

Structures of Aromatic Compounds

Acta Crystallogr. B 45, 473 (1989).

Herringbone (θ -type) : Side dominant

phenanthrene biphenyl terphenyl

Dimer (κ -type) : Intermediate

perylene pyrene

γ -Structure (θ -type) : with large face

Stack (β -type) : Face dominant

coronene ovalene

Large molecular plane induces parallel stacking structures. 1

Photoconductivity

Time of Flight (TOF)

Pure crystals

$$v = \mu E = \frac{\mu V}{L}$$

$$t = \frac{L}{v} = \frac{L^2}{\mu V}$$

$$\mu = \frac{L^2}{tV}$$

オシロスコーブ

TOF Mobility (cm^2/Vs)

	Hole $a/b/c$	Electron $a/b/c$
Naphthalene	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 · Laser printer

(b) Monolayer

Light Photoconductor Electrode

(c) Multilayer

Light Charge Transport Layer Charge Generation Layer Electrode

3

Space-charge-limited current (SCLC)

Carrier injection into an insulator

$$J = en\mu E \rightarrow \frac{\partial E}{\partial x} = \frac{en}{\epsilon} = \frac{J}{\epsilon\mu E}$$

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

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

Integrate for x up to the thickness $L \rightarrow V$

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

$J \propto V^2$ Non ohmic
 \rightarrow Mobility μ

log J

Saturated

SCLC $\propto V^2$

Trapped

Ohmic $\propto V$

log V

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 $E_F = \text{const.}$

N_p , N_c , N_p' , N_c'

5

Forward bias

Reverse bias

attraction leads to current flow

電子注入 electron injection

ホール注入 hole injection

Potential is lowered to $V_D - V$.

No current flows

6

Majority carrier in N

$$N_e = N_c^0 e^{-\frac{E_c - E_F}{k_B T}}$$

Minority carrier in P

$$N_e' = N_c^0 e^{-\frac{E_c - E_F + eV_D}{k_B T}} \rightarrow N_c' = N_c e^{-\frac{eV_D}{k_B T}}$$

Under bias V , this leads to

$$N_e' = N_c e^{-\frac{e(V_D - V)}{k_B T}}$$

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 $I \propto N_e' - N_e = I_0 (e^{eV/k_B T} - 1)$

(The same equation for holes)

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

順方向 forward bias

reverse bias 逆バイアス

Current flows only for forward bias. (Diode)

7

Diodes for specialized uses

Light Emitting Diode

Recombination of injected carriers at forward bias generates light.

