2019年7月16, 17日
京都大学

集中講義（化学特別講義３）

金属錯体の電子移動と電子機能

Electron Transfer and Electronic Functions of Metal Complexes

東京大学大学院理学系研究科化学専攻

西原　寛

一日目
1) 自己紹介と研究歴
2) 電子移動反応とマーカス理論
3) 光合成とバイオフォトセンサ
4) 混合原子価錯体
5)フォトクロミック錯体

二日目
6)レドックス分子ロータ
7)ドナー・アクセプター共役錯体
8)レドックス錯体分子ワイヤ
9)拡張メタラジオレン系
10) 配位ナノシート（講演会）

研究歴　(西原　寛)

東京大学　理科Ⅰ類　→　理学部化学科
→　大学院理学系研究科化学専門課程　　佐佐木行美先生 齋藤太郎先生

1976-1979 卒論－修士課程　「有機金属錯体の金属蒸気合成」

1979-1982 博士課程
「窒素錯体とヒドリド錯体の反応によるアンモニア、ヒドラジンの合成（窒素固定）」

慶應義塾大学　荒牧国次先生

1982-1996 理工学部化学科界面化学研究室
助手、専任講師、助教授
「腐食抑制剤の研究」
「電子機能分子材料の研究」

Prof. Royce W. Murray
1987－1989
米国ノースカロライナ大学チャペルヒル校

1993－1996　本多健一先生
新技術事業団さきがけ研究２１
「光と物質」領域研究員

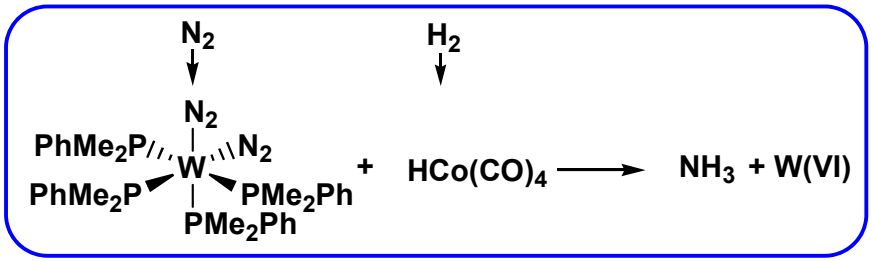
東京大学
1996年9月 大学院理学系研究科化学専攻　教授

東京大学　［佐佐木行美教授、齋藤太郎助教授］

空気中で不安定な有機金属錯体に没頭した学生時代

1976-1979 卒論－修士課程　「有機金属錯体の金属蒸気合成」
金属原子と配位子の気相反応
1979-1982 博士課程

"Reaction of Dinitrogen Complexes with Hydridometal Carbonyls"



Nishihara et al. *J. Am. Chem. Soc.* **1982**, *94*, 4367

Nitrogen fixation 窒素固定

Cleavage of N≡N : 944 kJ mol^{-1}

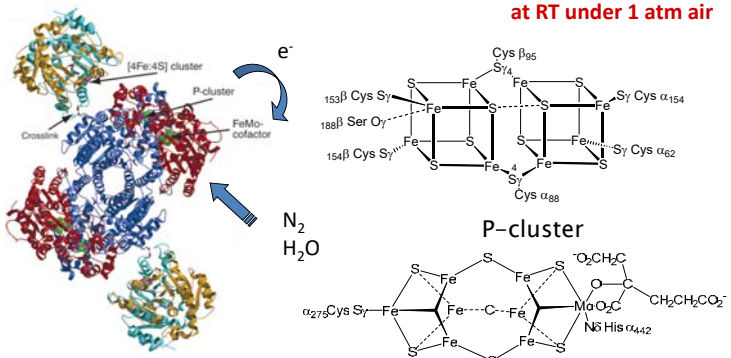
Harber–Bosch process (1908) $N_2 + 3H_2 \rightarrow 2NH_3$

at High T (500 °C), high P (20 MPa)　30 GJ /ton of NH_3

Nitrogenase

$N_2 + 8H^+ + 8e^- + 16\ ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16Pi$

at RT under 1 atm air



MoFe–protein
(1992, X-ray structure)

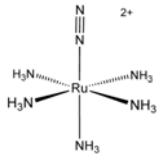
P–cluster

FeMo–cofactor

二窒素錯体 dinitrogen complex と人工窒素固定の歴史（１）

A. D. Allen, C. V. Senoff (1965). "Nitrogenopentammineruthenium(II) complexes". *Journal of the Chemical Society, Chemical Communications*: 621.

N_2H_4



A. Yamamoto, S. Kitazume, L. S. Pu, S. Ikeda *Chem. Commun*. 79 (1967)　山本明夫
A. Misono, Y. Uchida, T. Saito, *Bull. Chem. Soc. Jpn*., 40, 700 (1967)　齋藤太郎

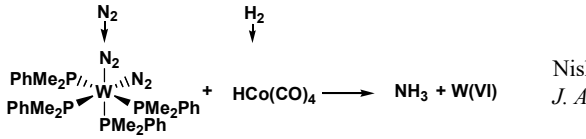
$Co(acac)_3 + PPh_3 + AlR_3 + N_2 \longrightarrow CoH(N_2)(PPh_3)_3$

1970s, 1980s

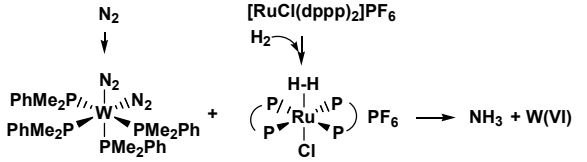
Mo, W dinitrogen complexes + HX $\longrightarrow$ NH_3, N_2H_4

Joseph Chatt, University of Sussex
Masanobu Hidai, The University of Tokyo, Faculty of Engineering　千鯛真信

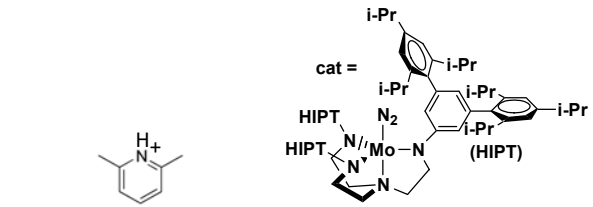
二窒素錯体 dinitrogen complex と人工窒素固定の歴史（２）



Nishihara et al.
J. Am. Chem. Soc. **1982**, *94*, 4367



Hidai et al.
Science **1998**, *279*, 540.



Catalytic

Schrock et al.
Science **2003**, *301*, 76.

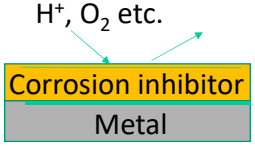
西林（東大）
830 cycles (2017)

慶應義塾大学　［荒牧国次教授］

腐食抑制剤と錯体の共通性に迫る

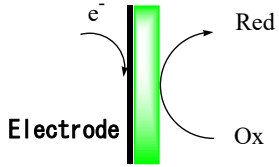
1982–1996 界面化学研究室 助手、専任講師、助教授

「腐食抑制剤の研究」



吸着型（配位結合）
沈殿被膜型（不溶性錯体生成）

「修飾電極」



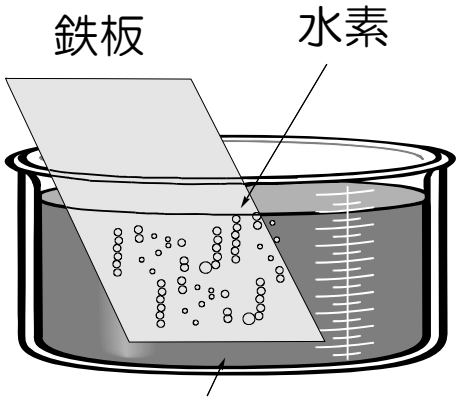
Corrosion protection
ET mediator
Catalyst
Chiral center
Photosensitizer

電気化学を学ぶ:
分極測定、交流インピーダンス測定
表面増強ラマン散乱(SERS)

サイクリックボルタンメトリ
回転電極ボルタンメトリ
分光電気化学

分子ー電極接合の受動的性質から能動的役割へ

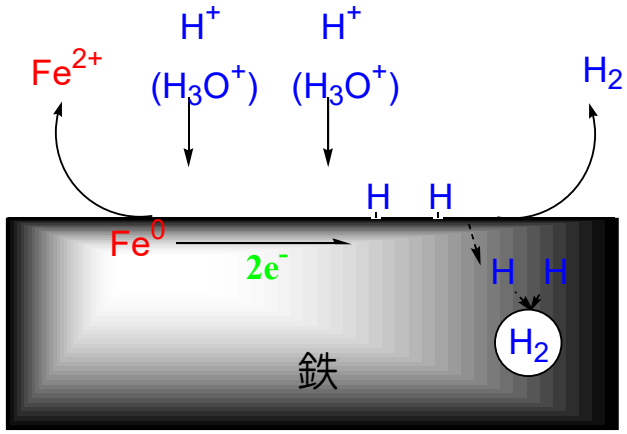
腐食 corrosion



	E^0
$Fe^{2+} + 2e^- = Fe$	-0.44
$2H^+ + 2e^- = H_2$	0.00
$Pt^{2+} + 2e^- = Pt$	+1.188

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2\uparrow$$

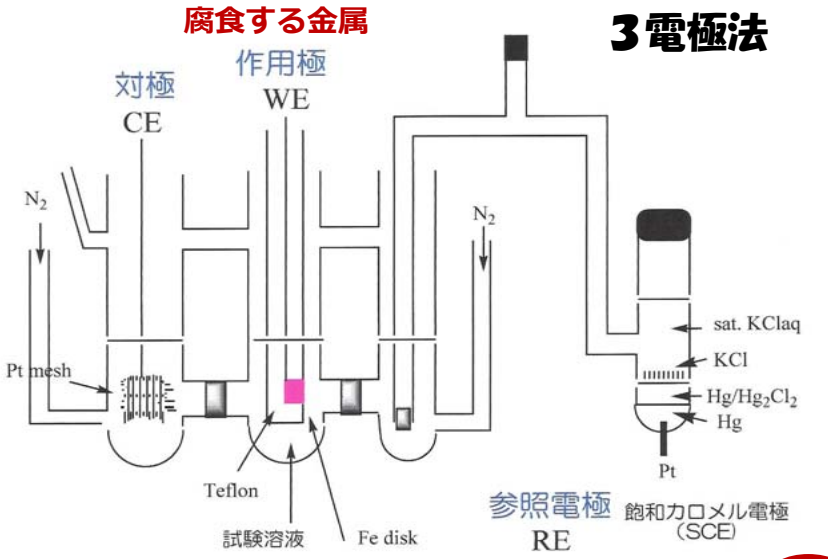
酸性溶液の腐食のメカニズム



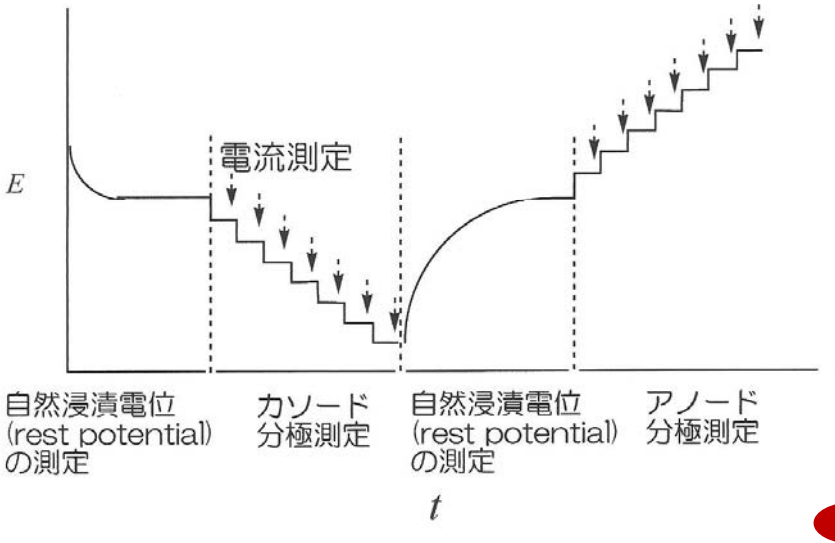
$Fe = Fe^{2+} + 2e^-$ アノード面

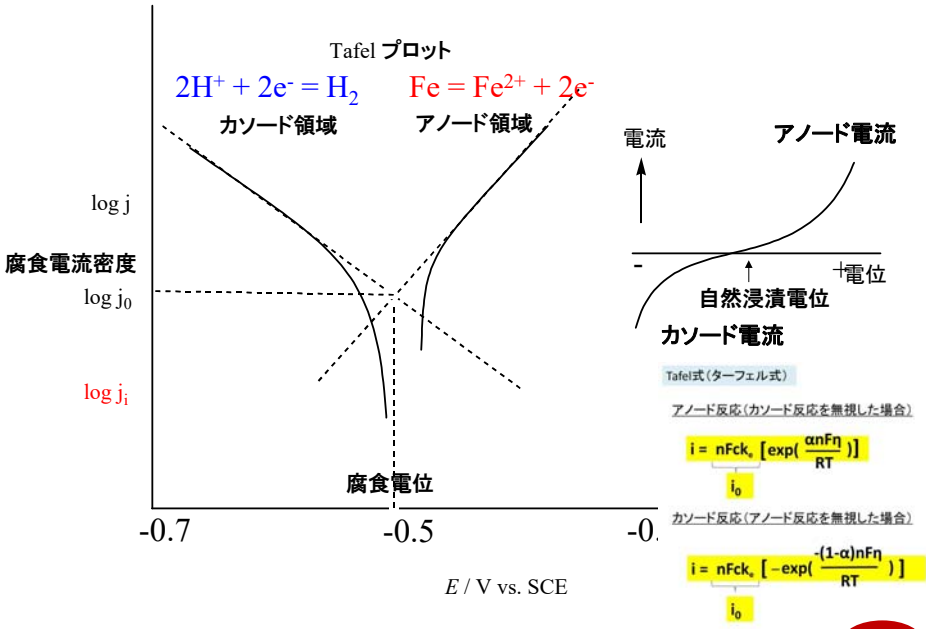
$2H^+ + 2e^- = H_2$ カソード面

腐食速度の電気化学的な測定法

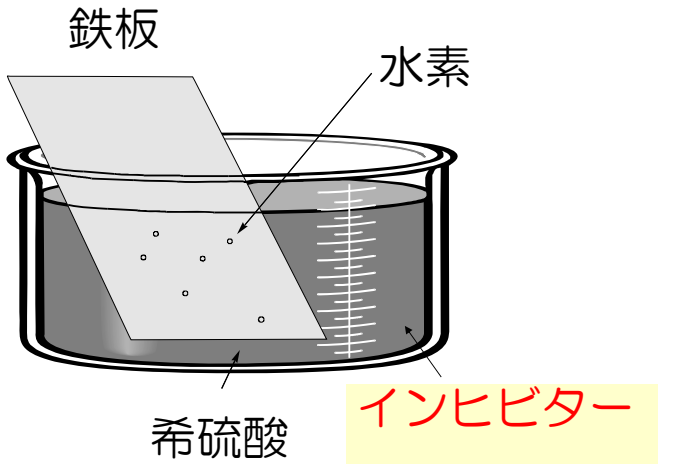


ポテンシオスタットを用いて、定電位における電流の測定
（定電位分極測定）





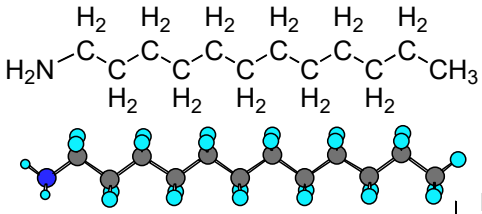
13

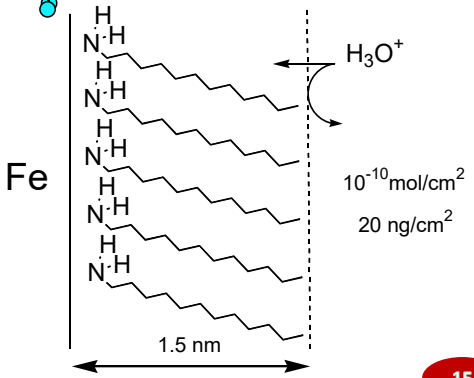


防食 corrosion inhibition

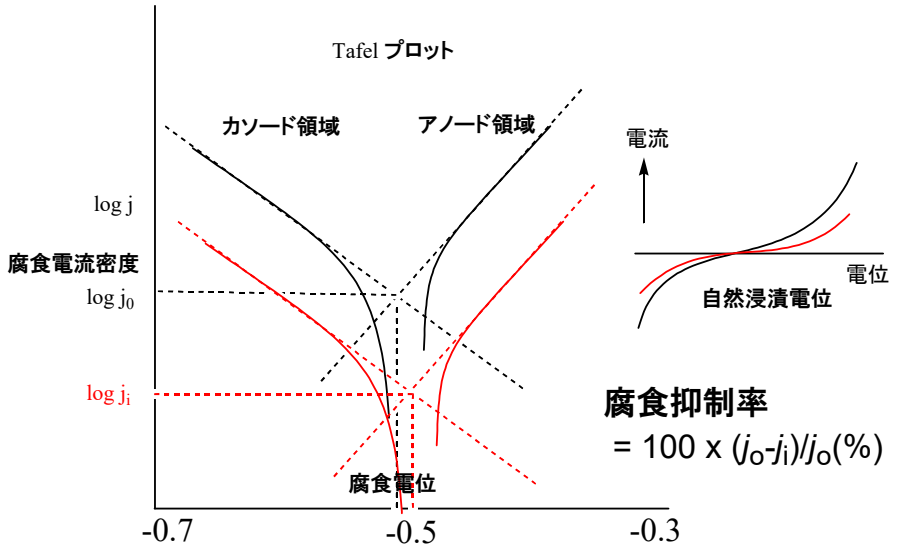
14

dodecylamine





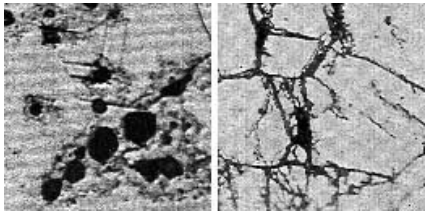
15



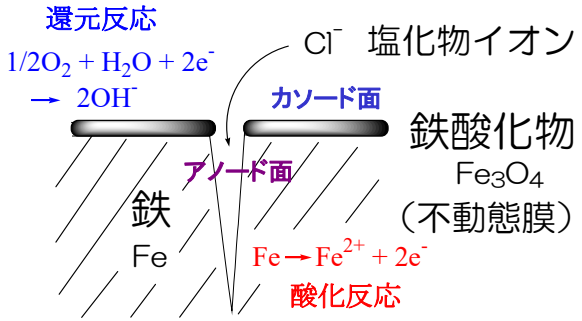
腐食抑制率
= 100 x $(j_o-j_i)/j_o$(%)

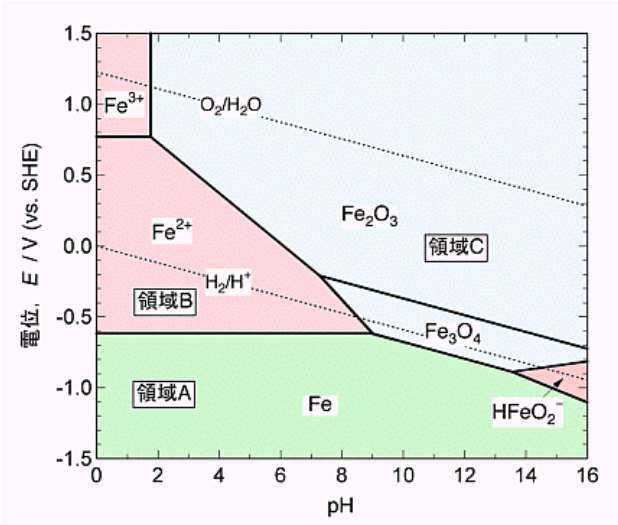
16

孔食



中性溶液





鉄のPourbaix（プールベ）図 （電位 *vs.* pH）

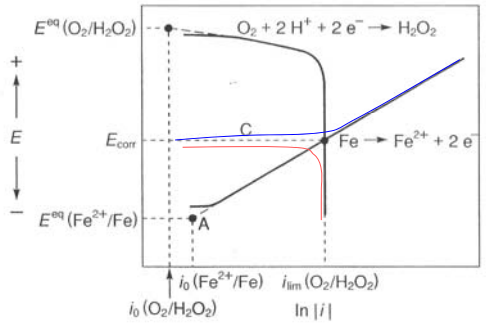


図 8.4　中性からアルカリ性水溶液中の鉄電極のターフェルプロット
(酸素存在下)
この図のように，ターフェル式の成立しない拡散限界電流が示されるようなプロットは，厳密にはターフェルプロットとはいわない．

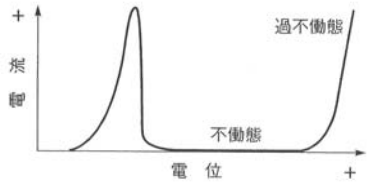
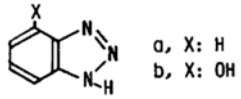
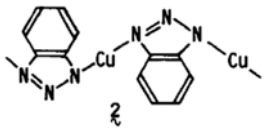


図 8.9　不働態化する金属を電極に用いて電位走査を行ったときに得られる電流－電位曲線の概略図

銅の腐食抑制剤、ベンゾトリアゾールの作用機構の解明



a, X: H
b, X: OH



表面増強ラマン散乱

交流インピーダンス法

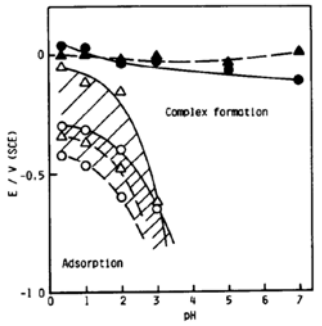


Fig 6 *E*–pH diagram obtained from SERS spectra for BTAH (○) and 4-OH-BTAH (△). Hatched zones show coexistence of complex and adsorbed molecule. Solid marks indicate open-circuit potentials of the electrode inhibited with BTAH (●) and 4-OH-BTAH (▲)

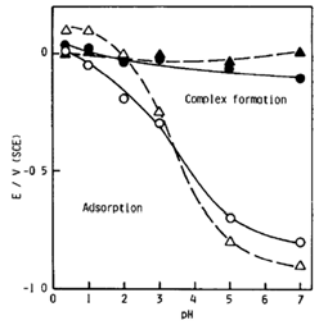
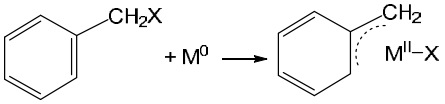


Fig 11 Potential *E*–pH diagram obtained from interfacial capacitance of copper electrode inhibited with BTAH (○) and 4-OH-BTAH (△). Solid marks indicate open-circuit potentials of the electrode inhibited with BTAH (●) and 4-OH-BTAH (▲)

Electrochim. Acta, **35**, 1011-1017 (1990)

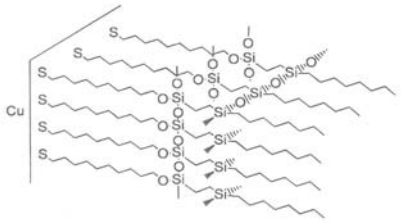
酸化的付加型インヒビター　ナノコーティングによる腐食防止



酸化的付加　Oxidative addition

$C_6H_5CH_2I$, $C_6H_5CH_2SCN$が鉄の酸性溶液中の優れた腐食抑制剤、促進剤となる。

Langmuir, **6**, 816-821 (1990)



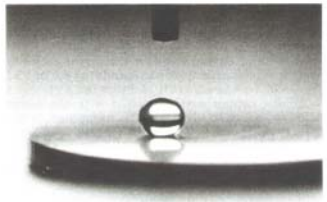
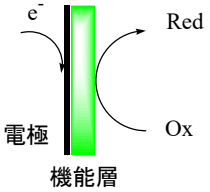


Fig. 7. Water-repellent surface of copper covered with the BTCSE and C_8TCS-modified MUO self-assembled monolayer.

J. Electrochem. Soc., **142**, 3936-3704 (1995).

修飾電極 Modified electrode



機能　速い外圏電子移動試薬
- 不斉中心
- 電子移動メディエータ、触媒
- 微量成分の濃縮
- 光増感剤（半導体電極）
- 腐食防止

電極表面修飾法

1．化学吸着　1973 R．F. Lane, A. T. Hubbard, Pt/quinone-olefin

2．共有結合形成 1974 NSF Energy Workshop in **Chapel Hill, NC**

Watkins (1975) 光学活性種

Murray (1976), Burt (1976) レドックス活性種

Evans (1977) 触媒活性種

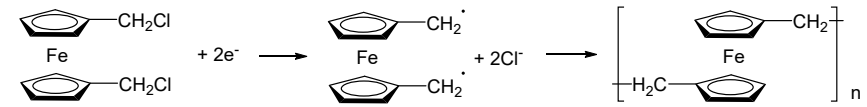
3．フィルムディポジション

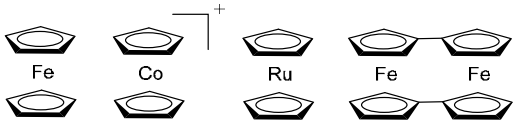
Miller and Van De Mark (1978), Merz and Bird (1978), Wrighton (1978)

Novak and Murray (1978), Anson and Oyama (1979)

メタロセンポリマー修飾電極

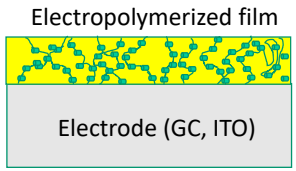
Electroreductive polymerization　1985-



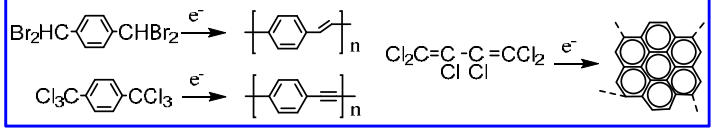


BFD

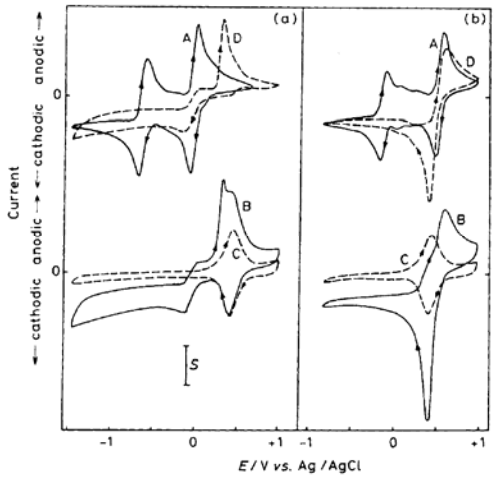
Class III mixed valence complex

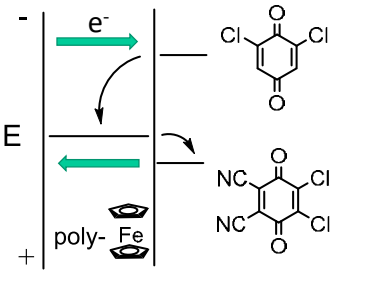


Electroreductive synthesis of conducting polymers



Irreversible Charge Transport through Polyferrocene Films



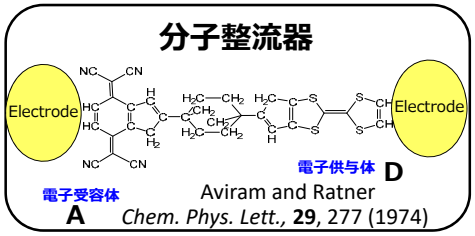


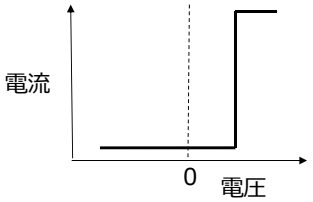
in Bu_4NClO_4-MeCN

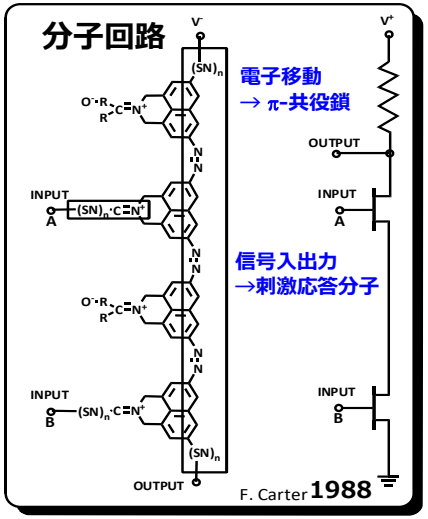
Solid-liquid interface

Nishihara and Aramaki, *J. Chem. Soc. Chem. Commun.* **1985**, 705.

