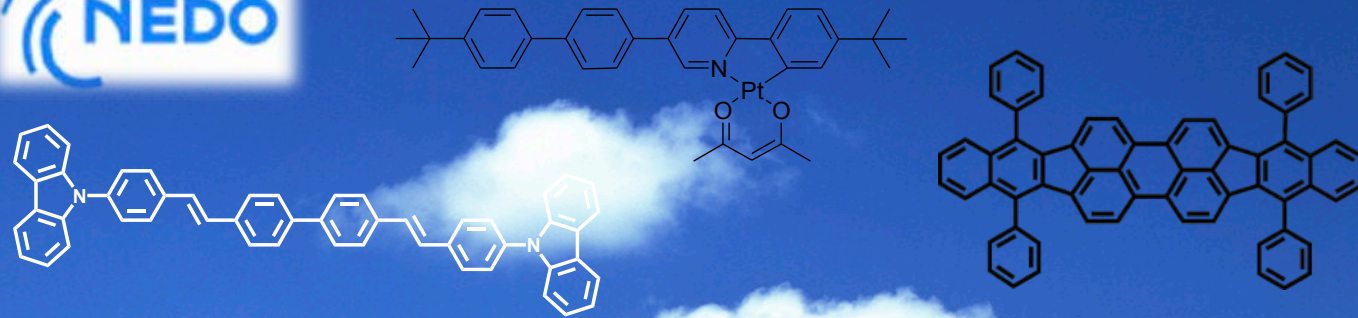




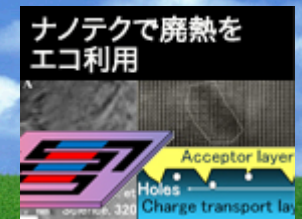
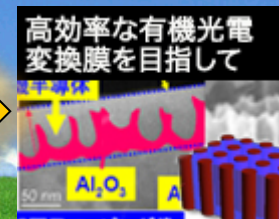
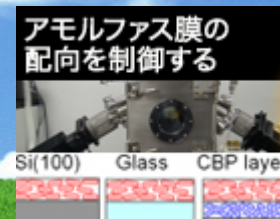
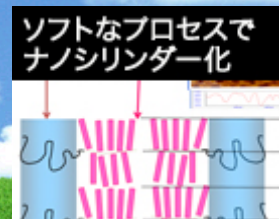
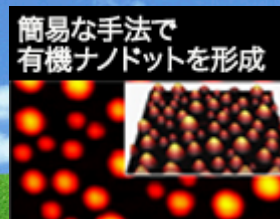
BEANS:
Bio Electro-
mechanical
Autonomous Nano
Systems



有機分子のナノ構造・配向制御が創り出す 次世代有機・熱電デバイス

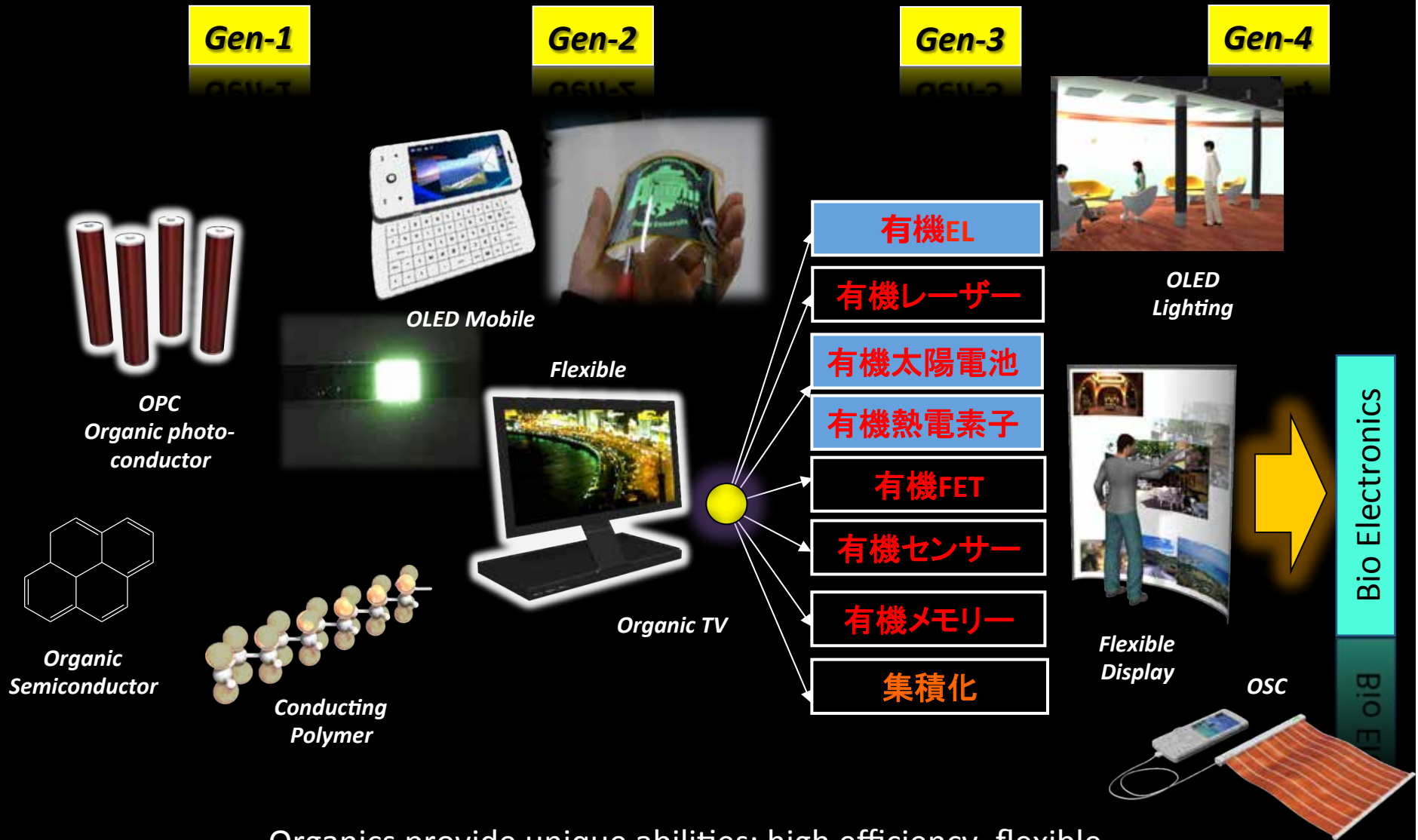
—次世代エレクトロニクス・MEMSへの要素技術—

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



Life Beans 九州
九州大学未来化学創造センター

有機半導体エレクトロニクスの工業化へ向かって



Organics provide unique abilities; high efficiency, flexible, low-cost, low-temp fabrication, and high compatibility with bio-applications

1960

1990

2000

2010

2020

低コスト・大面積化による工業化が可能な有機半導体層製造プロセス開発

100 nm程度の有機半導体ナノ構造形成

期待される成果

①高性能有機発光デバイス
(超低電圧、高光取り出しデバイス)



高効率発光デバイス



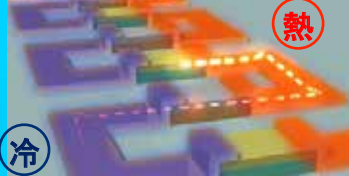
電荷移動度が高い有機薄膜

②高効率有機太陽電池



高効率光電変換特性

③高効率熱電デバイス



廃熱や体温で発電

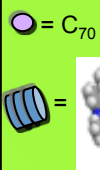
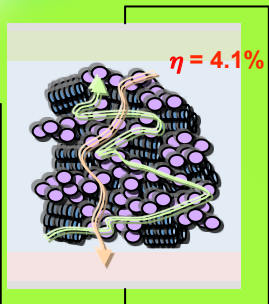
☆有機薄膜デバイスの利点



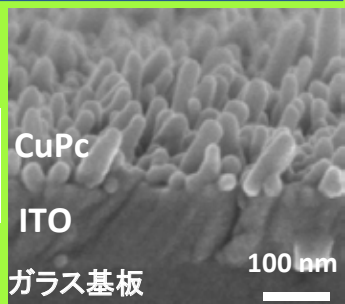
超軽量フレキシブルデバイス

BEANSプロジェクト

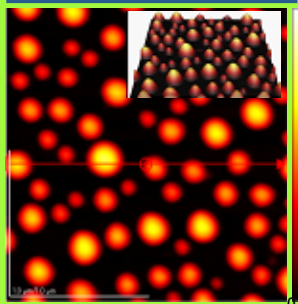
①バルクヘテロ構造による高効率太陽電池



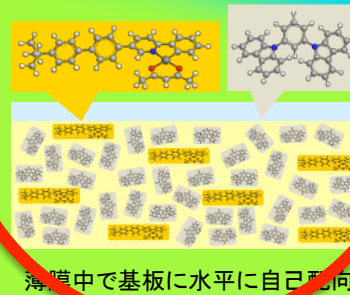
②配向制御による有機ナノピラー形成



③SAM膜による有機ナノドット形成

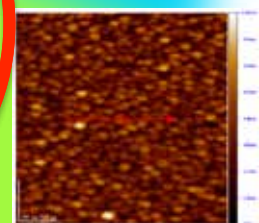


④有機分子の自己配向制御

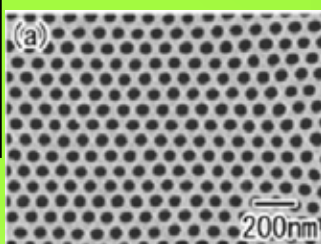


薄膜中で基板に水平に自己配向

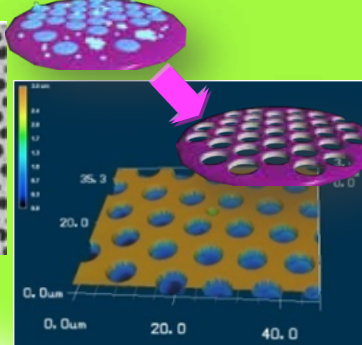
⑤中性粒子ビームによるナノ構造形成



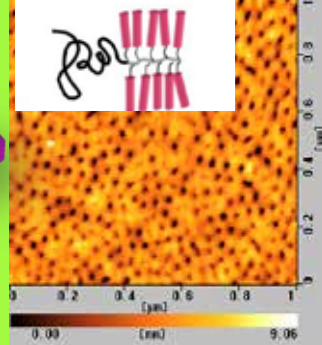
⑥ナノポーラスアルミナの形成



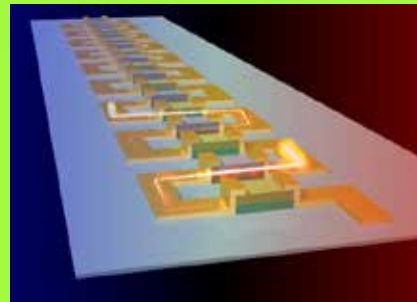
⑦ナノミスト相分離構造



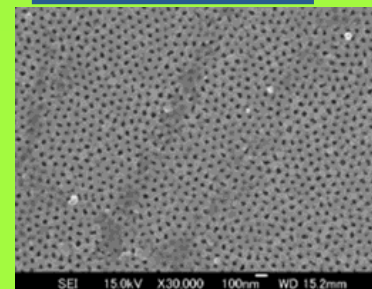
⑧ブロック共重合体によるナノ構造形成



⑨高次ナノ構造による新規有機熱電デバイス



⑩ポーラス膜への熱電薄膜作製



自己組織化ナノポーラス熱電薄膜 (ZT = 1.8)

Highly Efficient Organic Solar Cells with PCE > 15%

Advantage of Organic Solar Cells

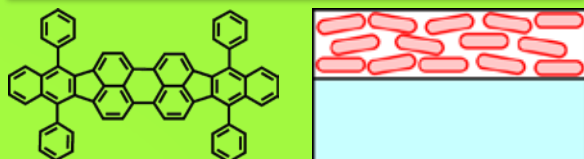
- 1) Low-cost: Organic Materials
- 2) Large Area and Flexible
- 3) Energy Saving for Production
- 4) Large Absorption Coefficient
- 4) Unlimited Molecular Design

Disadvantage

* Power Conversion Efficiency is limited.

