

Charge-transfer complex 電荷移動錯体

**Electron donor** 電子供与体

**Compounds easily oxidized to  $D^0 \rightarrow D^+$  with high HOMO levels**

**Electron acceptor** 電子受容体

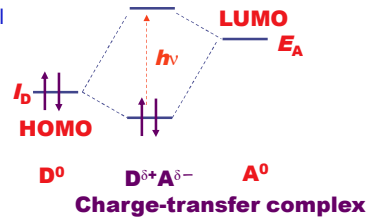
**Compounds easily reduced to  $A^0 \rightarrow A^-$  with low LUMO levels**

Lowest Unoccupied Molecular Orbital

LUMO conduction band

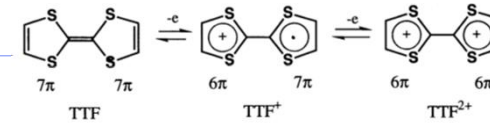
HOMO valence band

Highest Occupied Molecular Orbital

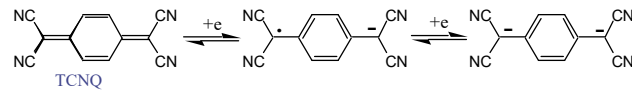


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**(a)  $7\pi$  electron  $\rightarrow$  Donor**

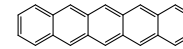


**(b)  $6\pi$  recovers from quinoido + electron withdrawing  $\rightarrow$  Acceptor**



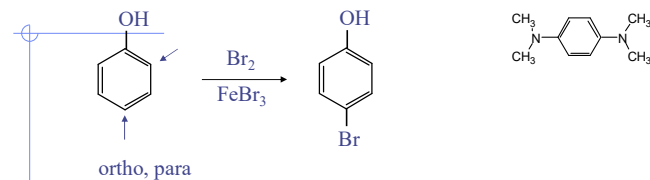
**(c) Aromatic hydrocarbons: Donor > Acceptor**

$\leftarrow$  In general,  $C^+$  is stabler than  $C^-$

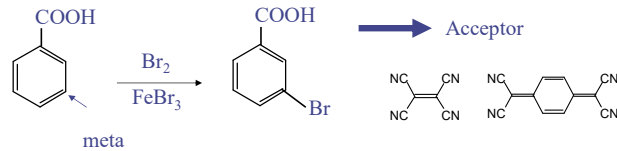


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El donating: -OH, -OCH<sub>3</sub>, -NH<sub>2</sub>  $\rightarrow$  Donor