分子エレクトロニクス

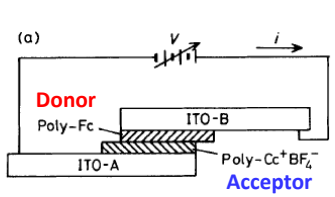






分子エレクトロニクス研究が1980年後半から活発化

Redox Diode made of Ferrocene and Cobaltoceium Electrode Films



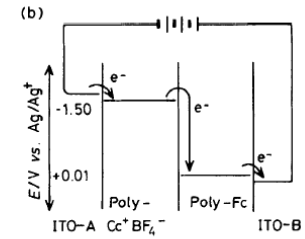


Figure 1. (a) A chemical diode composed of cobalticinium s ferrocene polymer films, and (b) the energetics of the device.

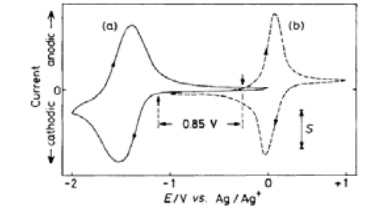


Figure 2. Cyclic voltammograms of (a) Poly-Cc⁺BF_4^- (Γ 7.3 × 10^{-9} mol cm^{-2}) and (b) Poly-Fc (Γ 1.3 × 10^{-8} mol cm^{-2}) on ITO electrodes in 0.1 M Bu_4NBF_4–MeCN at 0.1 V s^{-1}, S = 89 μA cm^{-2} for (a) 250 μA cm^{-2} for (b).

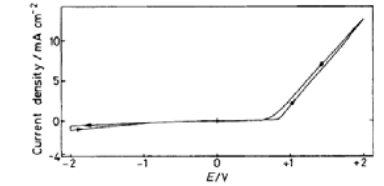


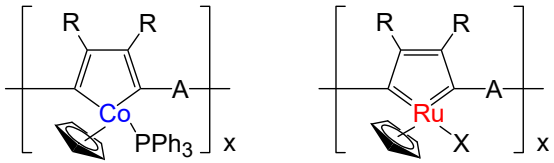
Figure 3. Current *vs.* voltage curves for the device ITO/Poly-Cc⁺BF_4^-/Poly-Fc/ITO at a potential sweep rate of 20 mV s^{-1}, Γ = 1.3 × 10^{-8} mol cm^{-2} for both polymers.

Solid-solid interface

Nishihara et al, *J. Chem. Soc. Chem. Commun.* **1987**, 628.

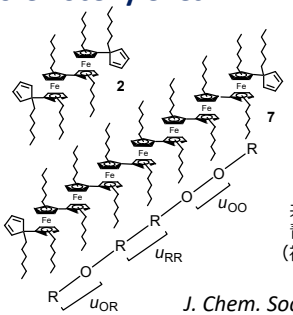
π共役金属錯体ポリマー（導電性高分子錯体）

Polymetallacyclopentadienes



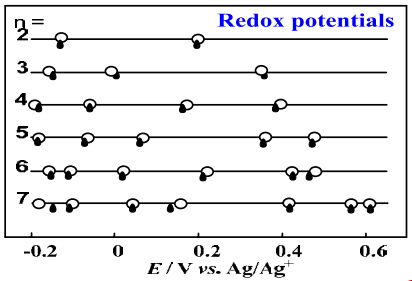
Adv. Mater. **1993**, *Chem. Mater.* **1996**, *J. Am. Chem. Soc.* **2003**, *Macromol. Symp.* **2004**.

Oligoferrocenylenes



共同研究
青木、陳
（福井大学）

隣接核間相互作用モデルで多段レドックス電位を解析可能



J. Chem. Soc., Dalton Trans. **1996**, **1999**, *Inorg. Chem.* **1999**.

無機化学研究室

配位プログラミングによる特異物性・化学機能を持つ新物質の開発と化学素子への展開

「配位」“Coordination”

金属 — 配位子

○化学結合の強さと可逆性を制御可能

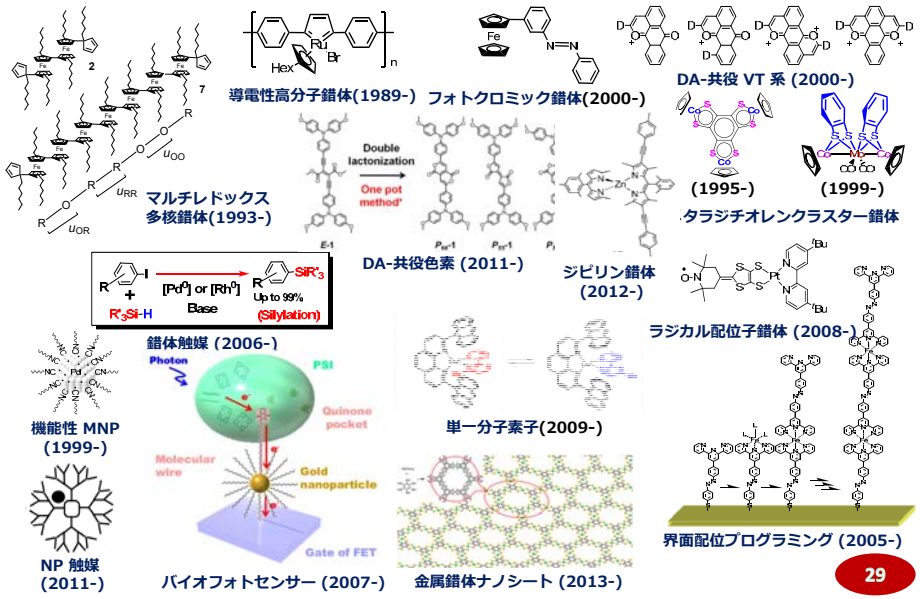
○配位結合による多彩な幾何構造

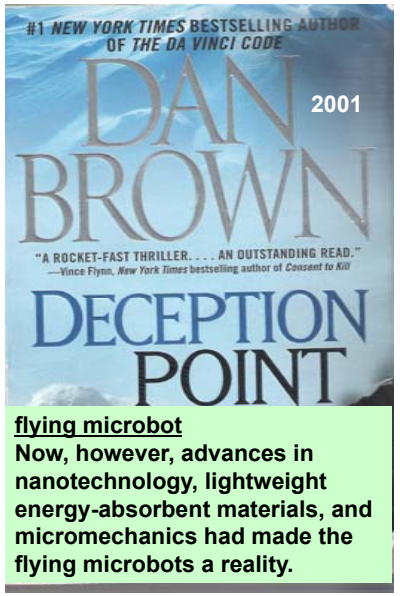
○配位化合物＝金属錯体の多様な化学反応性と物性

配位プログラミング (coordination programming)
＝ 化学結合・構造・物性を自在制御できる配位化学を武器として、特異な性質を持つ機能階層的な分子超構造体を精密設計して組み上げる方法

無機化学研究室

元素を活かした特異機能を持つ新物質の開発と化学素子への展開





flying microbot
Now, however, advances in nanotechnology, lightweight energy-absorbent materials, and micromechanics had made the flying microbots a reality.

2-2.5mg

1.5-2.5km/h

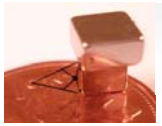
1日で5.1km

蚊は二酸化炭素の密度が多いところへ、周りより温度が高いところへ向かう習性がある。体温、におい、周りとの二酸化炭素の密度の違いなどで血を吸う相手を探している。
吸血の際は皮膚を痛点をはずして突き刺し、吸血を容易にする様々なタンパク質などの生理活性物質を含む唾液を注入（この唾液により血小板の凝固反応は妨げられる）した後に吸血に入る。

化学現象の連鎖

現状

Epson
(2008)



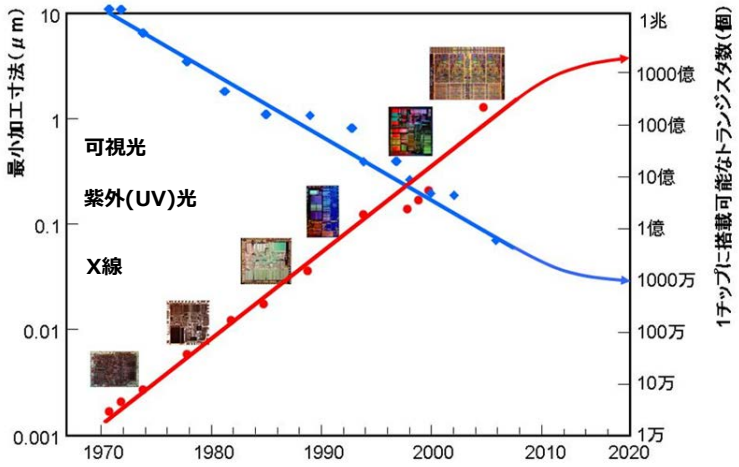
Univ. of Waterloo
(2009)

175 mg

Science
(2017)

ムーアの法則 【 Moore's law 】

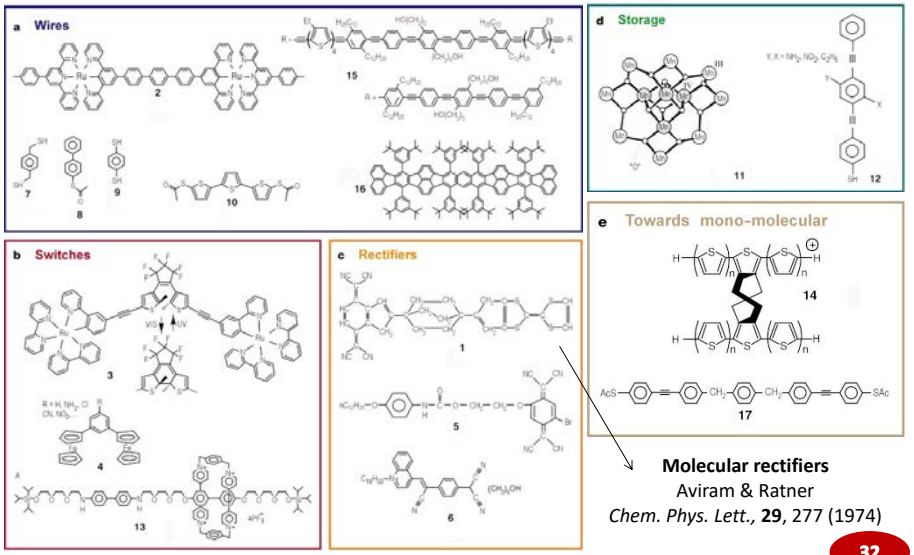
Gordon Moore博士が1965年に経験則として提唱
「半導体の集積密度は18～24ヶ月で倍増する」



http://special.nikkeibp.co.jp/ts/article/ab0c/118565/zu6.jpgより転載

Electronics using hybrid-molecular and mono-molecular devices

C. Joachim, J. K. Gimzewsld, and A. Aviram
Nature, **408**, 541 (2000)

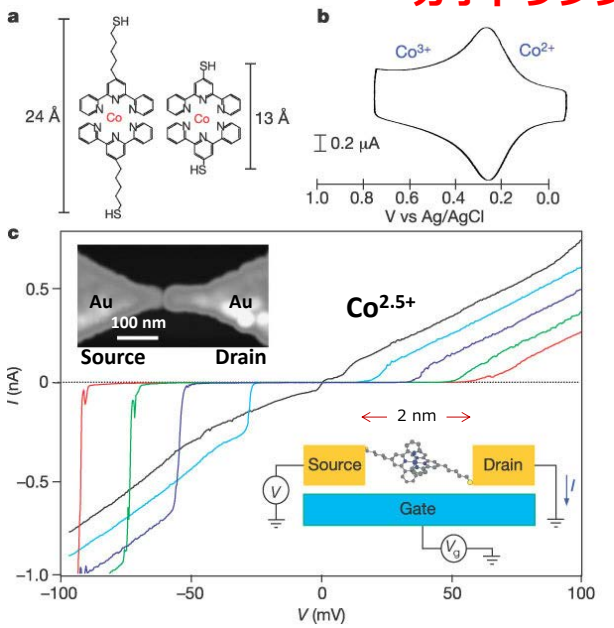


Molecular rectifiers
Aviram & Ratner
Chem. Phys. Lett., **29**, 277 (1974)

Coulomb blockade and the Kondo effect in single-atom transistors

J. Park et al., *Nature*, **417**, 723 (2002)

分子トランジスタ



電子デバイス　　ケミカルデバイス

ドライシステム
半導体 LSI
超高速応答
常温でのS/N比の高さ
トランジスタ増幅

京（けい）　10^{15}=10,000兆

ウェットシステム
生体分子系
イオン移動を伴うによる低速応答
単電子、単光子、単化学種検出
化学応答連鎖

神経の伝達速度：1 ～ 100 m s^{-1}

分子デバイス

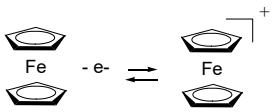
トップダウン型からボトムアップ型へ

2）電子移動反応とマーカス理論

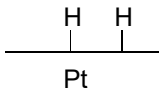
電子移動反応

	外圏反応 (outer sphere)	内圏反応 (inner sphere)
化学反応	$[Fe^{II}(CN)_6]^{4-} + [Ir^{IV}Cl_6]^{2-}$	$[Co^{III}Cl(NH_3)_5]^{2+} + [Cr^{II}(OH_2)_6]^{2+} + 5H_2O$
	$\rightleftarrows [Fe^{III}(CN)_6]^{3-} + [Ir^{III}Cl_6]^{3-}$	$\rightarrow [Co^{II}(OH_2)_6]^{2+} + [Cr^{III}Cl(OH_2)_5]^{2+} + 5NH_3$
	配位圏外での電子移動	架橋錯体の生成　Co^{III}-Cl-Cr^{II}

電極反応



$2H^+ + 2e^- \rightarrow H_2$

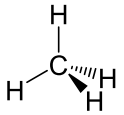


Molecules/Ions Undergoing Reversible Redox Reaction

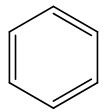
$$Ox \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} Red$$

stable　　stable

Thermodynamic reversibility
Chemical reversibility



×

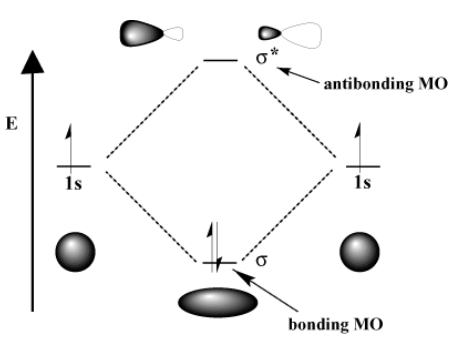


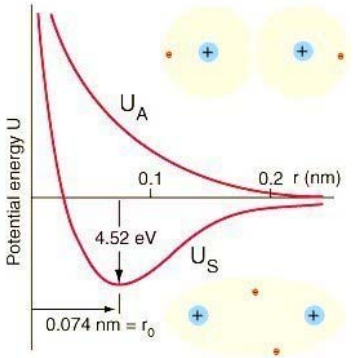
×

C_2H_5OH

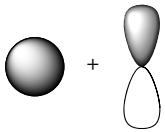
×

Molecular orbitals





non-bonding MO

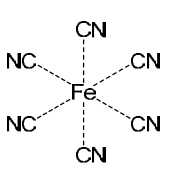


Molecules/Ions Undergoing Reversible Redox Reaction

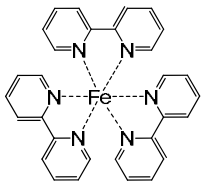
Metal complexes

Ox ⇌ Red (+ e⁻ / − e⁻)

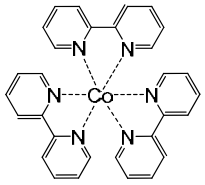
Ox: stable　　Red: stable



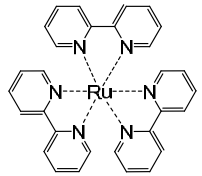
III/II



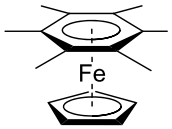
III/II



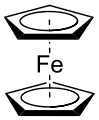
III/II　II/I



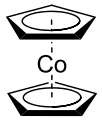
III/II　II/I　I/0



III/II



III/II



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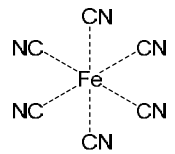
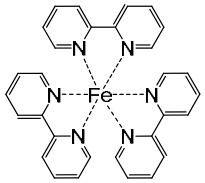
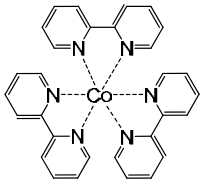


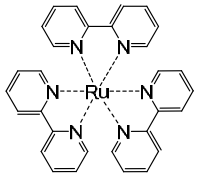
III/II



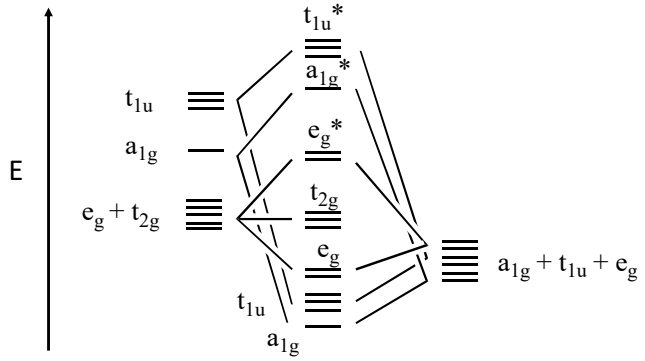
III/II



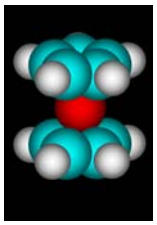
III/II　II/I

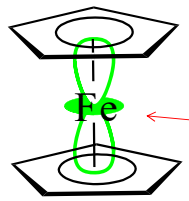


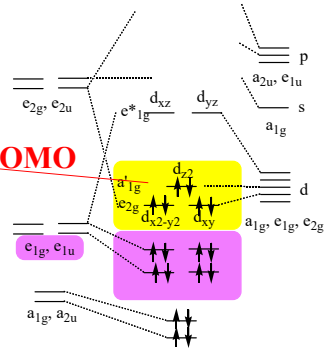
III/II　II/I　I/0



ferrocene







Benzene-like reactivity
Reversible 1e⁻ oxidation

R ⇌ O (-e⁻ / +e⁻)

Fe(II)　Fe(III)

金属錯体　可逆なレドックスを示すものがある。
非結合性軌道（non-bonding orbital)がHOMOかLUMO
遷移金属のd軌道が非結合性軌道になり得る
金属のｄ軌道のエネルギーレベルが程よい位置にある

1） 溶液内の電子移動 （外圏反応）

（1）Franck-Condonの原理 （電子移動）

e^-　9.1×10^{-31} kg　[1/1900]

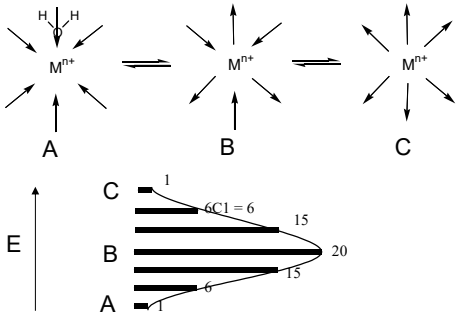
p, n　1.7×10^{-27} kg

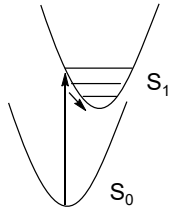
電子が移動する瞬間には、溶媒分子や酸化還元種の骨格は動かない。

（2） 電子エネルギー準位の拡がり

○ 分子の熱運動 （振動･回転）

○ 溶媒の配向変化

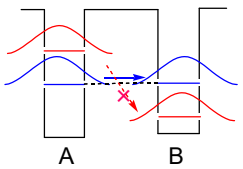


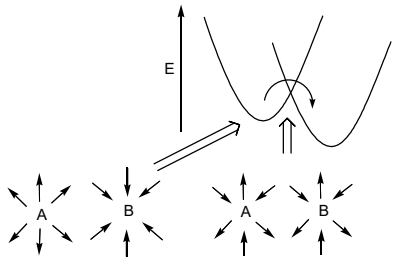


光励起における
Franck-Condonの原理

（3） 活性化状態

放出されるエネルギーが存在するような電子移動は起こらない





（4） 断熱性 (adiabaticity)

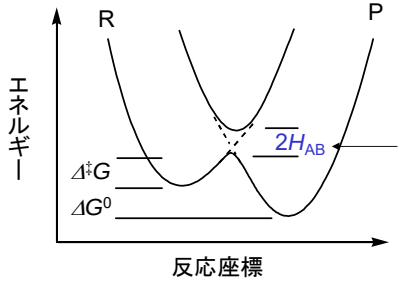
断熱的 adiabatic（$\kappa = 1$）

活性化状態（遷移状態）から100%の確率で電子が動く反応

非断熱的　non-adiabatic（$\kappa < 1$）

2） マーカス（Marcus） 理論

（1）遷移状態論



非交差則

同じ対称性をもつ二つの状態が接近したとき、混合して交差を回避する。

Electron coupling energy

$[Fe(OH_2)_6]^{3+/2+}$

$\Delta G^0 = 0$

$\Delta^{\ddagger}G = 32$ kJ mol^{-1}

$k = k_0 exp(-\Delta^{\ddagger}G / RT)$

$k = 3.0$ M^{-1}s^{-1}

（2） Marcus の式

化学反応

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [A|B] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [A^+|B^-]^* \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} A^+ + B^-$$

拡散ー出会い
溶媒再配向
分子内核変位

電荷移動

緩和
解離

$k_{et} = \kappa Z \, exp(-\Delta^{\ddagger}G / RT)$　Z: nuclear frequency factor, $Z_s \sim 10^{11}$ M^{-1}s^{-1}（溶液中）

$\Delta^{\ddagger}G = w_r + (\lambda/4)(1 + \Delta G^{0'}/\lambda)^2$

$\Delta G^{0'} = \Delta G^0 + w_p - w_r$

λ: 再配向エネルギー
reorganization energy

$w_r = (Z_A Z_B / D_s r_{AB})$　Z_D, Z_A: 電荷, D_s : 静的誘電率, r_{AB}: 電子移動距離

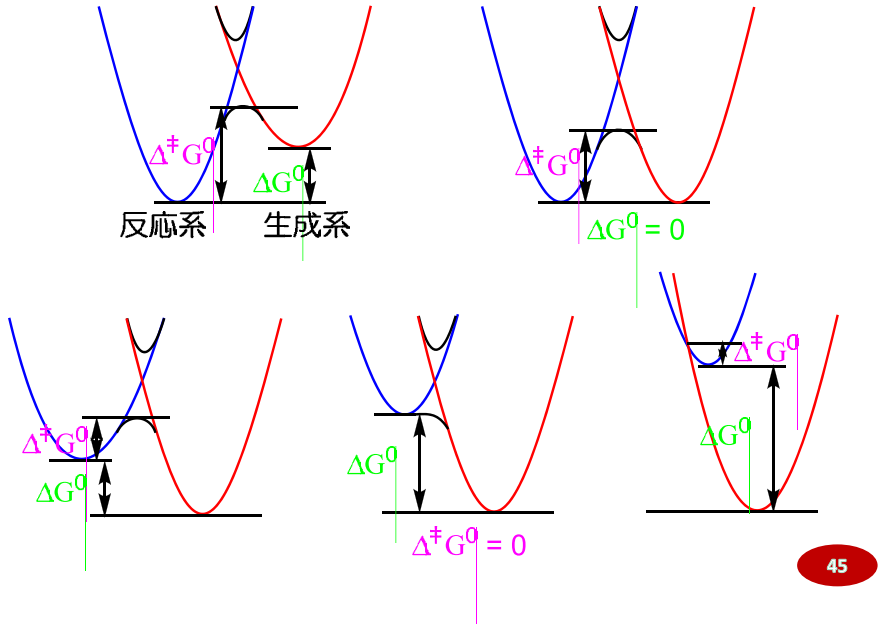
反応物を活性錯合体の平均距離まで近づけるのに要する静電的仕事

$w_p = (Z_{A+} Z_{B-} / D_s r_{AB})$　（反応物または生成物が中性なら0）

When $Z_{A+} = 1$, $Z_{B-} = -1$, $r_{AB} = 7$ Å, $D_s = 37$ (MeCN) , $w_p = -5.5$ kJ/mol.