Molecular Ordering

III) Control of Molecular Orientation (PCE=6.3%, V_{oc} =5.89 V)



Small molecular organic photovoltaic cells with exciton blocking layer at anode interface for improved device performance

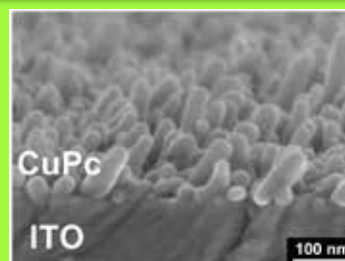
Appl. Phys. Lett., 99, 153302 (2011)

Top 20 Most Downloaded Articles

Very high open-circuit voltage of 5.89 V in organic solar cells with 10-fold-tandem structure

Appl. Phys. Lett. 100, 243302 (2012)

II) Preparation of Nano-pillars (PCE=1.2%)

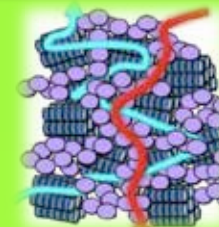
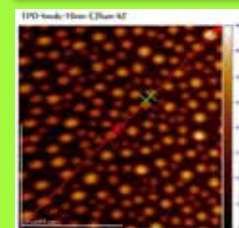


Formation of Organic Crystalline Nanopillar Arrays and Their Application to Organic Photovoltaic Cells

Appl. Mat. Int. 3, 80-83, (2011)

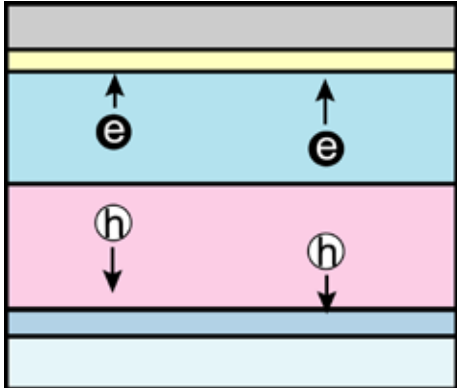
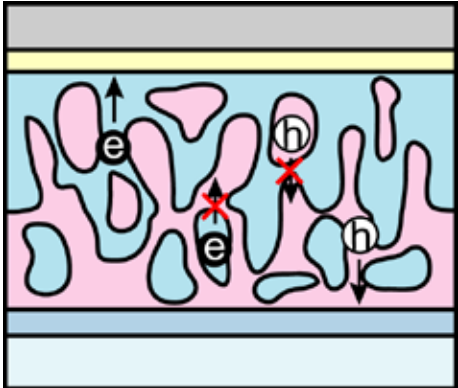
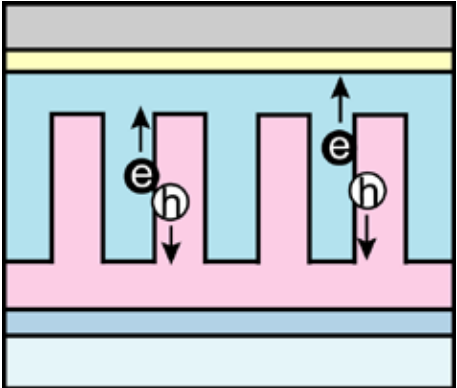
Top 10 Most Read Articles

I) Control of Nano-sized Grain Morphology (PCE=4.1%)



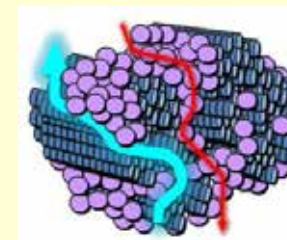
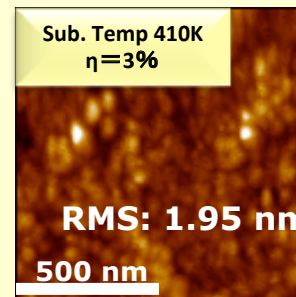
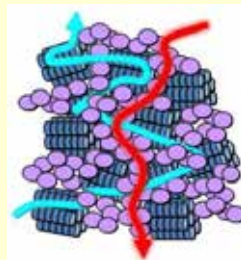
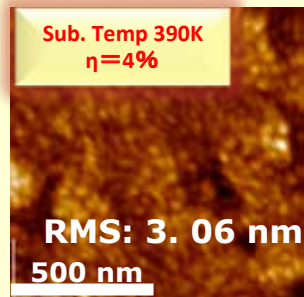
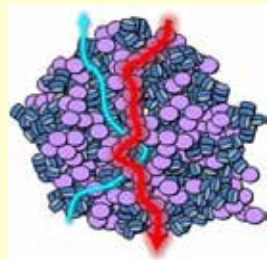
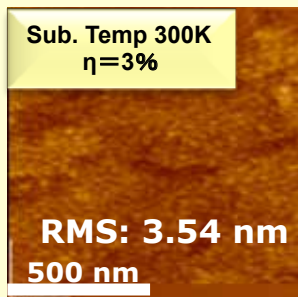
Nanocrystal growth and improved performance of small molecule bulk heterojunction solar cells composed of a blend of chloroaluminum phthalocyanine and C70
Appl. Phys. Exp. 3, 121602 (2010)

(II) 有機太陽電池の高性能化へ

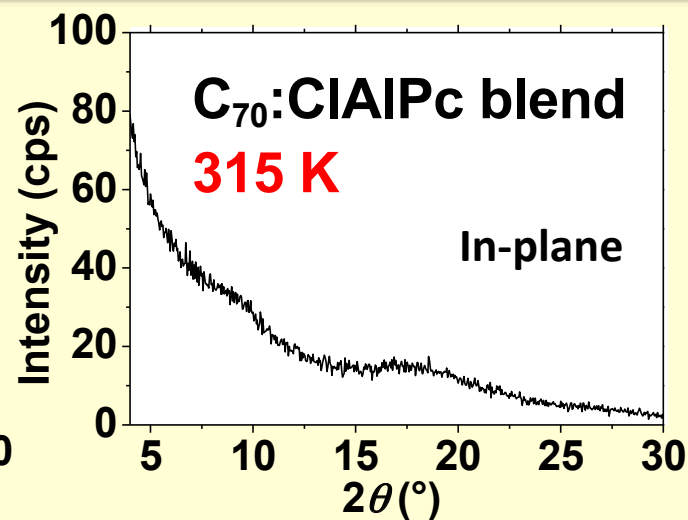
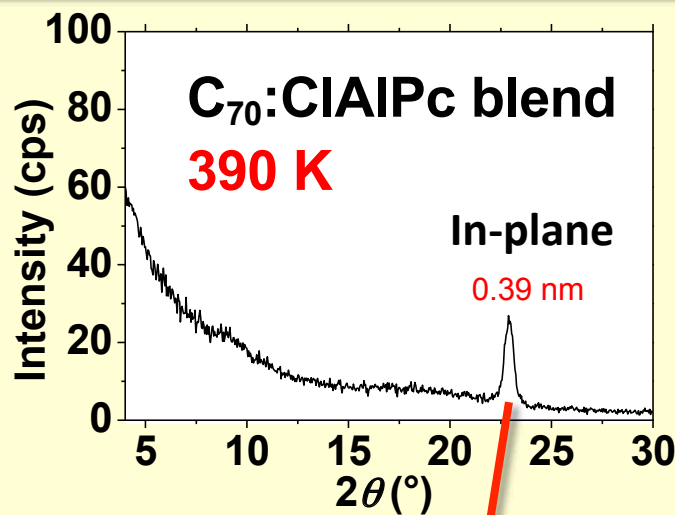
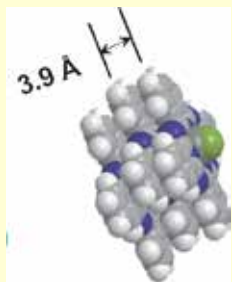
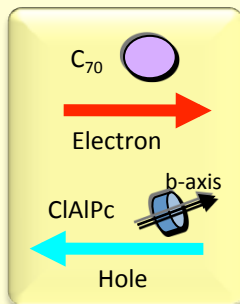
	Planer hetero structures	Bulk hetero structures	Nano-Pillar structures
	 <p>[2] C. W. Tang <i>Appl. Phys. Lett.</i>, 48, 183 (1986)</p>	 <p>[3] J. Xue et al., <i>Adv. Mater.</i> 17, 66 (2005)</p>	 <p>[4] J. S. Kim et al., <i>Adv. Funct. Mater.</i> 20, 1 (2010)</p>
η_A	△	△	⊙
η_{ED}	△	⊙	⊙
η_{CT}	⊙	⊙	⊙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