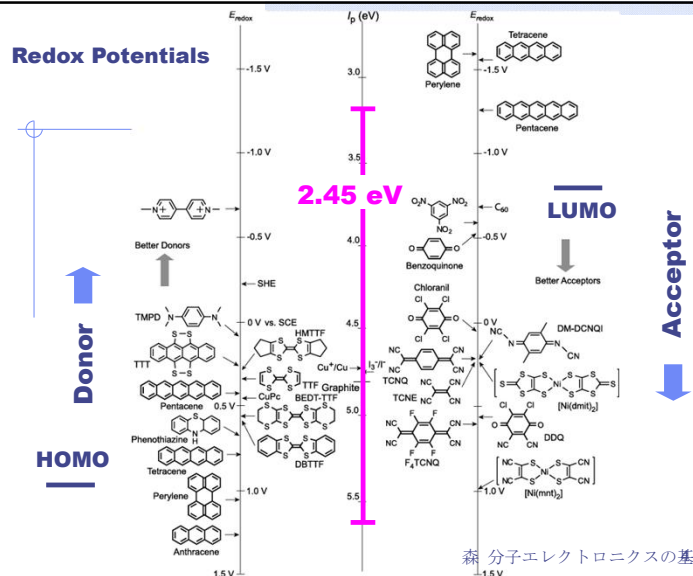


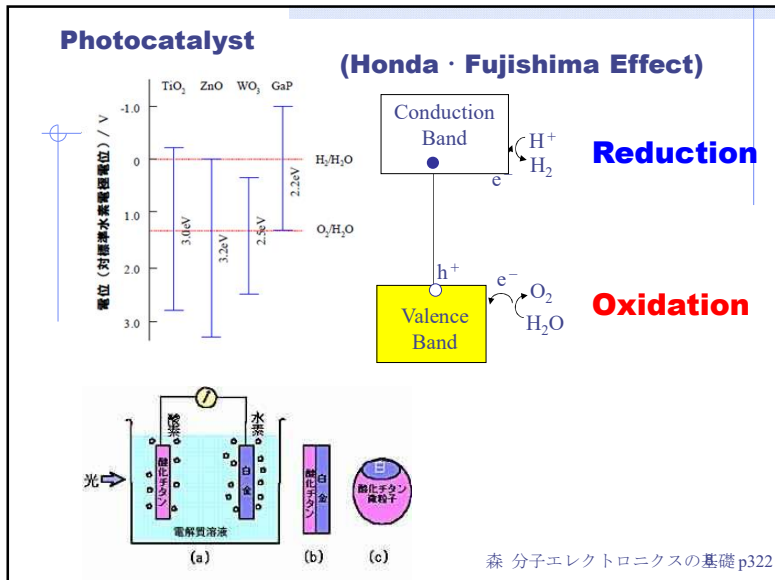
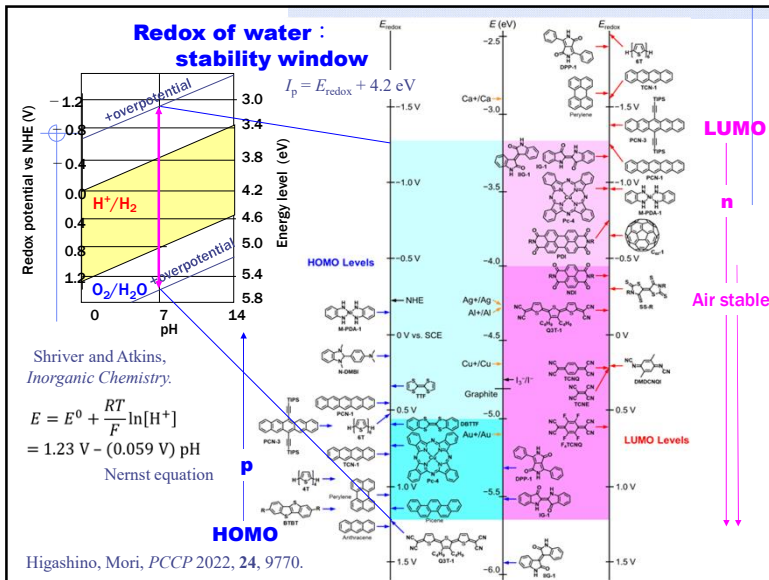
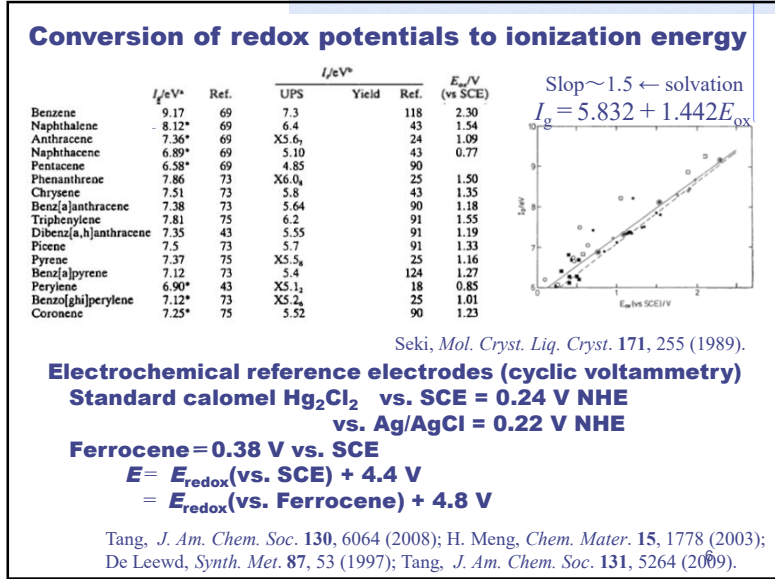
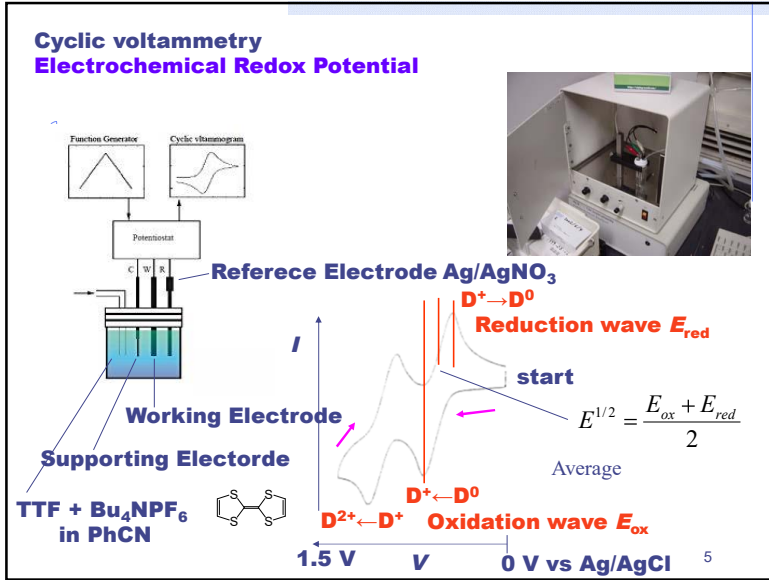
Elc withdrawing: -NO<sub>2</sub>, -CN, halogene, -COOH, -COOCH<sub>3</sub>, -CHO