電子注入 electron injection

ホール注入 hole injection

EL: Electroluminescence

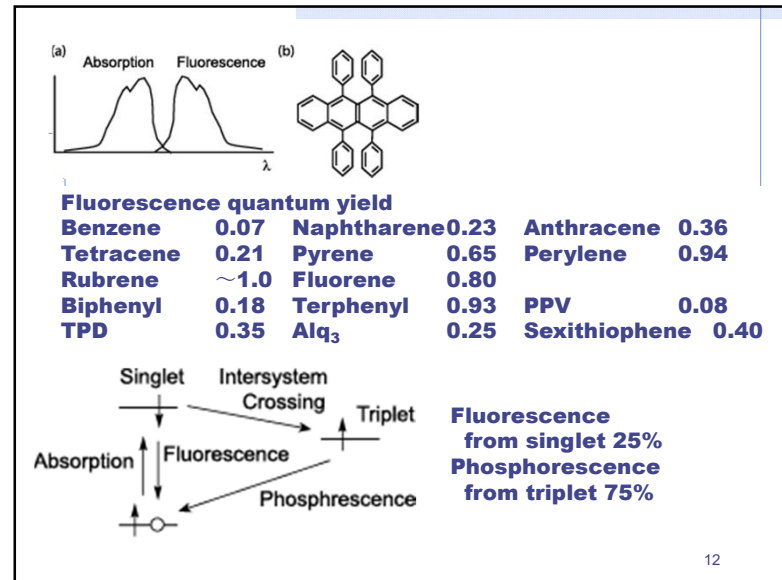
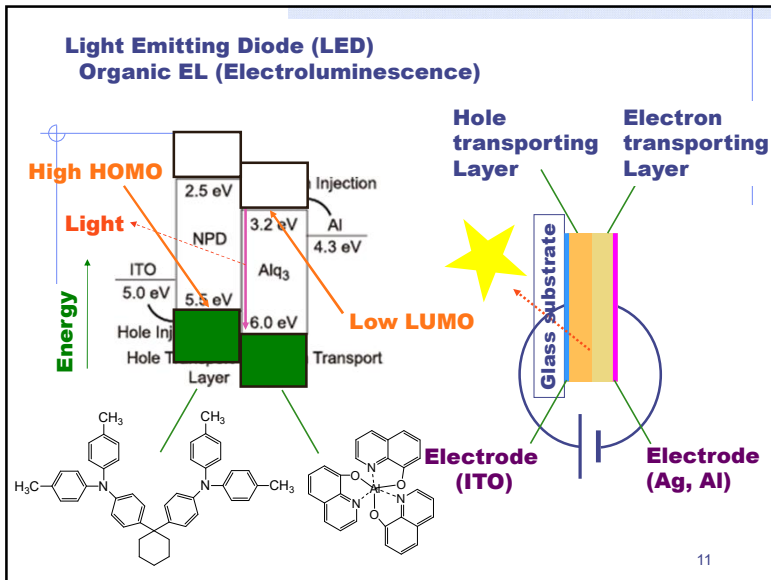
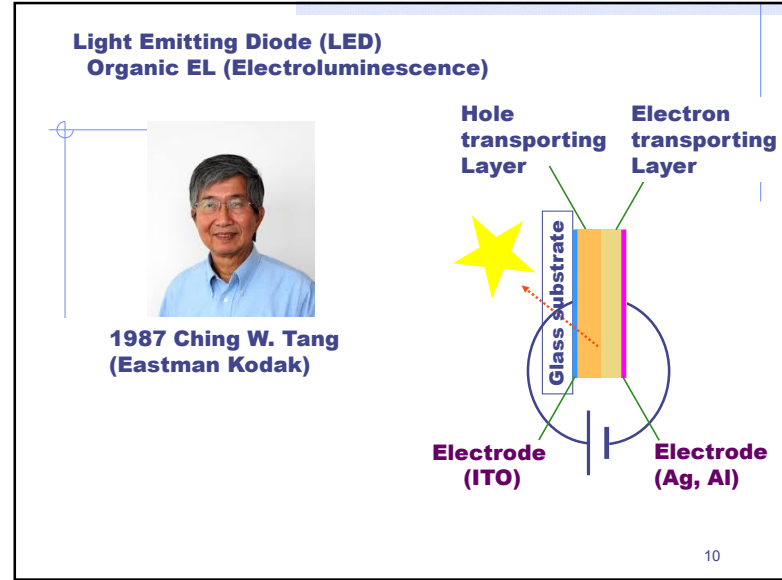
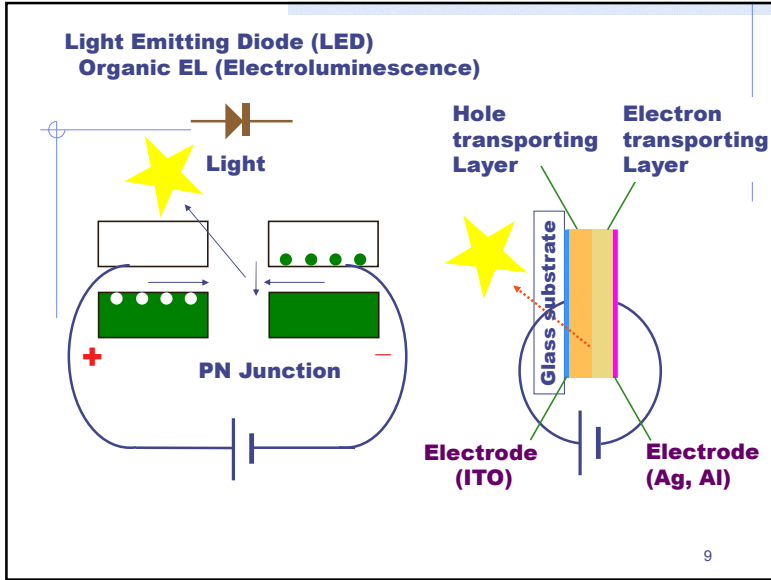
$h\nu$ depends on E_g .

