Organic Electronic Devices

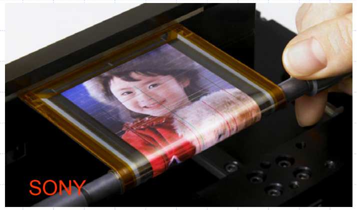
Organic LED Display

Organic LED Lighting

- Large area
- Low-cost (like an ink)
- High contrast (Self luminous)
  - Liquid crystal 10^3→Organic EL 10^6
- Flexible
- Thin
- Light-weight

Organic Electronic Devices

Organic LED + Organic transistor



Flexible

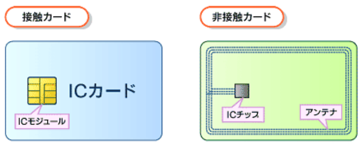
Flexible scanner

Organic Electronics
- LED (Electroluminescence)
- Transistor
- Solar cell (Photovoltaics)

Organic solar cell

Organic Electronic Devices

Printed Electronics



RF ID tag

Low cost
Easy process

↓

Printed electronics   Inkjet printing ...

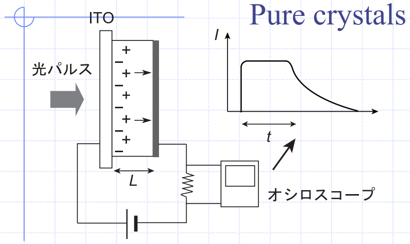
↓

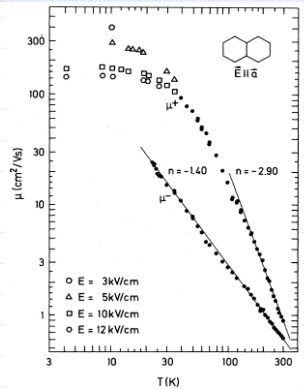
Fabricate IC by ink

Photoconductivity

Time of Flight (TOF)

Pure crystals





TOF Mobility (cm^2/Vs)

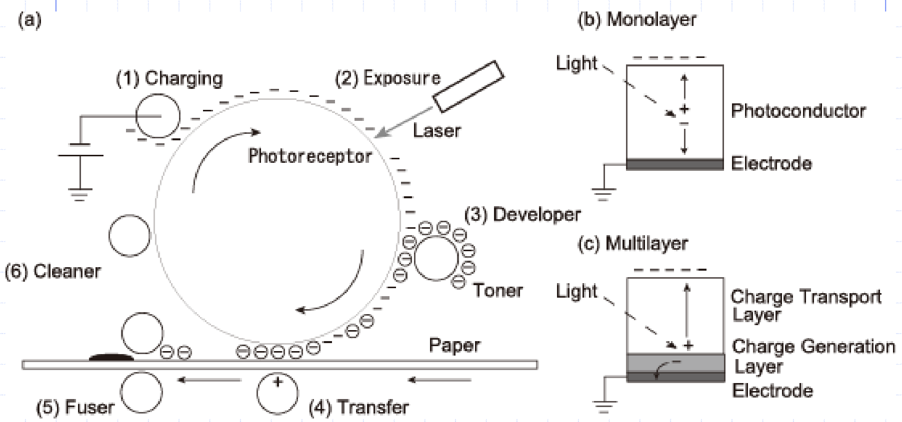
	Hole *a*/*b*/*c*	Electron *a*/*b*/*c*
Naphthlene	0.94/1.48/0.32	0.62/0.64/0.44
Anthracene	1.13/2.07/0.73	1.73/1.05/0.39
Perylene	Activated	2.37/5.53/0.78
Terphenyl	0.6/-/0.80	0.34/1.2/0.25

N. Karl, *Landort-Börnstein Numerical Data and Functional Relationships in Science and Technology*, New Series Group III 17a-i (1985).

Photoconductivity

Electrophotography C. F. Carlson (1938)

Copy·Lase printer

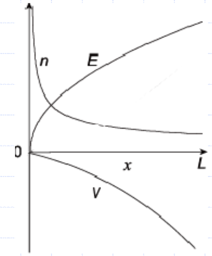


Space-charge-limited current (SCLC)

Carrier injection into an insulator

$J = en\mu E$ ➡ $\frac{\partial E}{\partial x} = \frac{en}{\varepsilon} = \frac{J}{\varepsilon \mu E}$

Integrate ➡ $E = \left(\frac{2J}{\varepsilon\mu}\right)^{1/2} x^{1/2}$

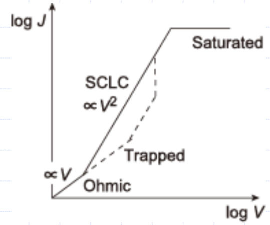


n **is accumulated around** x **= 0.**
E **is steep at** x **= 0.**

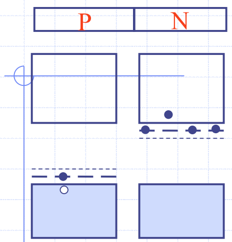
Integrate for x **up to the thickness** ***L*** **→** ***V***

$$V = \int_0^L E dx = \left(\frac{8J}{9\varepsilon\mu}\right)^{1/2} L^{3/2} \Rightarrow J = \frac{9}{8}\varepsilon\mu \frac{V^2}{L^3}$$

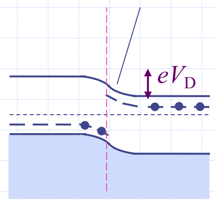
J **∝** ***V*****² Non ohmic**
→ Mobility ***μ***



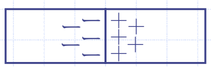
PN junction



Majority carrier is depleted around the junction to have net positive charge. →欠乏層 (Depletion Layer)

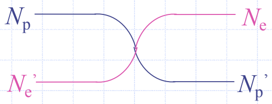


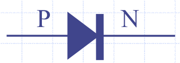
Junction polarizes so as to have opposite charges to the majority carriers.

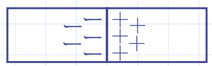


Most resistance come from the depleted junction.

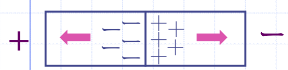
Potential surface bends so as to make E_F = const.



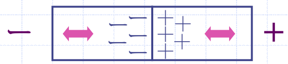




Forward bias



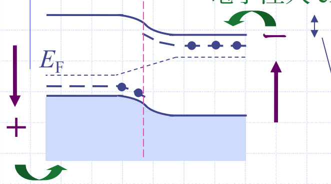
Reverse bias

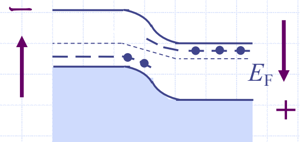


+ − attraction leads to current flow

No current flows

電子注入 electron injection





ホール注入
hole injection

Potential is lowered to V_D-V.