大学院物理化学（中）妹尾、広田、田隅、岩澤編、
講談社サイエンティフィック, pp.426-435 (1992)

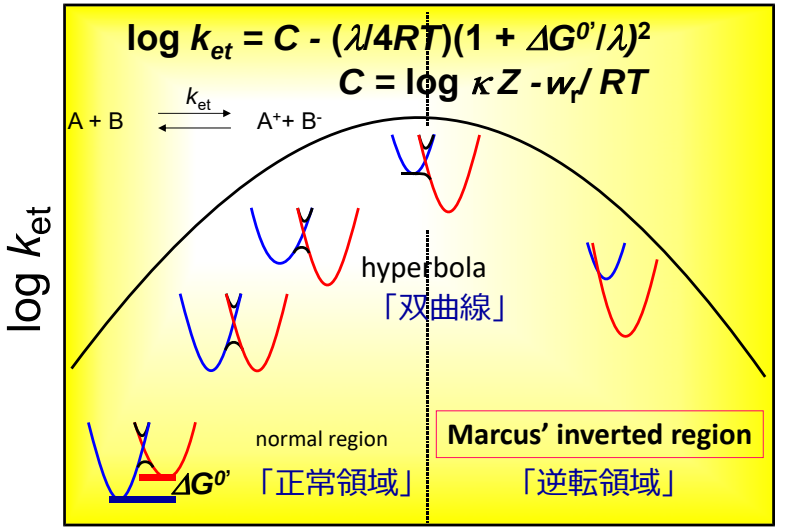
$\Delta G^{0'} = \Delta G^0 + w_p - w_r$



Marcus theory

$\log k_{et} = C - (\lambda/4RT)(1 + \Delta G^{0'}/\lambda)^2$

$C = \log \kappa Z - w_r / RT$



$-\Delta_r G^{O'} < \lambda$ $-\Delta_r G^{O'} = \lambda$ $-\Delta_r G^{O'} > \lambda$

再配向エネルギー、λ

$\lambda = \lambda_i + \lambda_o$

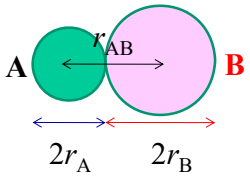
Inner sphere Outer sphere

$\lambda_i = \frac{1}{2} \Sigma k_j (\Delta x_j)^2$

静的誘電率

$\lambda_o = e^2 (1/2r_A + 1/2r_B - 1/r_{AB})(1/D_{op} - 1/D_s)$

光学的誘電率 $= n^2$（屈折率）



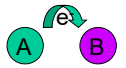
今、$r_A = r_B = r_{AB}/2 = a$ とすると

λ_o (eV)$= (7.20/a(\text{Å}))(1/n^2 - 1/D_s)$

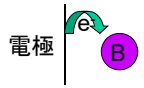
電極反応

$\lambda_e = \frac{1}{2} \lambda_o = (3.60/a(\text{Å}))(1/n^2 - 1/D_s)$

$Z_e \sim 10^4$ cm s^{-1}



どちらも主役



片方だけ主役

- 非極性溶媒　D_s (~D_{op}) ~ 1.5 – 4.0
  水　D_s = 78
  非極性溶媒中の方が電子移動が速い。
- 反応物の大きさが大きい方が電子移動が速い。

自己電子交換反応　$\Delta G^0 = 0$

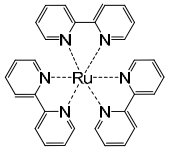
化学反応	電極反応
λ_s (eV) $= (7.20/a(\text{Å}))(1/n^2 - 1/D_s)$	λ_e (eV) $= (3.60/a(\text{Å}))(1/n^2 - 1/D_s)$
$\Delta^{\ddagger}G_s = \lambda_o/4$	$\Delta^{\ddagger}G = \lambda_e/4$
$k_{et,s} = \kappa Z_s \exp(-\Delta^{\ddagger}G_s / RT)$	$k_{et,e} = \kappa Z_e \exp(-\Delta^{\ddagger}G_e / RT)$
$Z_s \sim 10^{11}$ M^{-1}s^{-1}	$Z_e \sim 10^4$ cm s^{-1}

例1）

溶液内自己電子交換反応　　電極レドックス反応

$[Ru_A(bpy)_3]^{2+}$ + $[Ru_B(bpy)_3]^{3+}$ ⇀↽ $[Ru_A(bpy)_3]^{3+}$ + $[Ru_B(bpy)_3]^{2+}$

$[Ru(bpy)_3]^{2+}$ ⇀↽ $[Ru(bpy)_3]^{3+}$ + e^- / H_2O



H_2O　n = 1.33,　D_s = 78.5

錯体　a = 6.8 Å

λ_s = (7.20/6.8)(1/1.33² – 1/78.5) = 0.585 eV

λ_e = (3.60/6.8)(1/1.33² – 1/78.5) = 0.29 eV

$\Delta^{\ddagger}G_s \sim \lambda_e/4$ = 0.14 eV　14 kJ mol^{-1}

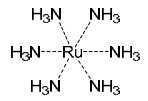
$\Delta^{\ddagger}G_e \sim \lambda_e/4$ = 0.07 eV　7 kJ mol^{-1}

$k_{et,s}$ = 10^{11} exp {-0.14 × 96500/ (8.31 × 298)} = 3.4 × 10^8 $M^{-1}s^{-1}$

$k_{et,e}$ = 10^4 exp {-0.07 × 96500/ (8.31 × 298)} = 580 cm s^{-1}

例2）

$[Ru(NH_3)_6]^{2+}$ ⇀↽ $[Ru(NH_3)_6]^{3+}$ + e^- / H_2O



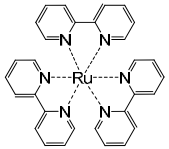
a = 3.5 Å

λ_e = 0.61 eV

$\Delta^{\ddagger}G_e$ = 0.15 eV　15kJ mol^{-1}

$k_{et,e}$ = 76 cm s^{-1}

$[Ru(bpy)_3]^{2+}$ ⇀↽ $[Ru(bpy)_3]^{3+}$ + e^- / H_2O



a = 6.8 Å

λ_e = 0.29 eV

$\Delta^{\ddagger}G_e$ = 0.07 eV　7 kJ mol^{-1}

$k_{et,e}$ = 580 cm s^{-1}

分子が大きい方が電子移動が速い。

例3）

フェロセン／フェロセニウム　　溶媒効果

a = 3.5 Å

H_2O　n = 1.33,　D_s = 78.5　λ_e = 0.570 eV　$k_{et,e}$ = 97 cm s^{-1}

ピリジン n = 1.51,　D_s = 12.0　λ_e = 0.366 eV　$k_{et,e}$ = 510 cm s^{-1}

溶媒極性の低い方が電子移動が速い。

Nitrogen fixation　窒素固定

Cleavage of N≡N : 944 kJ mol^{-1}

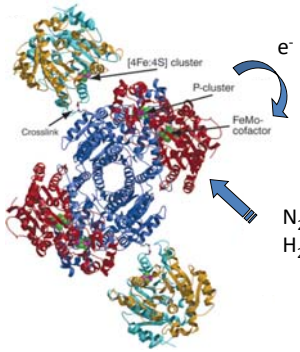
Harber–Bosch process (1908)　$N_2 + 3H_2 \rightarrow 2NH_3$

at High T (500 °C), high P (20 MPa)　30 GJ /ton of NH_3

Nitrogenase

$N_2 + 8H^+ + 8e^- + 16\ ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16Pi$

at RT under 1 atm air



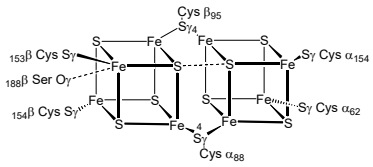
MoFe–protein

(1992, X-ray structure)

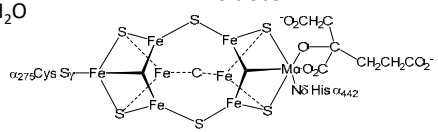
e$^-$

N_2

H_2O



P–cluster



FeMo–cofactor

Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions

Half-Reaction	$\mathscr{E}°$ (V)	Half-Reaction	$\mathscr{E}°$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^- + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

（3） Marcus の交差関係

$A + B \underset{k_{-AB}}{\overset{k_{AB}}{\rightleftharpoons}} A^+ + B^-$

$A + A^* \underset{k_{-A}}{\overset{k_A}{\rightleftharpoons}} A^+ + A^{*-}$

$B + B^* \underset{k_{-B}}{\overset{k_B}{\rightleftharpoons}} B^+ + B^{*-}$

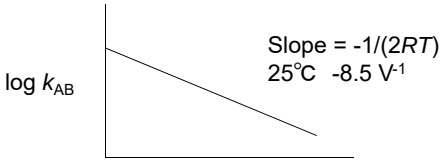
$K_{AB} = k_{AB}/k_{-AB}$

$$k_{AB} = (k_A k_B K_{AB} f)^{1/2}$$

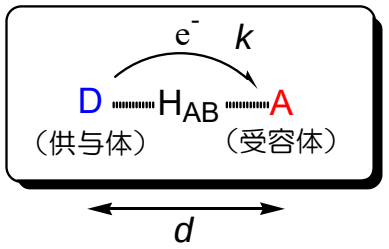
$$\log k_{AB} = (\log k_A k_B f)/2 - \Delta G^0_{AB}/2RT$$

$$\ln f = (\ln K_{AB})^2/(4\ln(k_A k_B/z^2))$$

f = 1と近似できる。

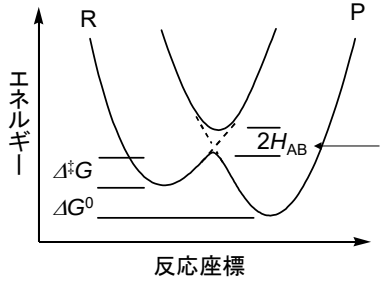


3）長距離電子移動



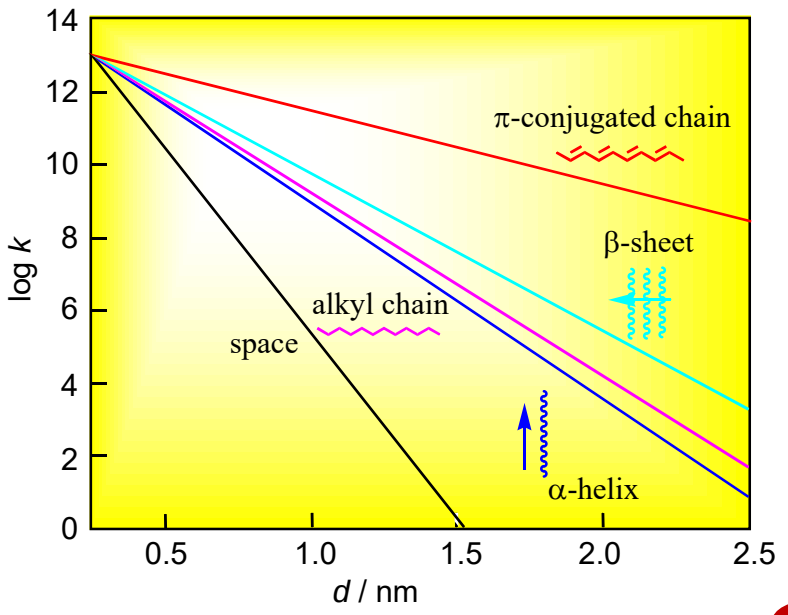
$H_{AB} = H_{AB}^0 \exp[-\beta(d-d_0)/2]$

$k = k^0 \exp[-\beta(d-d_0)]$



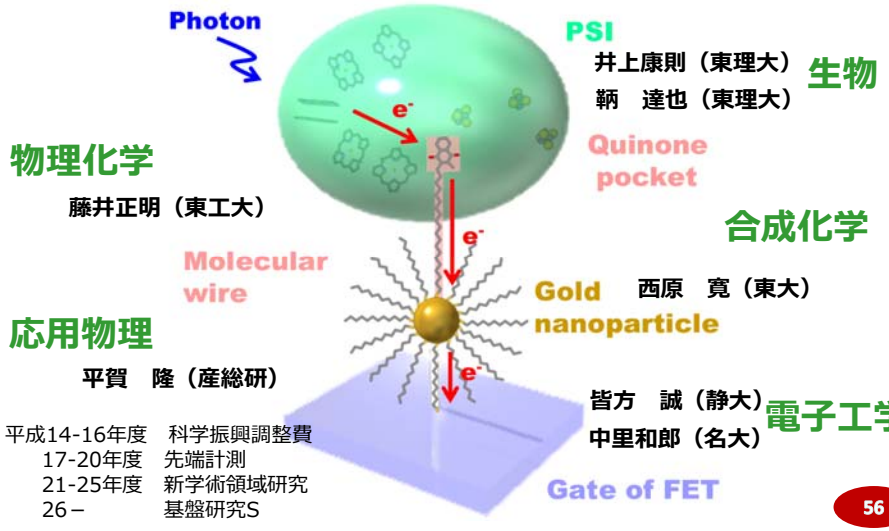
$H_{AB} = H_{AB}^0 \exp[-\beta(d-d_0)/2]$

spacer	β
space	2 - 4
alkyl chain	1
π-conjugated chain	0.2
α-helix	1.1
β-sheet	0.9



3) 光合成とバイオフォトセンサ

シアノバクテリア PSI ―分子ワイヤートランジスタ接合

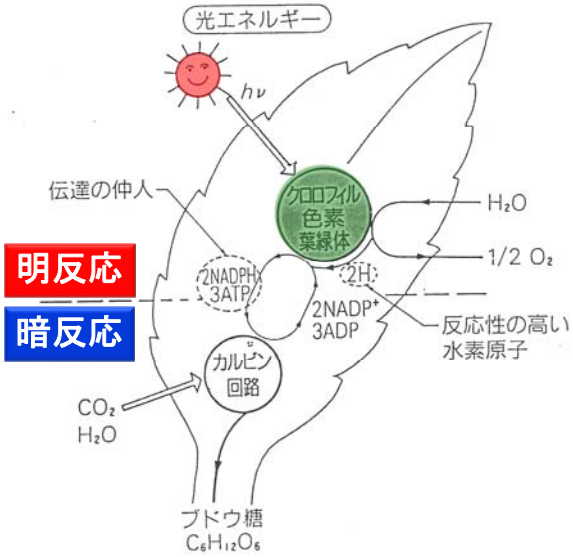


平成14-16年度 科学振興調整費
17-20年度 先端計測
21-25年度 新学術領域研究
26－ 基盤研究S

生物の進化は究極のコンビナトリアル化学

バイオ共役マテリアル

光合成 Photosynthesis



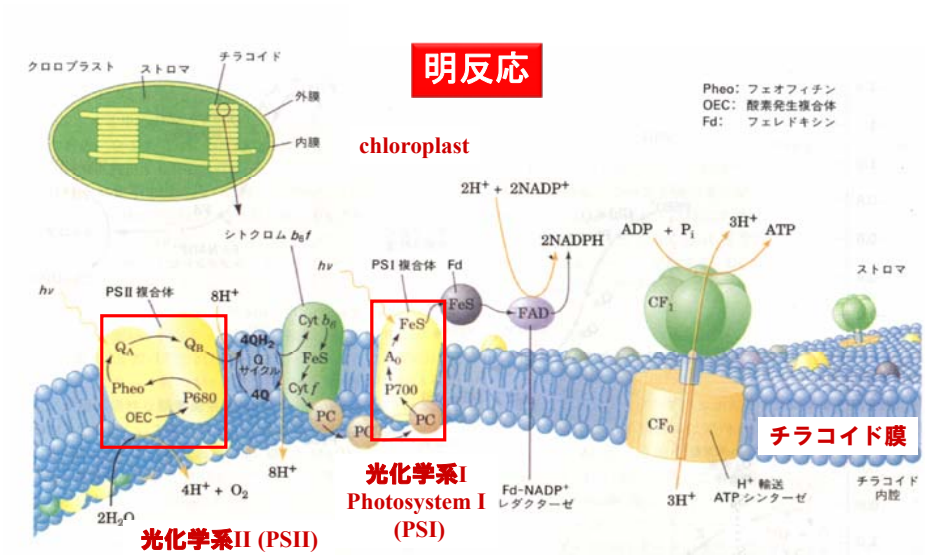
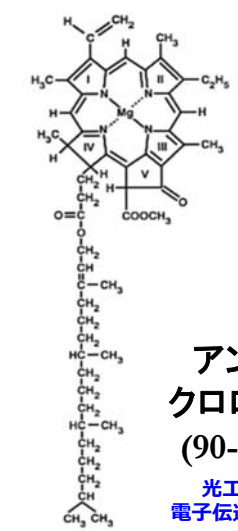
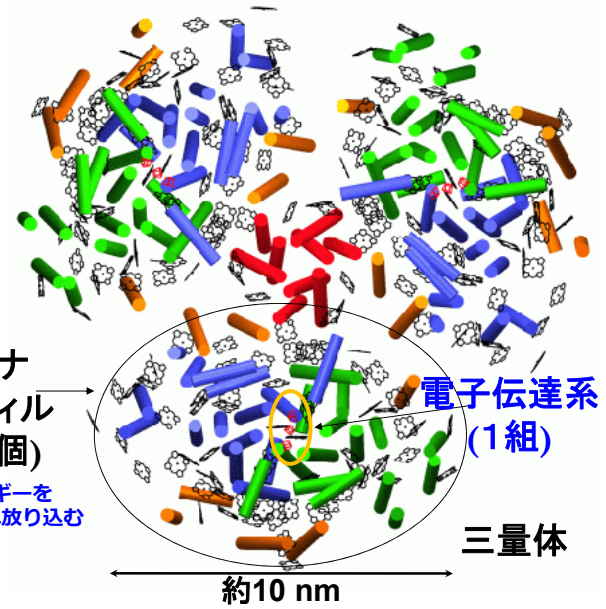


図 22・15 チラコイド膜の電子伝達系成分．PSⅡ，シトクロム b_6f 複合体，PSⅠの3種のタンパク複合体で構成され，この間を移動性電子キャリヤー，プラストキノン(Q)とプラストシアニン(PC)が結ぶ．H_2O から NADPH へ光の作用で電子が流れる(黒矢印)とプロトンがチラコイドの内部に流れ込む(赤矢印)．酸素発生複合体の作用で水が開裂して O_2 を発生するときもプロトンがチラコイド膜内に生じる．生じたプロトン濃度勾配の解消と共役して ATP が生産される(H^+ 輸送 CF_1CF_0- ATP シンターゼ)．膜には集光複合体もあり，その中のクロロフィルや他の色素が光励起エネルギーを PSⅠや PSⅡに伝える［D. R. Ort, N. E. Good, *Trends Biochem. Sci.*, **13**, 469 (1988)］

ヴォート生化学より引用



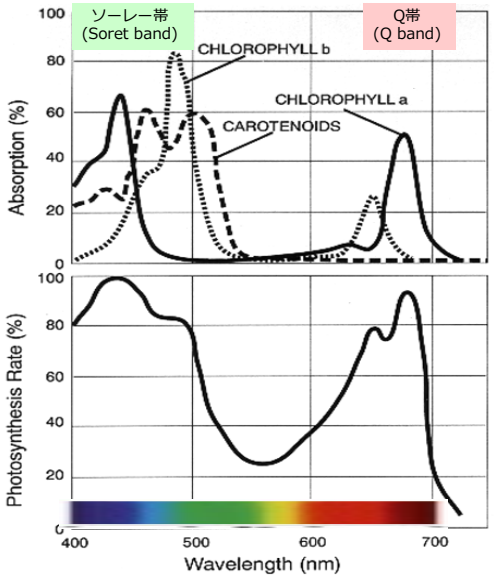


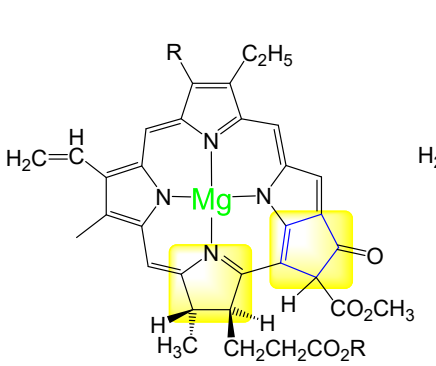
シアノバクテリアのPSIの構造

光合成色素の光吸収スペクトルと光合成効率

光吸収スペクトル

光合成効率

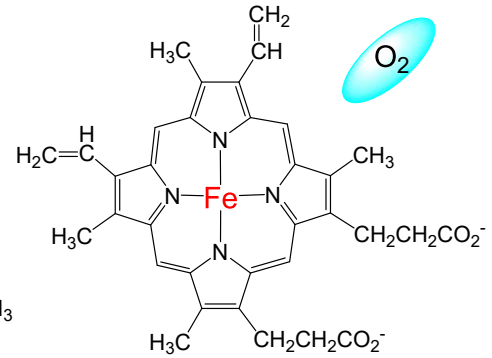




緑色

クロロフィルa

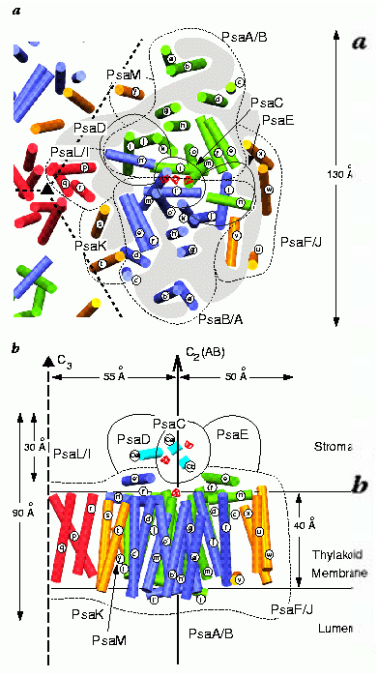
分子の対称性が崩れているので、
Q帯が許容遷移になる。

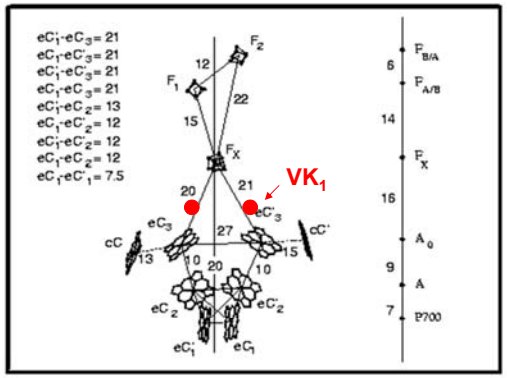


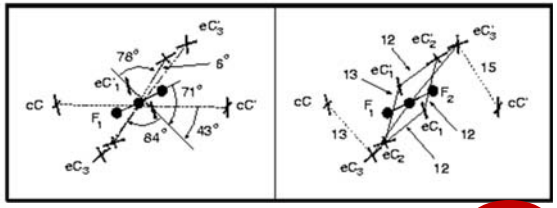
赤色

ヘム(赤血球)

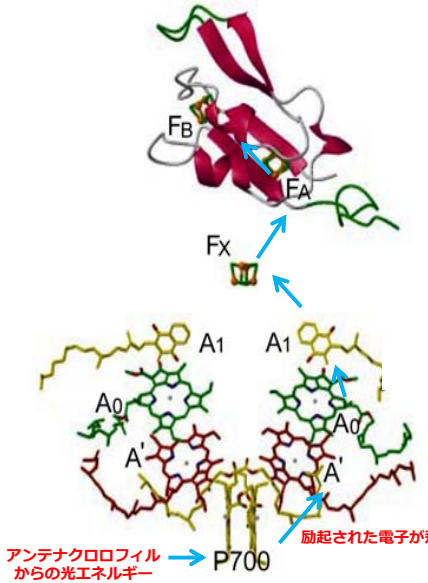
Q帯が禁制遷移なので、
ソーレー帯しか吸収がない。

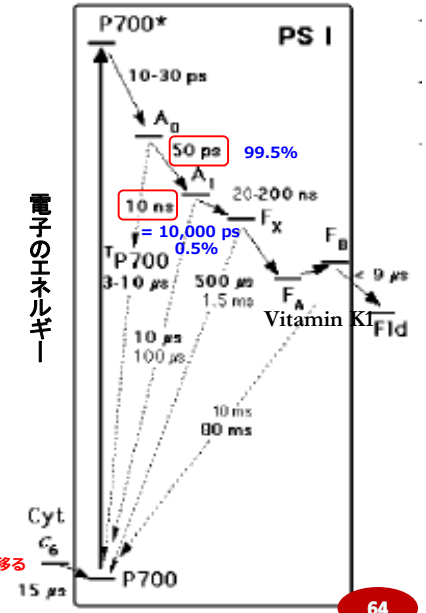






PSI内の電子移動とその速さ





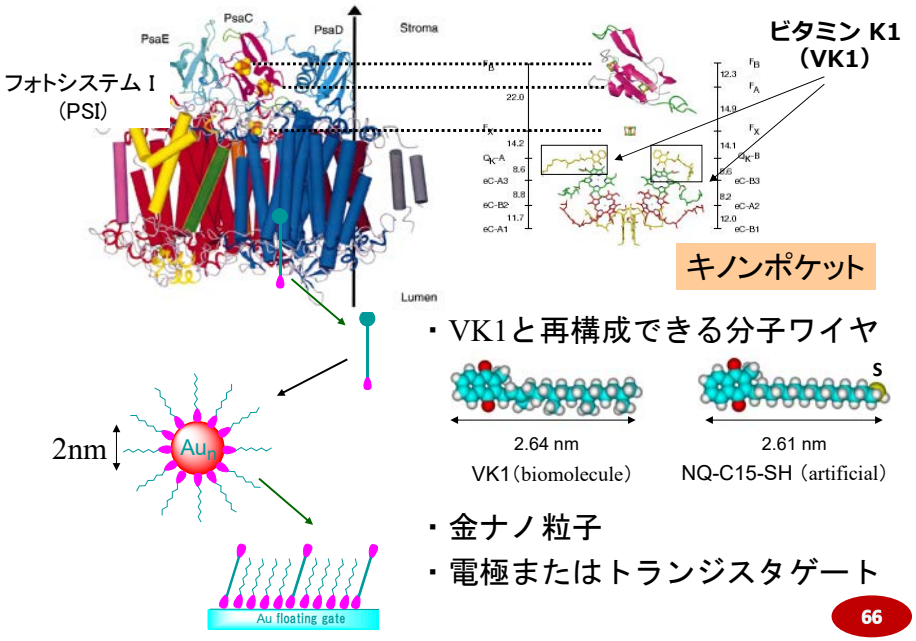
光合成系では何故，効率の良い電子移動が起こるのか？

逆の電子移動をどのようにして止めているのか？

電子移動の速度はどのようにして決まるのだろうか？

マーカス理論

バイオ共役フォトセンサー作製の戦略



・VK1と再構成できる分子ワイヤ

2.64 nm
VK1（biomolecule）

2.61 nm
NQ-C15-SH（artificial）

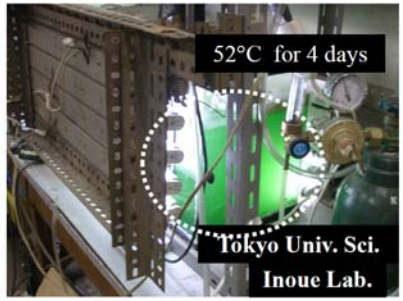
・金ナノ粒子

・電極またはトランジスタゲート

PSI の抽出

シアノバクテリアのサンプリング

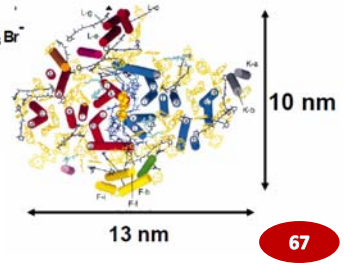
培養



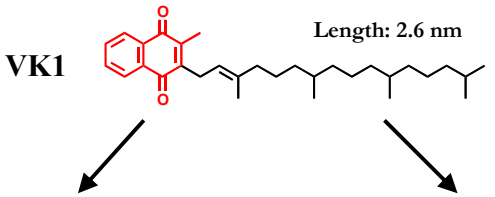
シアノバクテリア: *Thermosynechococcus elongatus*