Nano-pillar structures are ideal structure

Control of Grain Size, Molecular Stacking and Orientation



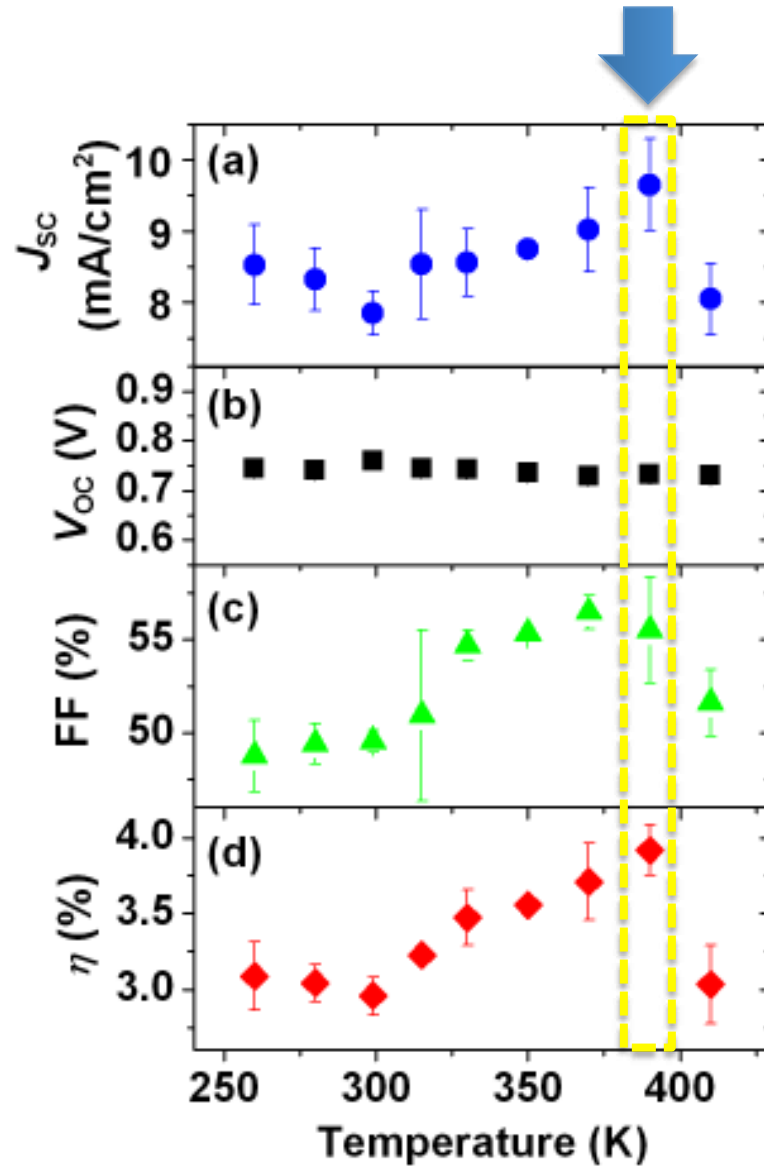
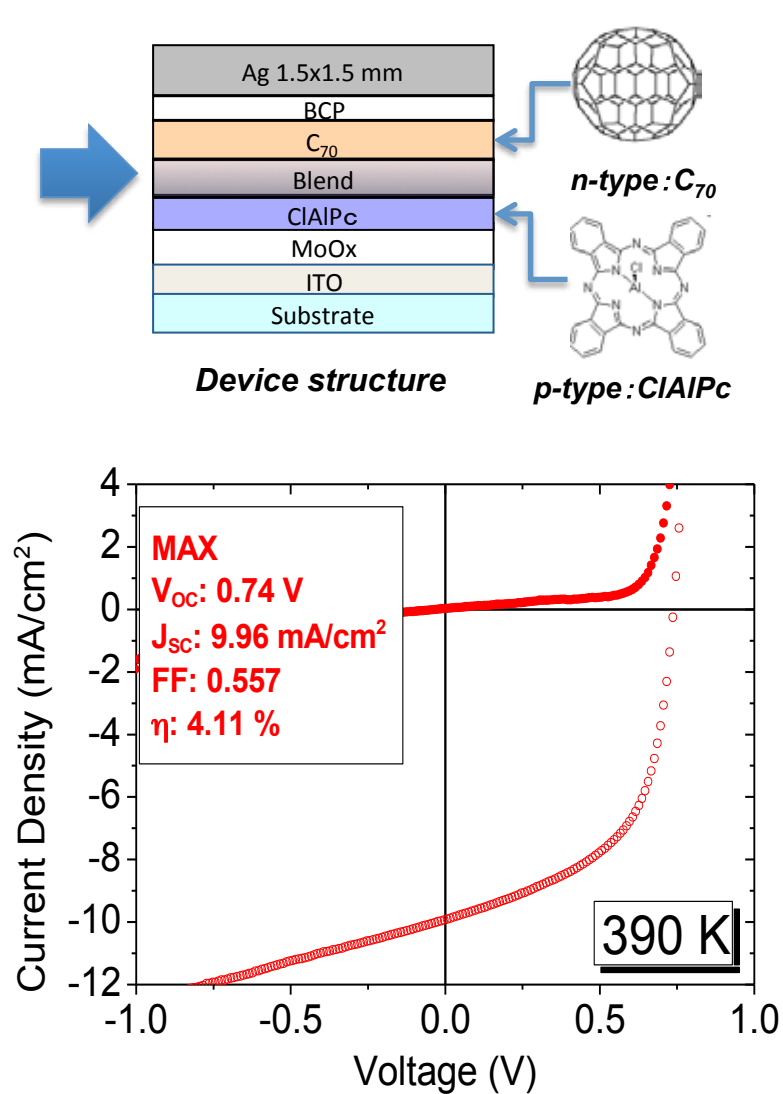
Large surface area



CIAIPc aligns to parallel orientation by π Stacking

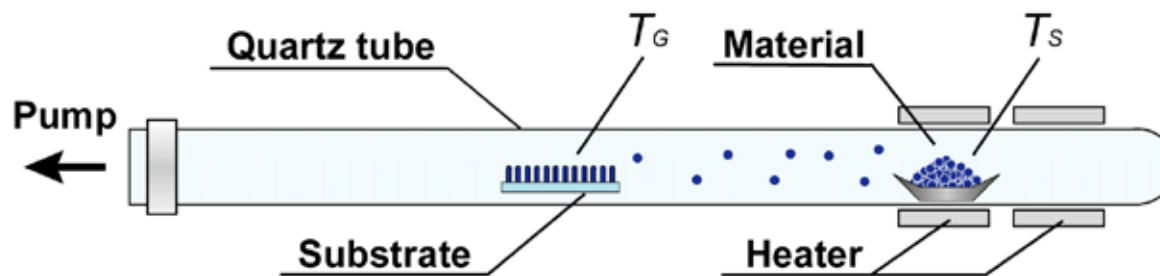
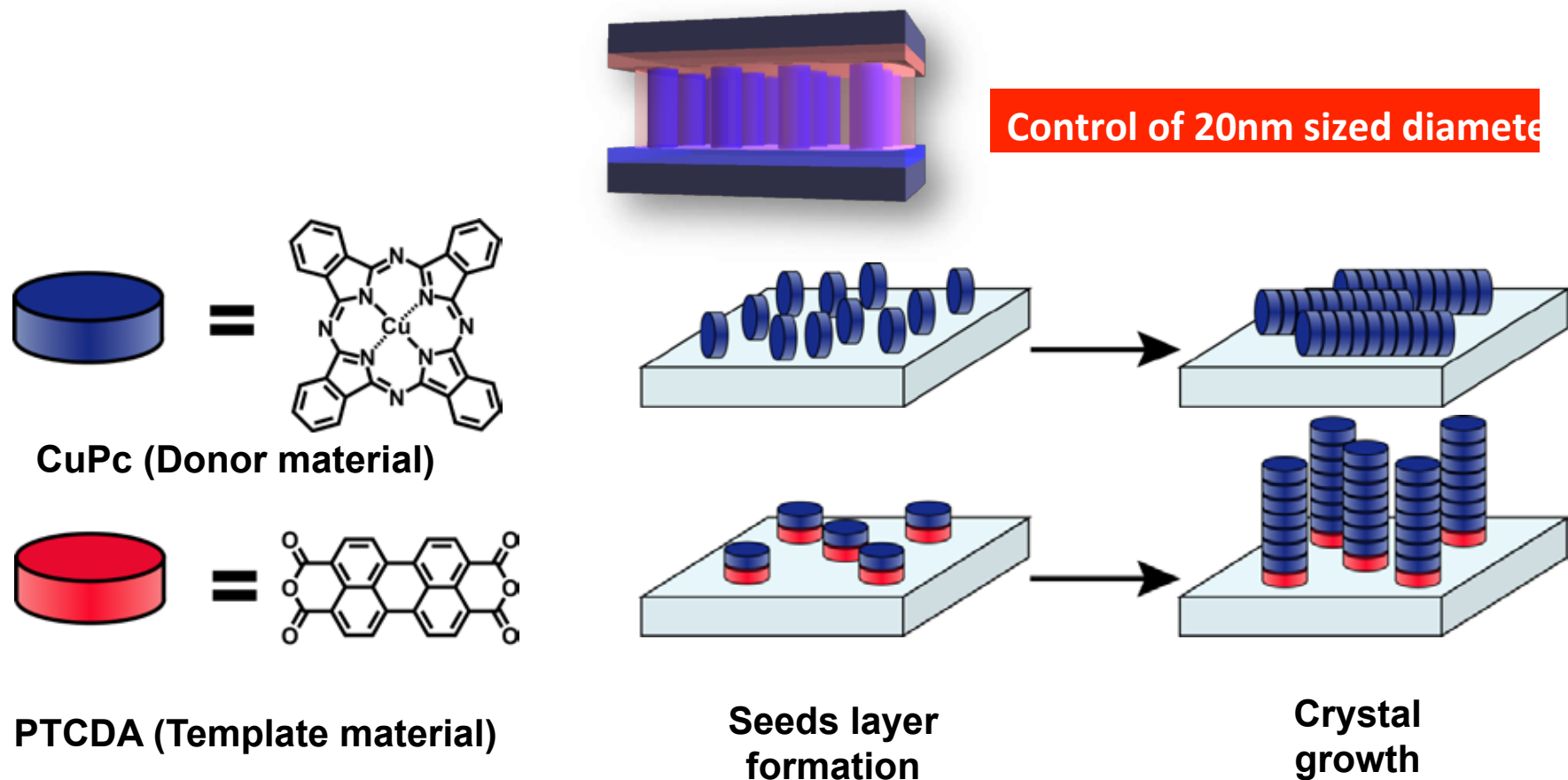


(3) 有機ナノグレイン制御



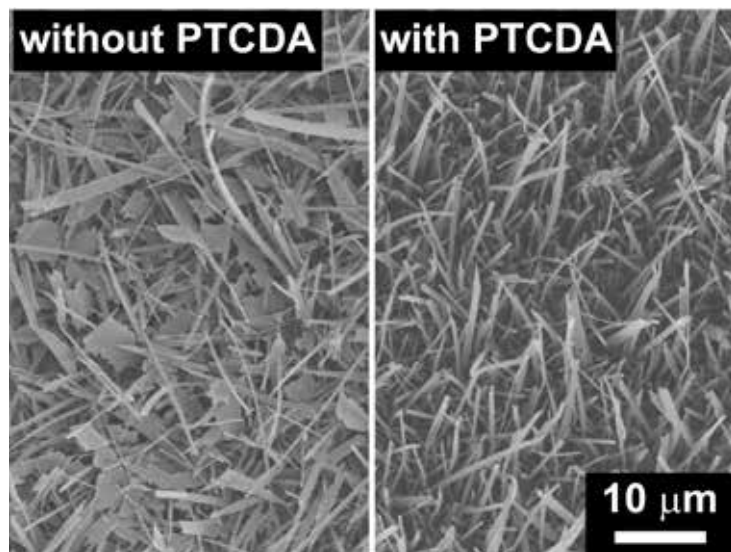
Appl. Phys. Exp. 3, 121602 (2010)
 Kentaro Harada, Tomohiko Edura, and Chihaya Adachi

II) Artificial Control of Organic Nano-Pillars

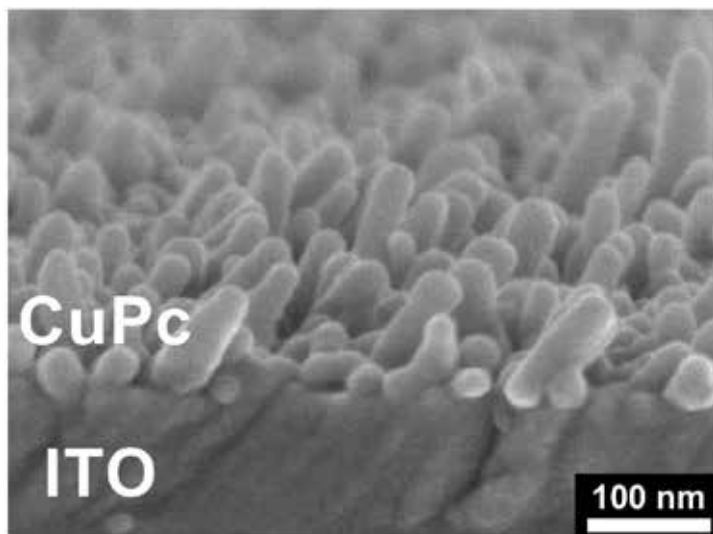


Orientation controlled CuPc molecules were used as seeds layer.

