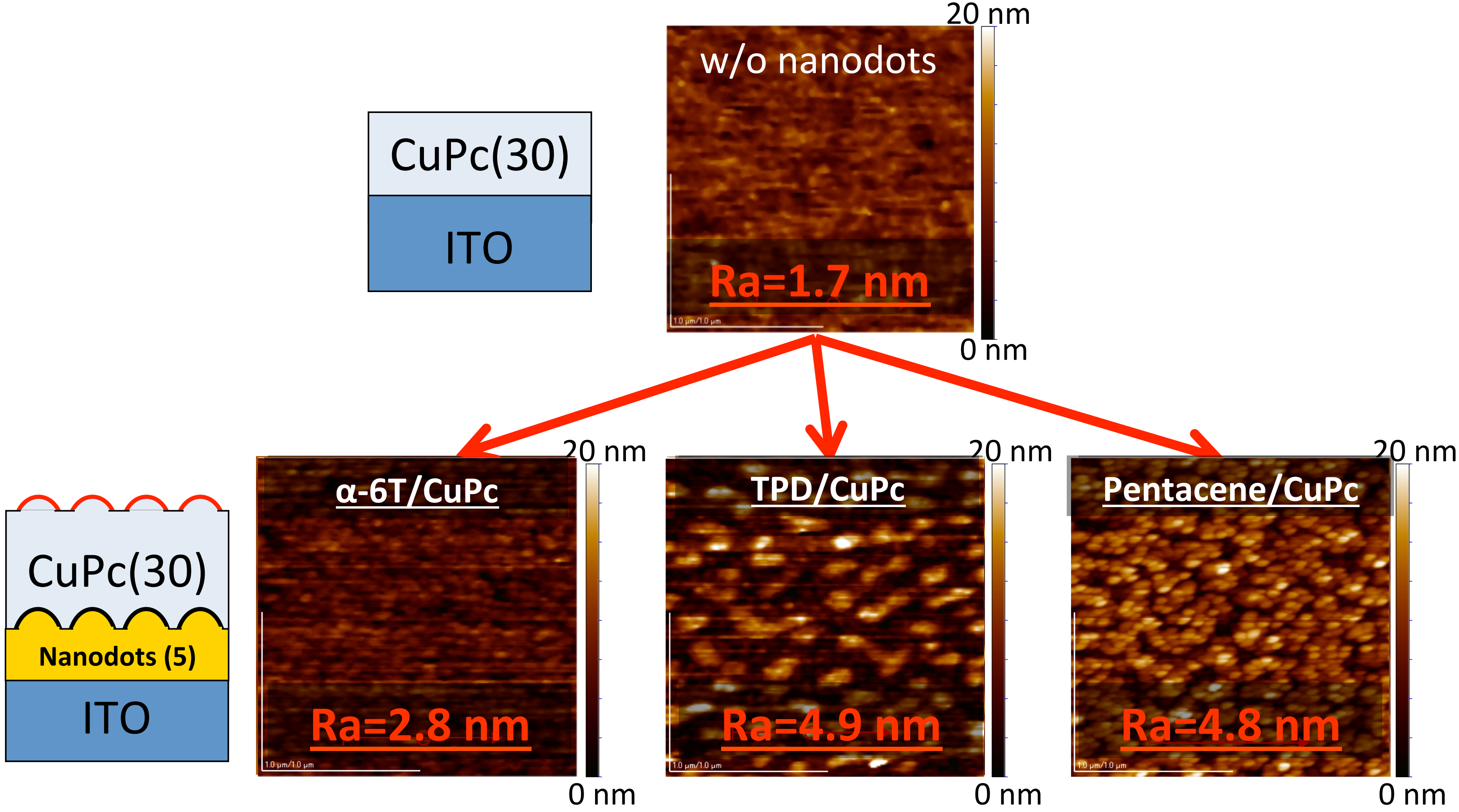
（1）有機ナノドット構造の導入



Organic semiconducting materials



有機ナノドット構造によるデバイス特性の向上

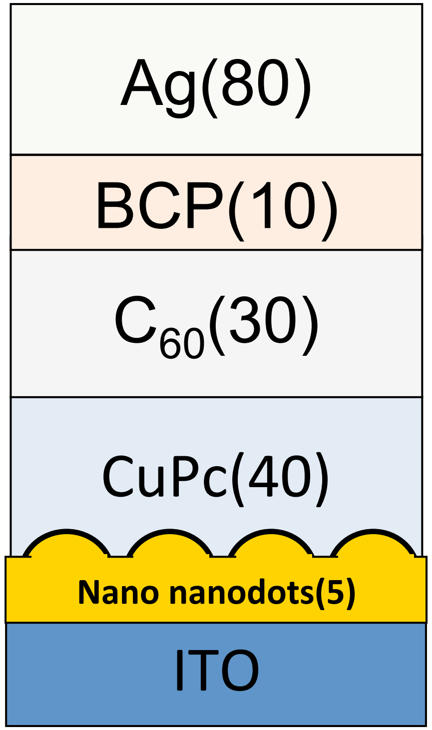


The surface of p-n interface was greatly increased

(Ra： α-6T＜TPD≒Pentacene)