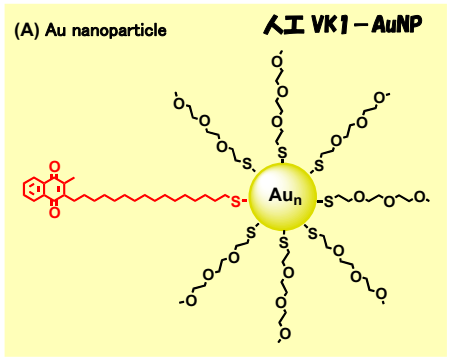
PSI

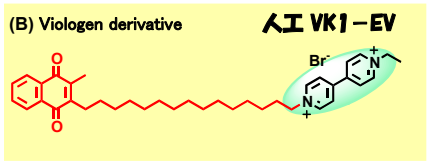
抽出と精製



人工 VK1



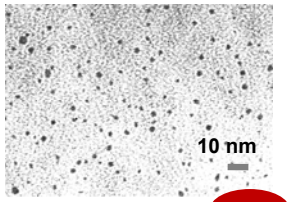




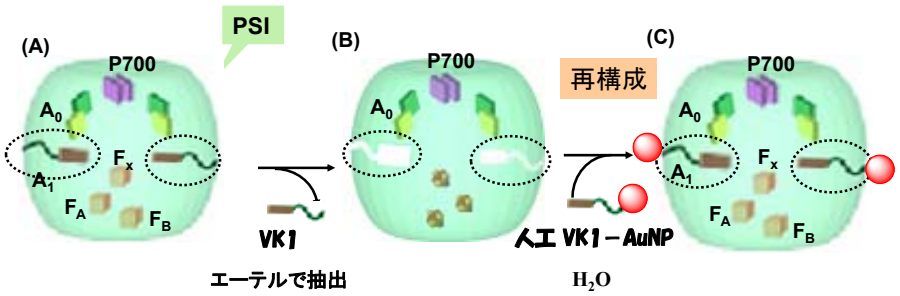
NQ-C15-SHで表面安定化した金ナノ粒子

ナノ粒子核の直径:
1.6 nm

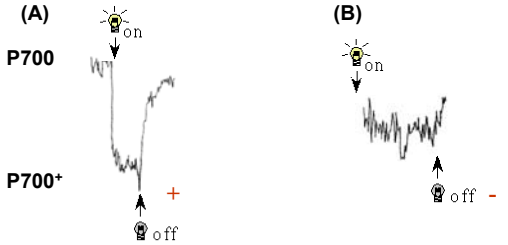
組成:
147 金原子
54 PEG-SH
2 NQ-C15-SH



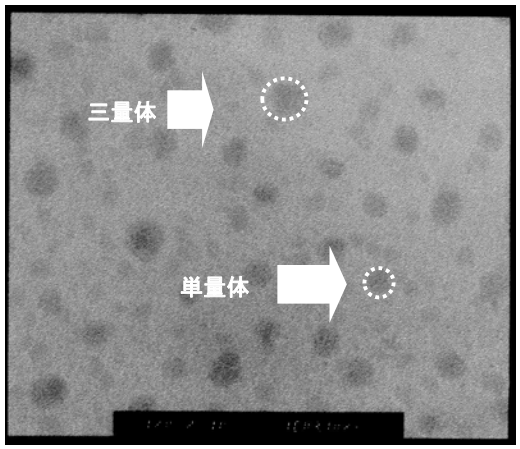
VK1を PSI から取り出し、人工VK1で再構成する。

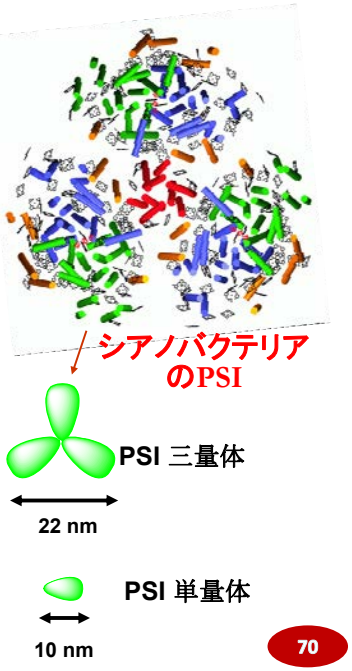


実験による検証—— 光照射時の701 nmの光吸収強度の変化

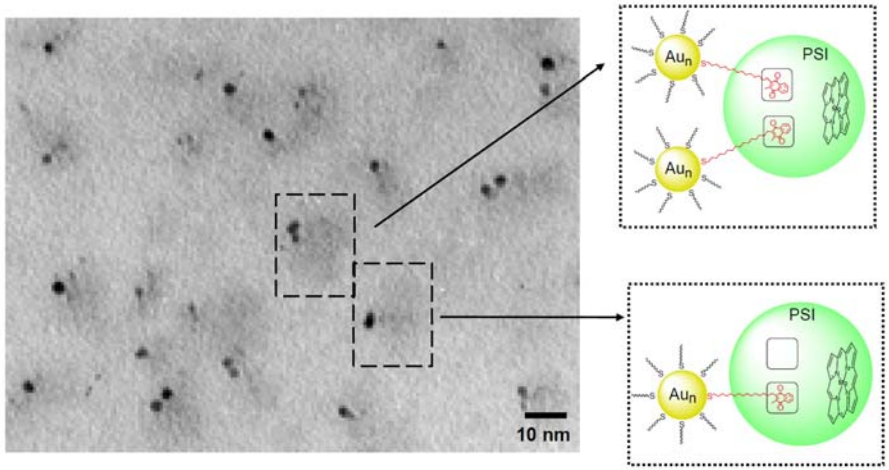


天然PSIの透過型電子顕微鏡（TEM）像 (x 120,000)



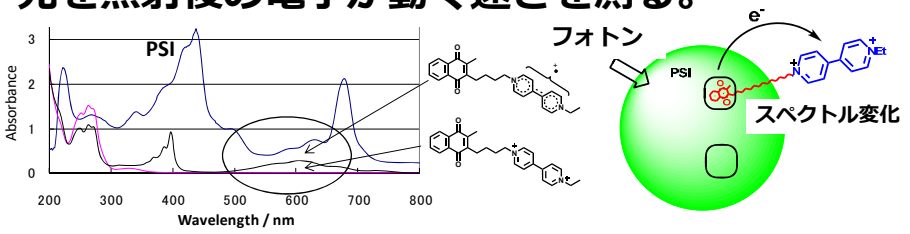


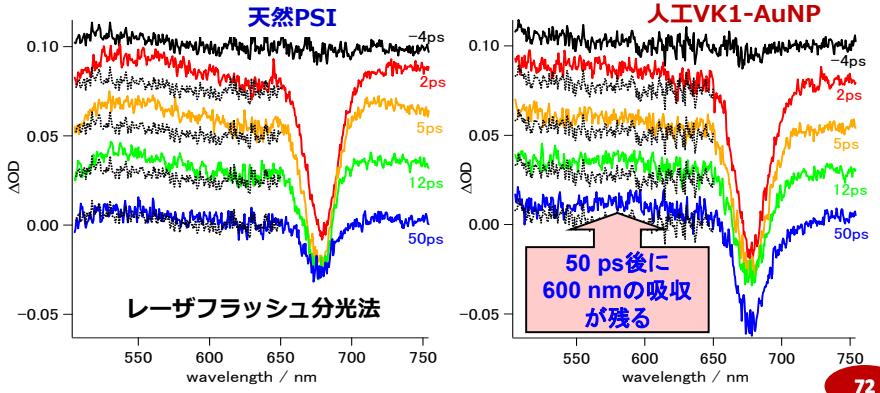
人工VK1–AuNPのTEM像



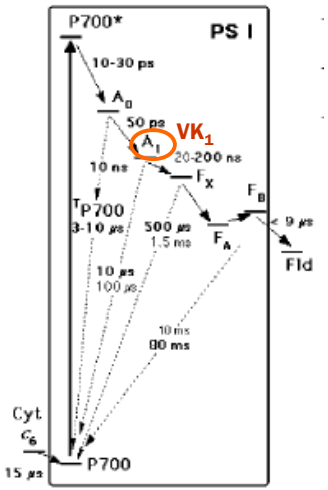
金ナノ粒子結合人工ビタミンK1が選択的に天然ビタミンK1を取り除いたPSIのキノンポケットに入っている。

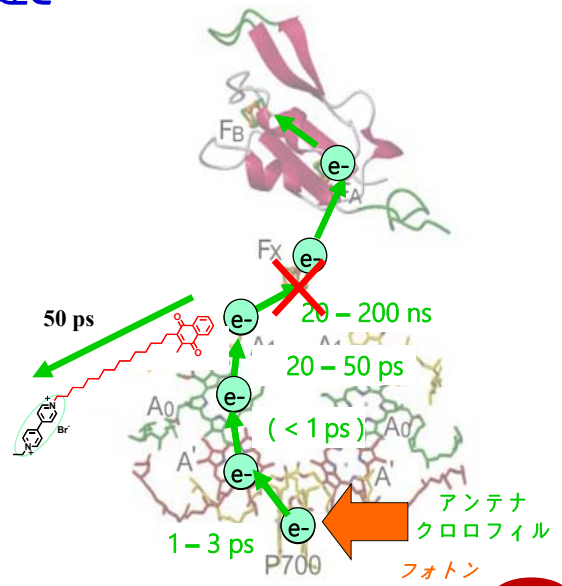
光を照射後の電子が動く速さを測る。



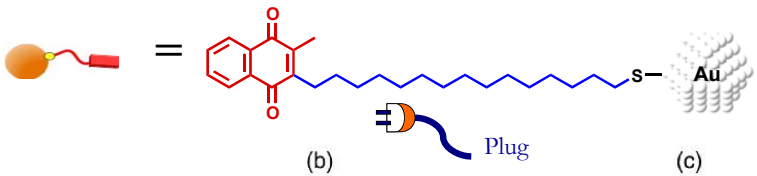


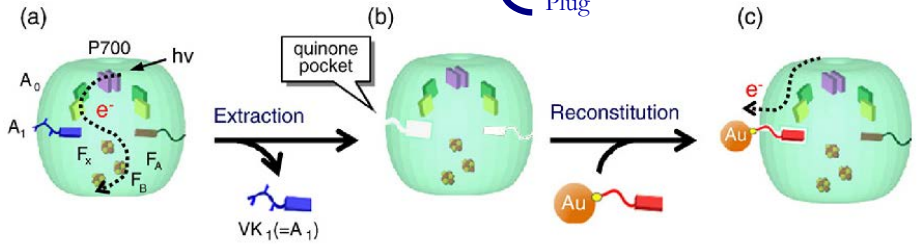
PSI内の電子移動の速さ



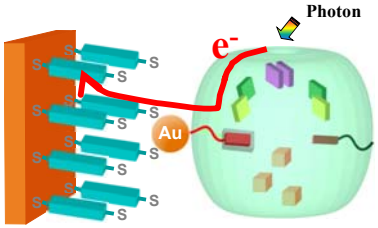


人工VK1を結合したPSIを電極に固定する。





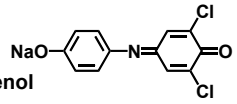
PSI-AuNP 修飾電極の光電流を測る。



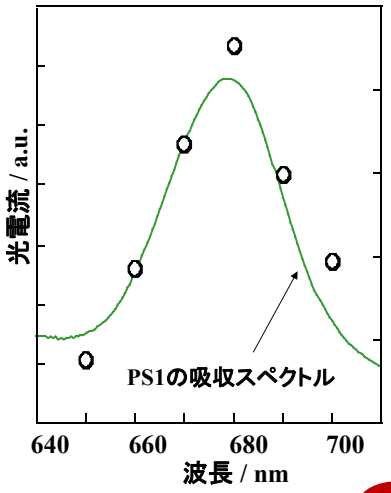
印加電位:
0 V vs. Ag/AgCl (sat. KCl aq.)

電解質溶液:
2.5 mM DCIP
250 mM NaAsA
0.1 M $NaClO_4$
20 mM Mes-NaOH aq. (pH = 6.4)

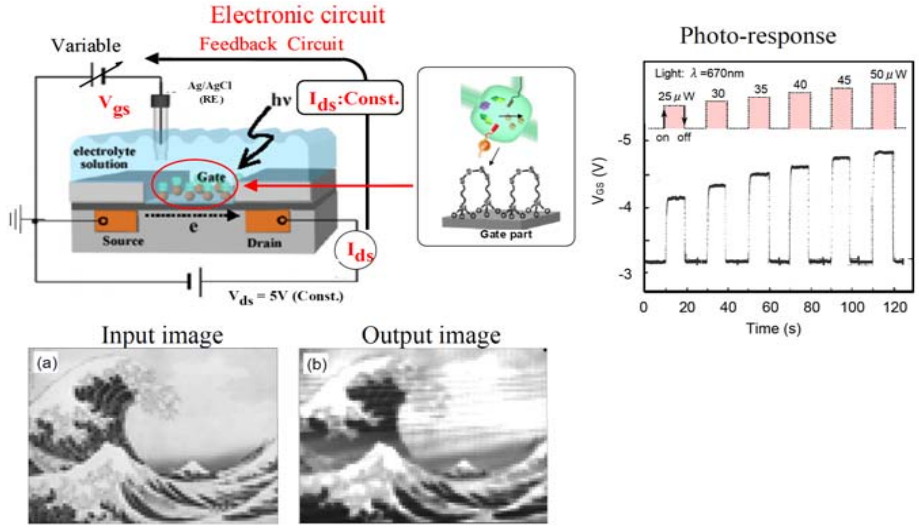
DCIP:
Sodium 2,6-dichloroindophenol



光電流アクションスペクトル



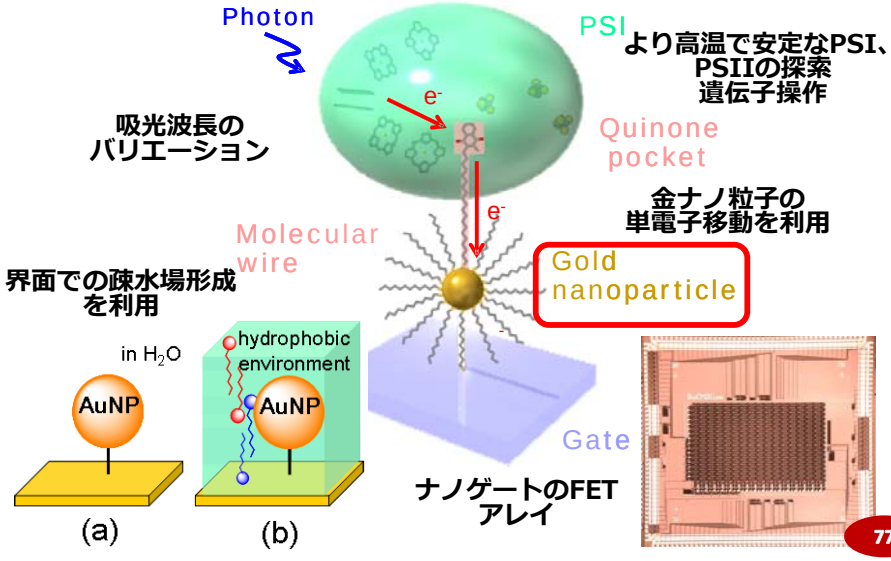
PSI-AuNP-トランジスタでイメージングセンサを作製



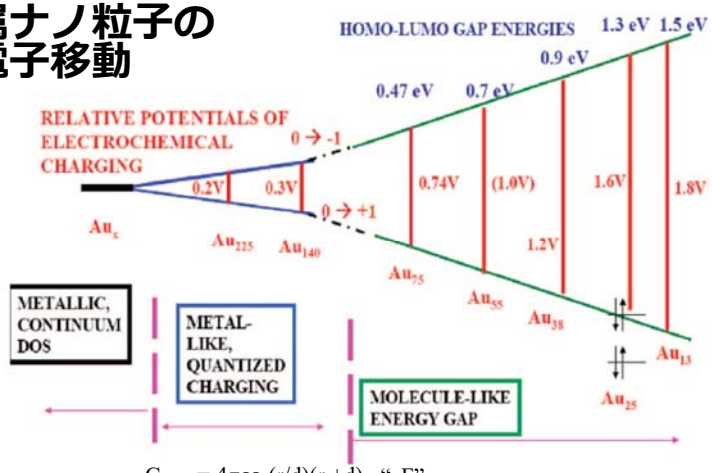
N. Terasaki et al., *BBA-Bioenerg.* **2007**, *1767*, 653.

最終目標

室温で単光子を検出できる超高感度センサ



金属ナノ粒子の単電子移動

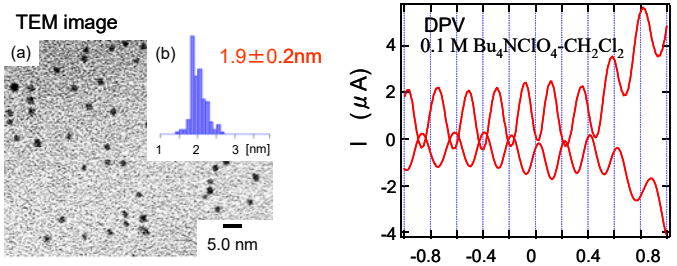


$C_{CLU} = 4\pi\varepsilon\varepsilon_0(r/d)(r+d)$ "aF"

Fig. Summary of electrochemical behavior by MPC core size, showing estimated energy gaps (HOMO–LUMO gaps) and electrochemical energy gaps (which is the spacing between the first oxidation peak and the first reduction current peak for the native nanoparticle).

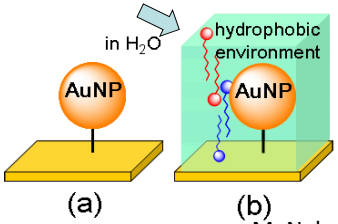
R. W. Murray, *Chem. Rev.*, **108**, 2688–2720 (2008).

水溶液中での AuNP 単電子移動の観察

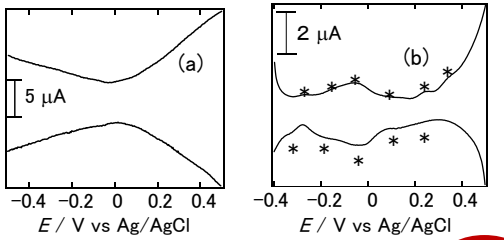


Double Surfactants

$C_6H_{13}N(CH_3)_3Br$ + PhSDS

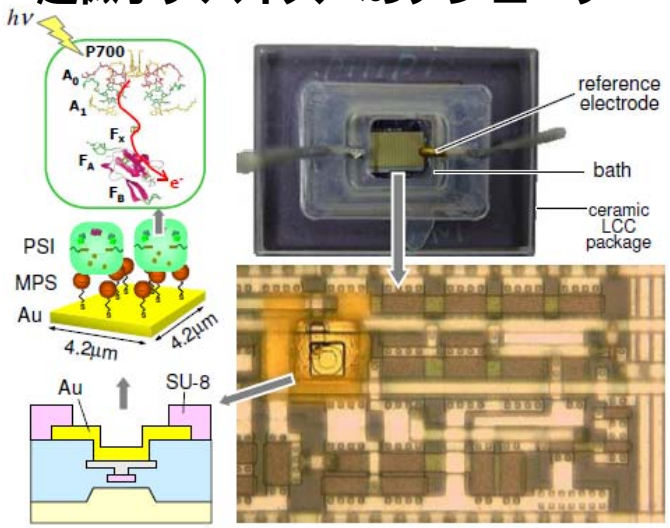


in NEt_4ClO_4 - H_2O



M. Nakai et al. *Angew. Chem. Int. Ed.* **2008**, *47*. 6699.

超微小デバイスへのアプローチ

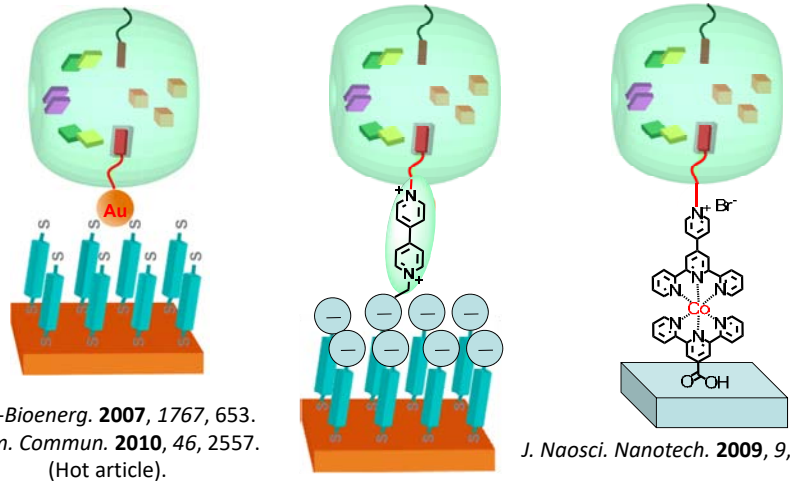


M. Miyachi et al., *Chem. Commun.* **2010**, *46*, 2557. (Hot article).

"Photosensors: Going for gold"
Nature-Asia Pacific, Featured highlight, *June 21, 2010*

Bio-photosensors

Cyanobacterial PSI–Molecular Wire–Electrode

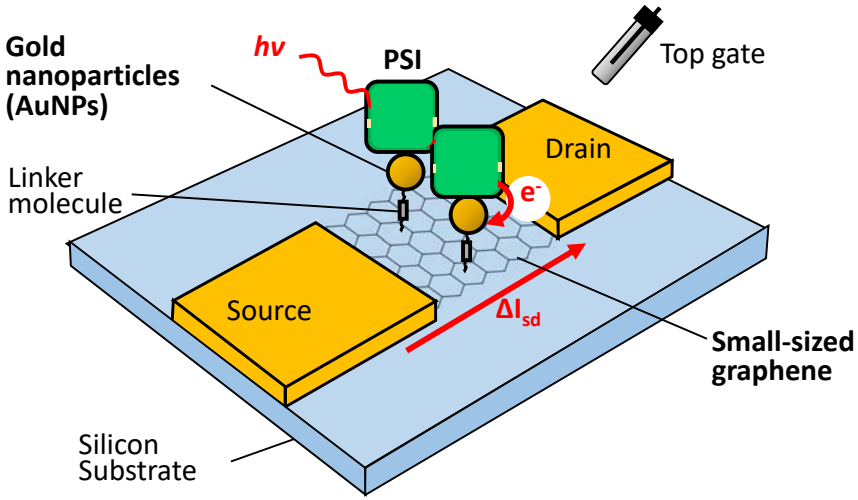


BBA-Bioenerg. **2007**, *1767*, 653.
Chem. Commun. **2010**, *46*, 2557.
(Hot article).

Angew. Chem. Int. Ed. **2009**, *121*, 1613 (Press release).
Thin Solid Films, **2012**, 520, 5123.

J. Naosci. Nanotech. **2009**, *9*, 1722.

Photosensor based on PSI, AuNPs and graphene FET



Electron transfer → Change in the source-drain current (I_{sd})

Nikon

ニコン チャンネル > 光と人の物語 > "見る力"の発展 > 生き物の力で人工の目を作る

"見る力"の発展
生き物の力で人工の目を作る
The Story of Light and People
ナビゲーター：横山広美 さん

太陽の光を浴びて育つ植物は、光の粒を効率よく電子に変換する力をもっている。生き物がもつこの機能を「部品」として利用し、研究室で作り出された細い分子のワイヤーとつなげることで、生物の機能を使った人工的な「目」ができた。生き物と人工の物質による「ハイブリッド」によって、ごくわずかの光であっても検出できる。つまり光の極限利用ができるようになるのだ。

人間になったガラテア

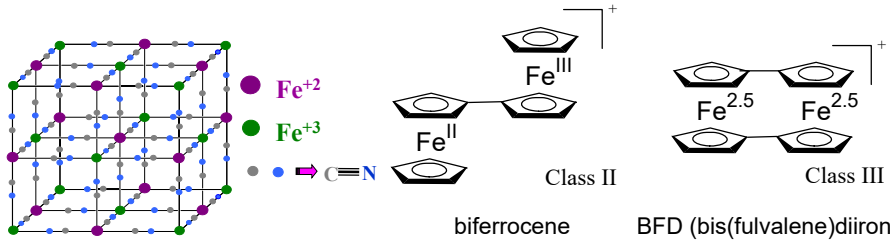
ギリシャ神話には彫刻の女性が人間になる話がある。キプロス島の王、ピグマリオンが自ら彫刻した女性、ガラテアに恋をし、ガラテアが人間になることを望んだ。それを知った神、アフロディーテが願いを聞き入れてガラテアを人間にする話である。

しかし現在の技術をもってしても、私たち人間は細胞ひとつゼロから人工的に作ることはできない。それくらい生命というのは複雑かつ精緻なものである。

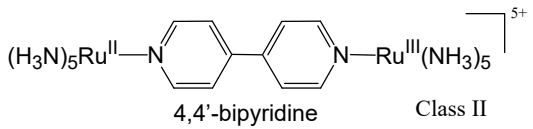
ならば、こうした生体の一部を使って、これまで達成しえなかった人工物を作ろうという考えが生まれるのも自然な流れである。化学者である西原寛東京大学教授は、現在主流の「ナノテクノロジー」研究の先に、何があるかを考えていた。そこで思い至ったのが、生体と人工物を組み合わせたまったく新たな物質を作ることだった。生体の一部を取り出す研究は1960年代に始まっていた。しかし、これを化学物質である「部品」として使おうとする研究はこれまでにない試みである。

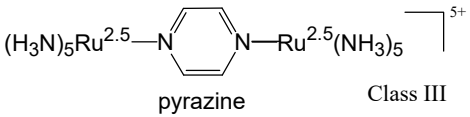
「ピグマリオンとガラテア」
©Erich Lessing/PPS

1）混合原子価錯体の例



Creutz-Taube salts



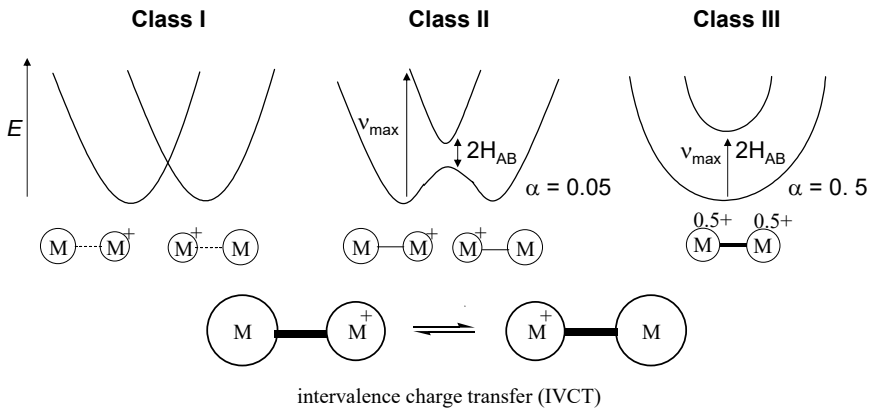


2）研究の歴史

1950	Prussian blue etc. （固体状態）
1956-1965	Marcus theory （電子移動速度論）
1967	Hush theory （IVCTバンドの理論）
1967	Robin and Day 混合原子価錯体の分類（Class I, II, III）
1969	Creutz-Taube錯体の合成（分子系）
1970's	Marcus-Hush theory の検証 様々な混合原子価錯体の合成と物性測定
1980's	溶媒効果など
1994	Creutz-Newton-Sutton (CNS) theory 架橋配位子の役割、電子輸送とホール輸送
1995	Aoki-Chen theory 二核系から多核系への拡張（レドックス挙動）
1996	Aoki-Nishihara オリゴフェロセニレンのレドックス挙動解析
1997	Ito-Kubiak IRによる混合原子価の電子交換速度論の解析
1999	Nishihara オリゴフェロセニレンのIVCTバンド解析
2002	Class II – Class III転移のthree-state model

3） 混合原子価錯体の分類

Robin-Dayの分類
レドックス核間相互作用の強さ Class I < Class II < Class III

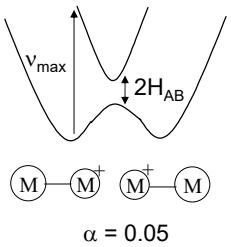


intervalence charge transfer (IVCT)

4） 原子価間遷移 (Intervalence-transfer, IVCT) (Class IIの場合)

$\Psi_g = \Psi A + \alpha\Psi_B$
$\Psi_e = \beta\Psi_A - \Psi_B$

重なり積分
$S_{AB} = \beta - \alpha = 0$

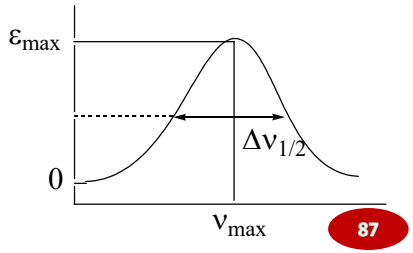


α = 0.05

$\alpha = -H_{AB}/h\nu_{IT}$
$= 2.06 \times 10^{-2} (\varepsilon_{max}\Delta\nu_{1/2}/\nu_{max})^{1/2}/r$

$H_{AB} = 2.06 \times 10^{-2} (\varepsilon_{max}\Delta\nu_{1/2}\nu_{max})^{1/2}/r$