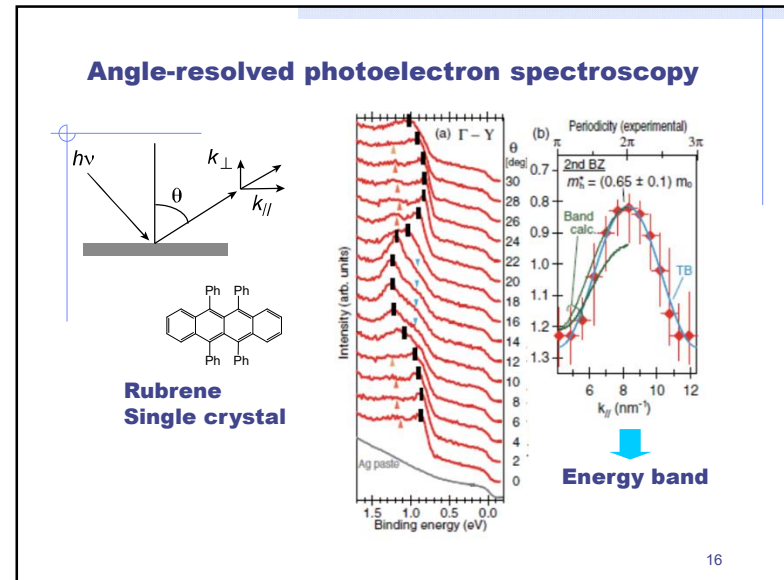
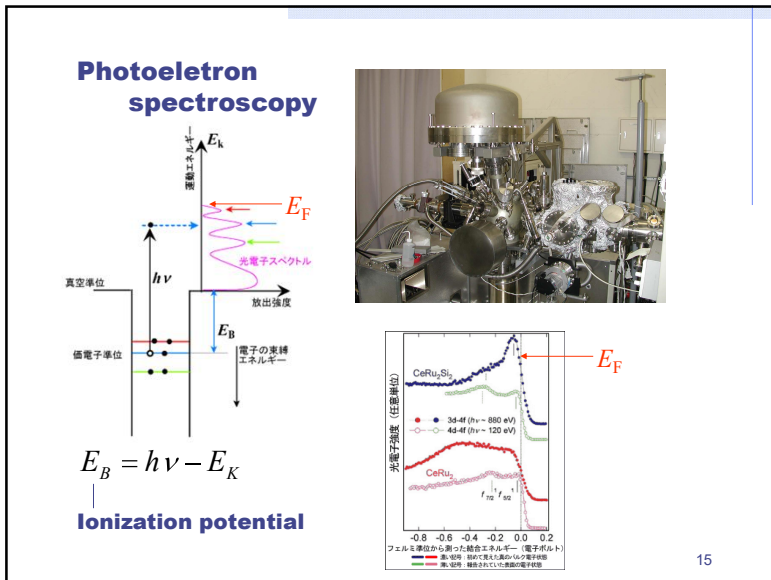
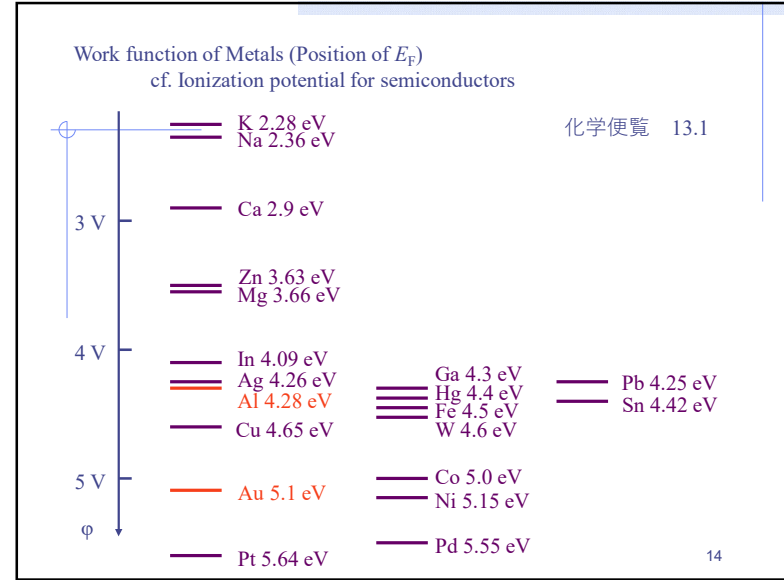
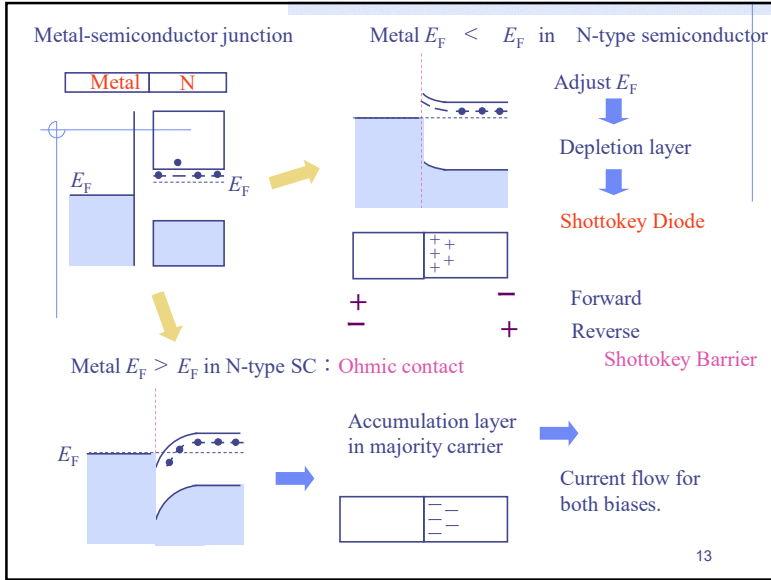
Zener Diode