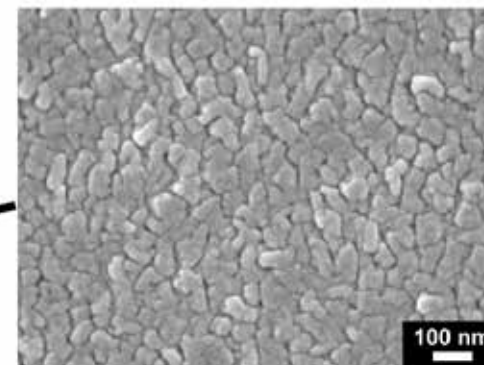
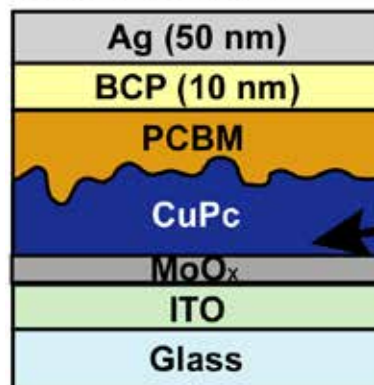
Artificial Control of Organic Nano-Pillars (センサーへの応用)



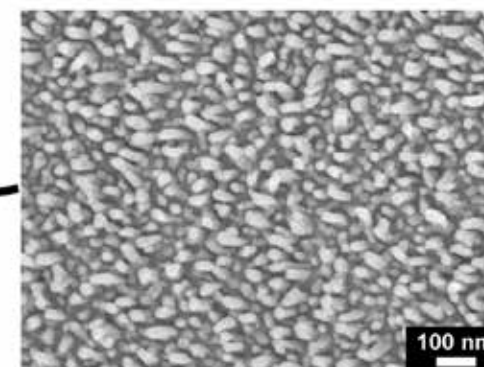
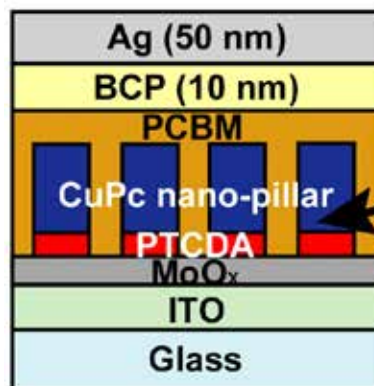
$T_S=370^\circ\text{C}$, $T_G=215^\circ\text{C}$



w/o PTCDA



with PTCDA

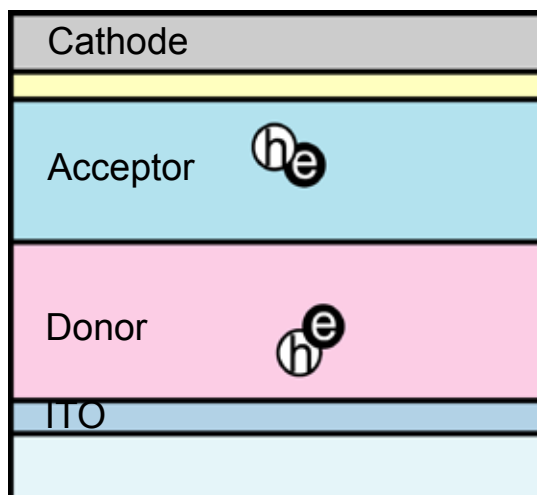
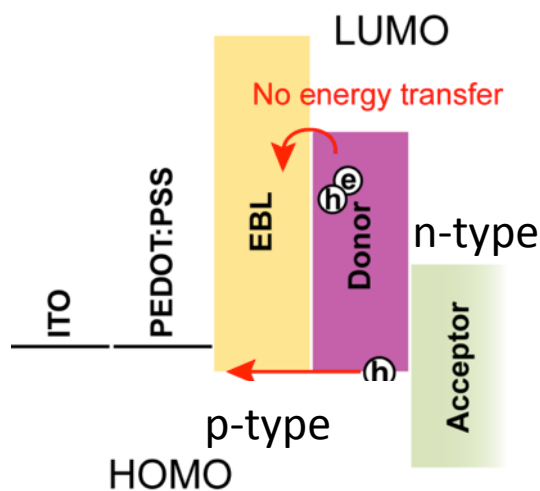


Masaya Hirade, Hajime Nakanotani, Masayuki Yahiro and Chihaya Adachi

Appl. Mat. Int. 3, 80-83, (2011)

Selected in Top 10 Most Read Articles for Q1 2011

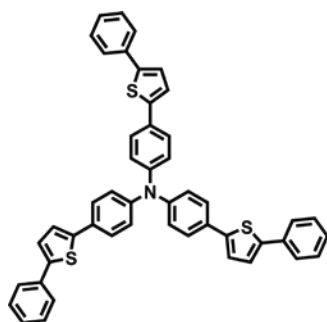
III) Introduction of molecular orientation in OSC



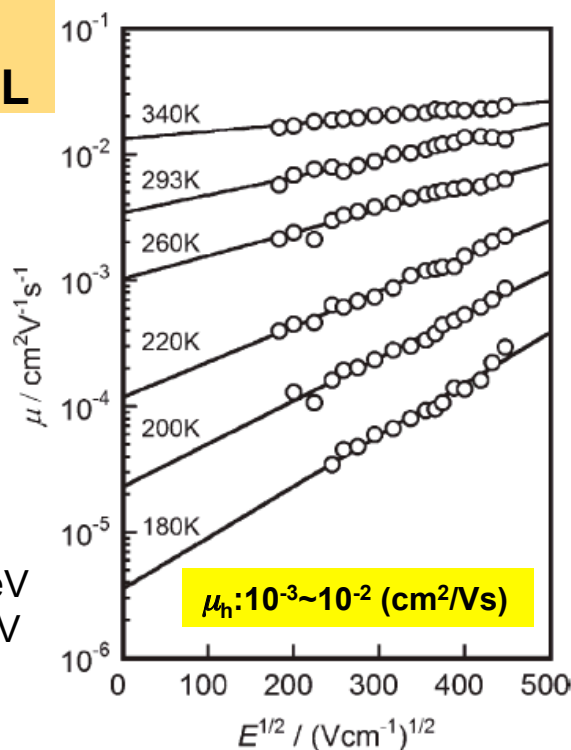
Confirmation of molecular orientation
Ellipsometry & Polarized emission



p-type
Material for EBL

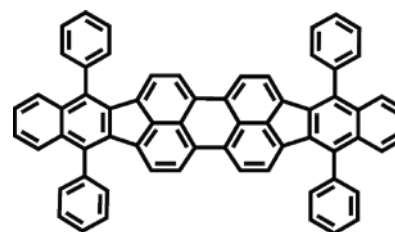


TPTPA
HOMO ~ 5.4 eV
LUMO ~ 2.7 eV
 $E_g = 2.7$ eV

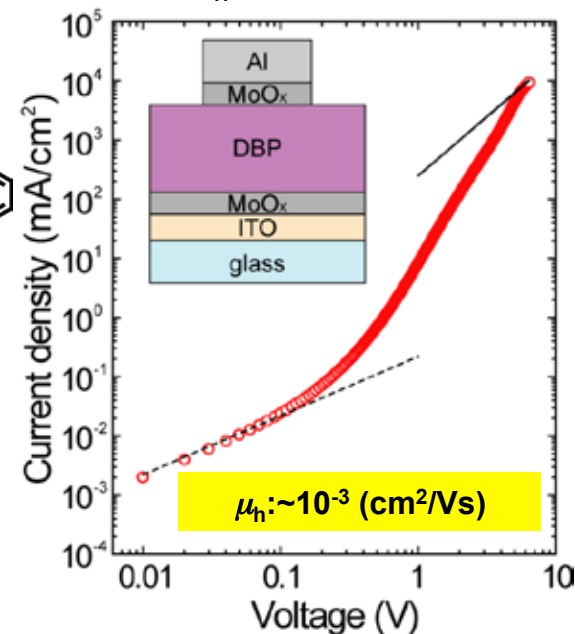


p-type: Material for Donor Layer

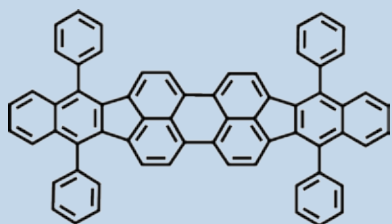
ITO/MoO_x(3 nm)/DBP(100 nm)/MoO_x(3 nm)/Al(100 nm)