Majority carrier in N $N_e = N_e^0 e^{-\frac{E_C - E_F}{k_B T}}$

Minority carrier in P $N_e' = N_e^0 e^{-\frac{E_C - E_F + eV_D}{k_B T}}$ ⇒ $N_e' = N_e e^{-\frac{eV_D}{k_B T}}$

Under bias V, this leads to $N_e' = N_e e^{-\frac{e(V_D - V)}{k_B T}}$

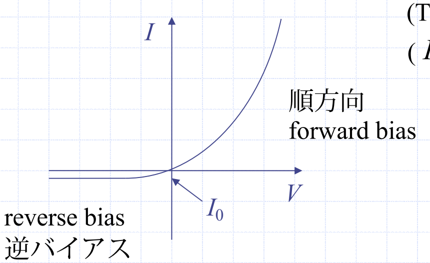
Majority carrier transport from N to P (electron diffusion current) $\propto N_e$

Minority carrier transport from P to N (electron generation current) $\propto N_e'$

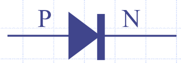
Total current $I \propto N_e' - N_e = I_0 (e^{eV/k_B V} - 1)$

(The same equation for holes)

($I_0 = N_e e^{-eV_D/k_B T}$ does not depend on V.)



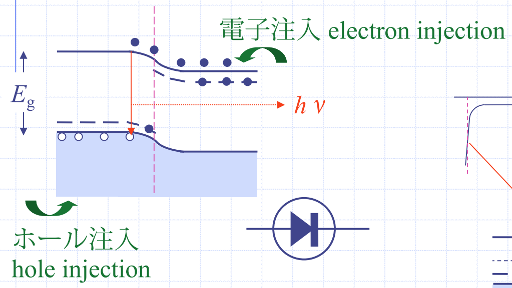
Current flows only for forward bias。
(Diode)



Diodes for specialized uses

Light Emitting Diode

Recombination of injected carriers at forward bias generates light.

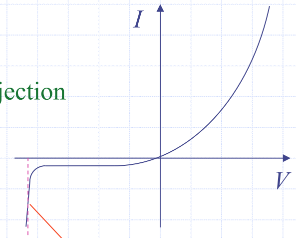


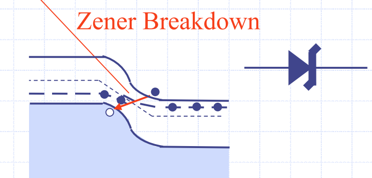
EL：Electroluminescence

$h\nu$ depends on E_g.

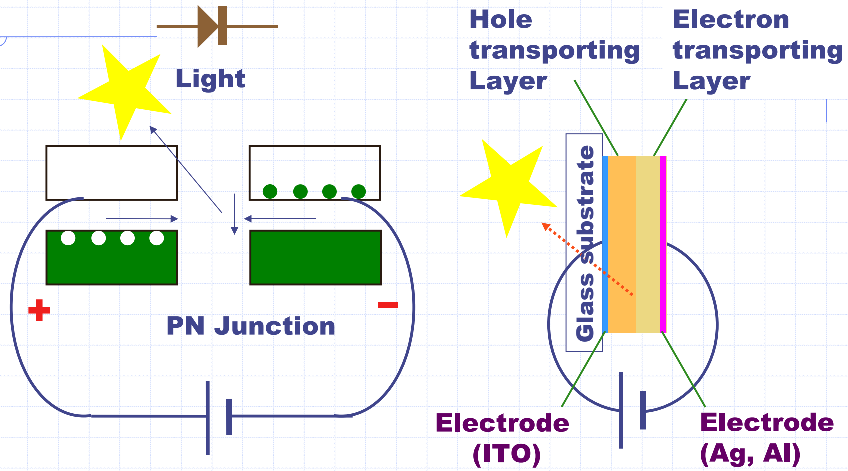
Zener Diode

Standard voltage at the reverse bias.

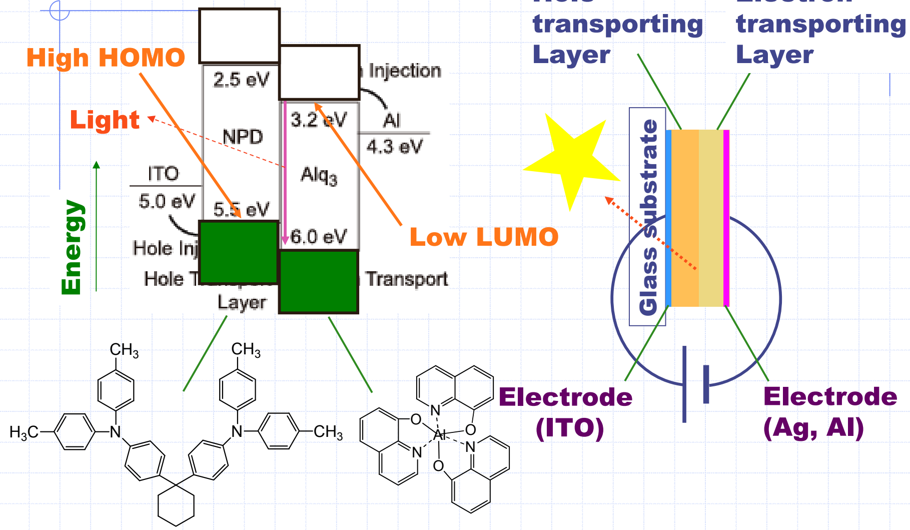


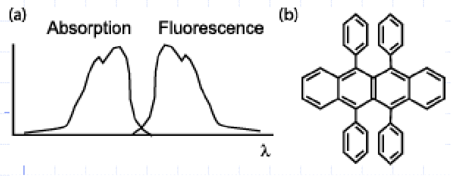


Light Emitting Diode (LED)
Organic EL (Electroluminescence)



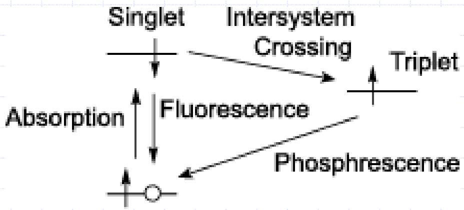
Light Emitting Diode (LED)
Organic EL (Electroluminescence)