Standard voltage at the reverse bias.

Zener Breakdown

8





Scanning Lines in a display

Passive matrix

$1/1600 \times 900$

Active matrix

Memorize the signal using a transistor

17

Organic transistor

I_D (μA)

V_D (V)

$V_G =$

- 80V
- 70V
- 60V
- 50V
- 40V
- 30V
- 20V
- 10V
- 0V

Linear Region

Saturated Region

Output characteristics

18

Organic transistor

I_D (A)

V_G (V)

$V_D = 80$ V

I_D (μA)

Transfer Characteristics

19

Organic transistor

$-I_D$ (A)

V_G (V)

$V_D = -80$ V

I_D (μA)

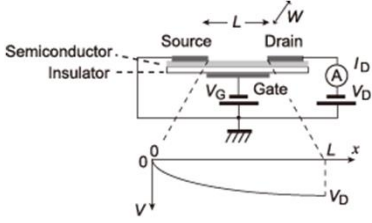
Transfer Characteristics

20

Quantitative transistor characteristics (Gradual Channel Approximation)

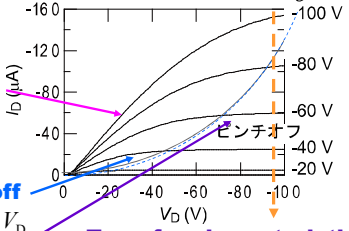
Charge on the interface
 $Q = C(V_G - V_T)$
Voltage $V(x)$ depends on x
 $Q(x) = C(V_G - V_T - V(x))$
 $ne \rightarrow Q(x)$ in $\sigma = ne\mu$
Electric field $E_x = -dV(x)/dx$
 $I_D = WQ(x)\mu(-dV(x)/dx)$

Integrate using $Q(x)$
 $\int_0^L I_D dx = \int_0^{V_D} WC\mu(V_G - V_T - V(x))dV$
 $I_D = \text{constant}$
 $I_D = C\mu \frac{W}{L} [(V_G - V_T)V_D - \frac{1}{2}V_D^2]$



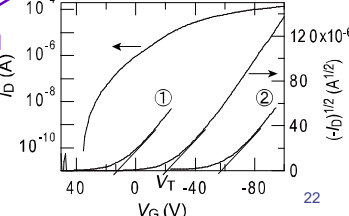
21

Output characteristics

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


Linear region
Pinch off
 $V_G - V_T = V_D$
Saturated region

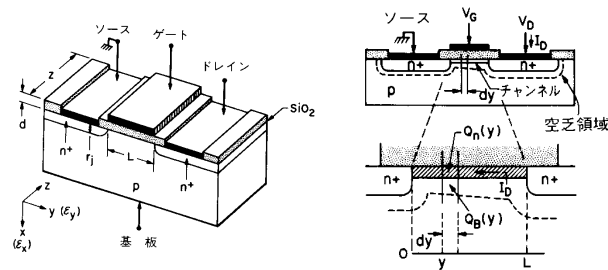
Transfer characteristics



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

22

cf. Si single-crystal 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)