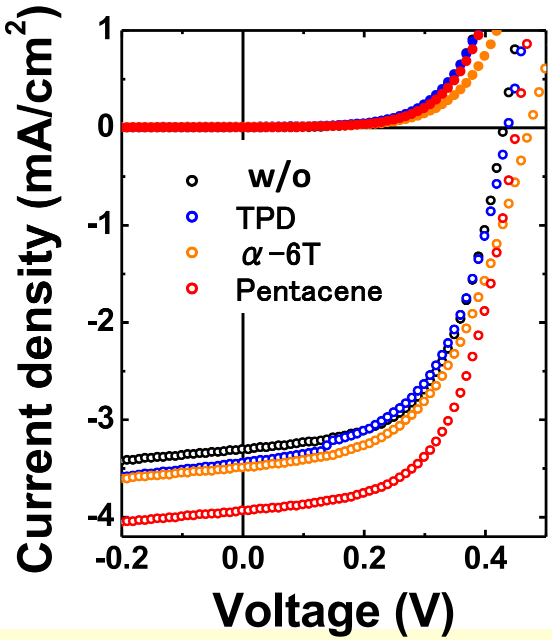
有機ナノドット構造によるデバイス特性の向上

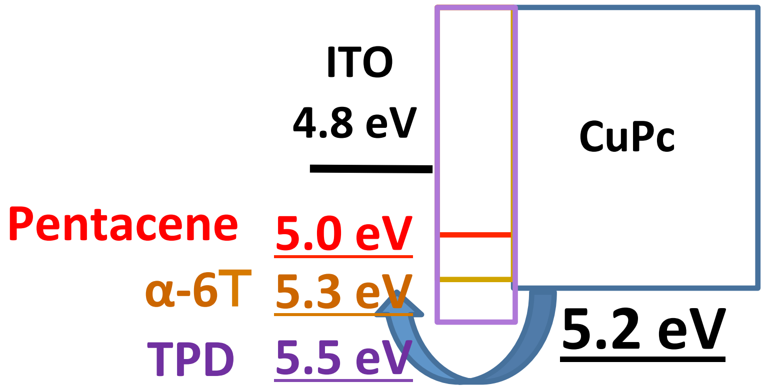
Device structure



Characteristics

	w/o	α-6T	TPD	Pentacene
Efficiency (η)	0.81 %	0.85 % ⇧	0.79% ⇩	1.04 % ⇧ (20%UP)

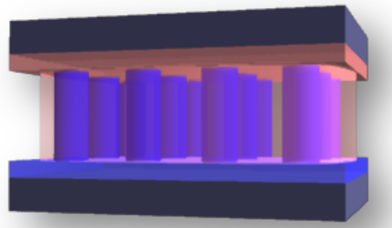




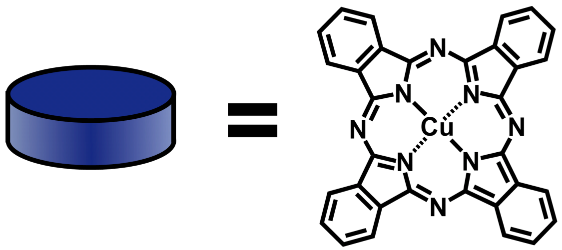
Conversion efficiency has improved by 20% by Pentacene nanodots

(η: TPD＜α-6T＜Pentacene)⇒Energy matching is important

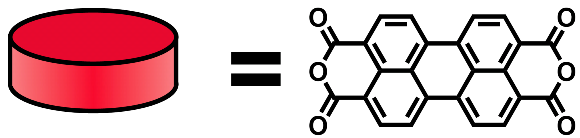
(2) 有機ナノピラー構造の導入



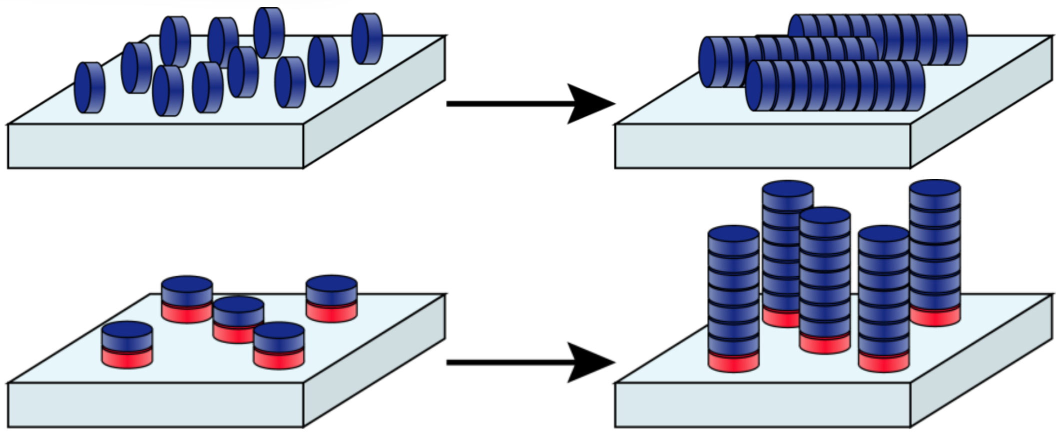
Control of 20nm sized diameter



CuPc (Donor material)

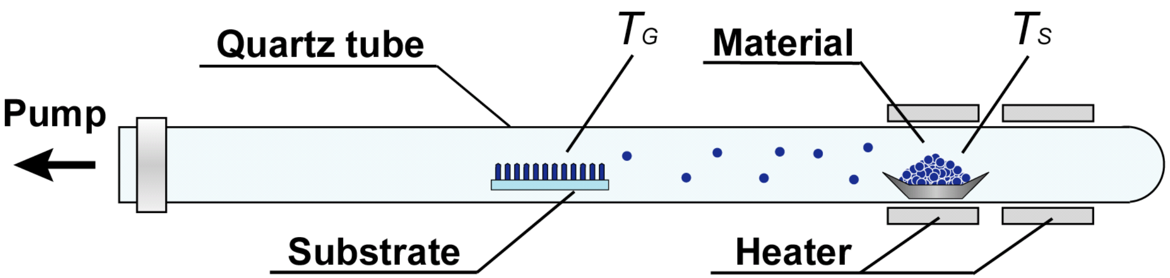


PTCDA (Template material)