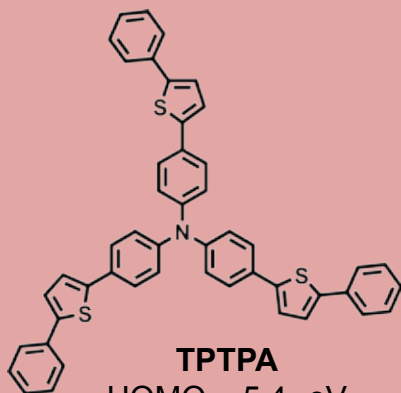
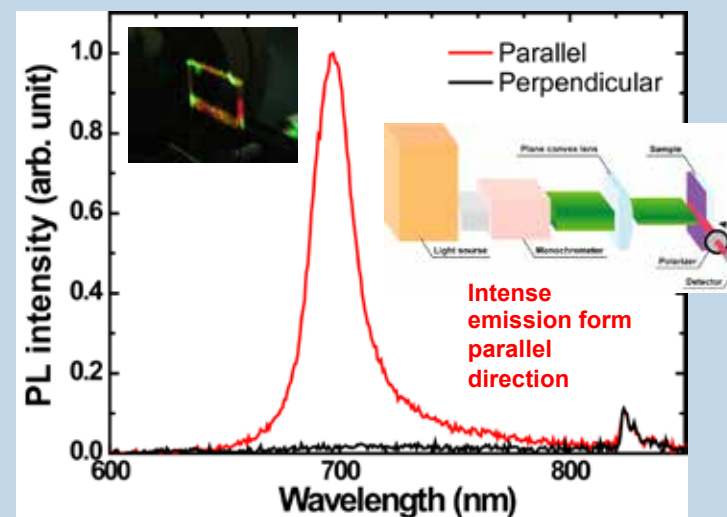
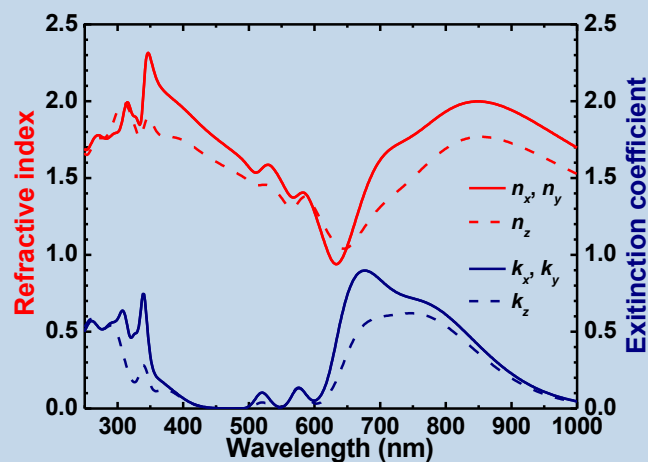
DBP
HOMO ~ 5.4 eV
LUMO ~ 3.4 eV
 $E_g = 2.0$ eV



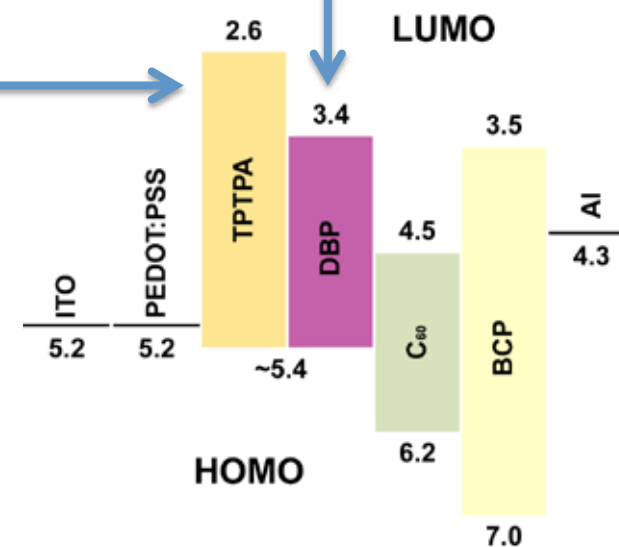
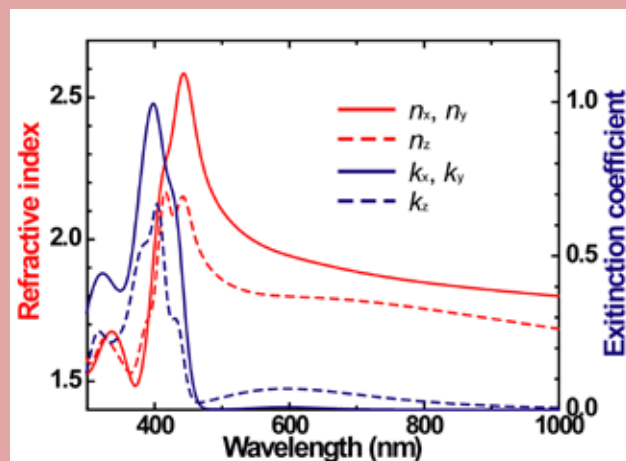
II) Introduction of Molecules Having Molecular Orientation



DBP
HOMO ~ 5.4₀ eV
LUMO ~ 3.4 eV

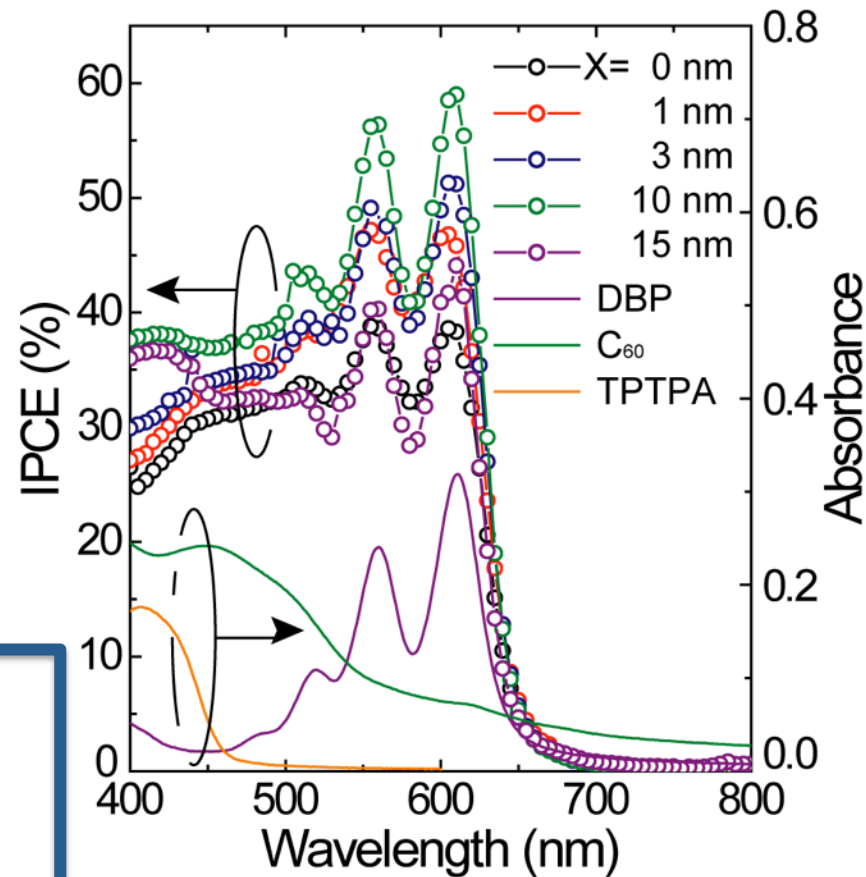
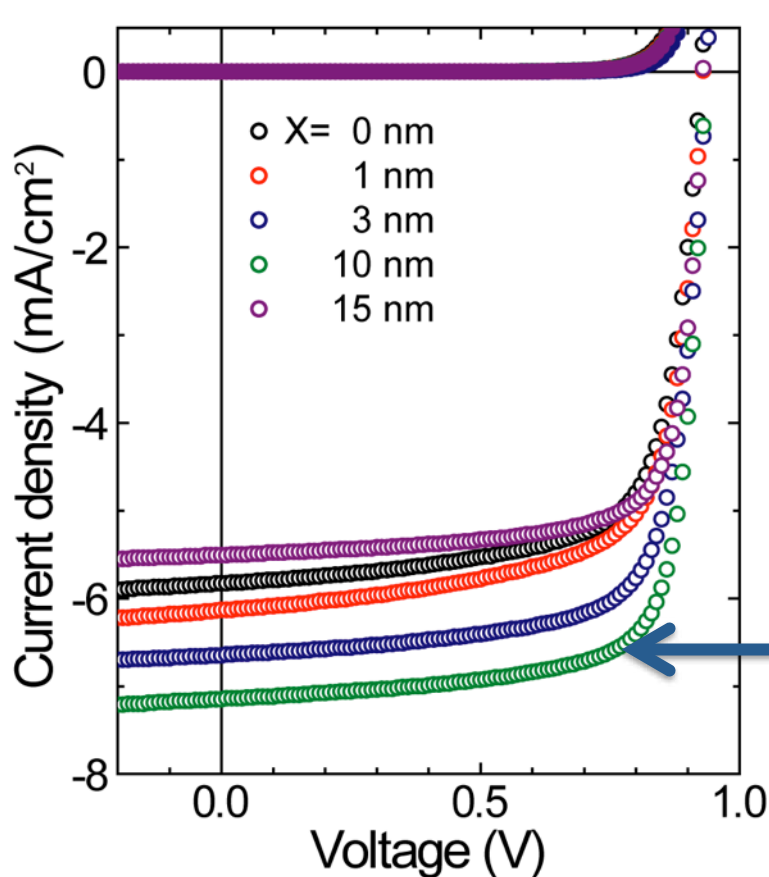


TTPA
HOMO ~ 5.4₀ eV
LUMO ~ 2.6 eV
 $\mu_h: 10^{-3} \sim 10^{-2} \text{ (cm}^2/\text{Vs)}$



OSC characteristics of DBP/TPTPA based OSC

ITO/PEDOT:PSS/TPTPA(X nm)/DBP(20-X nm)/C₆₀(50 nm)/BCP(10 nm)/Al(100 nm)

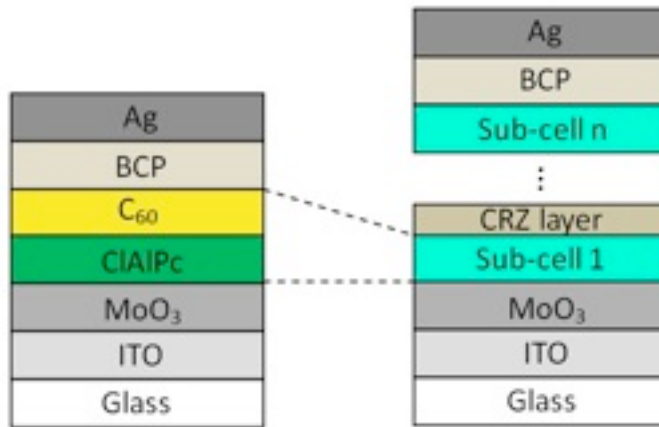


IPCE around DBP absorption range was increased.