Fluorescence quantum yield

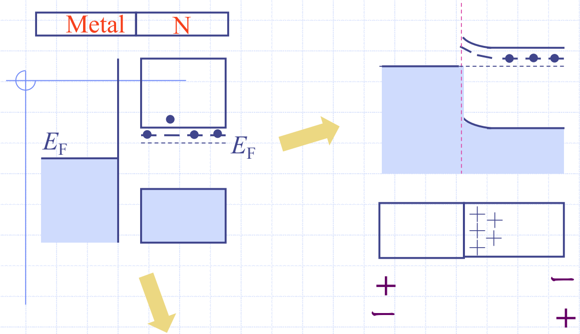
Benzene	0.07	Naphtharene	0.23	Anthracene	0.36
Tetracene	0.21	Pyrene	0.65	Perylene	0.94
Rubrene	~1.0	Fluorene	0.80		
Biphenyl	0.18	Terphenyl	0.93	PPV	0.08
TPD	0.35	Alq_3	0.25	Sexithiophene	0.40



Fluorescence from singlet 25%
Phosphorescence from triplet 75%

Metal-semiconductor junction

Metal E_F < E_F in N-type semiconductor



Adjust E_F

Depletion layer

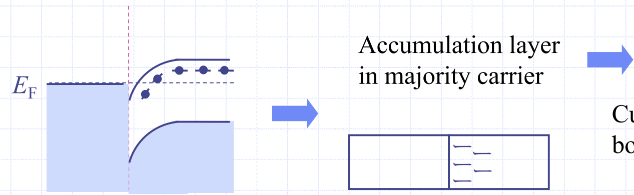
Shottokey Diode

Forward

Reverse

Shottokey Barrier

Meta E_F > E_F in N-type SC：Ohmic contact

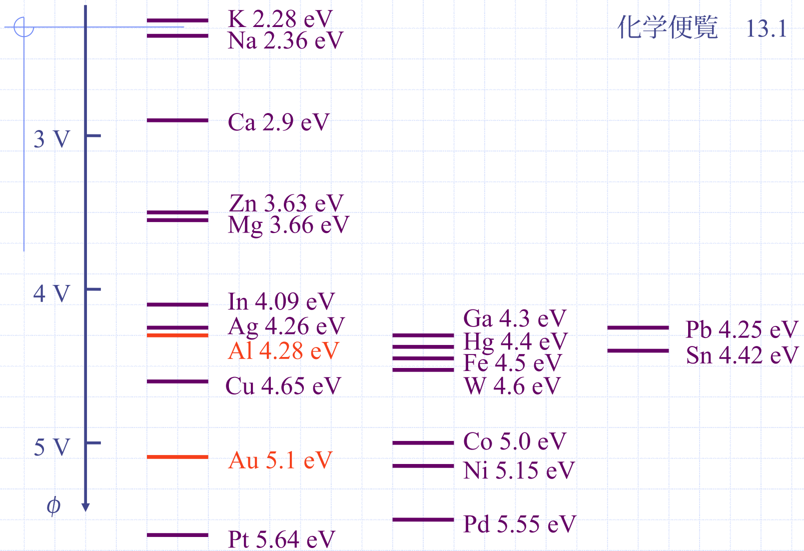


Accumulation layer in majority carrier

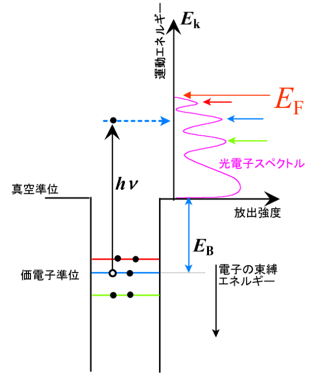
Current flow for both biases.

Work function of Metals (Position of E_F)