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**Redox Potentials**





**Mixed stack structure**  
 Neutral and ionic : low conducting  $10^{-11}$  S/cm  
 pyrene TCNE pyrene  
 Planer molecules make 1D stacks.

**Segregate stack structure**  
 Partial charge transfer : high conducting **170 S/cm**  
 TCNQ column  
 NMP column  
 TCNQ column

**(NMP)(TCNQ) : first 「Organic Metal」 1966**

$(TTF)_X$  : Typical 1D Metal (X = Cl, Br, I, SCN,  $x \sim 0.71$ )  
 Radical cation salt (Organic cation + Inorganic anion)

**500 S/cm**  
 Insulator Metal  
 Resistivity  
 Temperature (K)  
 Metal-insulator transition at 200 K

tetrathiafulvalene TTF

Planer molecules make 1D stacks.

**(TTF)(TCNQ)**  
 1973  
 $(TTF^{0.59+})(TCNQ^{0.59-})$

Diffusion method  
 From acetonitril solutions of TTF and TCNQ

Segregated stacks  
 TTF  
 TCNQ  
**600 S/cm**  
 Insulator Metal  
 Metal-insulator transition at 54 K

tetrathiafulvalene TTF  
 tetracyanoquinodimethane TCNQ

$\beta$ -(BEDT-TTF) $_2$ I $_3$   
 BEDT-TTF ( $T_c = 1.5$  K) First ambient-pressure superconductor  
**30 S/cm**  
 Superconducting metal  
 Resistivity  
 TEMPERATURE (K)  
**2D metal**

Transfer integrals  $\beta$  (meV)  
 方向 HOMO  
 p1 245  
 p2 84  
 c 50  
 q1 127  
 q2 68  
 Intercalin  $\sim$  p2  
 From MO calc.

### Various structures of BEDT-TTF

Mori, *Bull. Chem. Soc. Jpn.* 71, 2509 (1998); 72, 179 (1999); 72, 2011 (1999).

Ring over bond: slip along the long axis (RB)

"Ring over atom": slip along the short axis (RA)

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### $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$

1/2+ + -

Superconductivity at 10.4 K (1987)

Electrochemical Crystal Growth

$\text{BEDT-TTF} \rightarrow \text{BEDT-TTF}^+ [\text{Cu(NCS)}_2]^- \rightarrow (\text{BEDT-TTF})_2\text{Cu(NCS)}_2$

### $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$

First organic superconductor above 10 K ( $T_c=10.4$  K)

Urayama et al. *Chem. Lett.* 1988, 55; 1988, 463.

$\text{Cu(NCS)}_2$  Anion layer

BEDT-TTF Conducting layer

$\text{Cu(NCS)}_2$  Anion layer

Ideal 2D

Dimer Mott Insulator

### Metal-insulator transition in $\kappa$ phase organic superconductors

$\kappa\text{-(BEDT-TTF)}_2\text{Cu}[\text{C}(\text{CN})_2]\text{Cl}$   
 $\kappa\text{-(BEDT-TTF)}_2\text{Cu}[\text{C}(\text{CN})_2]\text{Br}$   
 $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$

Thermal contraction shifts the boundary right

Critical (end) point like Liquid-gas boundary

Temperature / K

Resistivity

Pressure

Chemical pressure

Universal phase diagram  $\kappa$  phase (Kanoda Diagram)

K. Kanoda, *Hyperfine Interact.* 104, 235 (1997).

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