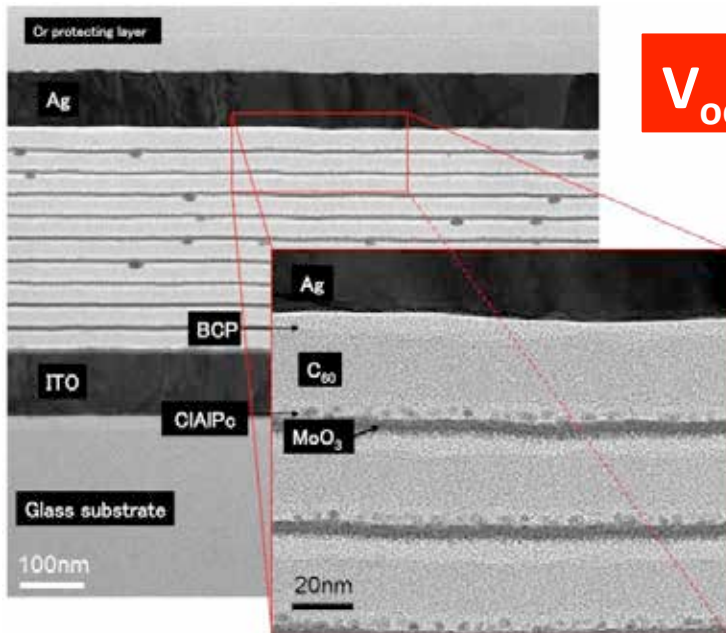
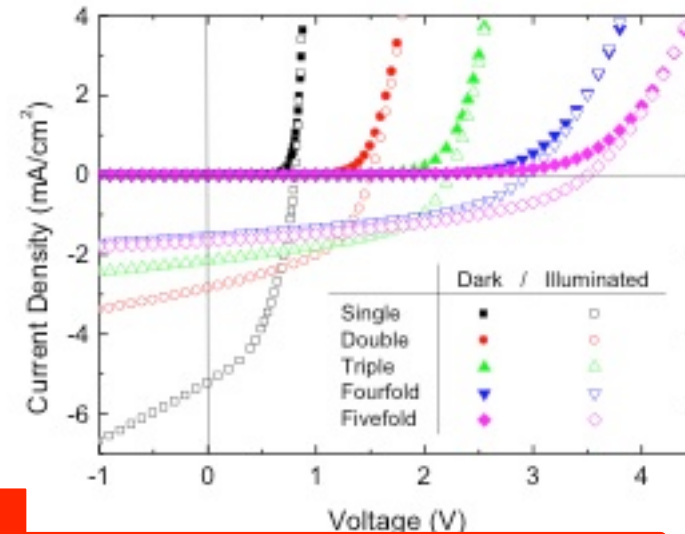
PCE=5.25%

X (nm)	J _{SC} (mA/cm ²)	V _{OC} (V)	FF	η _{PCE} (%)
0	-5.82±0.08	0.92±0.01	0.72±0.01	3.88±0.06
1	-6.22±0.10	0.93±0.01	0.70±0.02	4.05±0.09
3	-6.62±0.22	0.93±0.01	0.73±0.01	4.53±0.10
10	-7.15±0.25	0.93±0.01	0.74±0.03	5.04±0.20
15	-5.28±0.45	0.93±0.01	0.77±0.01	3.78±0.25
10 (Best)	-7.25	0.94	0.77	5.25

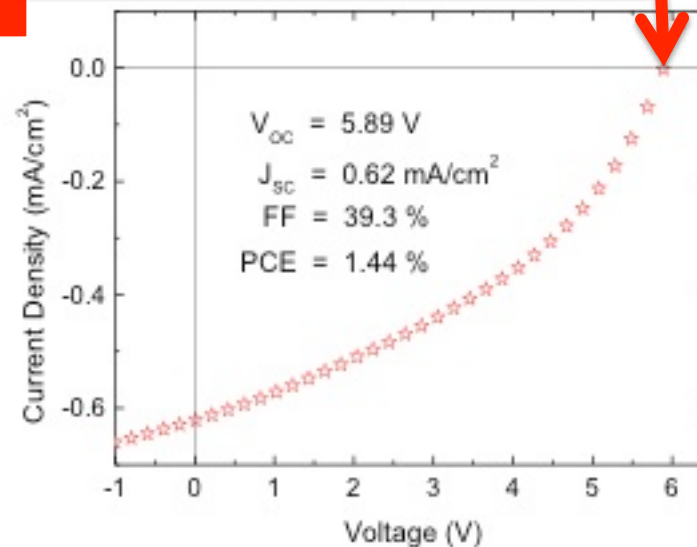
High V_{oc} : OSC characteristics of 10-fold Tandem OSC



Total 53 layers



$V_{oc} = 5.89$ V



Very high open-circuit voltage of 5.89 V in organic solar cells with 10-fold-tandem structure

Appl. Phys. Lett. 100, 243302 (2012)

Y. Zou, Z. Deng, W. J. Potscavage, M. Hirade, Y. Zheng and C. Adachi

高効率有機EL素子へ

$$\eta_{ext} = \eta_{int} \eta_p = \gamma \eta_r \eta_{PL} \eta_p$$

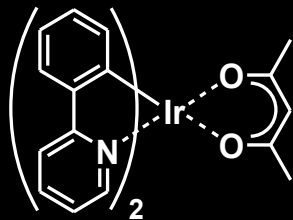
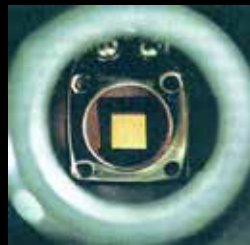
$\sim 100\%$ $\sim 100\%$ $\sim 100\%$ $\sim 20\%$

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

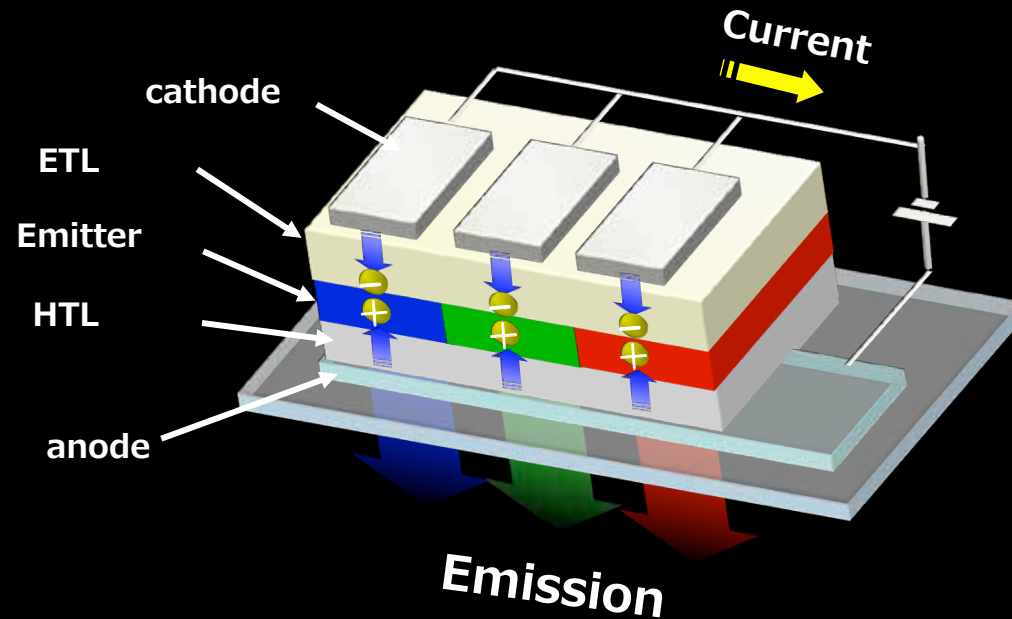
η_r : exciton production efficiency

η_{PL} : PL quantum efficiency

η_p : light out-coupling efficiency



Internal EL efficiency
~100%

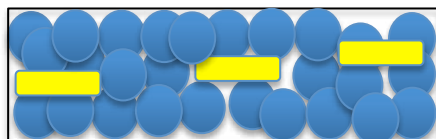
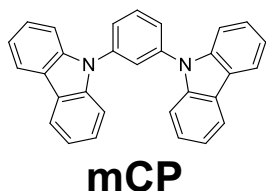
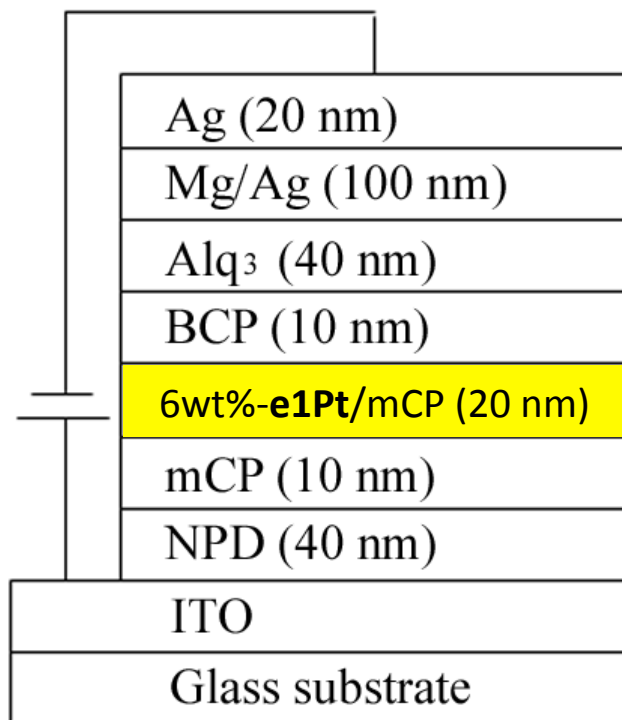


究極の高性能化へ

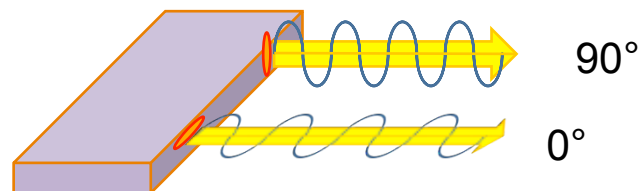
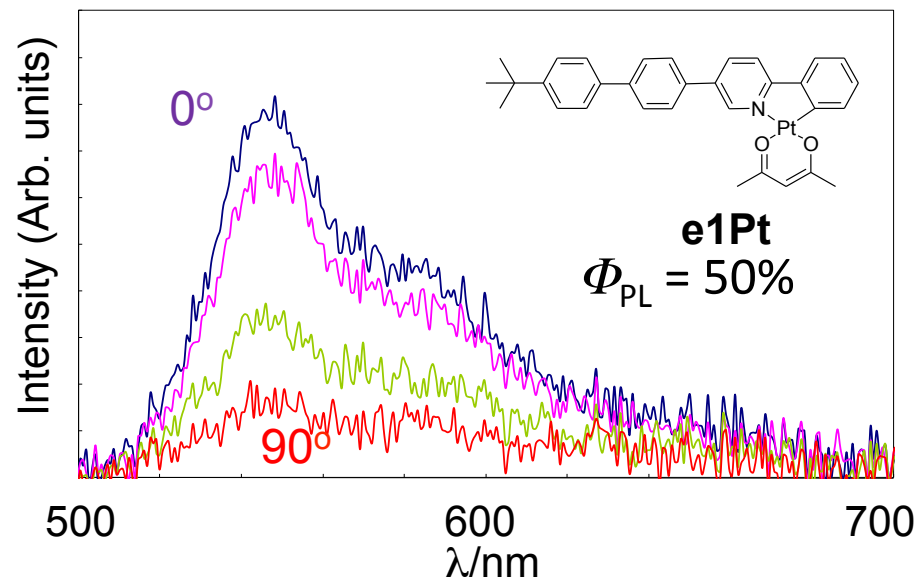