cf. Ionization potential for semiconductors

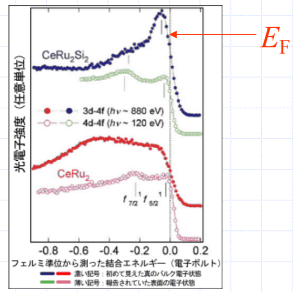


Photoeletron spectroscopy

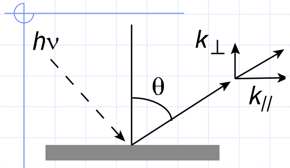


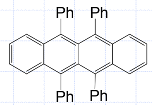
$$E_B = h\nu - E_K$$

Ionization potential

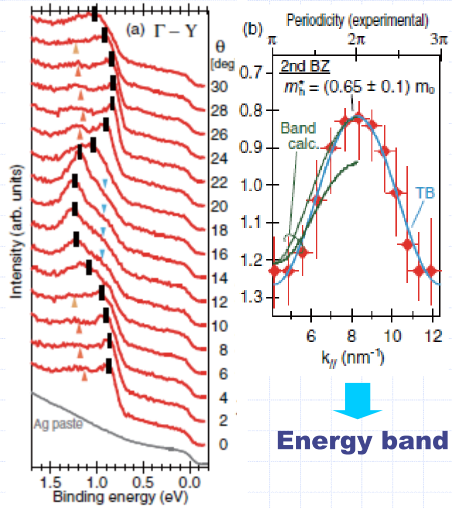


Angle-resolved photoelectron spectroscopy





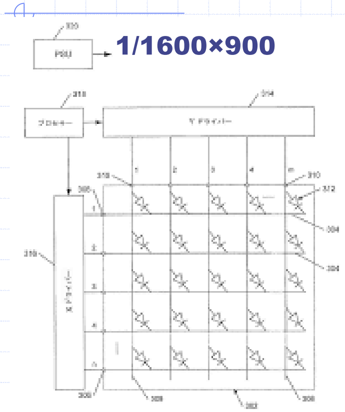
Rubrene Single crystal



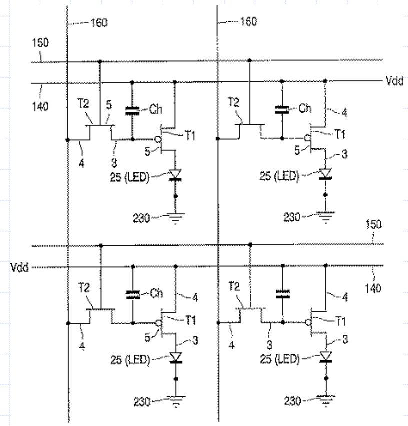
Energy band

Scanning Lines in a display

Passive matrix

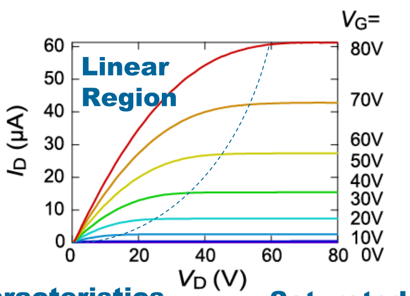


Active matrix



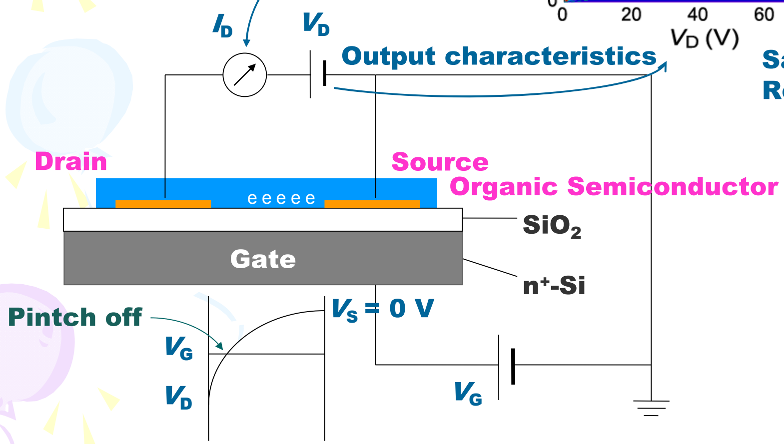
Momorize the signal using a transistor

Organic transistor

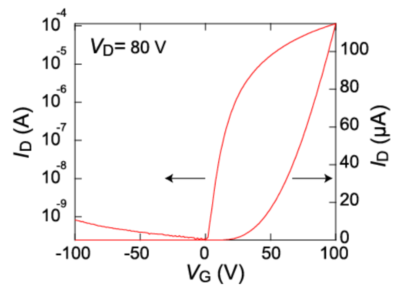


Output characteristics

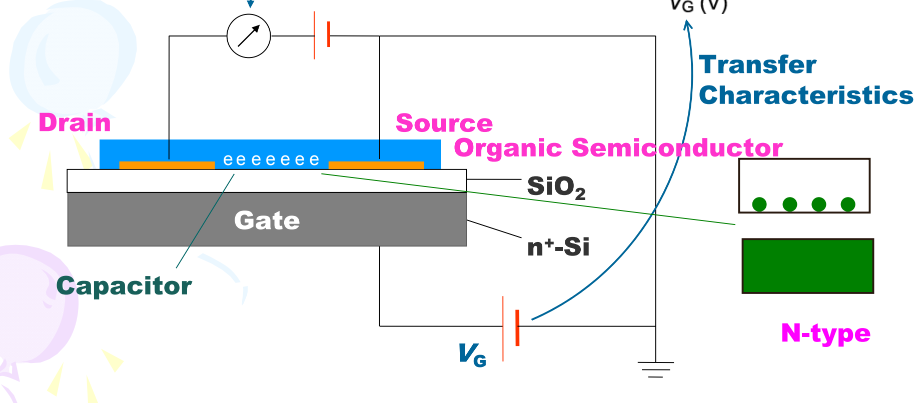
Saturated Region



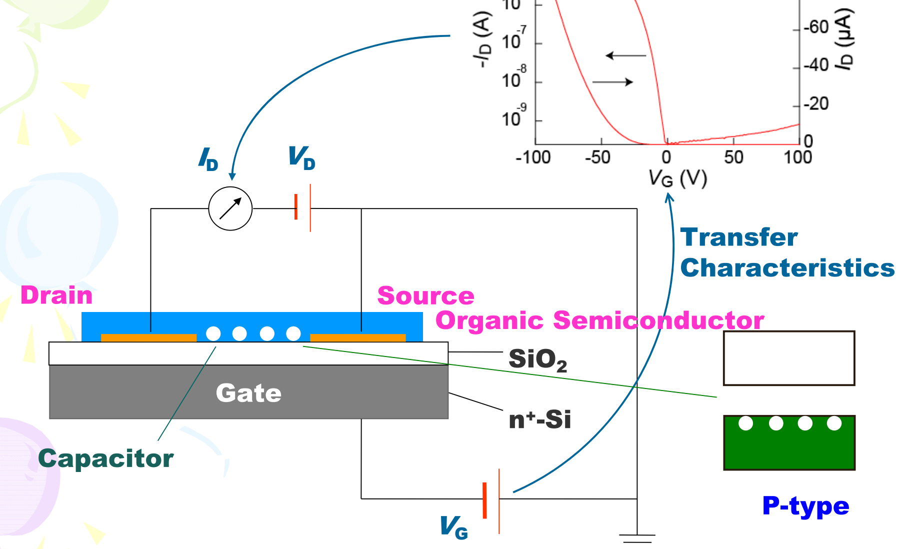
Organic transistor



Transfer Characteristics



Organic transistor



Quantitative transistor characteristics (Gradual Channel Approximation)