$\Delta\nu_{1/2} = (2310\nu_{max})^{1/2}$



5）酸化還元電位

Red-Red $\xrightarrow{E^0_1}$ Red-Ox $\xrightarrow{E^0_2}$ Ox-Ox

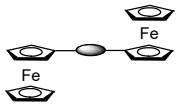
$\Delta E^0 = E^0_2$(Ox-Ox/Red-Ox) - E^0_1(Red-Ox/Red-Red) (1)
$K_c = \exp(\Delta E^0 F/RT)$ (2)
$\Delta G_c = \Delta G_s + \Delta G_e + \Delta G_i + \Delta G_r + \Delta G_r$ (3)

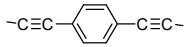
ΔG_s:the statistical distribution of the comproportionation equilibrium
ΔG_e:the electrostatic repulsion of the two like-charged metal nuclei
ΔG_i:an inductive factor dealing with competitive coordination of the bridging ligand by the metal nuclei
ΔG_r:the free energy of resonance exchange
ΔG_{ex}:the stabilization of one of the reactants

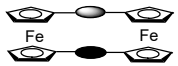
==========

u_{OR}: ΔG_r
u_{OO}: ΔG_e

6）フェロセン二量体の混合原子価状態



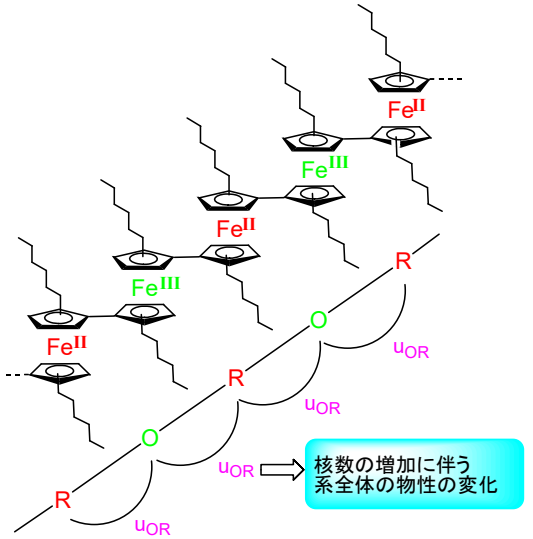
	ΔE_{12} / V
none	0.42
-CH=CH-	0.17
$-(CH=CH)_2-$	0.13
$-(CH=CH)_3-$	0.09
$-C\equiv C-$	0.13
$-(C\equiv C)_2-$	0.10
-N=N-	0.18
	0.07
	0.47
	0.30
	0.23



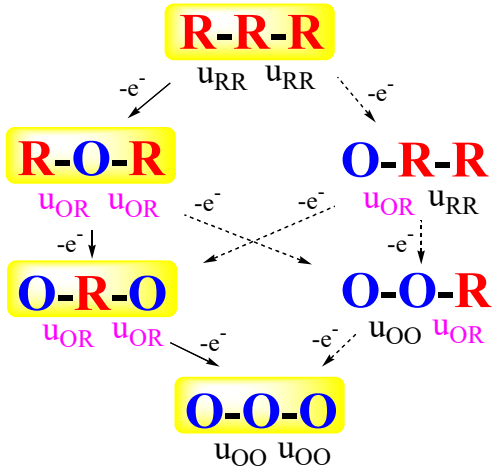
	ΔE_{12} / V
= none	0.59
$C\equiv C$	0.36
[= none, = N=N]	0.41

Oligo(1,1'-ferrocenylene)s

核（金属）間相互作用を調べるモデル



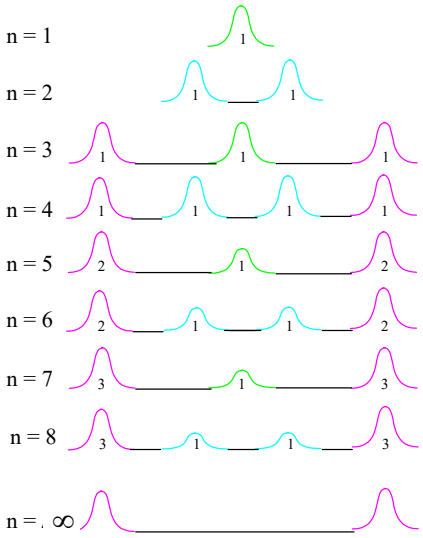
隣接核間相互作用モデル



K. Aoki and J. Chen, 1995

species	μ^0	$(E_{N,i+1} - E_{N,i})e$
RRRR	$4\mu_R^0 + 3u_{RR}$	
RORR	$3\mu_R^0 + \mu_O^0 + 2u_{OR} + u_{RR}$	$u_1 - u_2$
RORO	$2\mu_R^0 + 2\mu_O^0 + 3u_{OR}$	$2u_1$
OROO	$\mu_R^0 + 3\mu_O^0 + 2u_{OR} + u_{OO}$	$u_1 + u_2$
OOOO	$4\mu_O^0 + 3u_{OO}$	
RRRRR	$5\mu_R^0 + 4u_{RR}$	
RRORR	$4\mu_R^0 + \mu_O^0 + 2u_{OR} + 2u_{RR}$	0
ROROR	$3\mu_R^0 + 2\mu_O^0 + 4u_{OR}$	$2u_1 - 2u_2$
ORORO	$2\mu_R^0 + 3\mu_O^0 + 4u_{OR}$	$2u_1 + 2u_2$
OOROO	$\mu_R^0 + 3\mu_O^0 + 2u_{OR} + u_{OO}$	0
OOOOO	$4\mu_O^0 + 3u_{OO}$	
RRRRRR	$6\mu_R^0 + 5u_{RR}$	
RRRORR	$5\mu_R^0 + \mu_O^0 + 2u_{OR} + 3u_{RR}$	0
RORROR	$4\mu_R^0 + 2\mu_O^0 + 4u_{OR} + u_{RR}$	$u_1 - u_2$
RORORO	$3\mu_R^0 + 3\mu_O^0 + 5u_{OR}$	$2u_1$
OROORO	$2\mu_R^0 + 4\mu_O^0 + 4u_{OR} + u_{OO}$	$u_1 + u_2$
OOROOO	$\mu_R^0 + 5\mu_O^0 + 2u_{OR} + 3u_{OO}$	0
OOOOOO	$6\mu_O^0 + 5u_{OO}$	

$u_1 = (u_{OO} + u_{RR})/2 - u_{OR}$, $u_2 = (u_{OO} - u_{RR})/2$



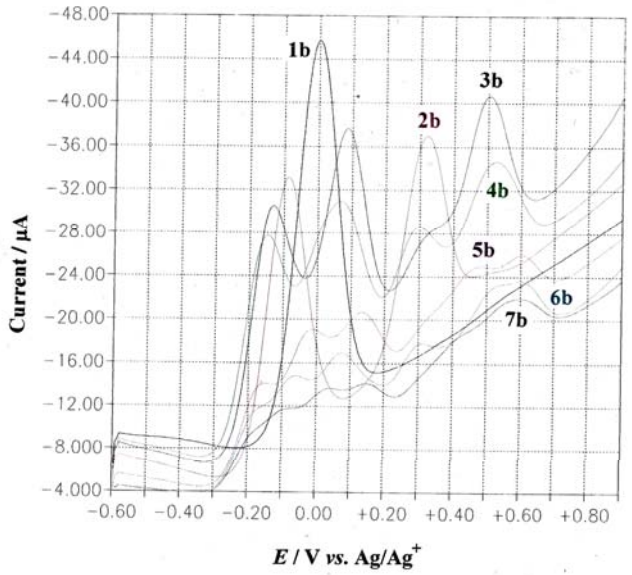
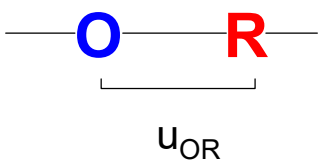
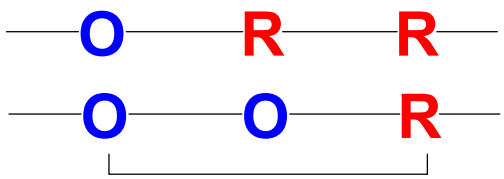


Fig. Osteryoung square-wave voltammograms of **1b** - **7b** at GC in 0.1 M TBAP-CH_2Cl_2 at a frequency of 15 Hz and a potential step of 4 mV.



u_{OR}



u_{OXR}

Estimation based on interaction energies over two and three redox nuclei

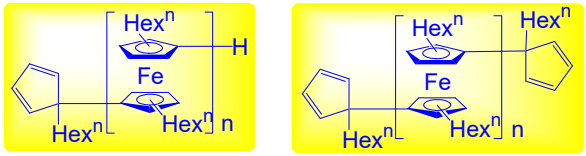
species	μ^0	$(E_{N,i+1} - E_{N,i})e$
RRRR	$4\mu_R^0 + 3u_{RR}$	
RORR	$3\mu_R^0 + \mu_O^0 + 2u_{OR} + u_{RR} + u_{OXR}$	$u_1 - u_2 - 2u_3$
RORO	$2\mu_R^0 + 2\mu_O^0 + 3u_{OR}$	$2u_1 + 2u_3$
OROO	$\mu_R^0 + 3\mu_O^0 + 2u_{OR} + u_{OO} + u_{OXR}$	$u_1 + u_2 - 2u_3$
OOOO	$4\mu_O^0 + 3u_{OO}$	
RRRRR	$5\mu_R^0 + 4u_{RR}$	
RRORR	$4\mu_R^0 + \mu_O^0 + 2u_{OR} + 2u_{RR} + 2u_{OXR}$	$-4u_3$
RORORO	$3\mu_R^0 + 2\mu_O^0 + 4u_{OR}$	$2u_1 - 2u_2 + 2u_3$
ORORO	$2\mu_R^0 + 3\mu_O^0 + 4u_{OR}$	$2u_1 + 2u_2 + 2u_3$
OOROO	$\mu_R^0 + 3\mu_O^0 + 2u_{OR} + u_{OO} + 2u_{OXR}$	$-4u_3$
OOOOO	$4\mu_O^0 + 3u_{OO}$	
RRRRRR	$6\mu_R^0 + 5u_{RR}$	
RRRORR	$5\mu_R^0 + \mu_O^0 + 2u_{OR} + 3u_{RR} + 2u_{OXR}$	$-2u_3$
RORROR	$4\mu_R^0 + 2\mu_O^0 + 4u_{OR} + u_{RR} + 2u_{OXR}$	$u_1 - u_2 - 2u_3$
RORORO	$3\mu_R^0 + 3\mu_O^0 + 5u_{OR}$	$2u_1 + 4u_3$
OROORO	$2\mu_R^0 + 4\mu_O^0 + 4u_{OR} + u_{OO} + 2u_{OXR}$	$u_1 + u_2 - 2u_3$
OOROOO	$\mu_R^0 + 5\mu_O^0 + 2u_{OR} + 3u_{OO} + 2u_{OXR}$	$-2u_3$
OOOOOO	$6\mu_O^0 + 5u_{OO}$	

$u_1 = (u_{OO} + u_{RR})/2 - u_{OR}$,
$u_2 = (u_{OO} - u_{RR})/2$, $u_3 = u_{OXR}$

species	μ^0	$(E_{N,i+1} - E_{N,i})e$
RRRRRRR	$7\mu_R^0 + 6u_{RR}$	
RRRORRR	$6\mu_R^0 + \mu_O^0 + 2u_{OR} + 4u_{RR} + 2u_{OXR}$	$-u_3$
RORRORR	$5\mu_R^0 + 2\mu_O^0 + 4u_{OR} + 2u_{RR} + 3u_{OXR}$	$-4u_3$
RORORORO	$4\mu_R^0 + 3\mu_O^0 + 6u_{OR}$	$2u_1 - 2u_2 + 3u_3$
ORORORO	$3\mu_R^0 + 4\mu_O^0 + 6u_{OR}$	$2u_1 - 2u_2 + 3u_3$
OROOROO	$2\mu_R^0 + 5\mu_O^0 + 4u_{OR} + 2u_{OO} + 3u_{OXR}$	$-4u_3$
OOOROOO	$\mu_R^0 + 6\mu_O^0 + 2u_{OR} + 4u_{OO} + 2u_{OXR}$	$-u_3$
OOOOOOO	$7\mu_O^0 + 6u_{OO}$	

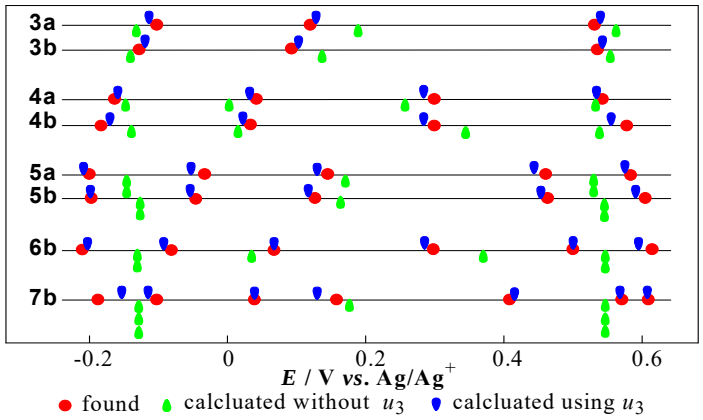
$u_1 = (u_{OO} + u_{RR})/2 - u_{OR}$, $u_2 = (u_{OO} - u_{RR})/2$, $u_3 = u_{OXR}$

酸化還元電位



1a - 5a

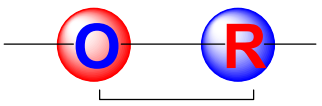
1b - 7b



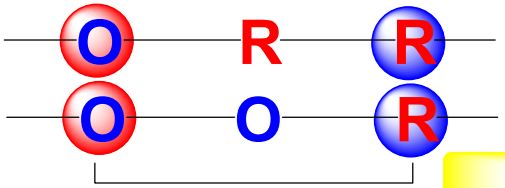
K. Aoki, J. Chen, H. Nishihara, T. Hirao, *J. Electroanal. Chem.* **1996**, *416*, 151.

97

$u_1 = 15.0$ kJ mol^{-1}
$u_2 = 4.5$ kJ mol^{-1}
$u_3 = -3.7$ kJ mol^{-1}

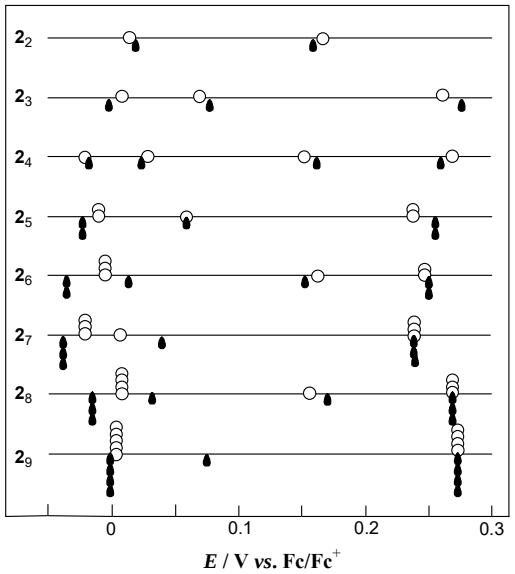


$u_{OR} = -15$ - -24 kJ mol^{-1}



$u_{OXR} = -3.7$ kJ mol^{-1}

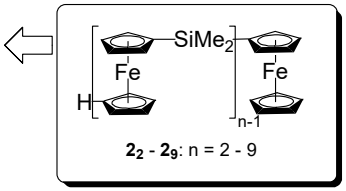
98



I. Manners et al.

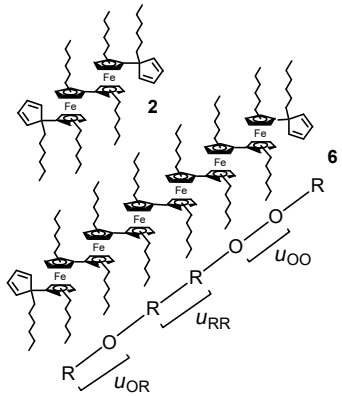
○ Found

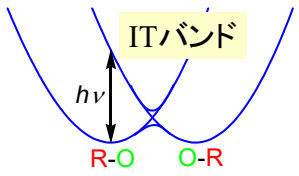
● Calcd using u_{OX}, u_{RR}, and u_{OO}



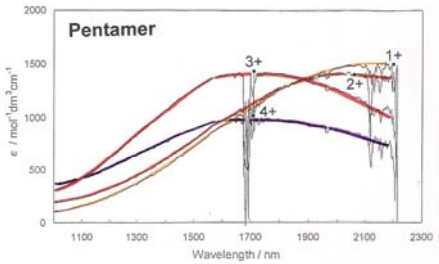
2_2 - 2_9: n = 2 - 9

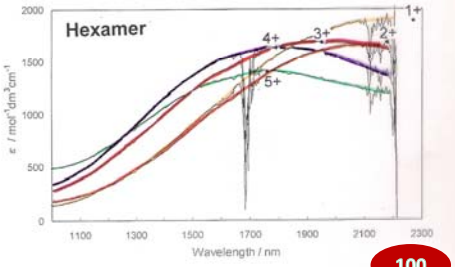
99



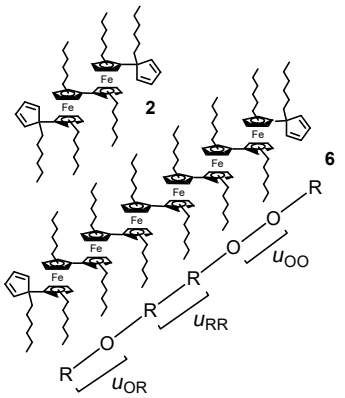


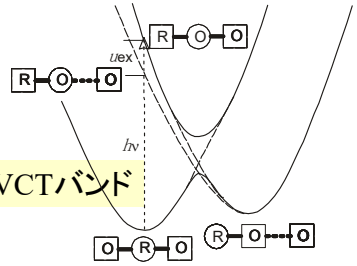
IT bands of oligo(dihexylferrocenylene)s





100





IVCTバンド

O-R-O → R-O-O → R-O—O

u_{ex} = 13 kJ mol^{-1}

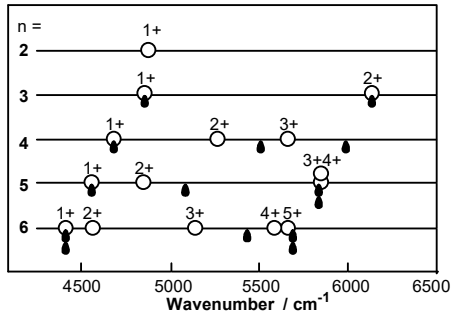
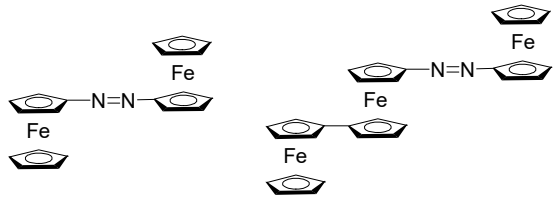


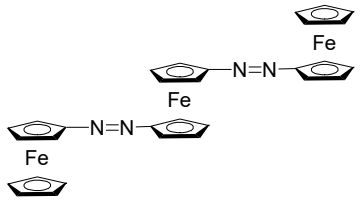
Fig. ν_{max} of IT bands for oligo(dihexylferrocenylene)

○ Found ● Calcd based on neighboring site interaction energies

*J.C.S.Dalton Trans.***1999**, 3355–3360

"**Redox Chemistry and Functionalities of Conjugated Ferrocene Systems**",
H. Nishihara, *Adv. Inorg. Chem.*, 53, 41-86 (2002).





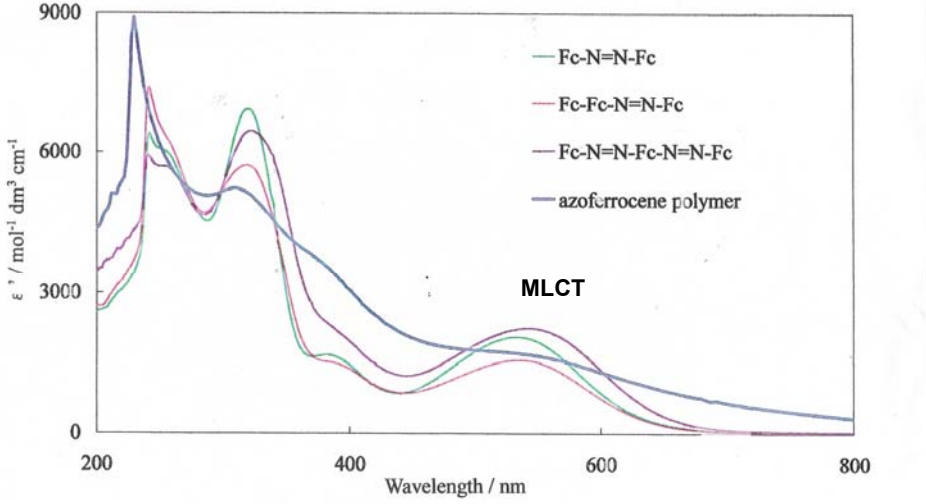
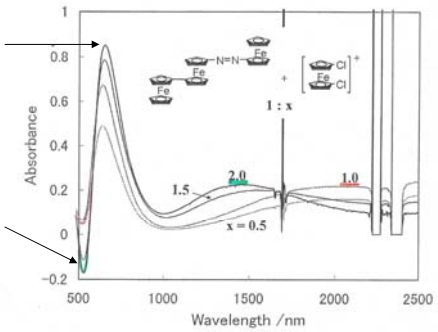
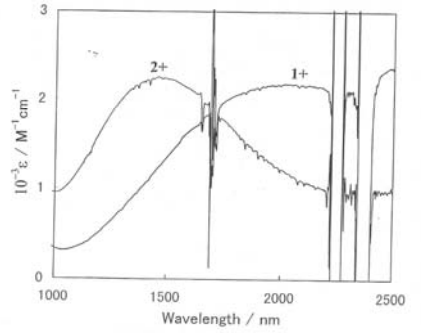


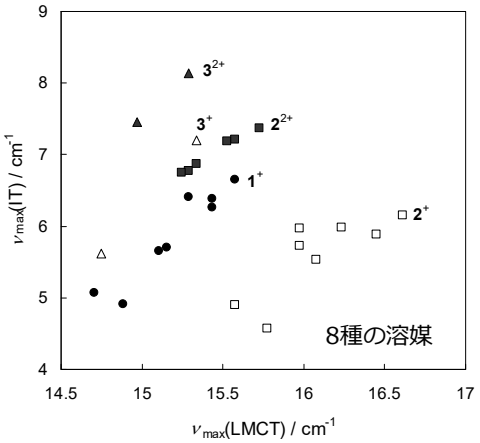
Fig. UV-VIS absorption spectra of **1** , **2** , **3** , and **4** in CH_2Cl_2.
$\varepsilon' = \varepsilon / n$, where n is the number of ferrocenyl units in a molecule.

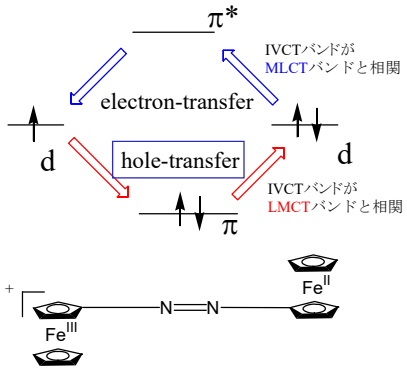
LMCT

MLCT

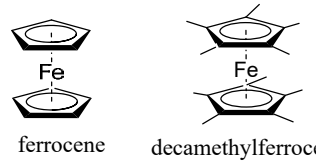






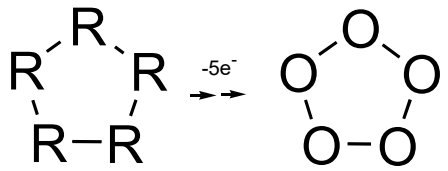


問1 フェロセン($[Fe(\eta^5\text{-}C_5H_5)_2]$)とデカメチルフェロセン($[Fe(\eta^5\text{-}C_5Me_5)_2]$)はともに$Bu_4NPF_6$ーアセトニトリル中で可逆な1電子酸化反応を起こす。このニ種の錯体を比較して
1）酸化還元電位の正負および、
2）電子移動の反応速度定数の大小
について考察せよ。



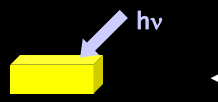
ferrocene　　decamethylferrocene

問2 図に示すような正五角形型にレドックス核が結合した系で、トータル5電子の酸化還元反応が起る場合に、その酸化還元電位の分布がどのようになるか、隣接核間相互作用モデルで考察せよ。
ただし、u_{OR} = -10 kJ/mol, u_{OO} = 10 kJ/mol, u_{RR} = 0 とする。
1 eV (particle)$^{-1}$ = F [C mol^{-1}] × 1 [V] = 96.5 kJ mol^{-1}



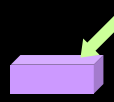
Photochromism

photochromic molecules



Form A

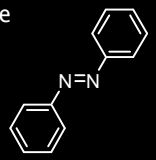
bistability



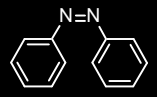
Form B

Molecular memory
Molecular switch

◆ azobenzene



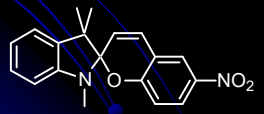
trans



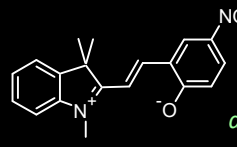
cis

geometry

◆ spiropyran



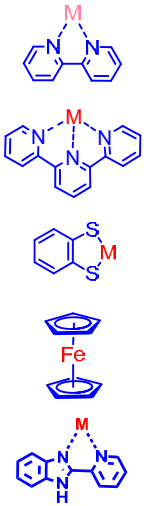
spiropyran



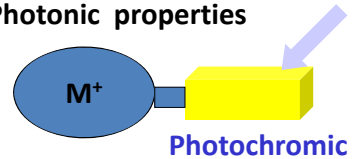
merocyanine

dipole

Photochromic complexes



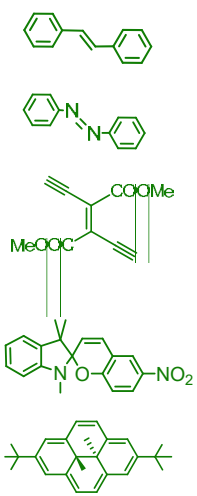
Electronic, magnetic, and Photonic properties



Molecular memories and switches

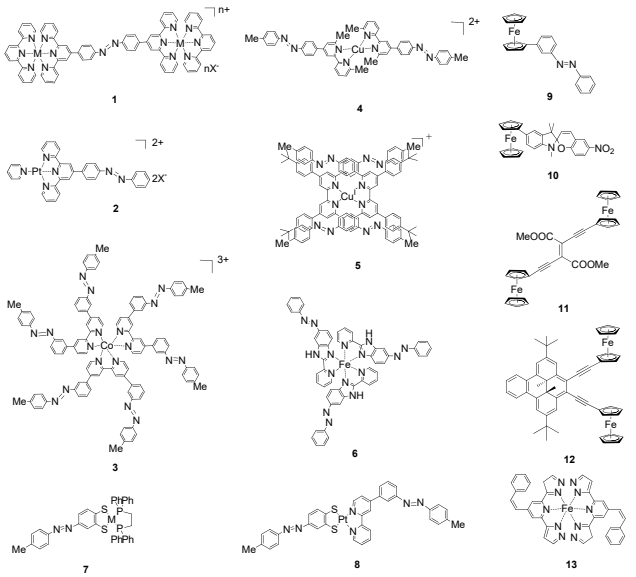
geometry
dipole

Multi-functionalities by the interaction of photochromic moieties with transition metals



Struct. Bond. **2007**, *123*, 79. *Dalton Trans.(Perspective)*, **2008**, 3260.
Comprehensive Inorganic Chemistry II, **2012** in press.