- ✓ 分子配向による光取り出し効率の向上
- ✓ 駆動電圧の低下

リン光デバイスによる高効率化の実現

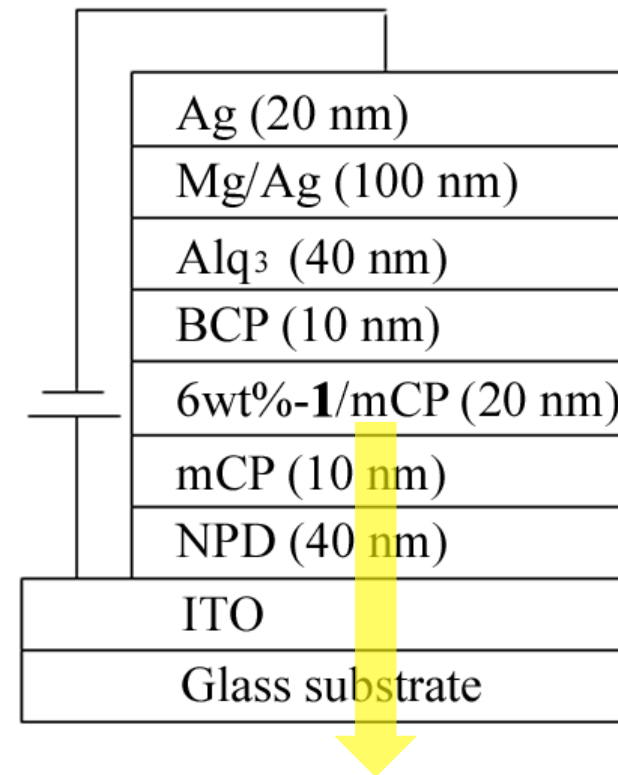
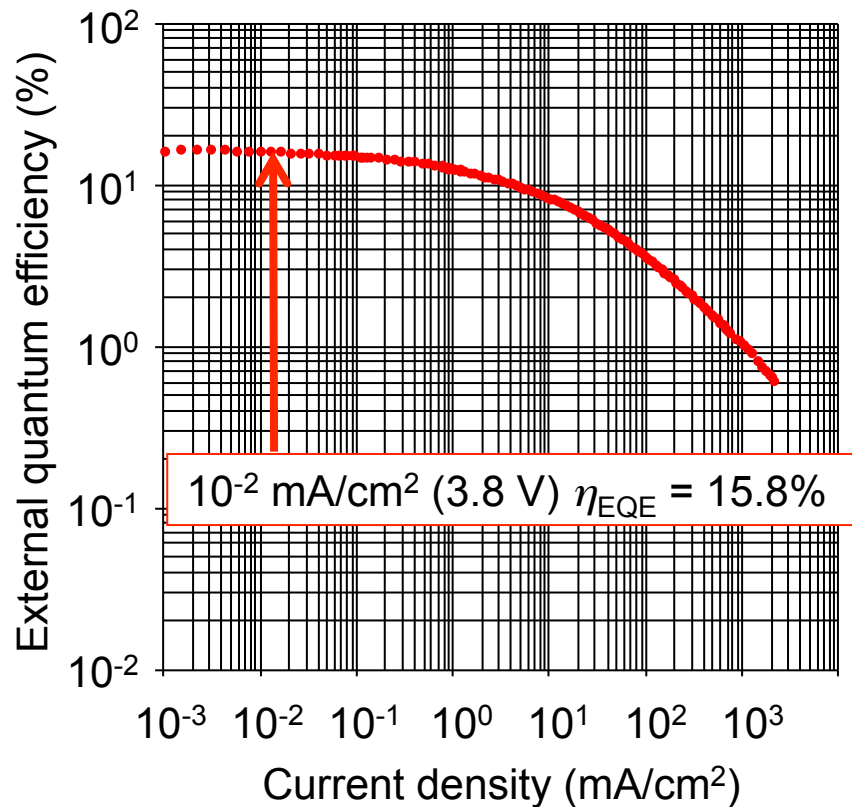
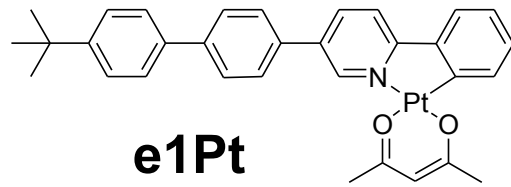


6wt%-e1Pt / mCP (100 nm)



ゲスト-ホスト系
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

リン光デバイスによる高効率化へ



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

$$= \gamma \times \eta_{ST} \times \Phi_{PL} \times \Phi_{out}$$

$$\Phi_{out} = 32\%!$$

$$(\Phi_{PL} = 50\%, \gamma = 100\%, \eta_{ST} = 100\%)$$

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)

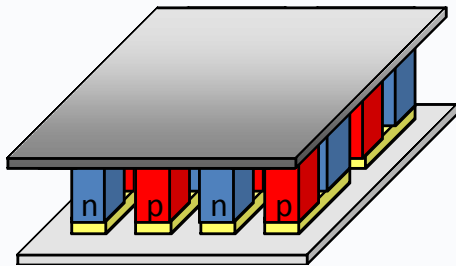
Masatsugu Taneda, Takuma Yasuda, and Chihaya Adachi

日本の工場における年間排熱量： 1×10^{15} KJ/年

↳ 日本全国の1か月間の発電量に相当

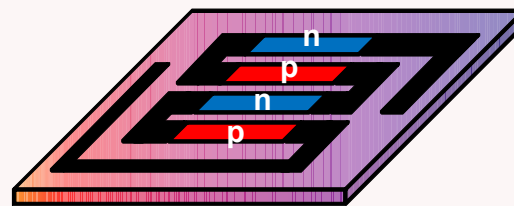
熱電変換デバイス

無機熱電材料 (Bi-Te系半導体)



- 熱電能が高い
- 高コスト
- 脆性
- 毒性が高い

有機薄膜熱電材料

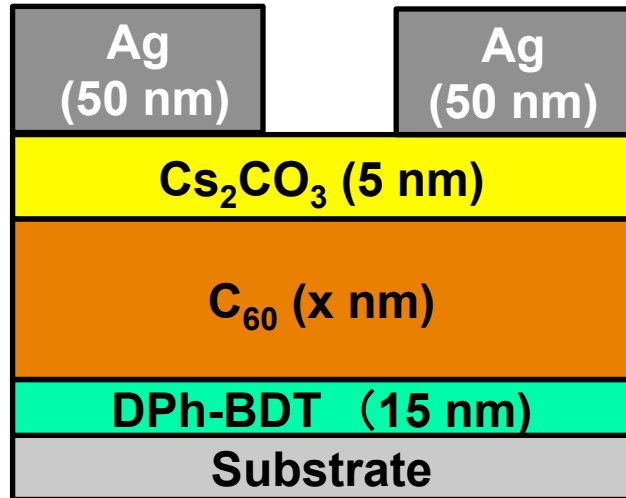


- 低コスト
- フレキシブル
- 大面積
- 熱電能が低い

従来のバルク型無機熱電デバイスにはない
新しいアプリケーションの可能性が期待できる

例) ウェアラブル熱電デバイス

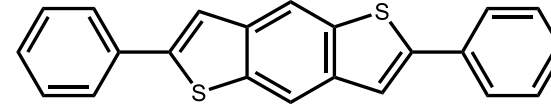
有機熱電デバイスの展開



x: 10, 15, 20, 30, 50, 70, 100

S.Kinoshita et al./Solid State Comm. 145 (2008) 114-117

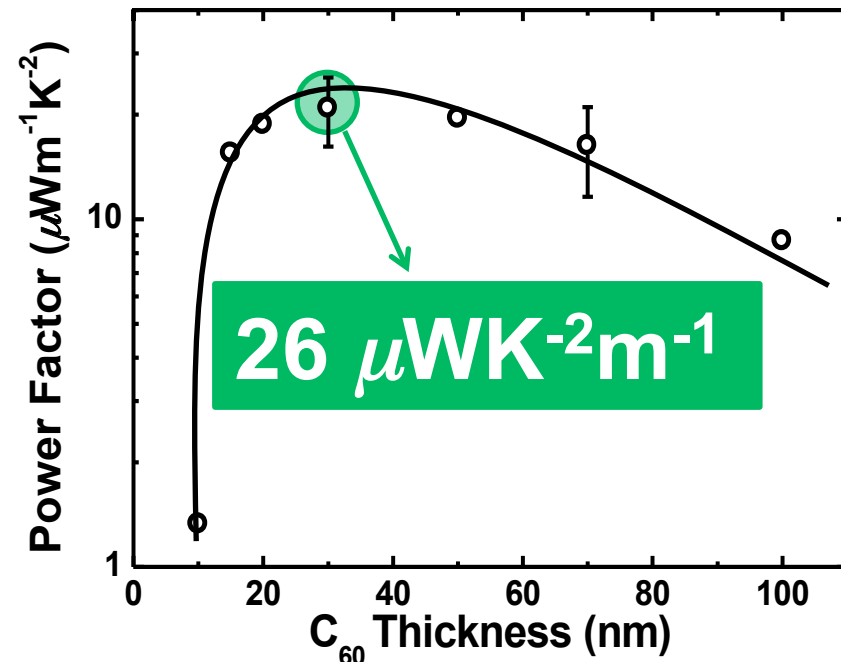
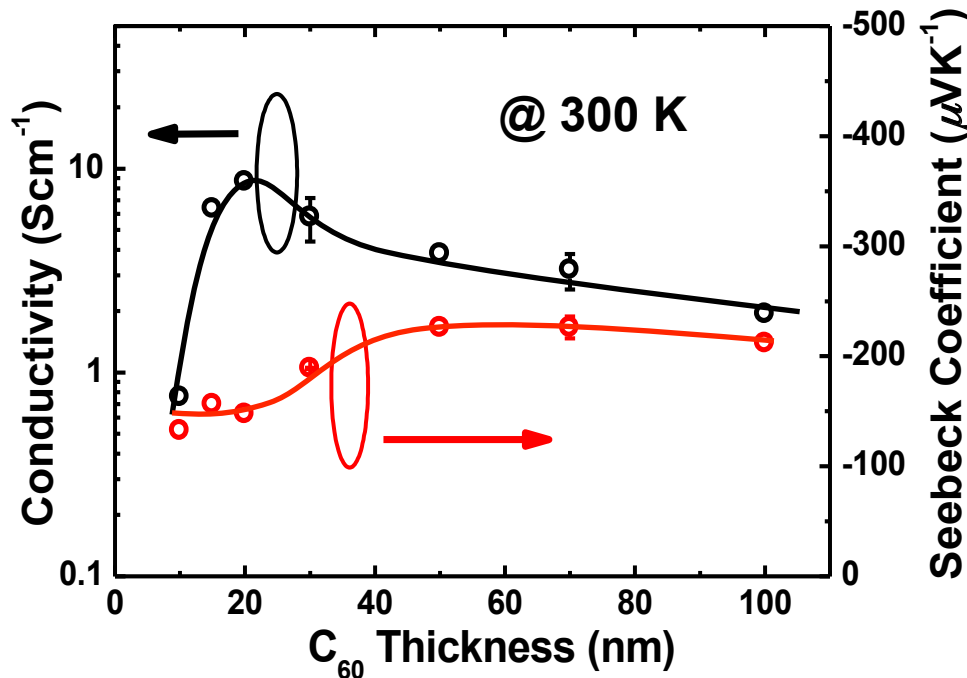
DPh-BDT