23

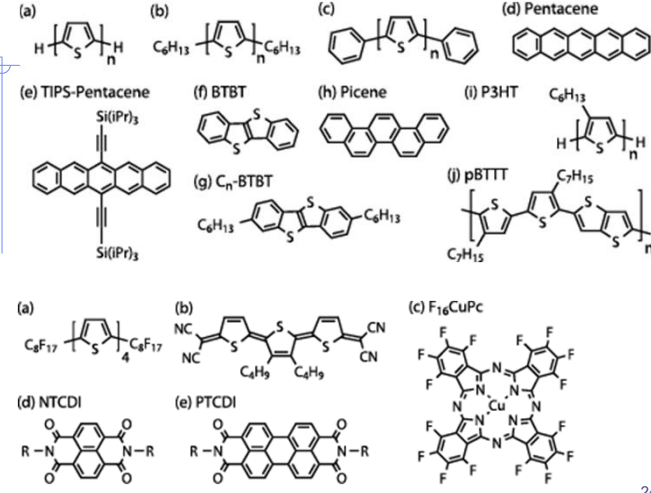
Organic Transistor Materials

P

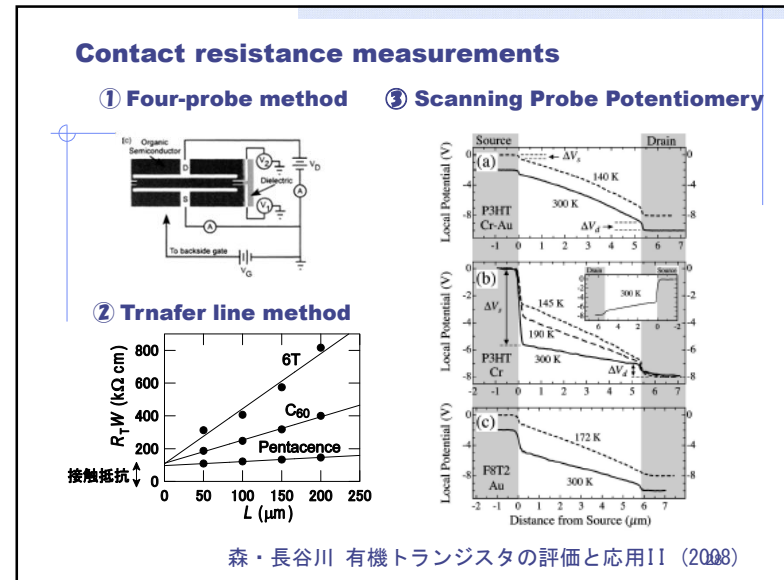
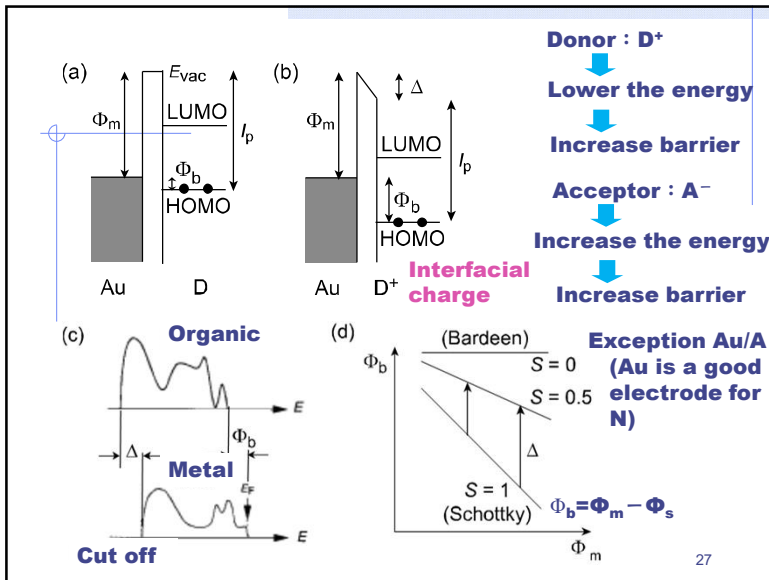
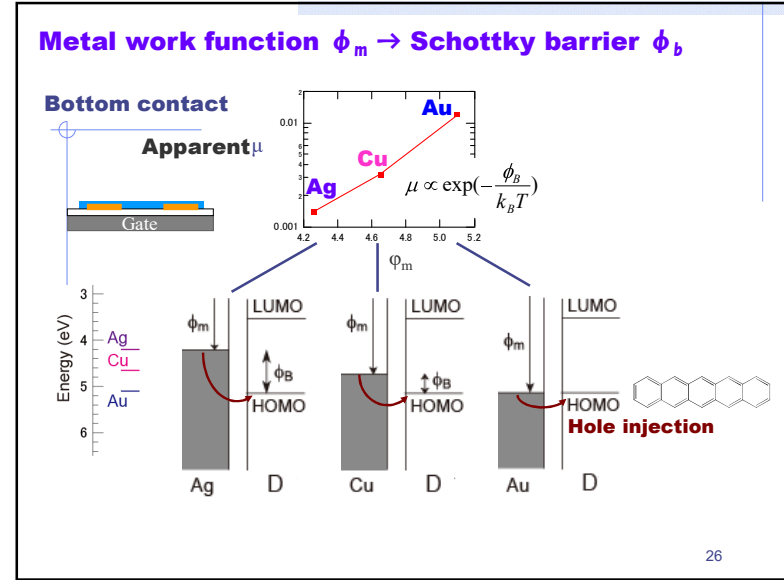