Photochromic complexes in Nishihara group

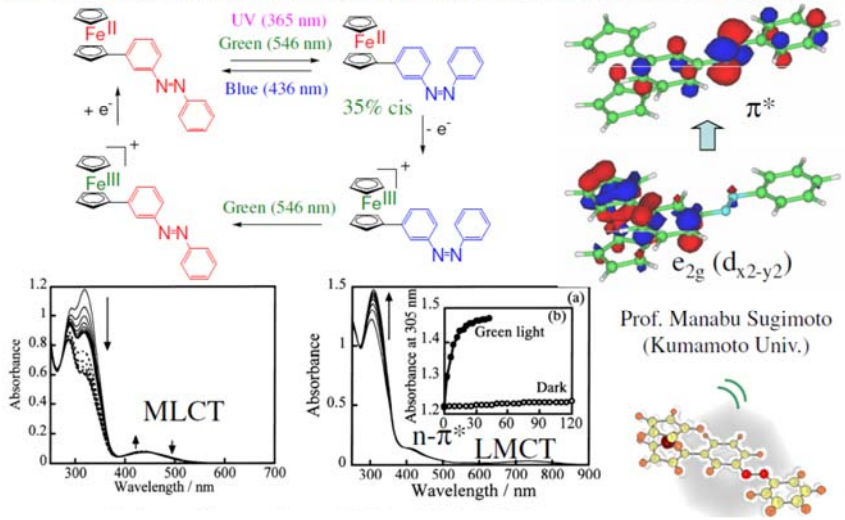


Struct. Bond. **2007**, *123*, 79. *Dalton Trans.(Perspective)*, **2008,** 3260.
Comprehensive Inorganic Chemistry II, **2012**.

Inorg. Chem. **2000**, *39*, 3438
JACS **2000**, *122*, 12373
Chem. Commun., **2001**, 1656
Inorg. Chem. **2001**, *40*, 4986
Chem. Lett. **2001**, 852
JACS **2002**, *124*, 8800
Inorg. Chem. **2002**, *41*, 7143
Inorg. Chem. **2003**, *42*, 2194
Inorg. Chem. **2003**, *42*, 6306
JACS **2003**, *125*, 2964
JACS **2005,***127*, 490
Chem. Comm. **2005**, 1215
Inorg. Chem. **2005** , *44*, 7547
Inorg. Chem. **2005** , *44*, 9056
Chem. Eur. J. **2005** , 11, 7322
Chem. Lett. **2006** , *35*, 38
ACIE **2006** , *45*, 4298
ACIE **2006** , *45*, 4793
Chem. Commun. **2007**, 4650
JACS **2008**, *130*, 7204
Chem. Eur. J. **2008**, *14*, 6978
Dalton Trans. **2009**, 280
Chem. Eur. J. **2009**, *15*, 1429
Chem. Commun. **2009**, 1993
Chem. Lett. **2010**, *39*, 204
Inorg. Chem. **2011**, 50, 4925
Chem. Commun. **2011**, *47*, 6846
New J. Chem. **2011**, *35*, 2146
Inorg. Chem. **2012**, *51*, 5188
Chem. Eur. J. **2012**, *18*, 8610
Chem. Lett. **2013**, *42*, 17
Inorg. Chem. **2013**, *52*, 1658
Chem. Eur. J. **2013**, *19*, 17314
New J. Chem. **2014**, *38*, 6114
JACS **2014**, *136*, 4809

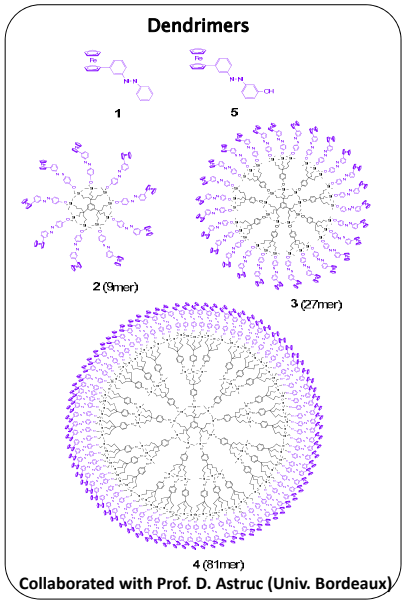
3-Ferrocenylazobenzene

Reversible photoisomerization using a single green light source and a redox reaction



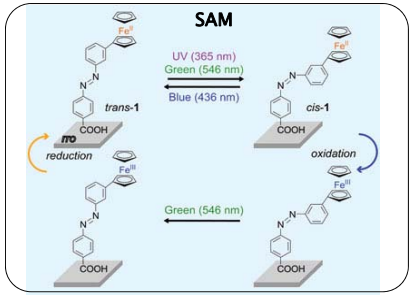
M. Kurihara et al., *J. Am. Chem. Soc.*, **2002**, *124*, 8800.
A. Sakamoto et al., *Inorg. Chem*. **2005**, *44*, 7547.

Dendrimers



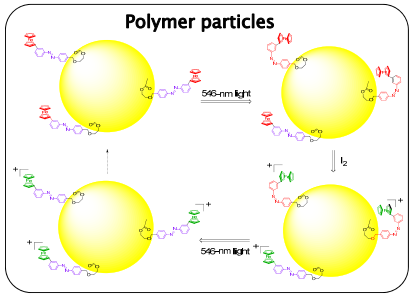
M.-C. Daniele et al.,*Chem. Lett.* **2006**, *35*, 38.

SAM



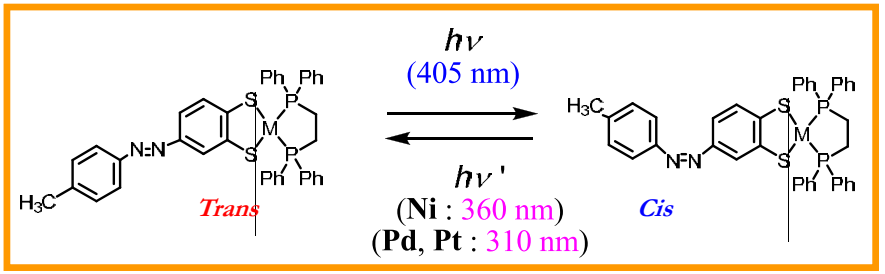
K. Namiki et al.,*Chem. Commun.* **2007**, 4650.

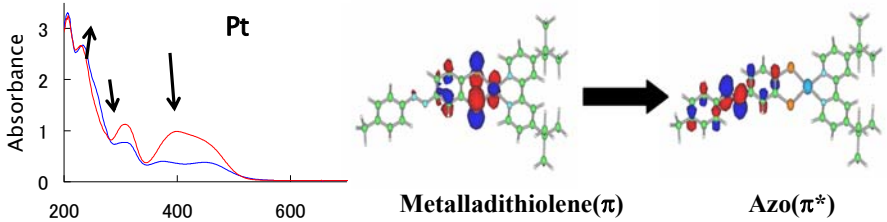
Polymer particles



K. Namiki et al., *New J. Chem.* **2011**, *35*, 2146.

Azobenzene-metalladithiolene conjugated system



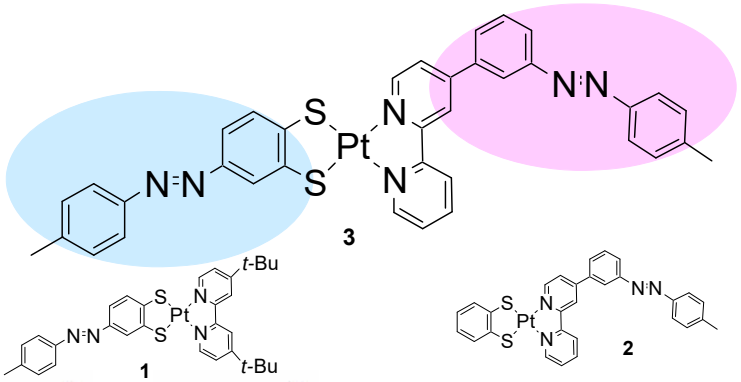


Low energy (ca. 400 nm) trans-to-cis photoisomerization with high thermal stability of the cis form.

M. Nihei et al., *J. Am. Chem. Soc*. **2003**, *125*, 2964.

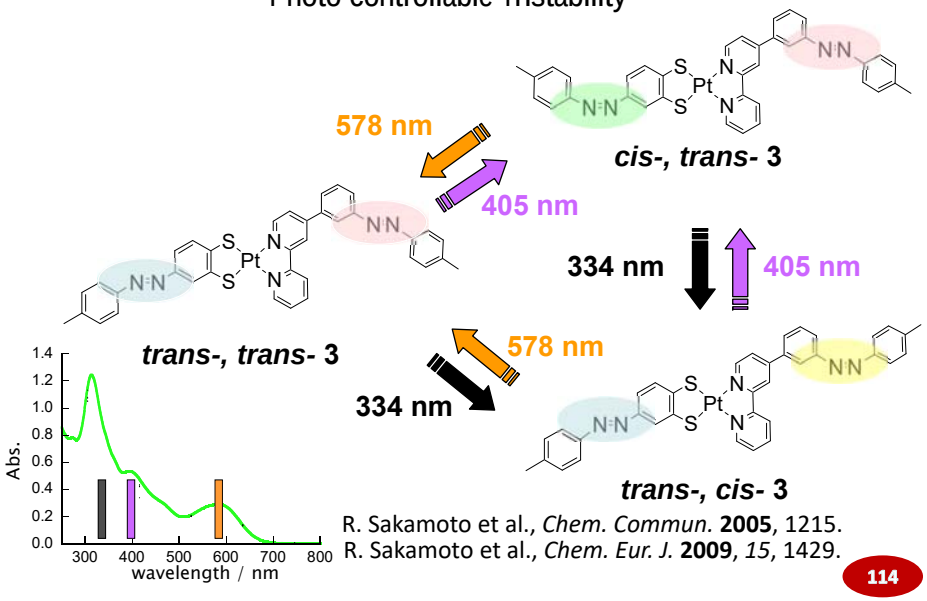
Bipyridine–dithiolato Pt Complex with Two Azobenzenes

- Photo-controllable Tristability –



Bipyridine–dithiolato Pt Complex with Two Azobenzenes

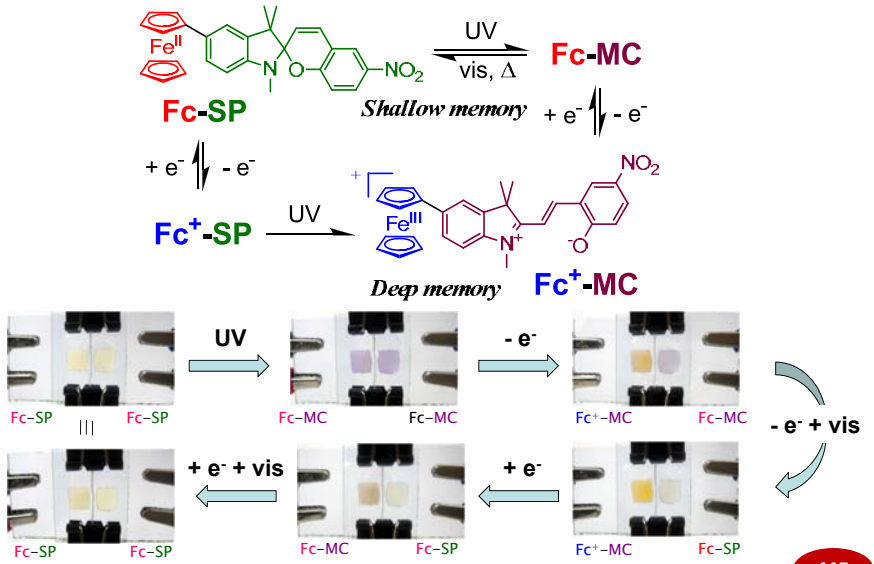
- Photo-controllable Tristability –



R. Sakamoto et al., *Chem. Commun.* **2005**, 1215.
R. Sakamoto et al., *Chem. Eur. J.* **2009**, *15*, 1429.

Ferrocenylspiropyran

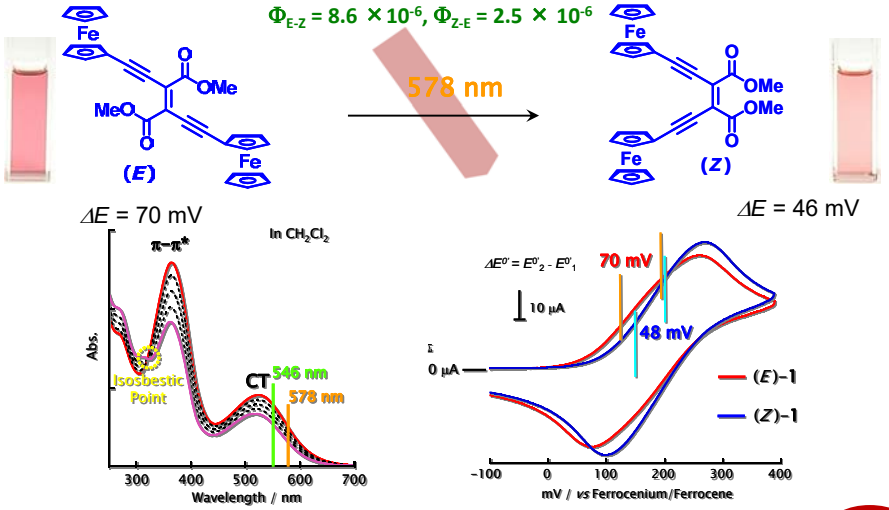
- Depth-controllable molecular photo-memory -



S. Nagashima et al., *Angew. Chem. Int. Ed.* **2006**, *45*, 4298.

Bis(ferrocenylethynyl)ethene

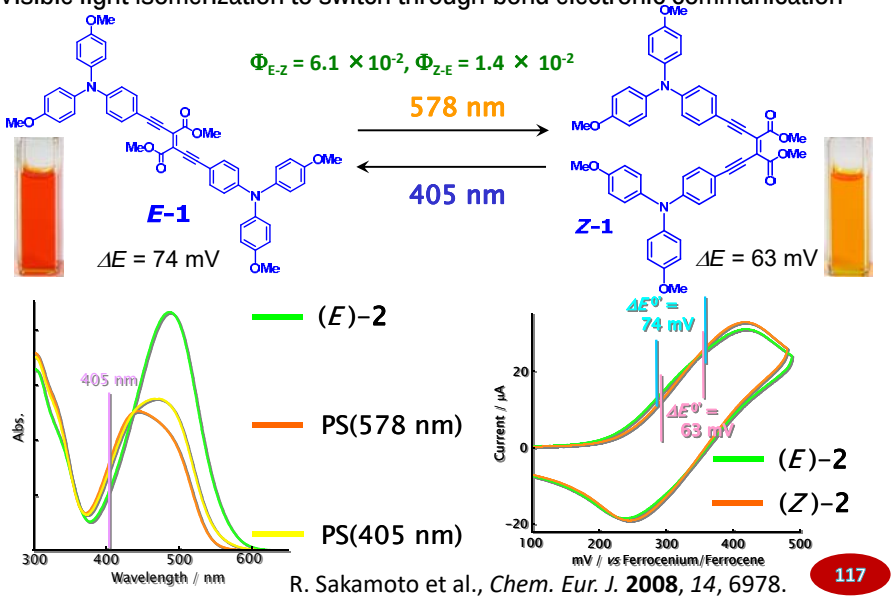
Visible light isomerization to alter through-bond electronic communication



R. Sakamoto et al., *Angew. Chem. Int. Ed.* **2006**, *45*, 4793.

Bis(arylethynyl)ethene

Visible light Isomerization to switch through-bond electronic communication

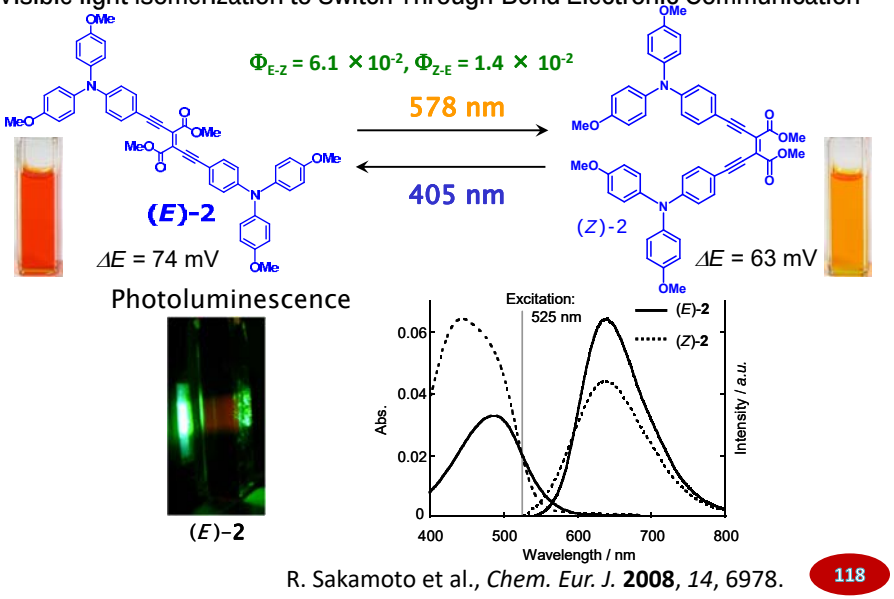


R. Sakamoto et al., *Chem. Eur. J.* **2008**, *14*, 6978.

117

Bis(arylethynyl)ethene

Visible light Isomerization to Switch Through-Bond Electronic Communication

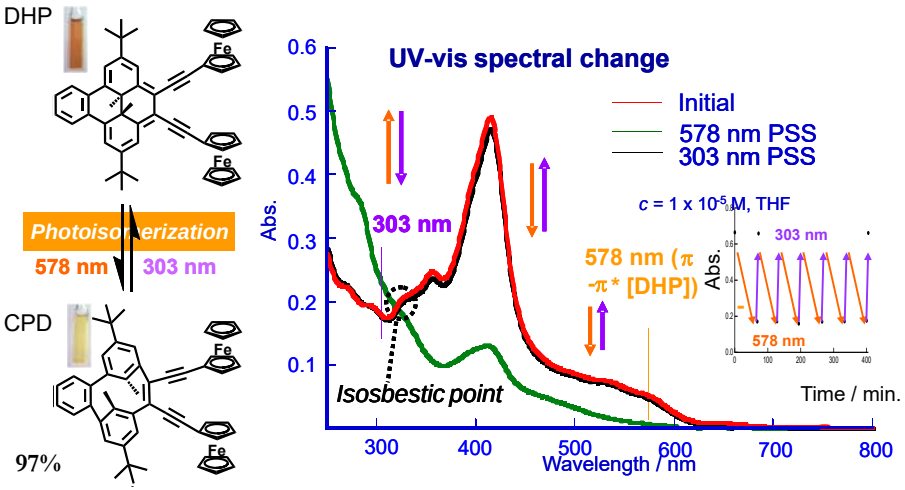


R. Sakamoto et al., *Chem. Eur. J.* **2008**, *14*, 6978.

118

Bis(ferrocenyl)dimethyldihydropyrene

High efficiency of photoisomerization

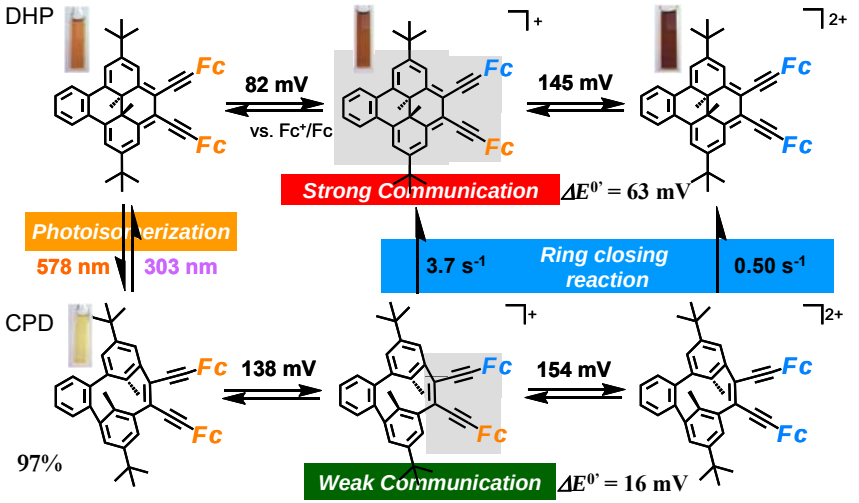


S. Muratsugu et al., *J. Am. Chem. Soc.* **2008**, *130*, 4204.

119

Bis(ferrocenyl)dimethyldihydropyrene

Redox-assisted ring closing with electronic communication switching

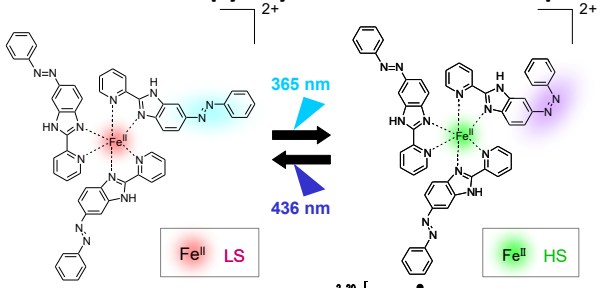


S. Muratsugu et al., *J. Am. Chem. Soc.* **2008**, *130*, 4204.

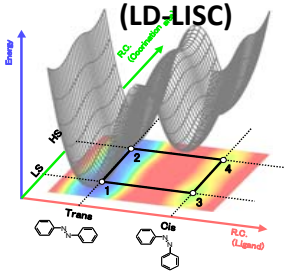
120

Reversible Light-induced Magnetization Change at RT

Azobenzene-attached pyridylbenzimidazole complex of Fe(II)



Ligand-driven light-induced spin change (LD-LISC)



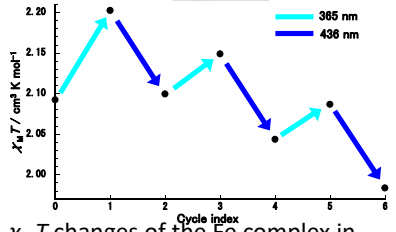
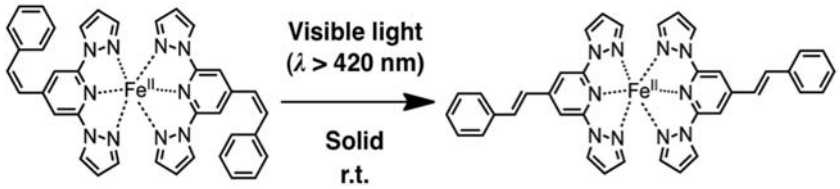


Fig. $\chi_M T$ changes of the Fe complex in acetone-d_6, upon photoirradiation at 293 K.

Y. Hasegawa et al, *Dalton Trans.* **2009**, 280.

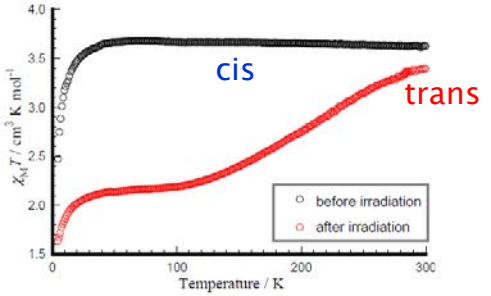
121

Modulation of Magnegtism through Photochromism



bis(dipyrazolylstyrylpyridine)iron(II)

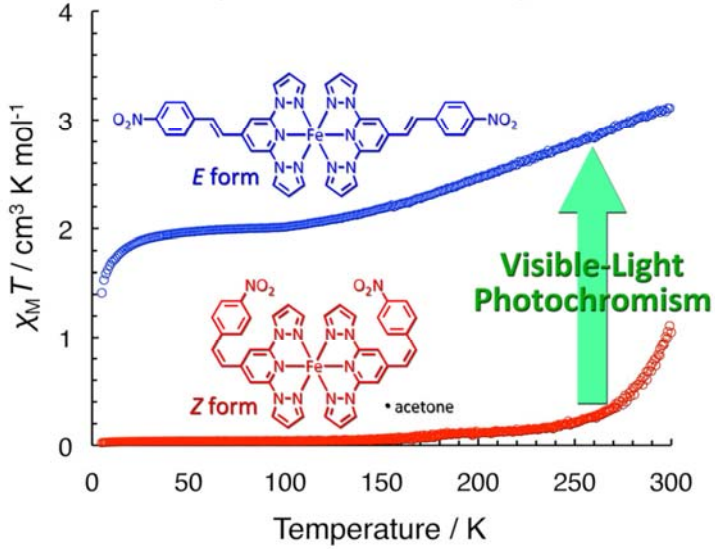
Magnetic properties



Y. Hasegawa et al., *Chem. Commun.* **2011**, 47, 6846.

122

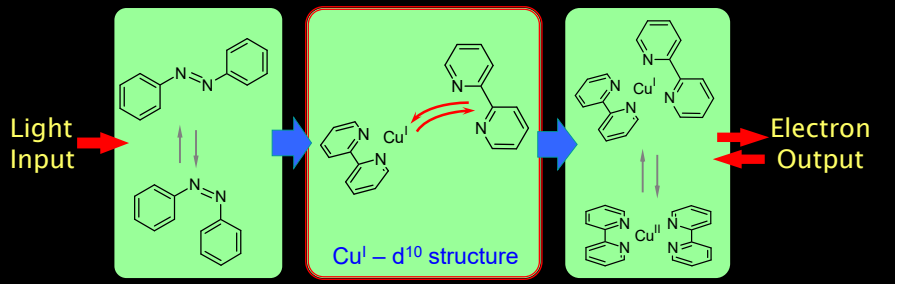
Solid State LD-LISC at Ambient Temperatures With a Large Modulation of Magnetism



K. Takahashi et al, *Inorg. Chem.* **2012**, *51*, 5188.

123

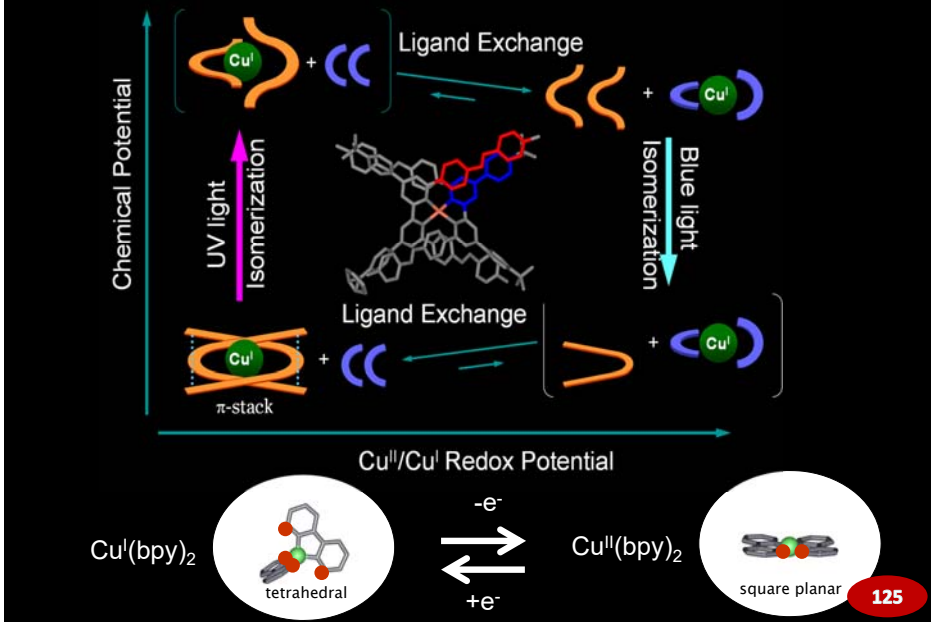
Reversible Photoelectronic Signal Conversion Based on Photoisomerization-Controlled Coordination Change



S. Kume et al., *J. Am. Chem. Soc.* **2005**, *127*, 490.

124

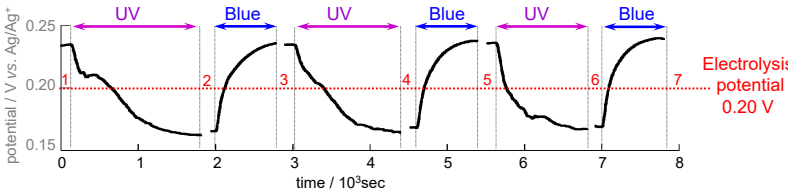
Energy Processing



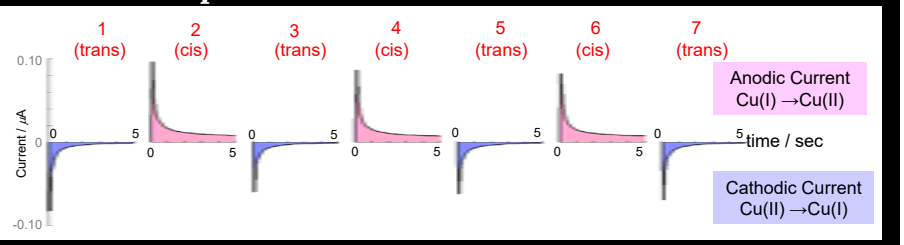
125

Electrochemical Output

Potential response



Current Response



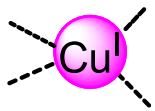
Changes in rest potential (upper) and electrolysis current (lower) of oAB-$[Cu^{I}(bpy^{*})_2$-$[Cu^{II}(bpy^{*})_2]^{2+}$ mixture with UV (365 nm) and Visible (436 nm) irradiation in 0.1M Bu_4NClO_4-dichloromethane.