$\mu_{\text{C}_{60}} : \sim 3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$
@ DPh-BDT: 15 nm

*HMDSのときは $\mu_{\text{C}_{60}} : \sim 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$

n型有機薄膜熱電デバイスにおいて最高の値



有機熱電デバイスの展開

- n型有機二層積層構造においてもp型と同様に高いパワーファクターを得た
- 移動度の高いデバイス構造を設計することでより高性能な熱電デバイスの作製に成功
- 表面ラフネスが小さい、グレインサイズが大きい膜ほど μ が高くその結果Pも高くなる。
- p-nプロトタイプデバイスにおいて熱起電力がp型、n型ユニットセルの熱起電力の和になることを確認

タイプ	分類	材料	κ ($\text{Wm}^{-1}\text{K}^{-1}$)	Z (K^{-1})	P ($\mu\text{Wm}^{-1}\text{K}^{-2}$)
p型	ポリマー	Polythiophene ¹	0.1—0.2	1.0×10^{-4}	10
	低分子	Pentacene ²	0.48 ^(a)	2.1×10^{-5}	10
n型	無機	BiTe ³	1.6	1.8×10^{-3}	2900
	電荷移動錯体	TTF-TCNQ ⁴	0.34	6.2×10^{-7}	0.21
	低分子	C ₆₀ ⁵	0.16 ^(a)	1.6×10^{-4}	26

(a) 3 ω 法による測定

n型有機薄膜熱電デバイスにおいて
最高レベルのパワーファクター

¹Hiraishi *et al.*, Jpn. J. Appl. Phys. (2009).

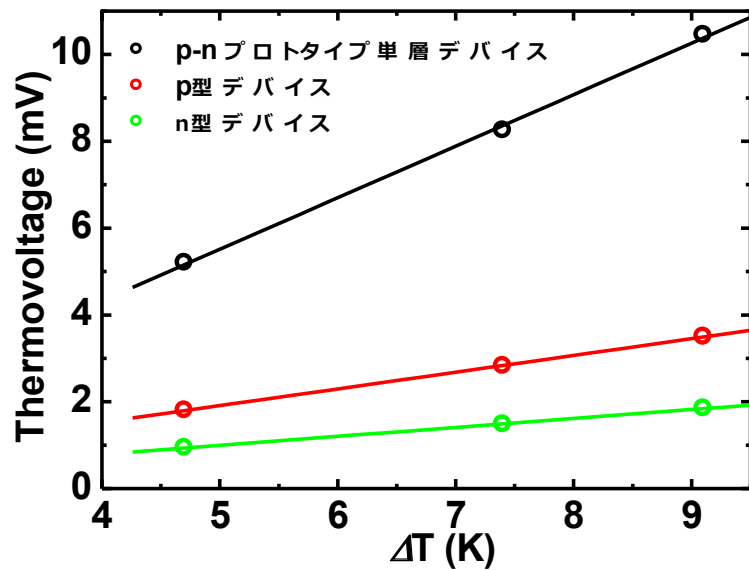
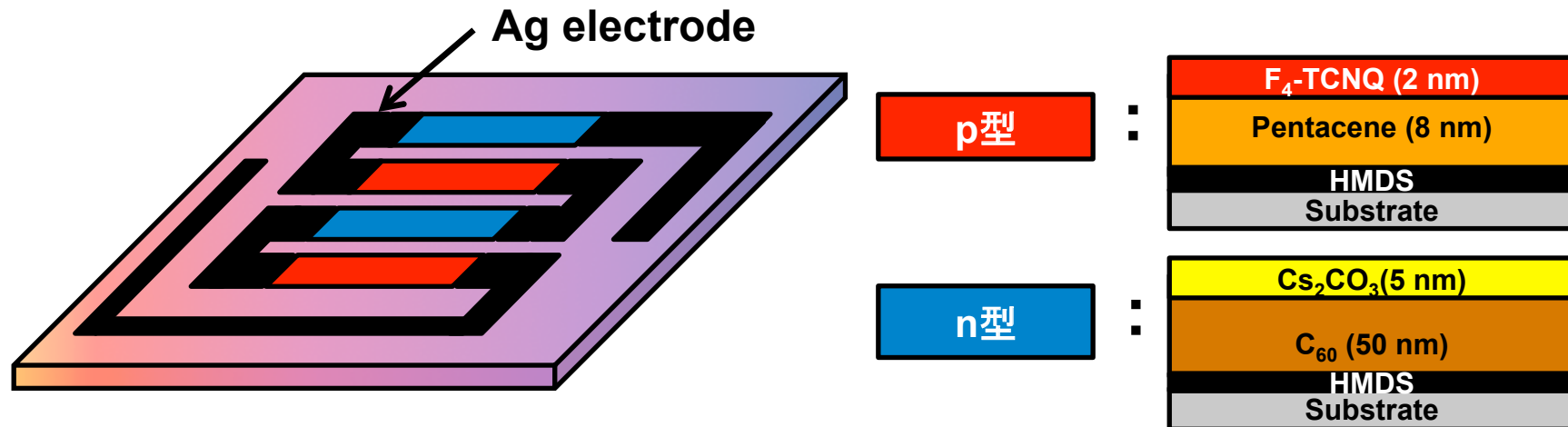
²K. Harada, M. Sumino, C. Adachi, S. Tanaka and K. Miyazaki, Appl. Phys. Lett. 96, 253304 (2010)

³Takashiri *et al.*, J. Appl. Phys. (2007).

⁴Itahara *et al.*, J. Electr. Mater. (2009).

⁵M. Sumino, K. Harada, M. Ikeda, S. Tanaka, K. Miyazaki, and C. Adachi, Appl. Phys. Lett, [99 093308 \(2011\)](#)

p-nプロトタイプ有機熱電デバイスの作製

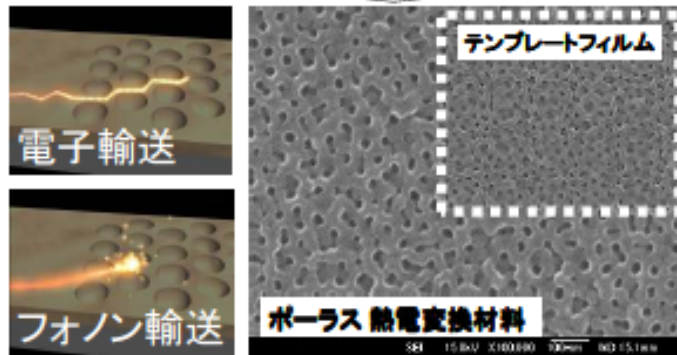


セル	熱起電力 (mVK ⁻¹)	抵抗値 (MΩ)
p型	0.39	1.1×10 ⁶
n型	0.19	2.5×10 ⁵
p-nプロトタイプ	1.20	3.6×10 ⁷

ポーラス熱電デバイスの作製

アルミナ陽極酸化を利用したナノ構造熱電変換材料

- アルミナ陽極酸化を用いたポーラス構造の作製
- ポーラス構造への蒸着でポーラス熱電薄膜を作製
- 作製したポーラス熱電薄膜の熱電特性向上を確認

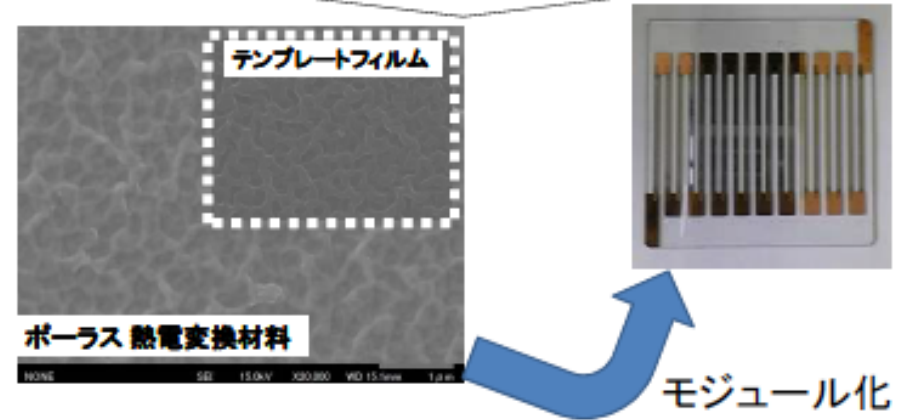


	σ [S/cm]	S [$\mu\text{V}/\text{K}$]	κ [W/(m·K)]	ZT at 300K
Bulk $\text{Bi}_{0.4}\text{Te}_{3.0}\text{Sb}_{1.6}$	840	213	1.5	0.8
Thin Film $\text{Bi}_{0.4}\text{Te}_{3.0}\text{Sb}_{1.6}$	649	234	1.0	0.9
Porous Film $\text{Bi}_{0.4}\text{Te}_{3.0}\text{Sb}_{1.6}$	398	198	0.25	1.87

M. Kashiwagi et al., Appl. Phys. Lett, 98, 023114(2011).

ポリマーテンプレートを利用したナノ構造熱電変換材料

- ブロックコポリマーを用いたポーラス構造の作製
- p-,n- Bi_2Te_3 材料で熱電特性向上を確認
- モジュール化した際にナノ構造の効果により出力向上を確認



	σ [S/cm]	S [$\mu\text{V}/\text{K}$]	κ [W/(m·K)]	ZT at 300K
Porous $\text{Bi}_{0.4}\text{Te}_{3.0}\text{Sb}_{1.6}$	198	200	0.27	0.88
Porous $\text{Bi}_{2.0}\text{Te}_{2.7}\text{Se}_{0.3}$	460	-131	0.23	1.03

有機光エレクトロニクスが切り開く近未来

次世代有機半導体デバイス



低環境負荷型大面積
有機太陽電池



フレキシブル
有機EL・太陽電池



大面積有機EL照明・
ディスプレイ



高効率有機太陽電池
(エネルギー変換効率10%へ)

>5%

高性能有機ELディスプレイ・照明

光取り出し効
率の向上
>30%

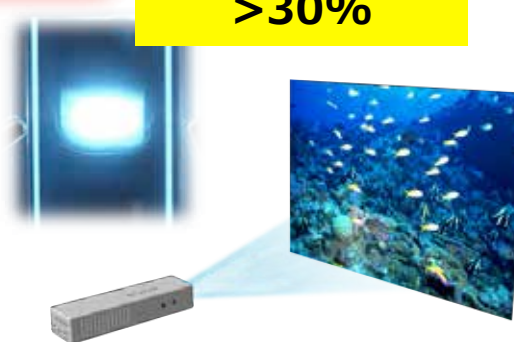
次々世代有機半導体デバイス



ウェアブル有機デバイス



デスクトップ製造装置



液体有機半導体、有機半導体レーザー
(次世代有機材料・デバイス)

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Mitsuharu Noto: Daiden Co.

Kunihisa Kato, Yasu Nakata : Lintec Co.

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