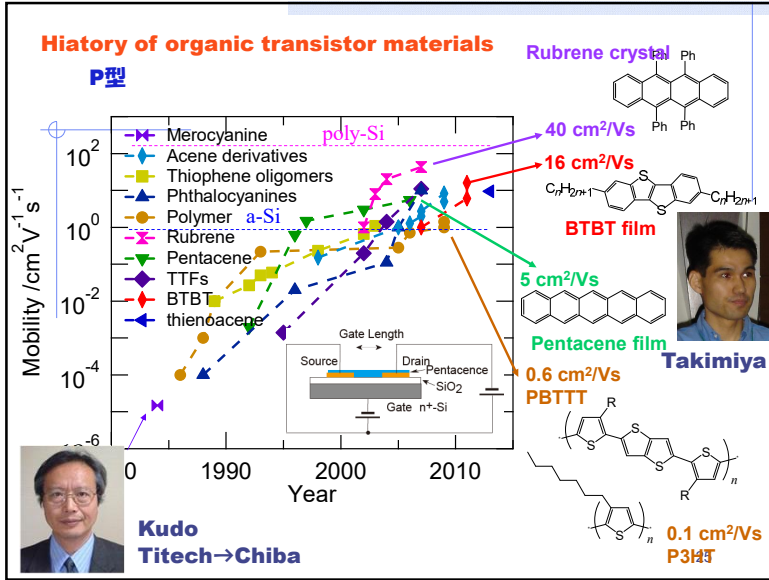
(a) TIPS-Pentacene, (b) BTBT, (c) Picene, (d) P3HT, (e) TIPS-Pentacene, (f) BTBT, (g) C_n-BTBT, (h) Picene, (i) P3HT, (j) pBTTT