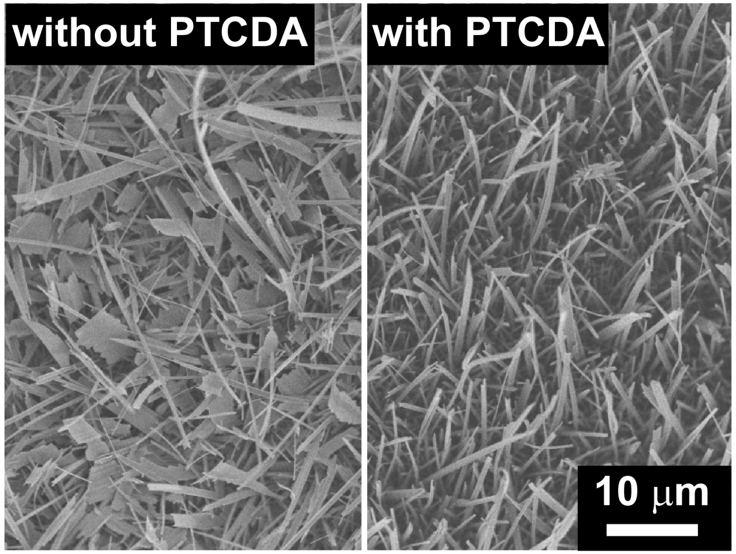
Seeds layer formation

Crystal growth

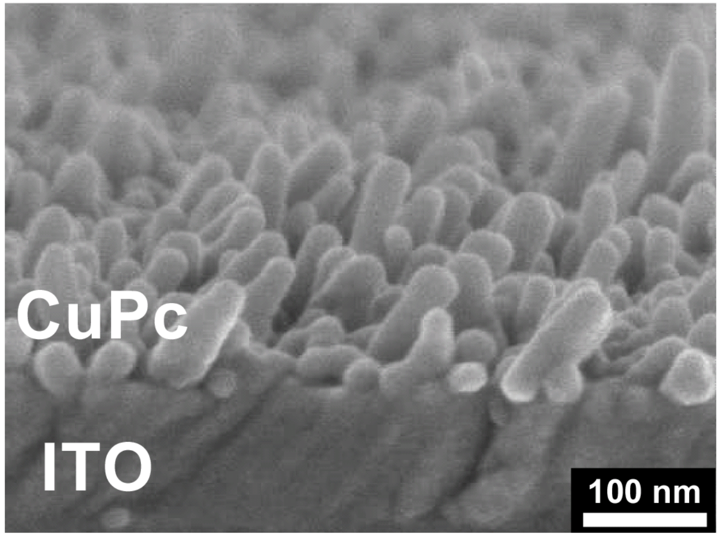


Orientation controlled CuPc molecules were used as seeds layer.

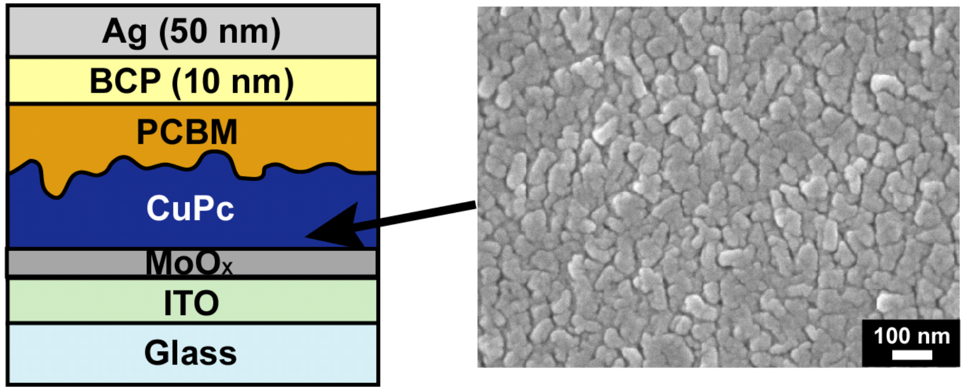
(2) Artificial Control of Organic Nano-Pillars