Charge on the interface

$Q = C(V_G - V_T)$

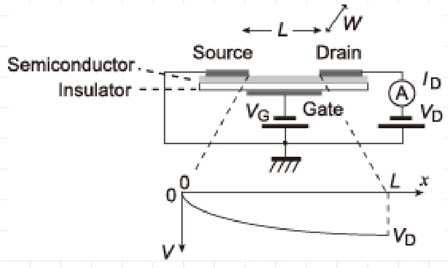
Voltage $V(x)$ **depends on** x

$Q(x) = C(V_G - V_T - V(x))$

$ne \rightarrow Q(x)$ in $\sigma = ne\mu$

Electric field $E_x = -dV(x)/dx$

$I_D = WQ(x)\mu(-dV(x)/dx)$



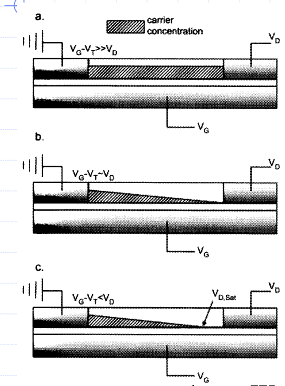
Integrate using $Q(x)$

$$\int_0^L I_D dx = \int_0^{V_D} WC\mu(V_G - V_T - V(x))dV$$

I_D**=constant**

$$I_D = C\mu\frac{W}{L}[(V_G - V_T)V_D - \frac{1}{2}V_D^2]$$

$$I_D = \frac{W\mu C}{L}((V_G - V_T)V_D - \frac{1}{2}V_D^2)$$



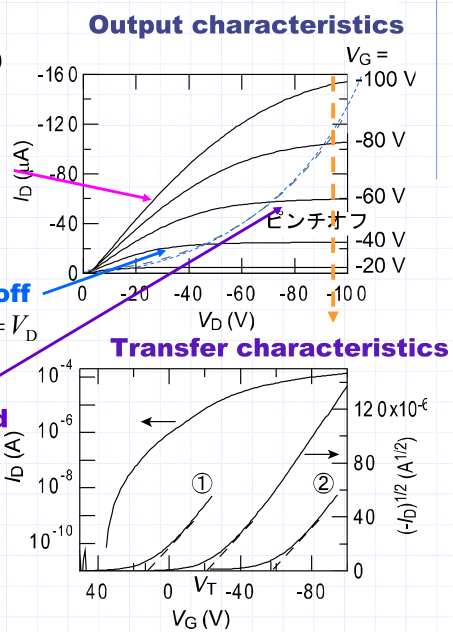
Linear region

Pintch off

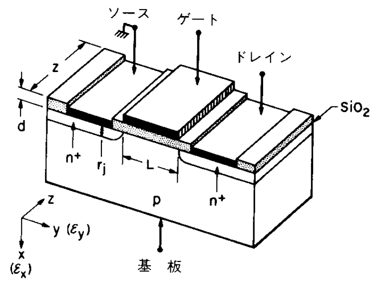
$V_G - V_T = V_D$

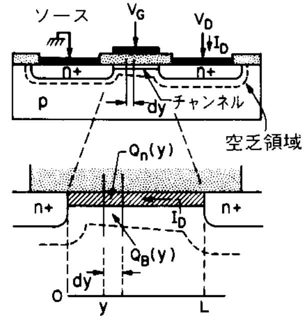
Saturated region

$$I_D = \frac{1}{2}C\mu\frac{W}{L}(V_G - V_T)^2$$



cf. Si single-srystal MOSFET





Minority carrier in the inversion layer in MOS

cf. Majority carrier in organics

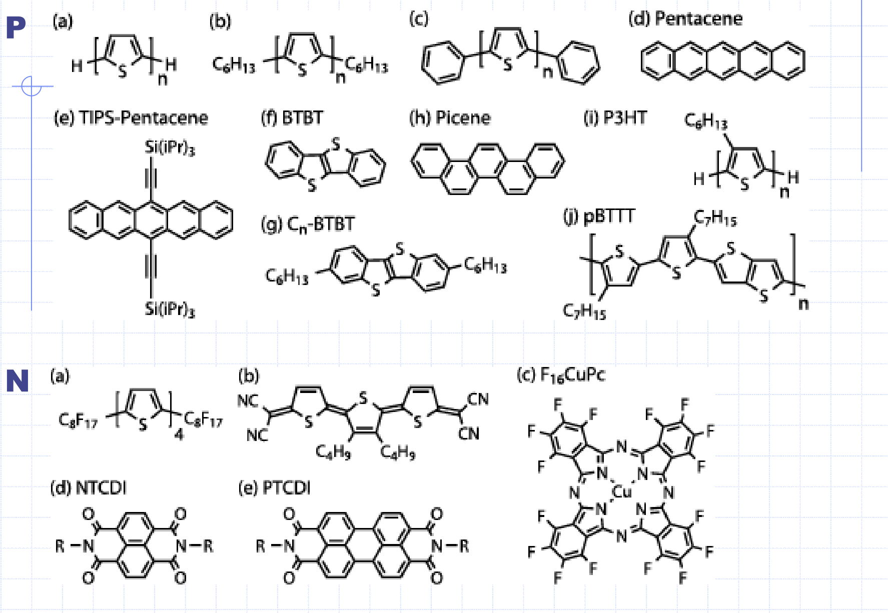
Inversely biased PN junction at source and drain

(Easily attain off current)

cf. Ohmic at source and drain in organics

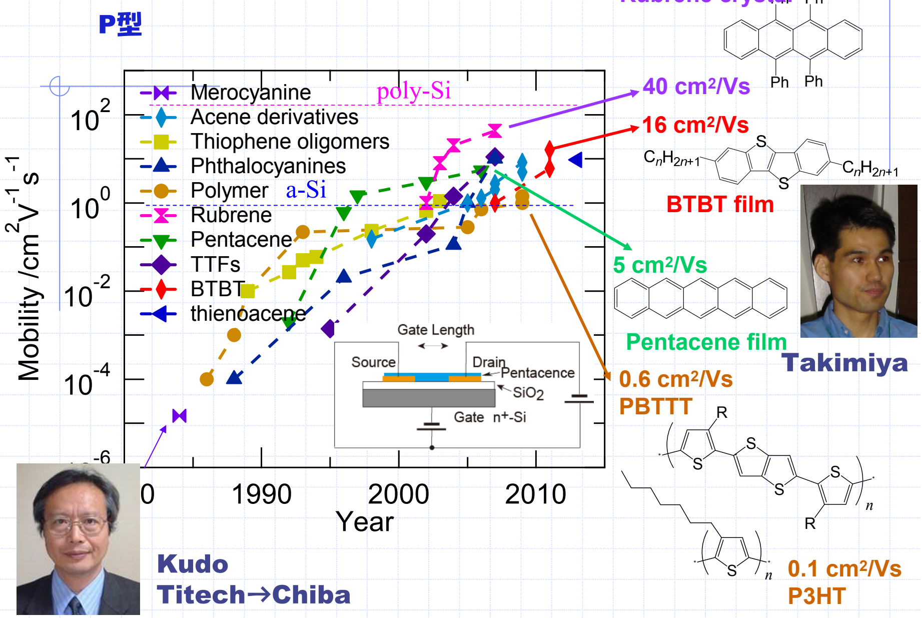
(Difficult to attain off current)