S. Kume et al., *J. Am. Chem. Soc.* **2005**, *127*, 490.

126

シンプルなジイミン銅錯体ー配位構造に依存する物性ー

d^{10}

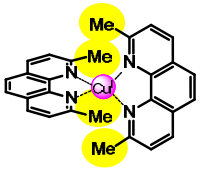


銅一価：正四面体形

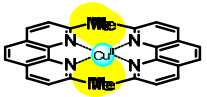
d^{9}

銅二価：平面四角形
三方両錐形

銅周辺が混んでいる

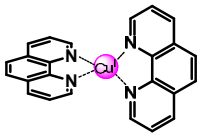


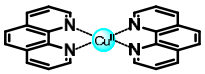
立体反発



銅一価は酸化されにくい
$Cu^{II/I}$ 酸化還元電位：正側

銅周辺が空いている

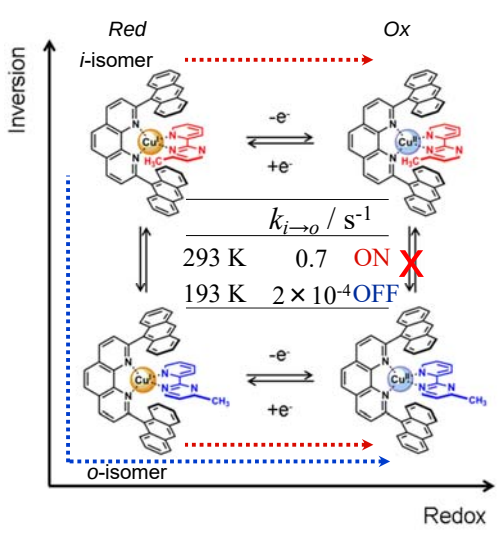


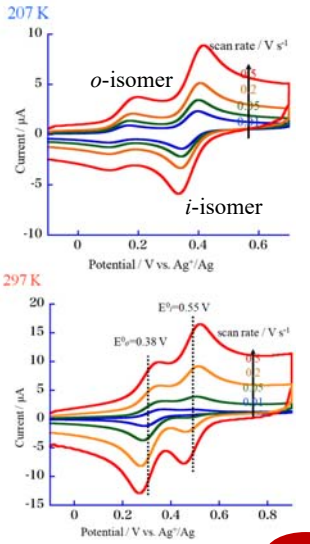


銅一価が酸化されやすい
$Cu^{II/I}$ 酸化還元電位：負側

127

A Single Molecular System Gating Electron Transfer by Ring Inversion of a Methylpyridylpyrimidine Ligand on Cu

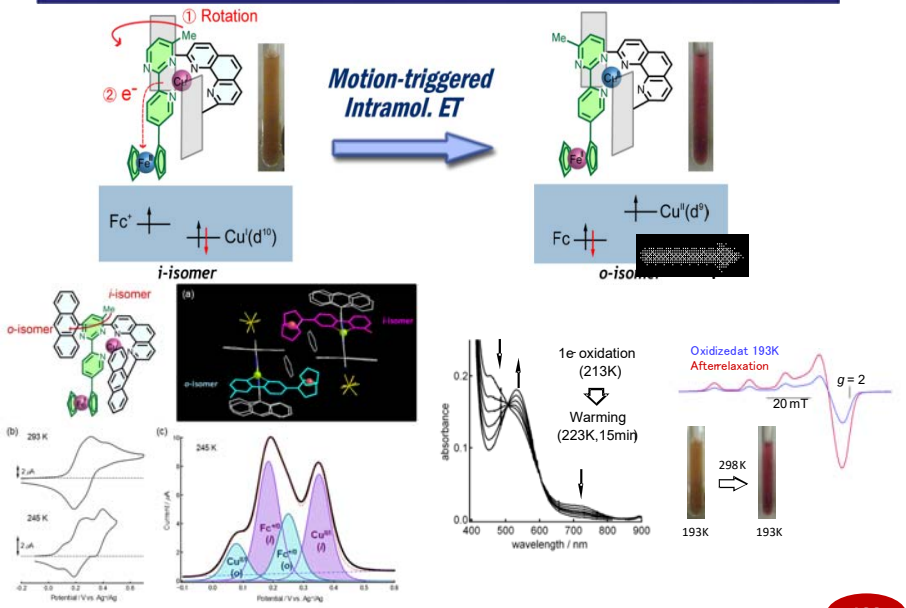




K. Nomoto et al., *J. Am. Chem. Soc.* **2009**, *131*, 3830.

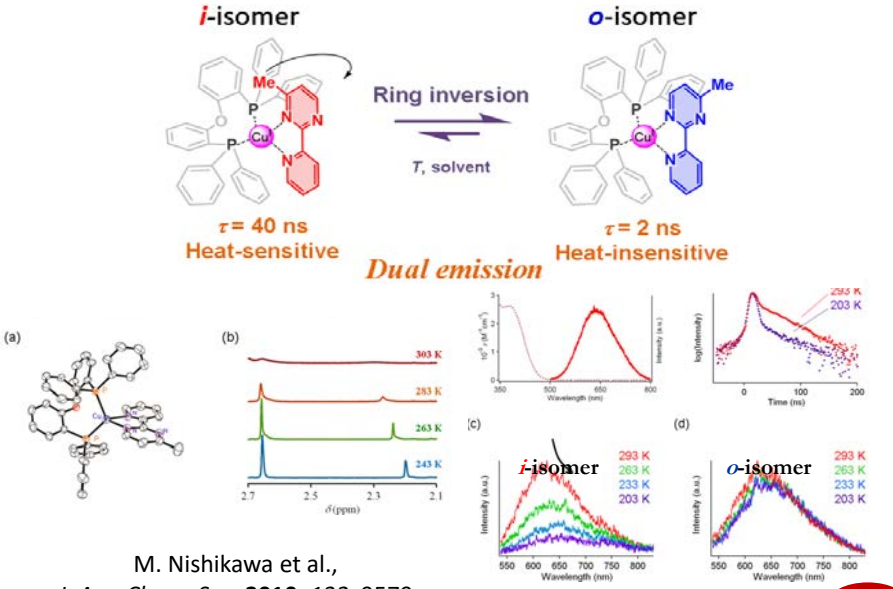
128

Intramolecular Electron Arrangement with a Rotative Trigger



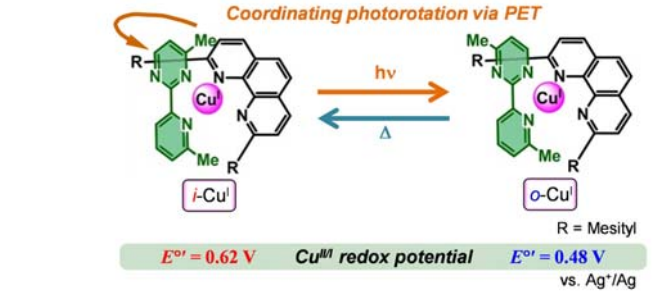
S. Kume et al., *J. Am. Chem. Soc.* **2009**, *131*,14198.

Dual Emission Caused by Ring Inversion Isomerization



M. Nishikawa et al.,
J. Am. Chem. Soc. **2010**, *132*, 9579.

Reversible Cu(II)/(I) Electrochemical Potential Switching Driven by Visible Light-Induced Coordinated Ring Rotation



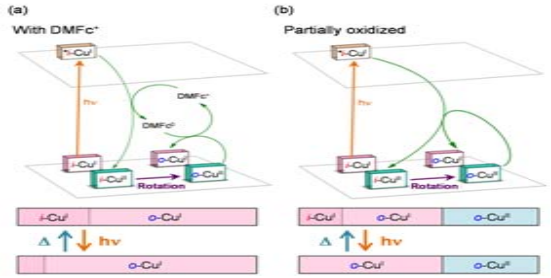
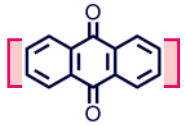


Photo-electric conversion without photochromism

M. Nishikawa et al.,
J. Am. Chem. Soc. **2002**, *134*, 10543

Design of Strong D-A Interaction Systems

Donor
Ferrocene (Fc)



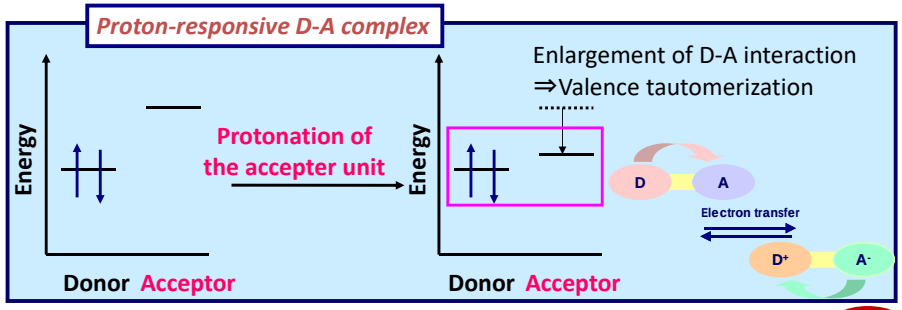
Acceptor
Anthraquinone (Aq)

FcAq , Fc_2Aq complexes

- $E^{0\prime}(Fc^+/Fc)$ is rather inert to pH.
- $E^{0\prime}(AQ/AQ^-)$ and $E^{0\prime}(AQ^-/AQ^{2-})$ are dependent of pH.

⇒Protonation-induced enlargement of D-A interaction

⇒ Valence tautomerization



J. Am. Chem. Soc. **2001,** *123,* 12903−12904

Structural Conversion and Spin Separation in Bis(ferrocenylethynyl)anthraquinones Triggered by Proton-Coupled Intramolecular Electron Transfer

Masaki Murata,† Mami Yamada,† Takako Fujita,† Kohei Kojima,† Masato Kurihara,† Kenya Kubo,† Yoshio Kobayashi,‡ and Hiroshi Nishihara*,†

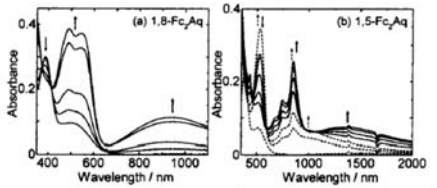
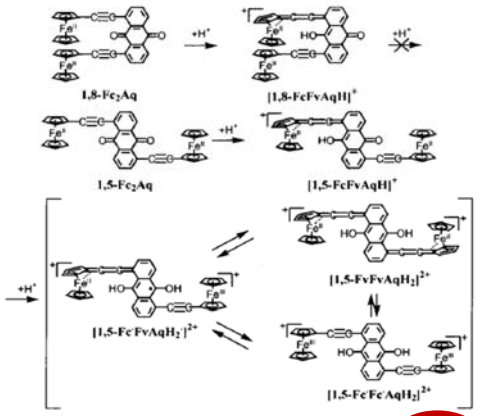
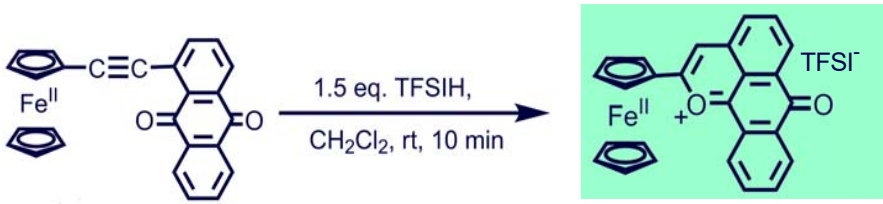


Figure 1. (a) UV−vis−near-IR spectral change of **1,8-Fc$_2$Aq** (5×10^{-5} M) in benzonitrile upon the addition of 0−2 equiv of CF_3SO_3H. (b) UV−vis−near-IR spectral change of **1,5-Fc$_2$Aq** (5×10^{-5} M) in benzonitrile upon the addition of 0−2 equiv (dotted lines and arrows) and 2−4 equiv (solid lines and arrows) of CF_3SO_3H.

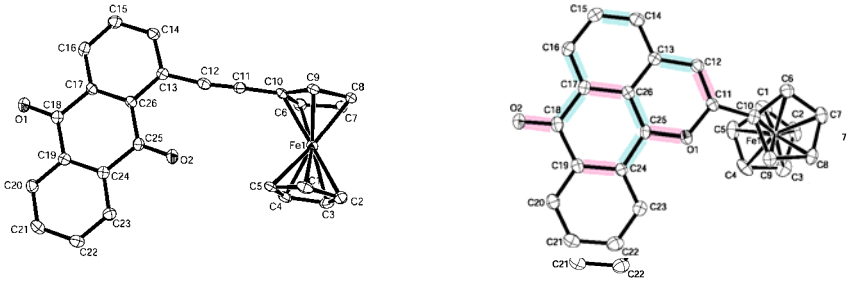
Scheme 1



Synthesis of protonated compound of 1-FcAq

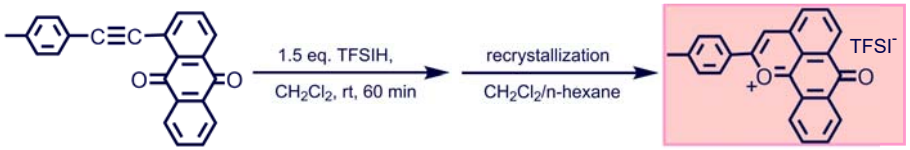


1-FcPyl yield : 82%



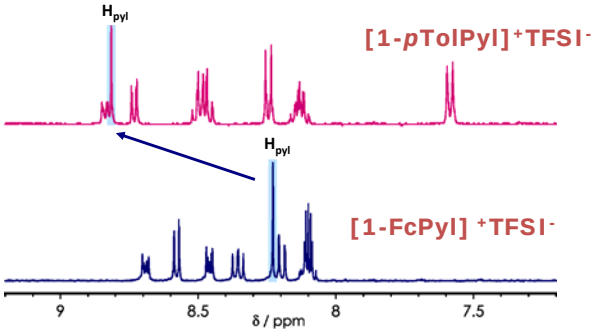
Angew. Chem. Int. Ed. **2007.** *J. Am. Chem. Soc.* **2009**.

Synthesis of protonated compound of 1-*p*-TolAq



1-*p*-TolPyl yield : 88%

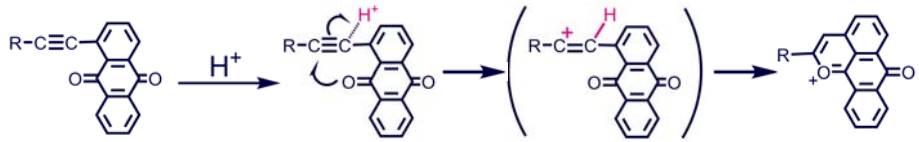
^{1}H NMR spectra

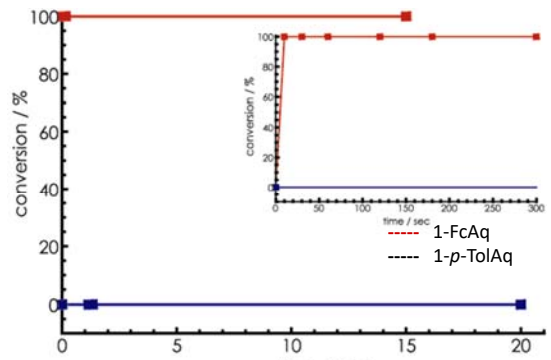


M. Kondo et al., *Angew. Chem. Int. Ed.* **2007**, *46*, 6271.

Reactivity of 1-RAq with TFSIH

[1-RAq]:[TFSIH]=1 : 1.5 [1-RAq]=0.1mM ⇒1/250 of the conc. for synthesis

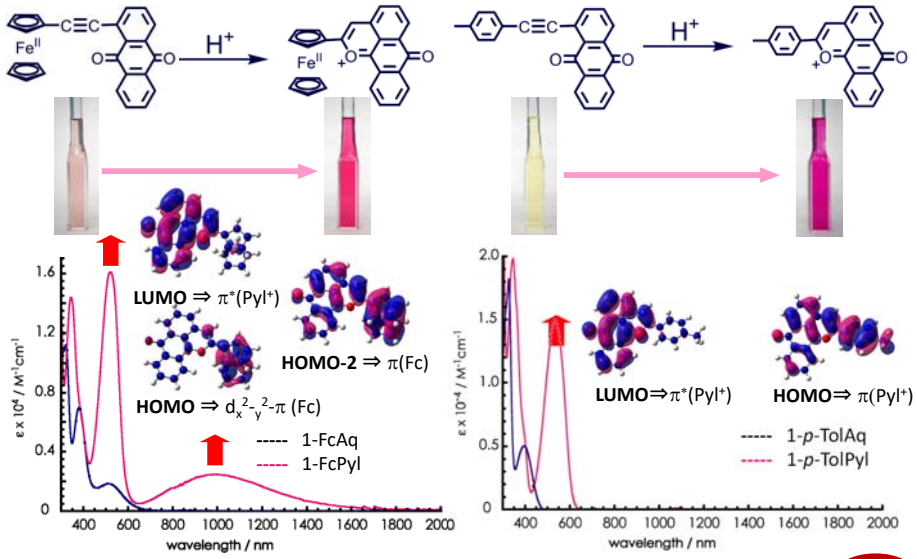




1-FcAq ⇒ reaction completed within 10 seconds.
1-*p*TolAq ⇒ reaction hardly proceeded even after 20 hours.

Angew. Chem. Int. Ed. **2007**, *46*, 6271.

UV-vis spectra of 1-RAq and [1-RPyl]$^+$TFSI$^-$



M. Kondo et al., *Angew. Chem. Int. Ed.* **2007**, *46*, 6271.

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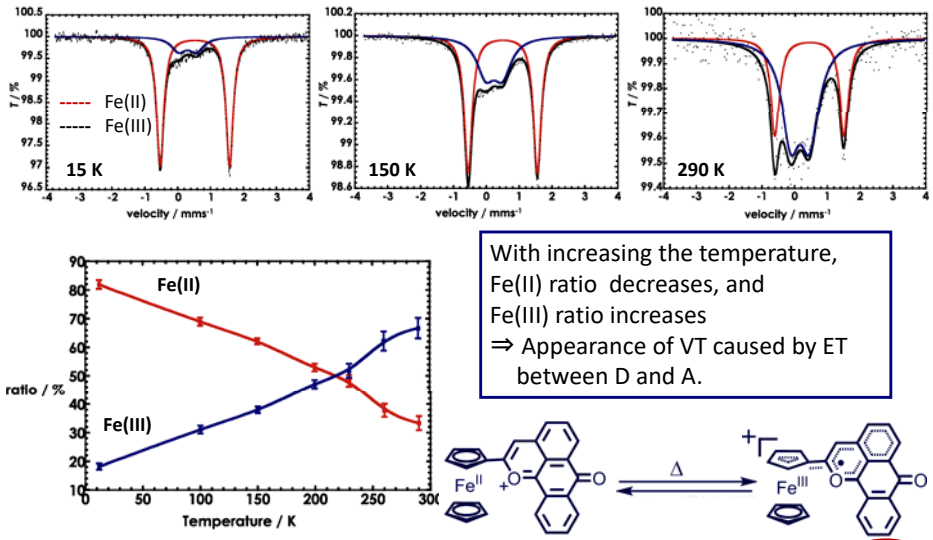
^{57}Fe Mössbauer Spectra of [1-FcPyl]$^+$TFSI$^-$



With increasing the temperature,
Fe(II) ratio decreases, and
Fe(III) ratio increases
⇒ Appearance of VT caused by ET between D and A.

M. Kondo et al., *Angew. Chem. Int. Ed.* **2007**, *46*, 6271.

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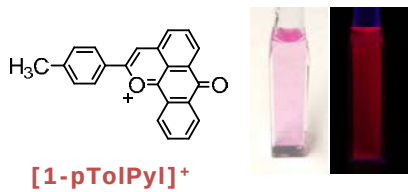
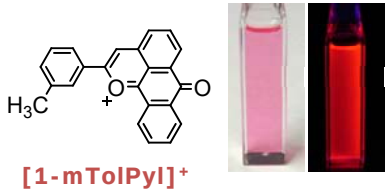
Photoluminescence properties of [1-RPyl]$^+$TFSI$^-$



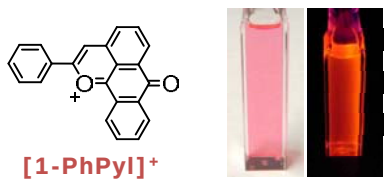
[1-pTolPyl]$^+$

λ_{max} = 550 nm, Φ = 0.09



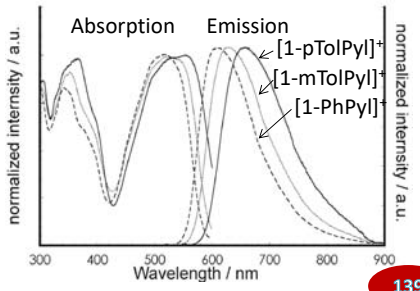
[1-mTolPyl]$^+$

λ_{max} = 520 nm, Φ = 0.20



[1-PhPyl]$^+$

λ_{max} = 520 nm, Φ = 0.19



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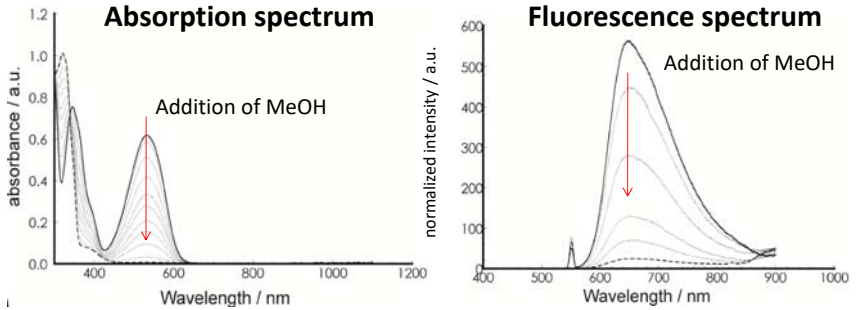
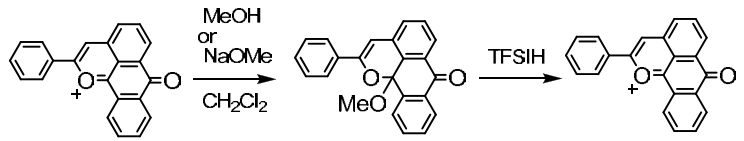
Reversible Switching of Luminescence of [1-RPyl]$^+$ Caused by MeOH (NaOMe) and Acid



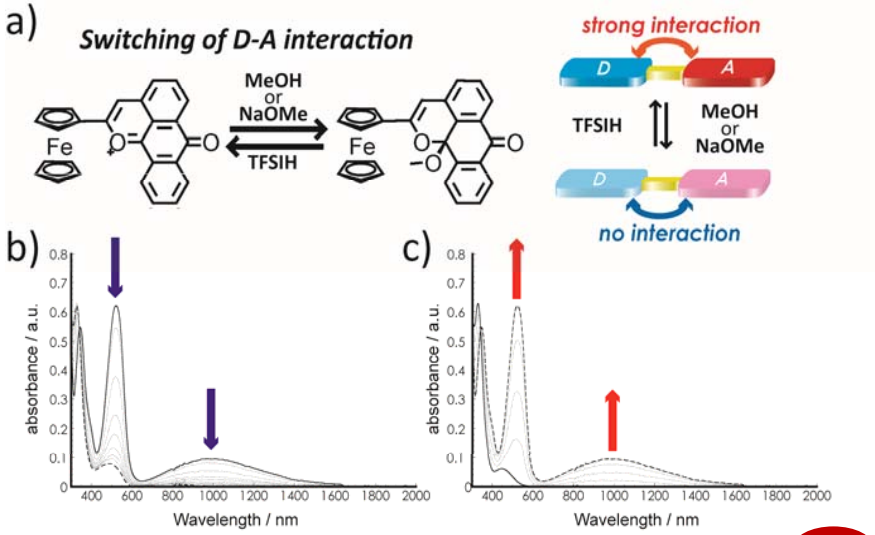


[1-PhPyl]$^+$ **1-PhPyl-OMe** [1-PhPyl]$^+$

M. Kondo et al., *Chem. Commun.* **2009**, 1993.

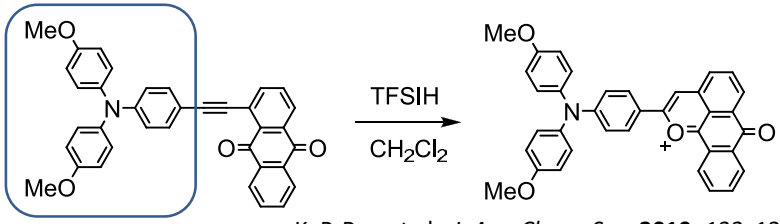
140

Reversible NIR Absorption Switching of [1-FcPyl]$^+$ Caused by MeOH (NaOMe) and Acid

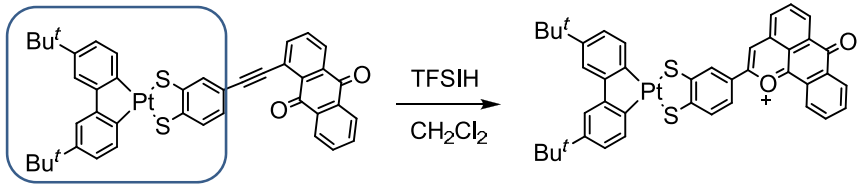


M. Kondo et al., *Chem. Commun.* **2009**, 1993.

Protonation-induced cyclization of RAq

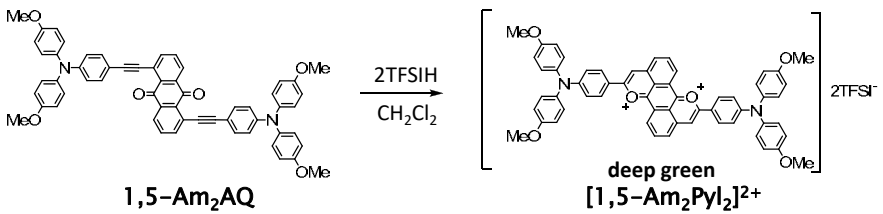


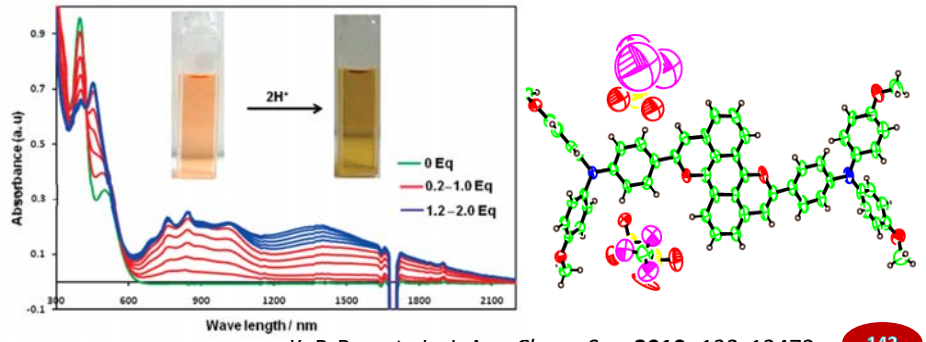
K. P. Rao et al., *J. Am. Chem. Soc.* **2010**, *132*, 12472.