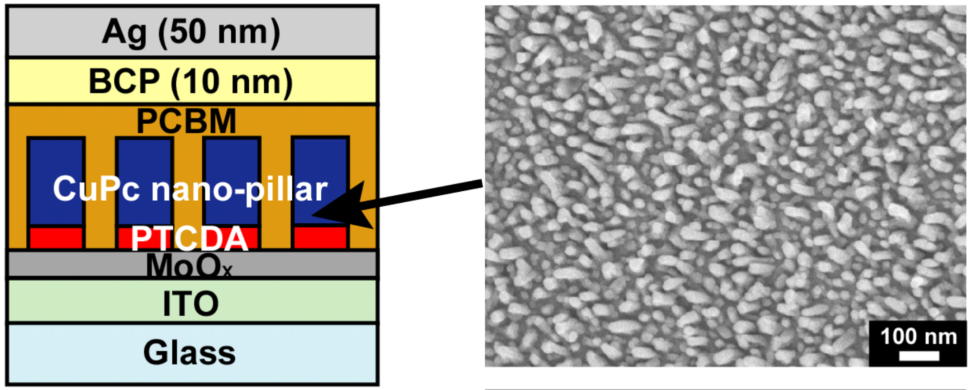
T_S=370℃, T_G=215℃



w/o PTCDA

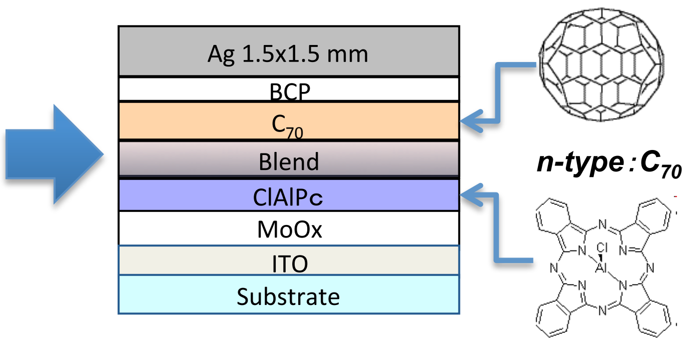


with PTCDA

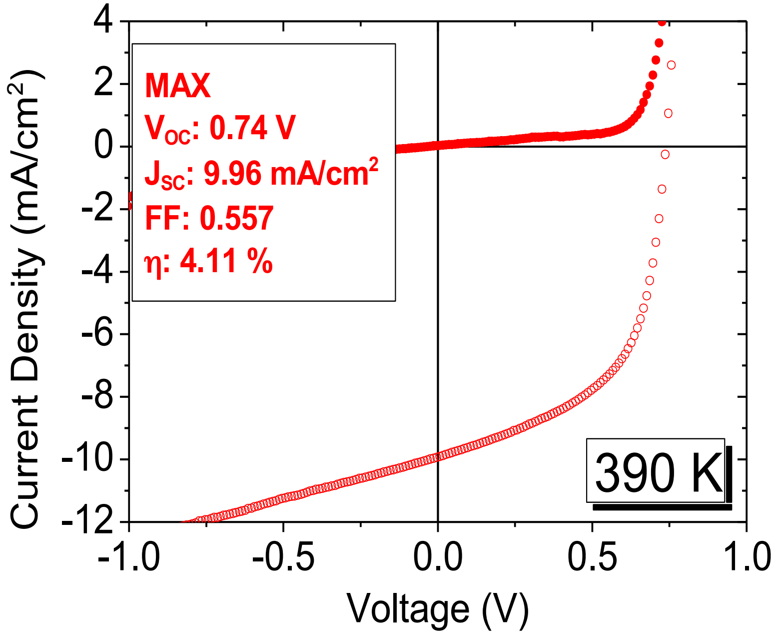


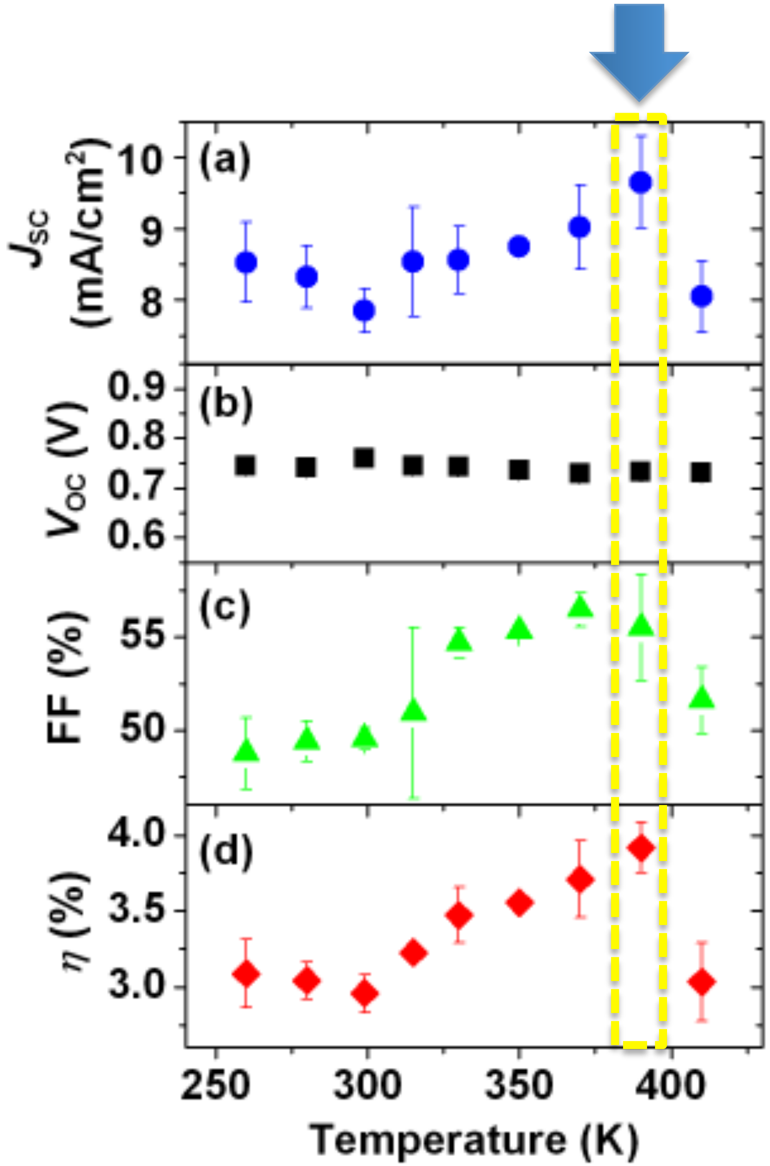
<u>Masaya Hirade</u>, Hajime Nakanotani, Masayuki Yahiro and Chihaya Adachi
Appl. Mat. Int. 3, 80-83, (2011)
Selected in Top 10 Most Read Articles for Q1 2011

(3) 有機ナノグレイン制御



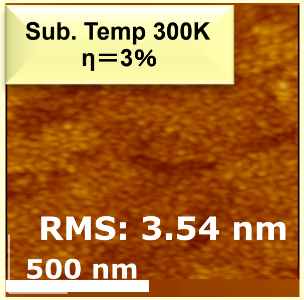
Device structure

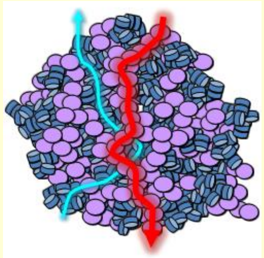


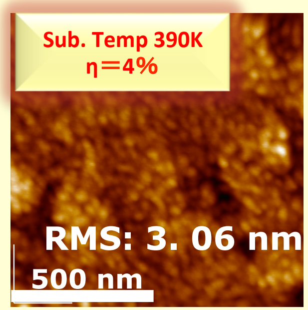


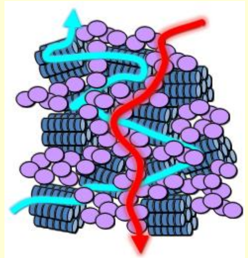
Appl. Phys. Exp. 3, 121602 (2010)
Kentaro Harada, Tomohiko Edura, and Chihaya Adachi