Organic Transistor Materials



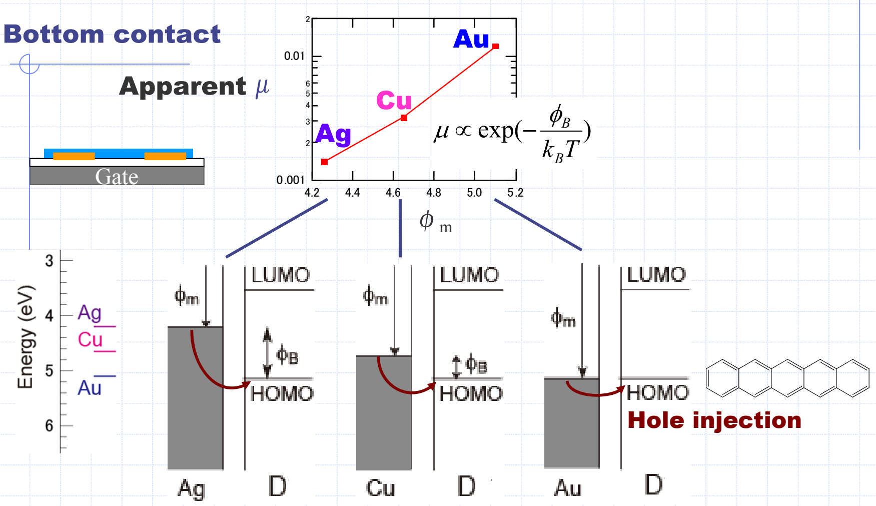
Hiatory of organic transistor materials

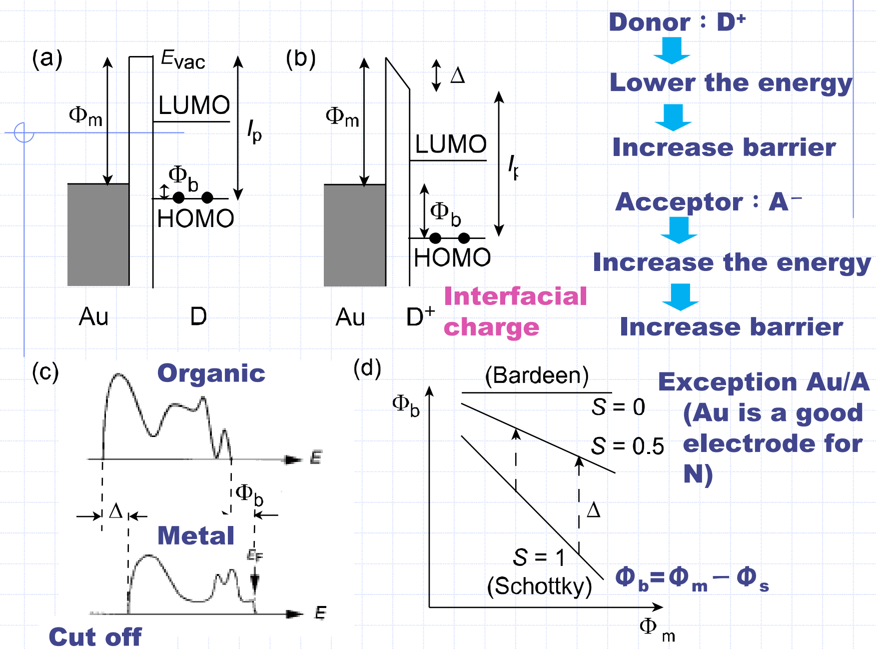
P型



Metal work function ϕ_m → Schottky barrier ϕ_b

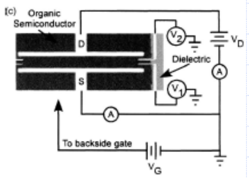
Bottom contact



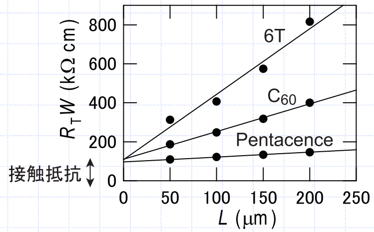


Contact resistance measurements

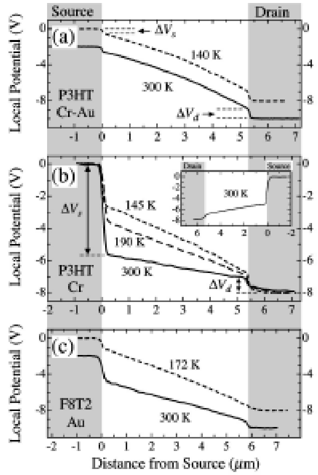
① Four-probe method



② Trnafer line method



③ Scanning Probe Potentiomery



森・長谷川　有機トランジスタの評価と応用II（2008）

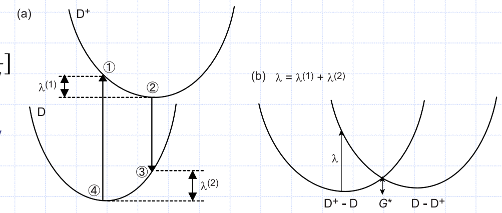
Theoretical calculation of mobility μ

①D⁺ on neutral D
②Optimized D⁺
③D on cationic D⁺
④Optimized D

Marcus theory

$$\mu = \frac{ea^2}{k_B T} k_{ET}$$

$$k_{ET} = \frac{2\pi}{\hbar} t^2 \sqrt{\frac{1}{4\pi\lambda k_B T}} \exp[-\frac{\lambda}{4 k_B T}]$$



Reorganization energy

$\lambda = \lambda^{(1)} + \lambda^{(2)}$

$D^+ - D \rightarrow D - D^+$

Chrge-transfer potential has Parabolic energy
→ Activation energy $G^* = \lambda/4$

λ : 0.1～0.3 eV

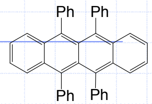
Bredas, *Chem. Rev.* **104**, 4971 (2004); **107**, 926 (2007).

Table 4. B3LYP/6-31G** Estimates of the Relaxation Energies Obtained from eqs 41 and 42 for the Thiophene Oligomers T*n* (with *n* the Number of Thiophene Rings)

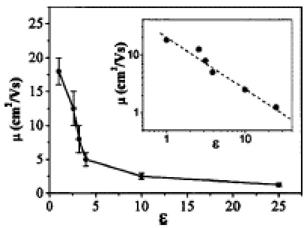
molecule	$\lambda_{rel}^{(1)}$ (meV)	$\lambda_{rel}^{(2)}$ (meV)
T1	200	204
T2	187	237
T3	162	211
T4	153	192
T5	142	172
T6	136	165
T7	126	147
T8	119	137

Single-crystal organic transistor

Rubrene



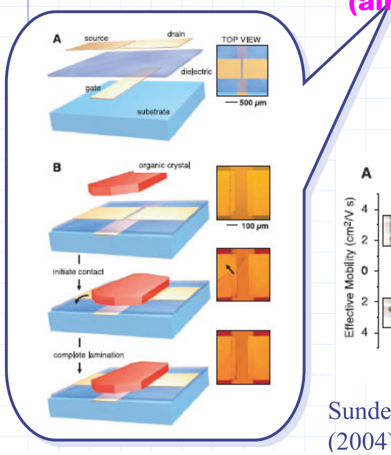
Single crystal
2003　1 cm²/Vs
2003　8 cm²/Vs
2004　20 cm²/Vs
(air-gap stamp

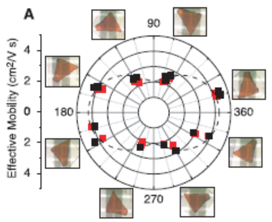


Dielectric constant of gate

cf. $C = \frac{\varepsilon S}{d}$

Stassen, *APL*, 85, 3899 (2004).