N

(a) C₈F₁₇, (b) F₁₆CuPc, (c) F₁₆CuPc, (d) NTCDI, (e) PTCDI



24



Theoretical calculation of mobility μ

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

Marcus theory

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

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

Reorganization energy

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

Charge-transfer potential has Parabolic energy

→ **Activation energy $G^* = \lambda$**

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	$\lambda^{(1)}$ (meV)	$\lambda^{(2)}$ (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 stam)

Dielectric constant of gate

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

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**

Glass substrate

Electrode (ITO) **Electrode (Ag, Al)**

Scramble → Bulk heterojunction
Yield ~10%

Photocatalyst **Dye sensitized solar cell**

Reduction **Oxidation**

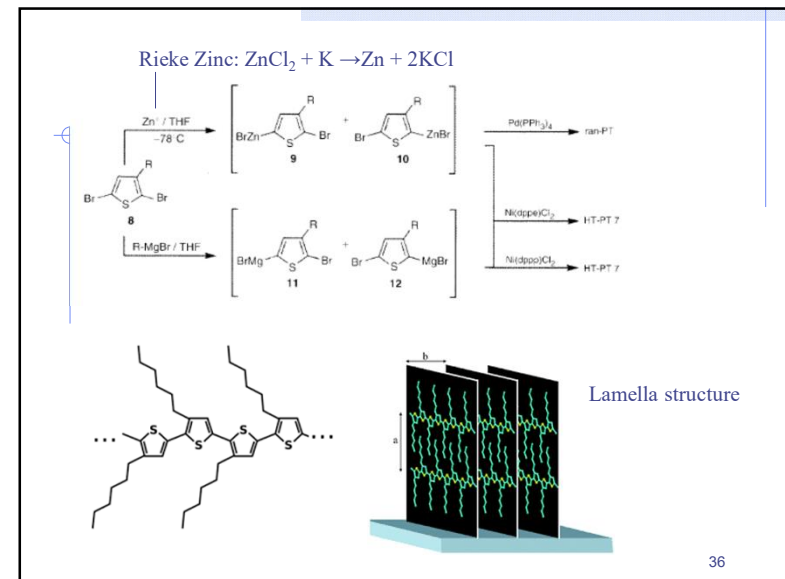
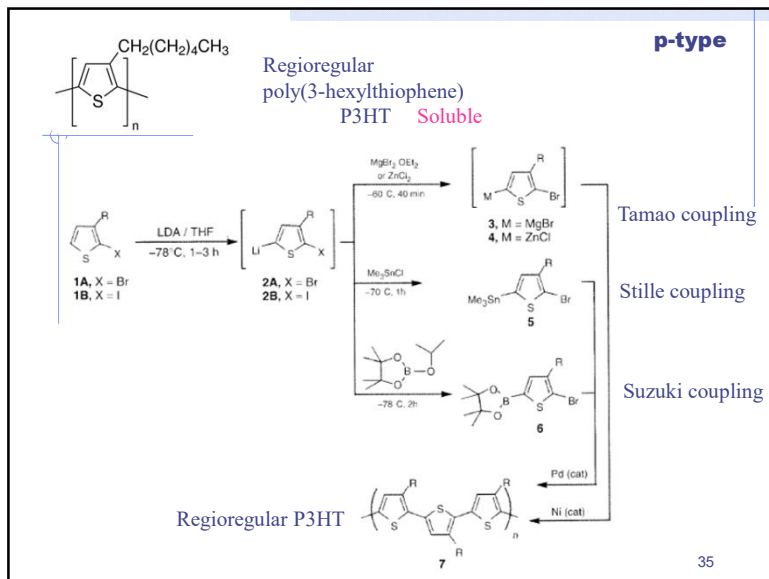
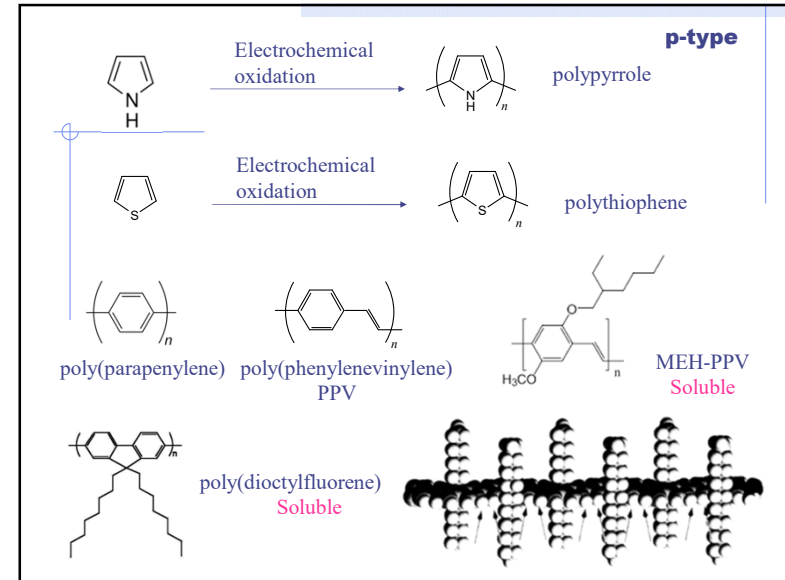
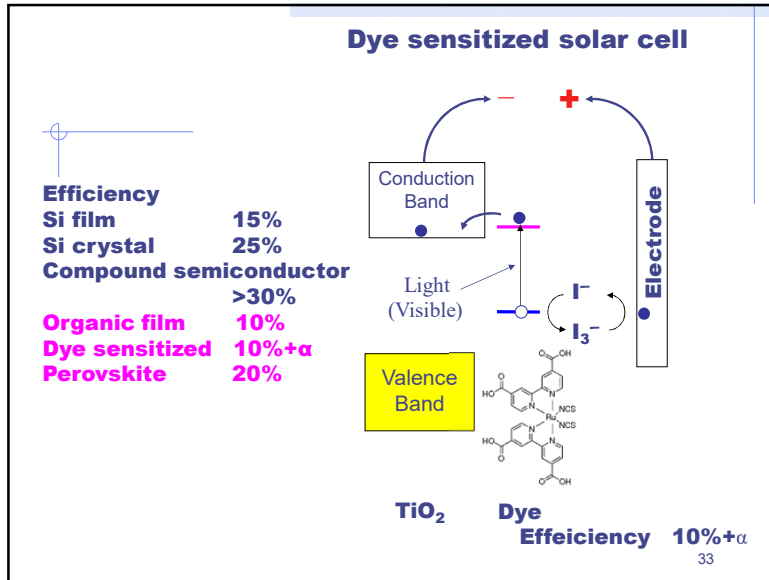
Conduction Band Conduction Band