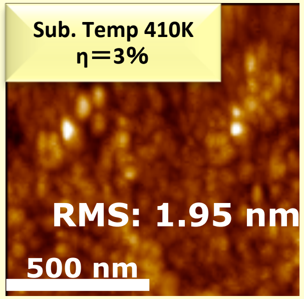
Control of Grain Size, Molecular Stacking and Orientation

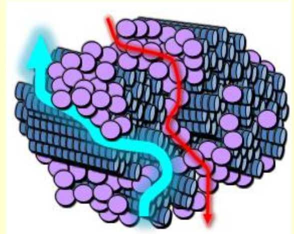




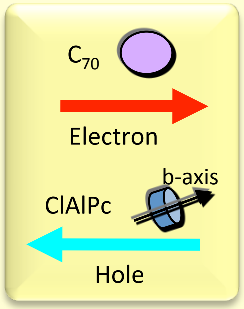


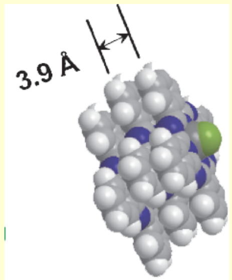


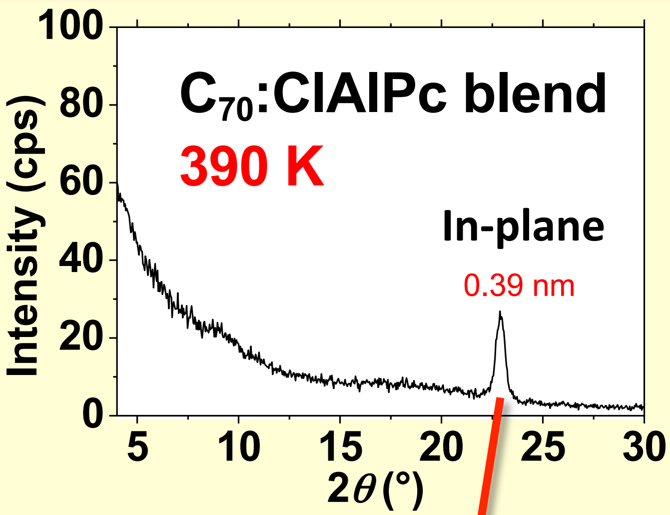


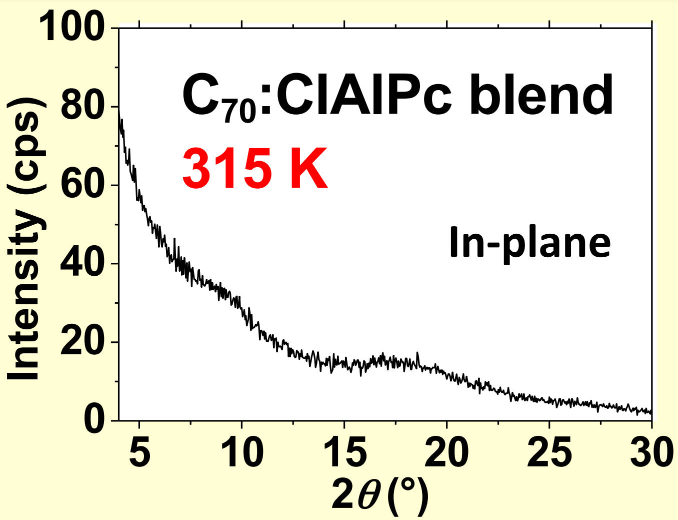


Large surface area

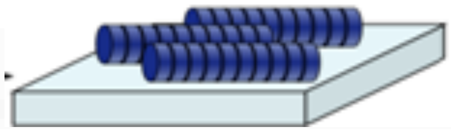




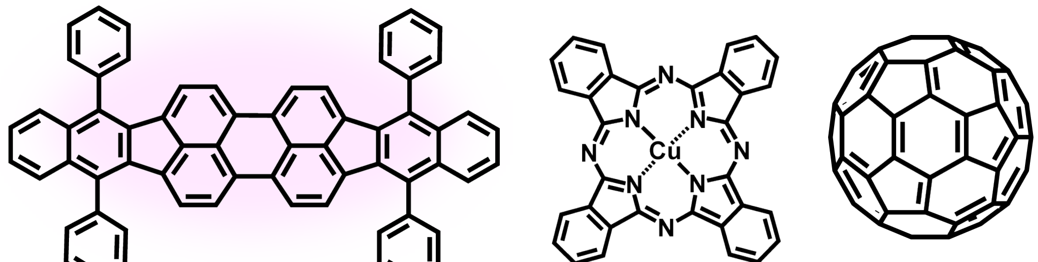




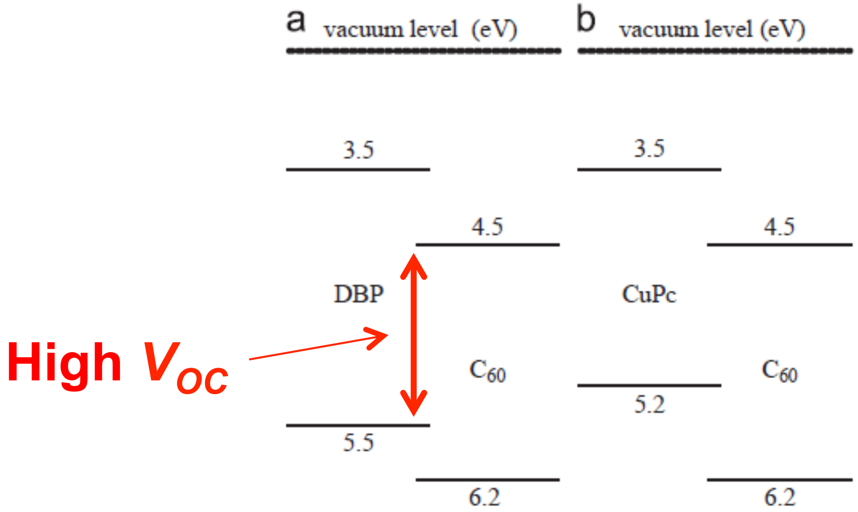
ClAlPc aligns to parallel orientation by π Stacking