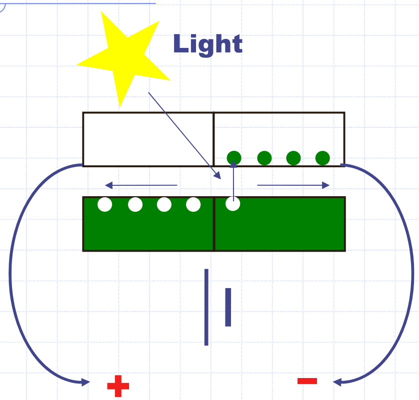




Single-crystal anisotropy

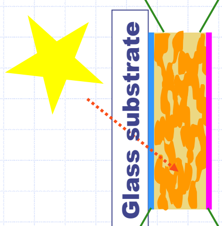
Sunder, *Science*, 303, 1644 (2004).

Organic solar cell　Reverse operation
Electricity ← Light



Hole transporting Layer

Electron transporting Layer

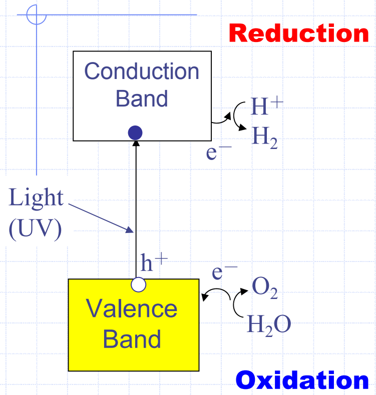


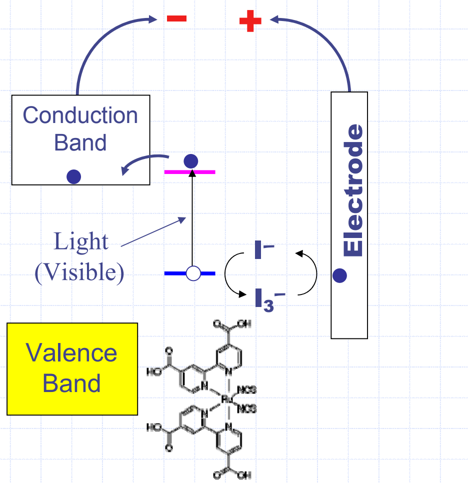
Electrode (ITO)

Electrode (Ag, Al)

Scramble → Bulk heterojunction
Yield ～10%

Photocatalyst / Dye sensitized solar cell





TiO_2

TiO_2 Dye

Effeiciency 10%+α

Dye sensitized solar cell

Efficiency

Si film 15%

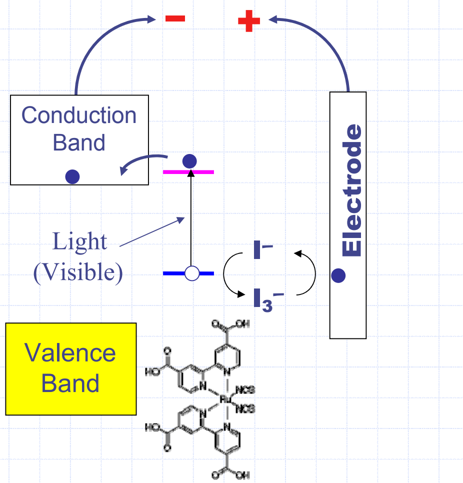
Si crystal 25%

Compound semiconductor >30%

Organic film 10%

Dye sensitized 10%+α

Perovskite 20%

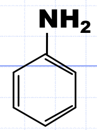


TiO_2 Dye

Effeiciency 10%+α

Polyaniline (PANI)

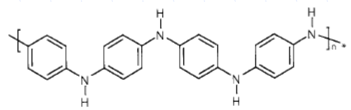
p-type



Electrochemical oxidation → **Polyaniline**

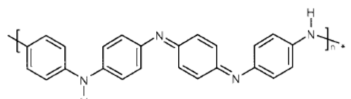
or $(NH_4)_2S_2O_8$

cf. Aniline black
black dye



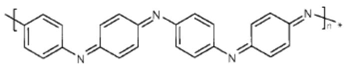
Leucoemeraldine

Coloeless insulator



Emeraldine

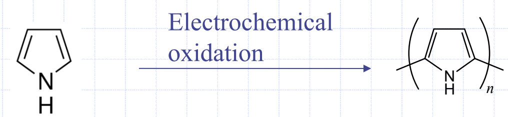
Blue or green (salt)



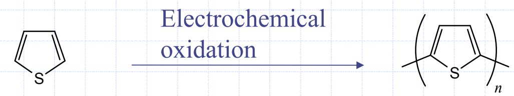
Pernigraniline

Blue/violet insulator

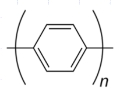
p-type



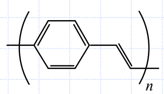
polypyrrole



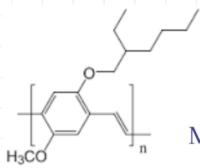
polythiophene



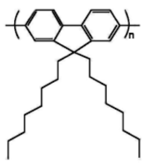
poly(parapenylene)