Valence Band Valence Band

Light (UV) Light (Visible)

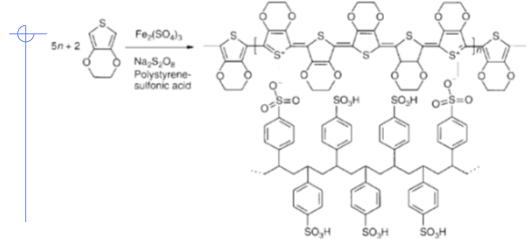


TiO₂ **TiO₂** **Dye**

Efficiency 10%+ α




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

Bayer

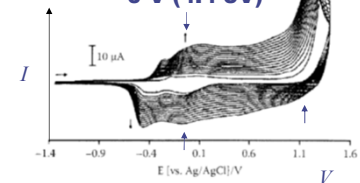
Transparent and flexible conducting film from aqueous solutions

37

 **Electrochemical oxidation of EDOT**

Irreversible oxidation of the monomer (polymerization)
~1.4 eV (5.8 eV)

Reversible oxidation of the polymer
~0 V (4.4 eV)

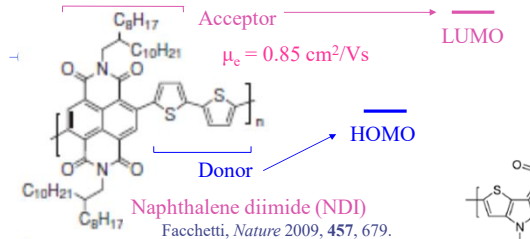


PEDOT/PSSの応用

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

38

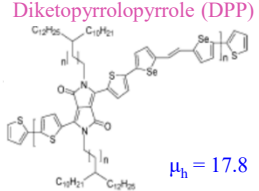
Donor-Acceptor-Type Polymers



$\mu_c = 0.85 \text{ cm}^2/\text{Vs}$

Naphthalene diimide (NDI)
Facchetti, *Nature* 2009, 457, 679.

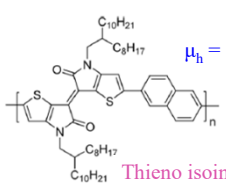
Diketopyrrolopyrrole (DPP)



$\mu_h = 17.8$

蔚山 *Chem. Mater.* 2015, 27, 1732.

Thieno isoindigo

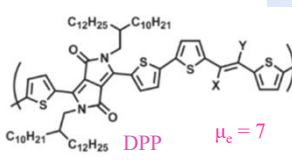


$\mu_h = 14.4$

蔚山 *JACS* 2014, 136, 9477.

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

39



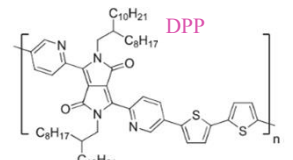
$\mu_c = 7$

慶尚 *Adv. Mater.* 2014, 26, 7300.

DPP

$\mu_c = 6.88$

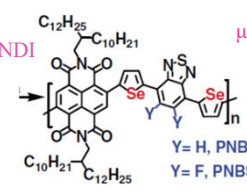
慶尚 *Chem. Mater.* 2016, 28, 2287.



$\mu_c = 6.3$

PDBPyBT

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



$\mu_c = 8.5$

NDI

Y = H, PNBS
Y = F, PNBSF

北京 *Adv. Mater.* 2017, 29, 1602410.

40