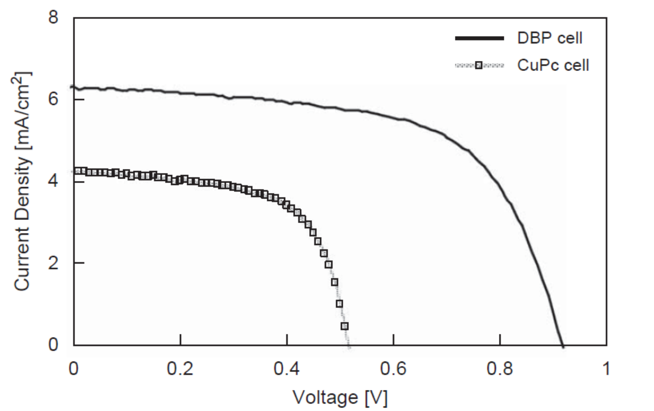
(4) 分子配向によるOSC特性の向上

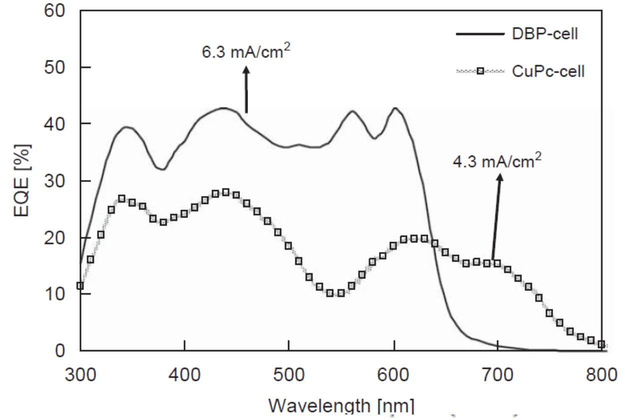


DBP CuPc C60



ITO/DBP or CuPc/C60/BCP/Al

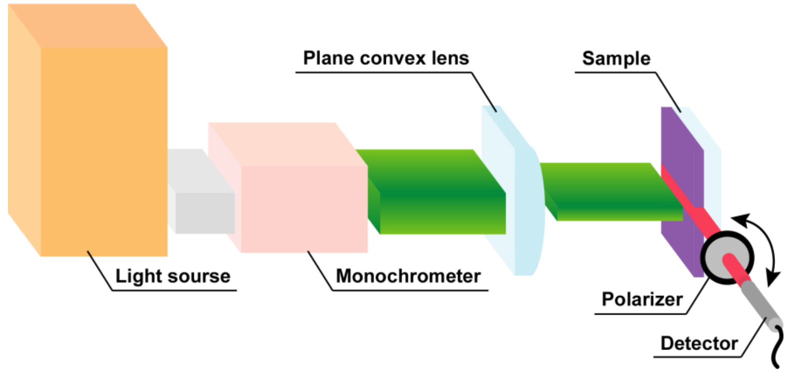


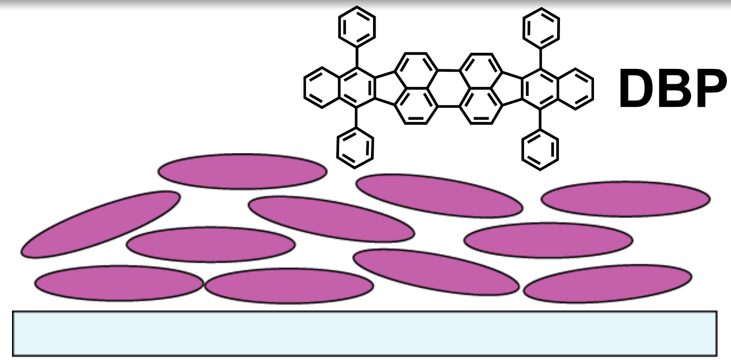


ED materials	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	Conversion efficiency (%)	Active cell area (cm^2)
DBP	6.3	0.92	0.62	3.6	0.033
CuPc	4.3	0.51	0.63	1.4	0.026
DBP(L)	5.7	0.91	0.51	2.6	1.6

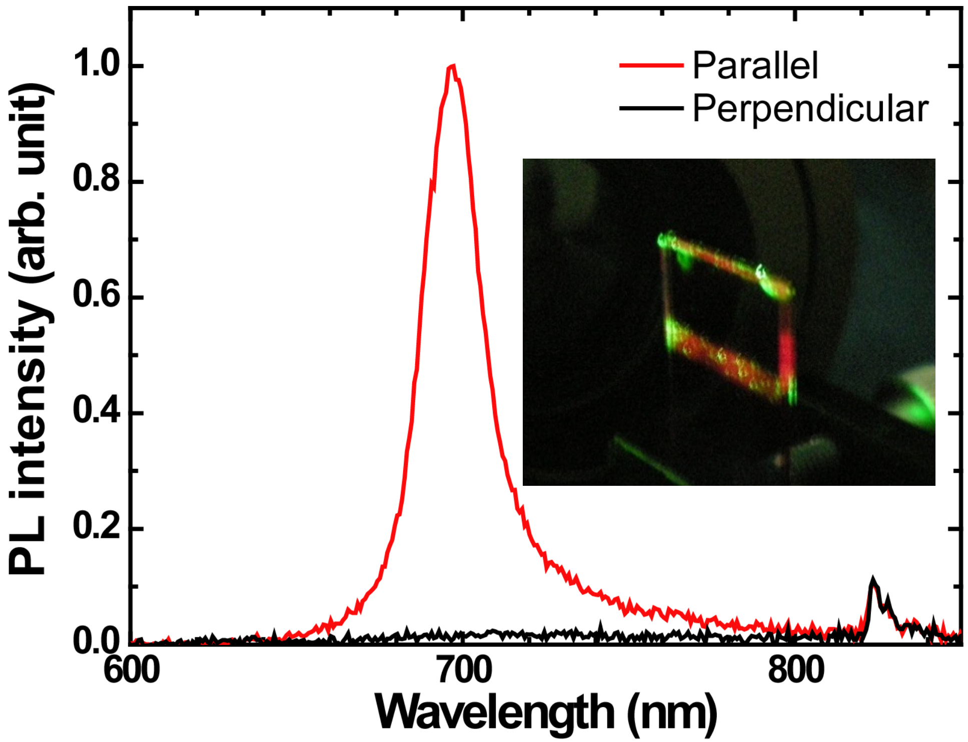
D. Fujishima et al. *Sol. Energy Mater. Solar Cells* **93**, 1029 (2009)