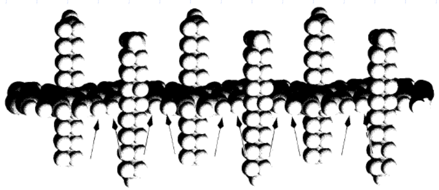
poly(phenylenevinylene)
PPV



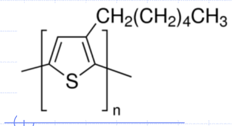
MEH-PPV
Soluble



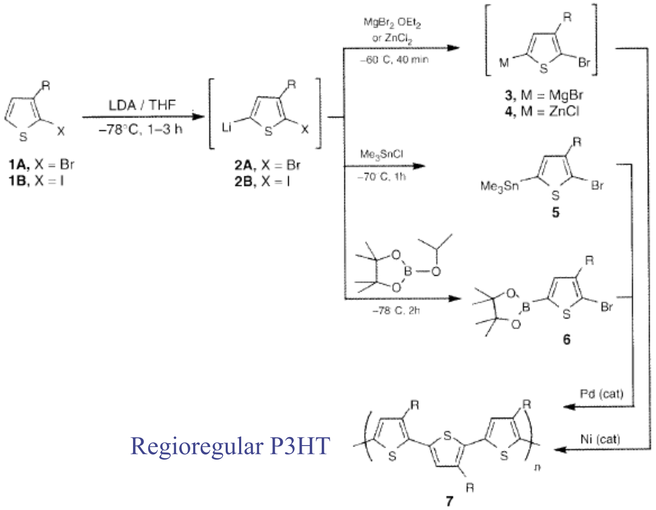
poly(dioctylfluorene)
Soluble



p-type



Regioregular
poly(3-hexylthiophene)
P3HT Soluble



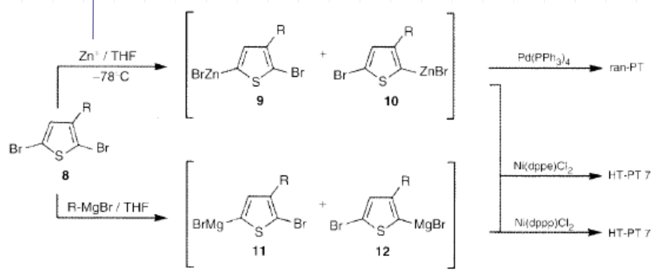
Tamao coupling

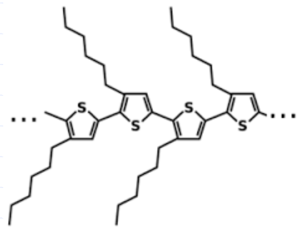
Stille coupling

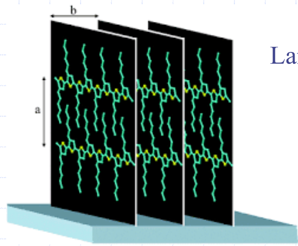
Suzuki coupling

Regioregular P3HT

Rieke Zinc: $ZnCl_2 + K \rightarrow Zn + 2KCl$

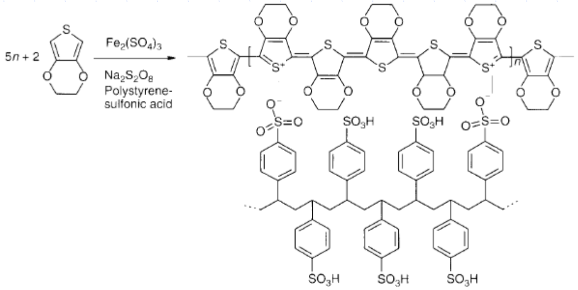






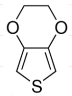
Lamella structure

PEDOT/PSS
Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)



Bayer

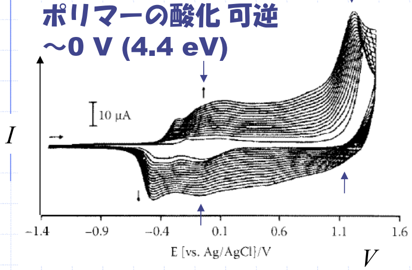
Transparent and flexible conducting film
from aquous solutions



EDOTの電気化学酸化

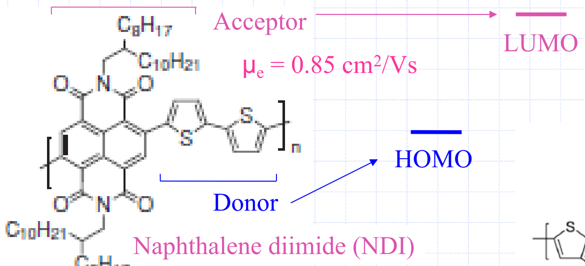
モノマーの酸化 (電解重合) 不可逆
～1.4 eV (5.8 eV)

ポリマーの酸化 可逆
～0 V (4.4 eV)

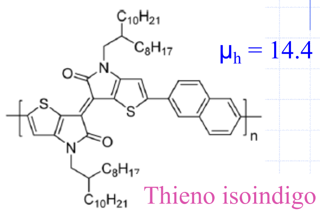


PEDOT/PSSの応用
1. 電解コンデンサ電極
   →直列抵抗の低下
2. 透明電極
3. 帯電防止塗料
4. 有機ELのホール注入層
5. 有機薄膜太陽電池電極
6. エレクトロクロミズム
7. 有機トランジスタ電極

Donor-Acceptor-Type Polymers

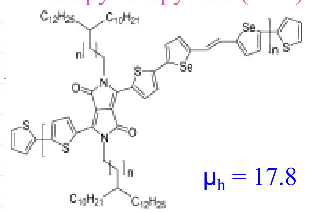


Facchetti, *Nature* 2009, **457**, 679.

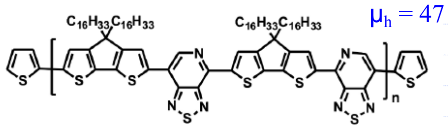


蔚山 *JACS* 2014, **136**, 9477.

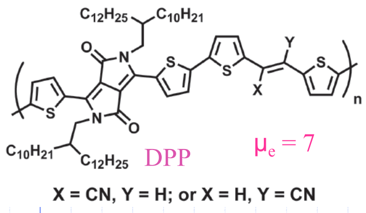
Diketopyrrolopyrrole (DPP)



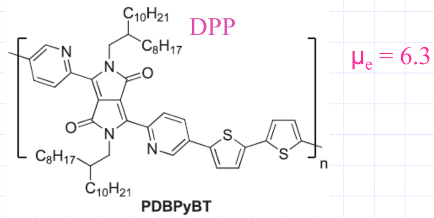
蔚山 *Chem. Mater*. 2015, **27**, 1732 .



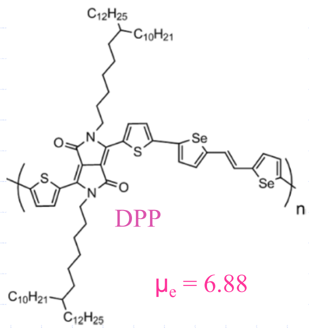
Heeger, *Nano Lett*. 2014, **14**, 2764.



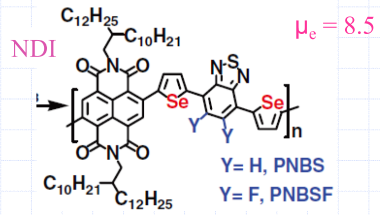
慶尚 *Adv. Mater*. 2014, **26**, 7300.



Waterloo *Adv. Mater*. 2014, **26**, 2636.



慶尚 *Chem. Mater*. 2016, **28**, 2287.



北京 *Adv. Mater*. 2017, **29**, 1602410.