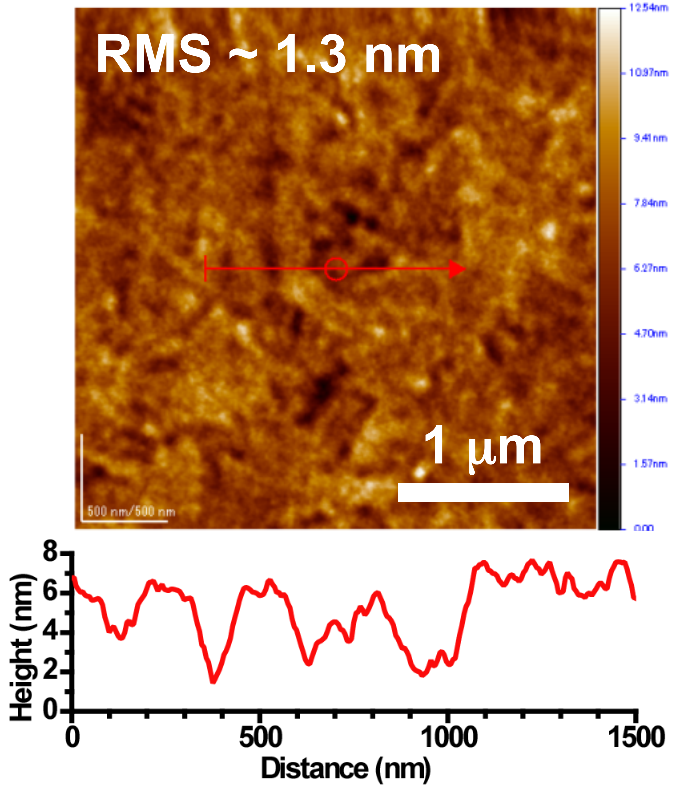
(4) 分子配向によるOSC特性の向上



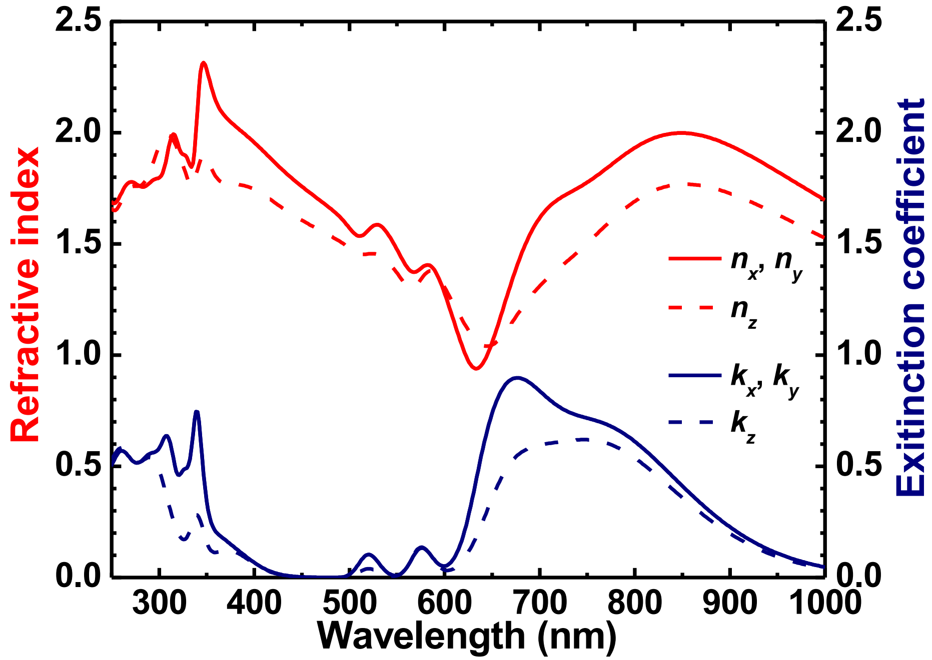


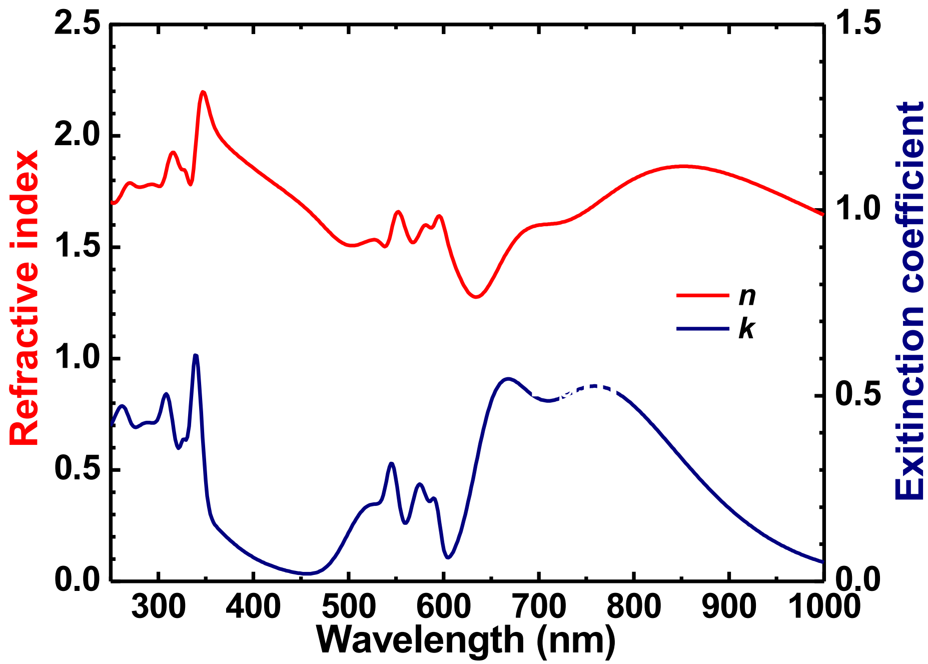
Intense emission form parallel direction





(4) 分子配向によるOSC特性の向上





<u>DBP film @ RT-depo.</u>

- ✓ Amorphous
- ✓ Optical anisotropy

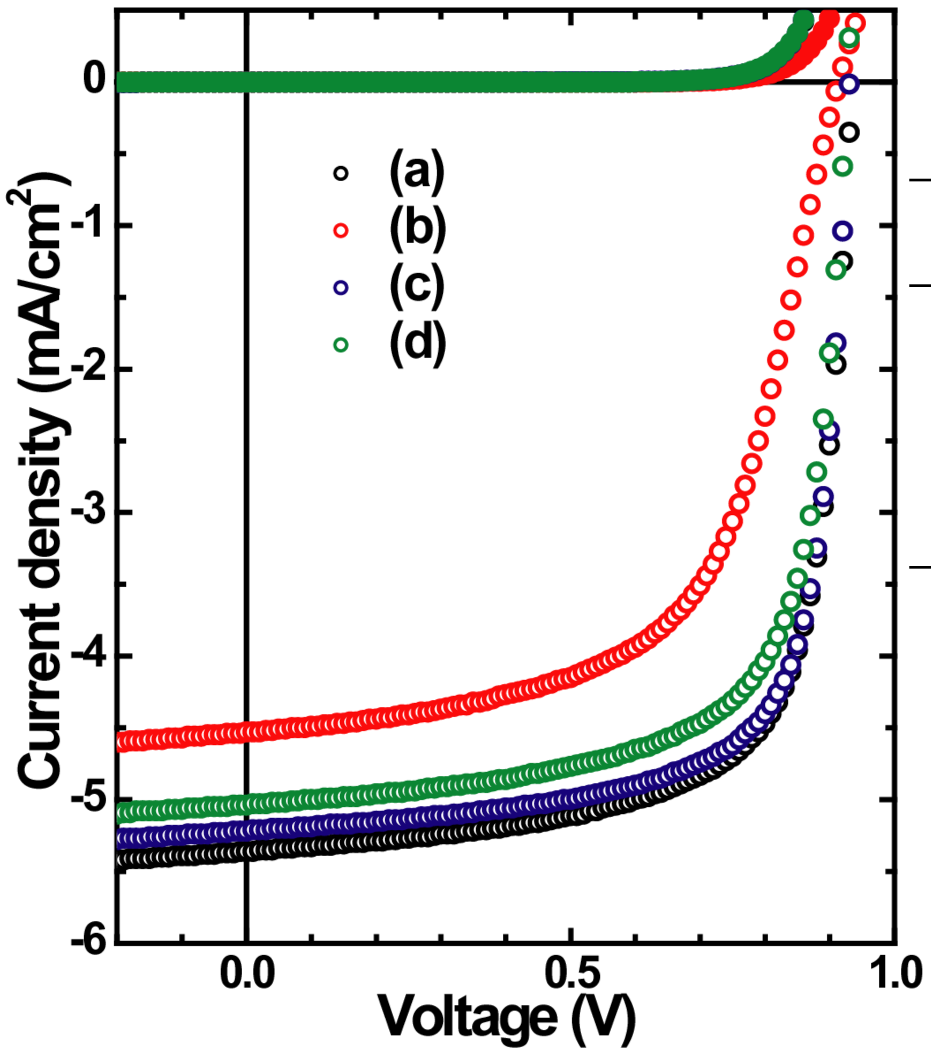
<u>DBP film @ 110 C</u>

- ✓ Amorphous
- ✓ Optically isotropic

Analyzed by Mr. Matsuda @ J. A. Woollam

(4) 分子配向によるOSC特性の向上

a) ITO/ o-DBP (20 nm) /C60 (50 nm)/BCP (10 nm)/Al (100 nm)
b) ITO/ r-DBP (5 nm)/o-DBP (15 nm) /C60 (50 nm)/BCP (10 nm)/Al (100 nm)
c) ITO/PEDOT/ o-DBP (20 nm) /C60 (50 nm)/BCP (10 nm)/Al (100 nm)
d) ITO/PEDOT/r-DBP (5 nm)/o-DBP (15 nm)/C60 (50 nm)/BCP (10 nm)/Al (100 nm)



O-DBP : Deposition at RT
R-DBP : Deposition at 110C

	J_{SC} mA/cm²	V_{OC} V	η %	FF	R_S Ωcm²	R_P Ωcm²
a	-5.36	0.94	3.58	0.71	0.080	1400
b	-4.53	0.92	2.47	0.60	38	1100
c	-5.22	0.94	3.52	0.72	0.086	1700
d	-4.04	0.93	3.25	0.70	0.059	1300

- ✓ Series resistance (R_S) was increased by using r-DBP at ITO interface.
- Face-on orientation decreases charge collection barrier.
- Carrier mobility enhancement of DBP layer

有機光エレクトロニクスが切り開く近未来

Acknowledgement

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