K. P. Rao et al., *Chem. Commun.* **2011**, *47*, 2330.

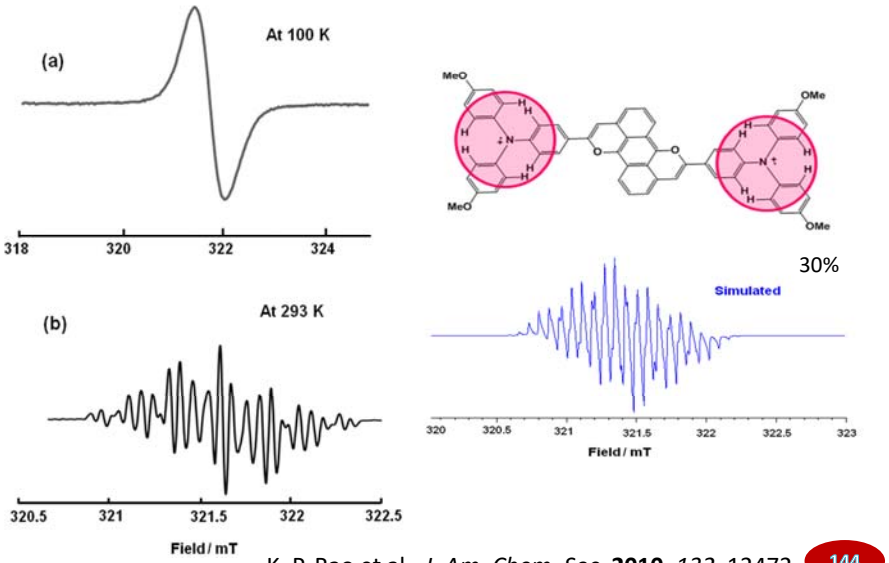
Double Protonation of [1,5-Am$_2$AQ$_2$]





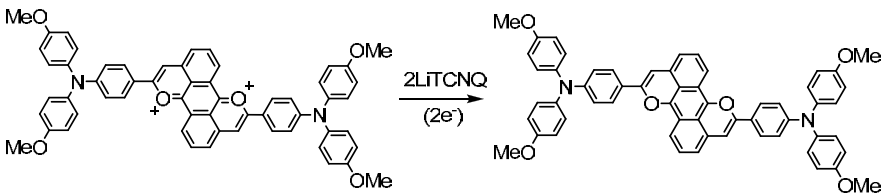
K. P. Rao et al., *J. Am. Chem. Soc.* **2010**, *132*, 12472.

EPR spectra of [1,5-Am$_2$Pyl$_2$](TFSI)$_2$

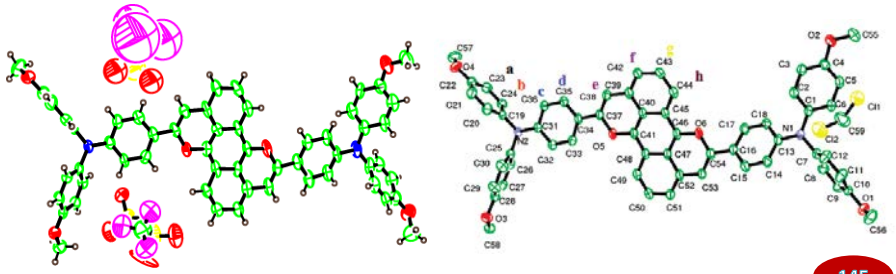


K. P. Rao et al., *J. Am. Chem. Soc.* **2010**, *132*, 12472.

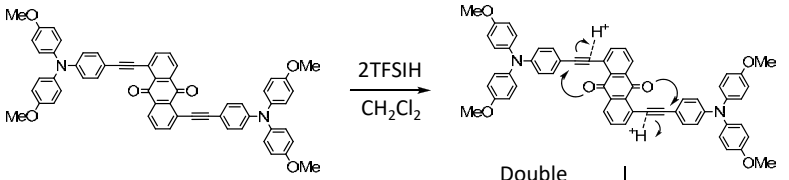
Preparation of the Neutral form $[1,5\text{-}Am_2Pyl_2]^0$



$[1,5\text{-}Am_2Pyl_2]^{2+}$ $[1,5\text{-}Am_2Pyl_2]^0$

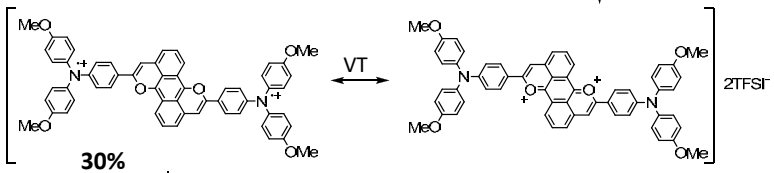


K. P. Rao et al., *J. Am. Chem. Soc.* **2010**, *132*, 12472.



$1,5\text{-}Am_2AQ$

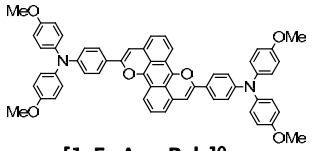
Double Annulation



30%

2LiTCNQ | CH_2Cl_2/MeCN

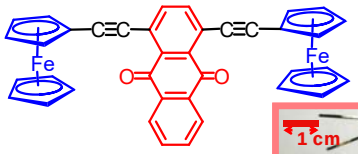
$[1,5\text{-}Am_2Pyl_2]^{2+}$



$[1,5\text{-}Am_2Pyl_2]^0$

K. P. Rao et al., *J. Am. Chem. Soc.* **2010**, *132*, 12472.

Guest-Induced Crystal-to-Crystal Transformation of $1,4\text{-}Fc_2AQ$



$1,4\text{--}Fc_2Aq$

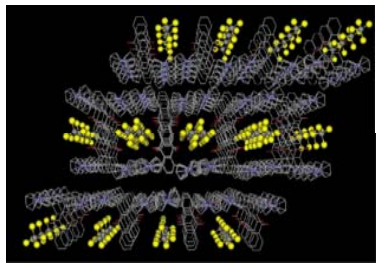
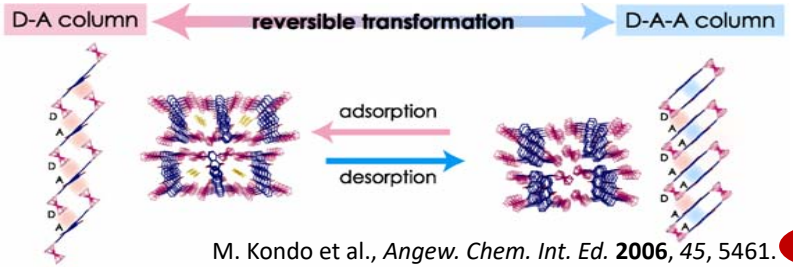
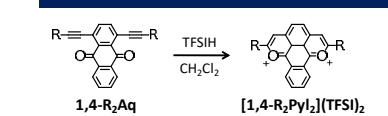


Fig. Crystal structure of **$1,4\text{-}Fc_2Aq$** along *b* axis.

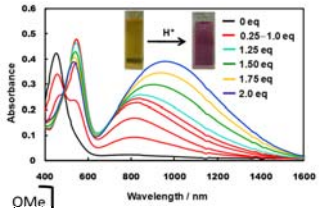


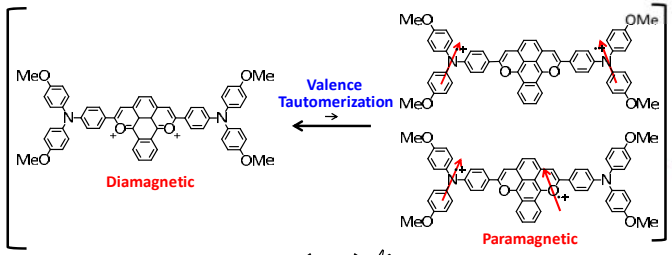
M. Kondo et al., *Angew. Chem. Int. Ed.* **2006**, *45*, 5461.

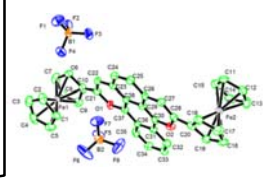
Double Protonation of $1,4\text{-}Fc_2AQ$

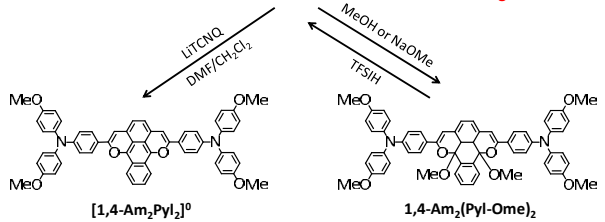


$1,4\text{-}R_2Aq$ $[1,4\text{-}R_2Pyl_2](TFSI)_2$

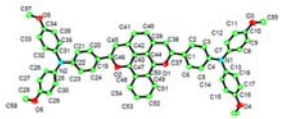






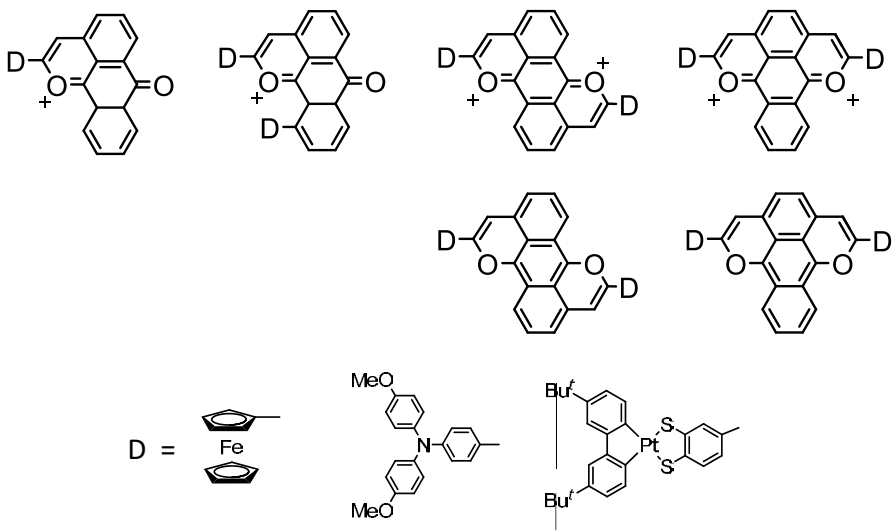


$[1,4\text{-}Am_2Pyl_2]^0$ $1,4\text{-}Am_2(Pyl\text{-}Ome)_2$

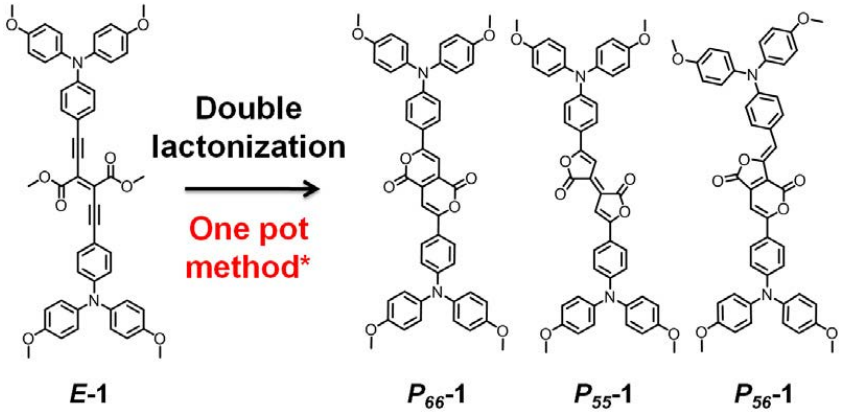


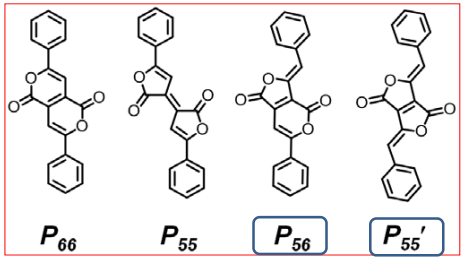
K. P. Rao et al., *Chem. Eur. J.* **2011**, *17*, 14010.

New Type of Strong D-A Interaction Systems



R. Sakamoto et al., *Chem. Lett.* **2011**, *40*, 1316 (Highlight Review)

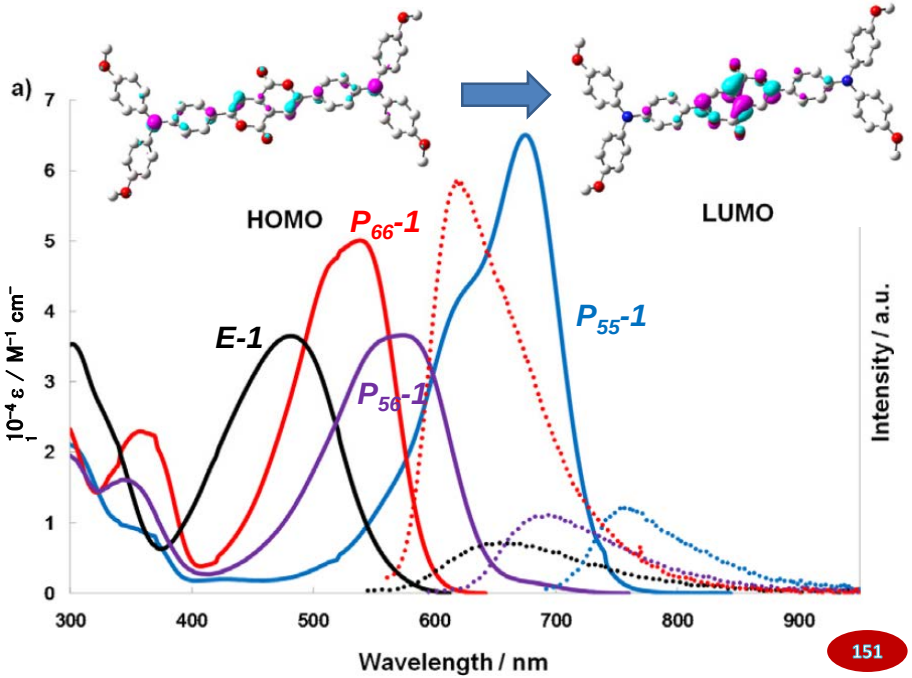


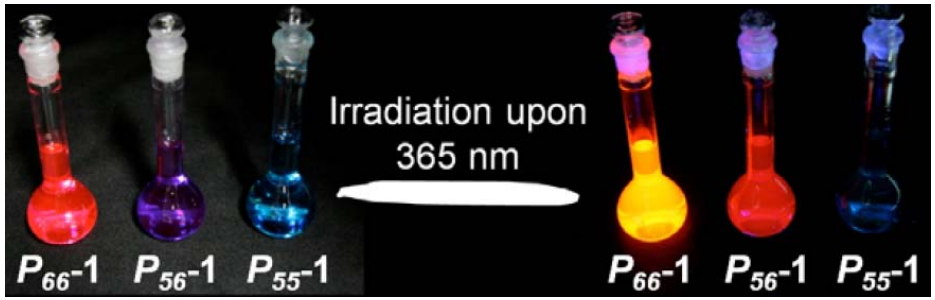


D-A-D

Pechmann dye frameworks

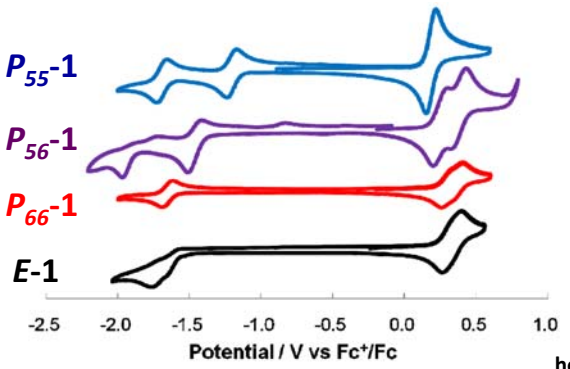
Unknown structure

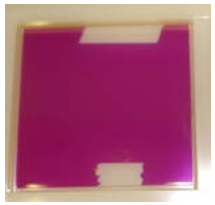




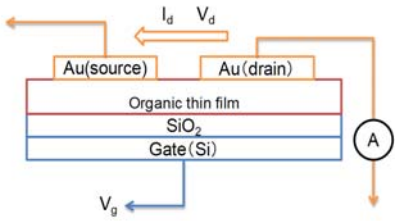
compounds	Absorption		Fluorescence	
	λ_{max} / nm	ε_{max} / M^{-1}cm^{-1}	λ_{max} / nm	Φ
P 66-1	538	50000	617	0.82
P 55-1	674	65000	753	0.27
P 56-1	574	37000	692	0.20
E-1	482	36000	660	0.15

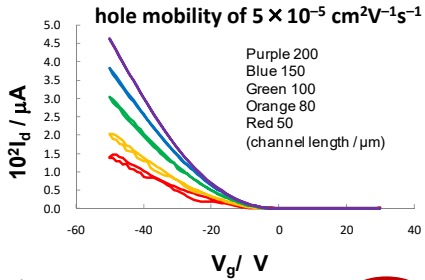
M. Hayashi et al., *J. Am. Chem. Soc.* **2011**, *133*, 14518.





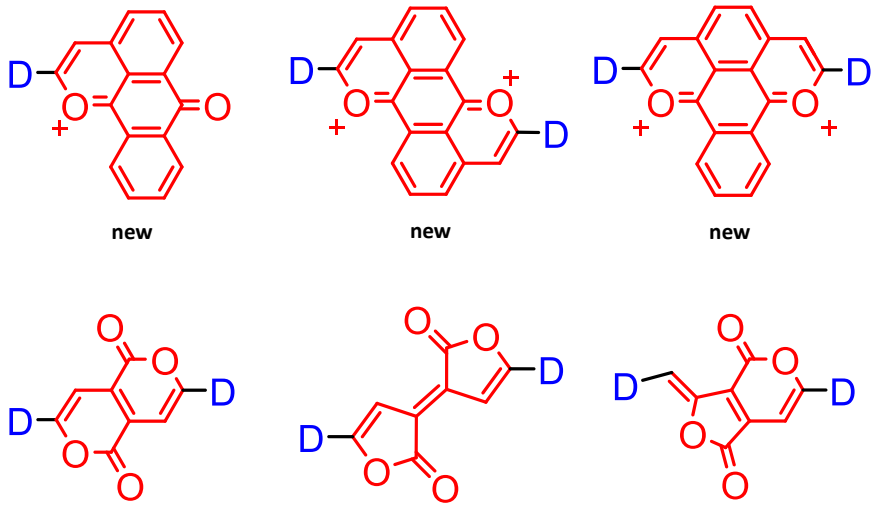
P_{66}-1 thin film





M. Hayashi et al., *J. Am. Chem. Soc.* **2011**, *133*, 14518.

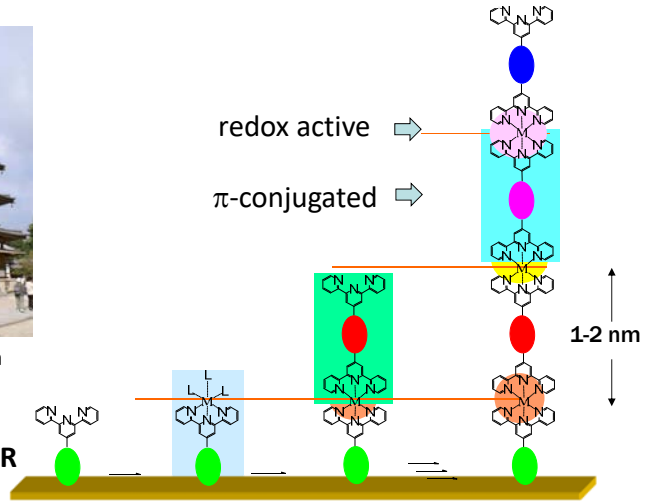
New Strong D–A Interaction Systems



Bottom-up Synthesis of Metal Complex Wires

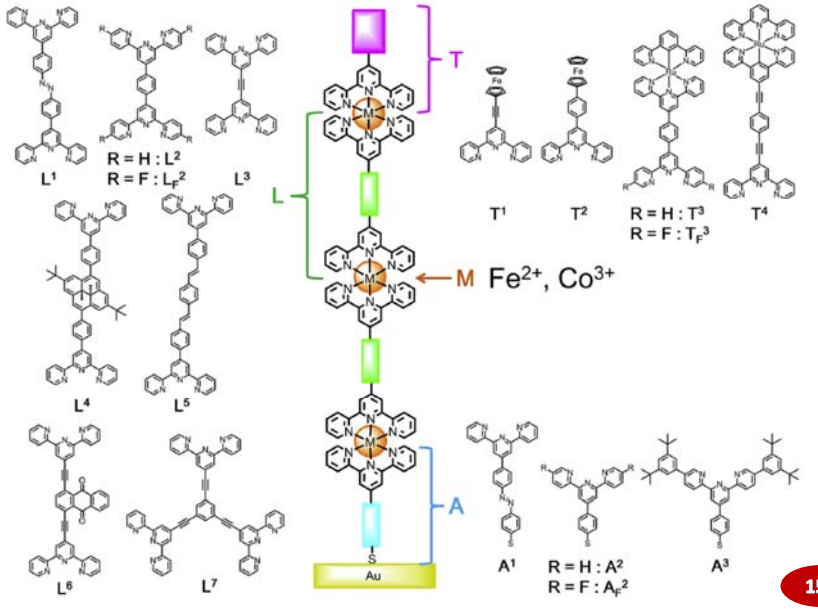
Vertical Coordination Programming

Five-story pagoda

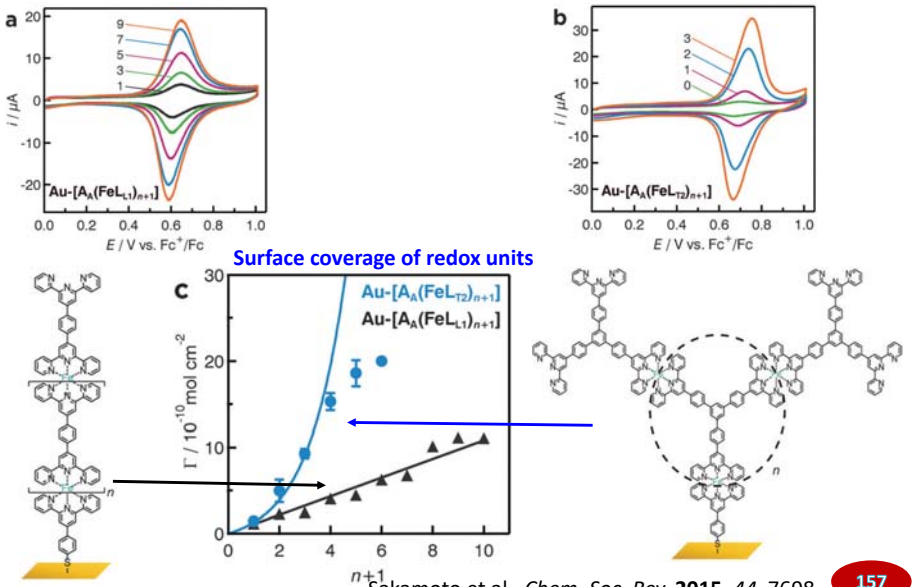


Chem. Commun. (Future Article), **2007**. *Coord. Chem. Rev.* **2007**. *Coord. Chem. Rev.* **2013**. *Polymer* **2013** (Feature Article). *Chem. Soc. Rev.* **2015**.

π-Conjugated Redox-active Molecular Wires

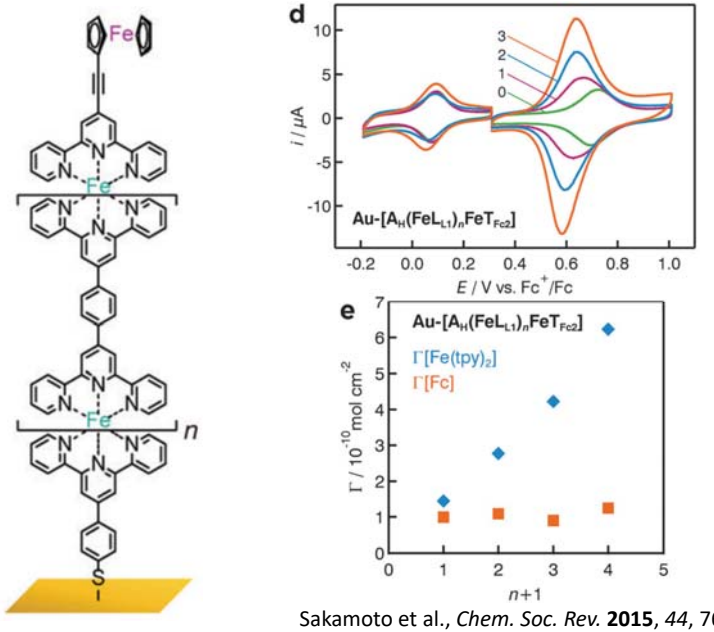


Redox Behaviors of π-Conjugated FeTPY Wires



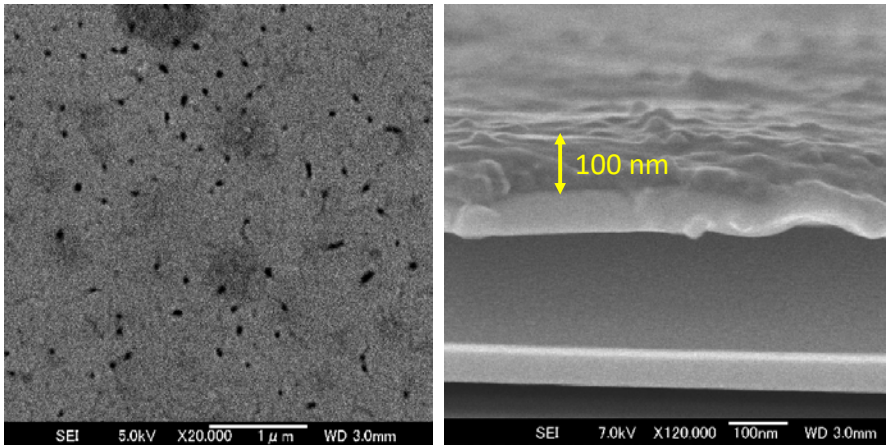
Sakamoto et al., *Chem. Soc. Rev.* **2015**, *44*, 7698.

Redox Behaviors of Fc-terminated FeTPY Wires

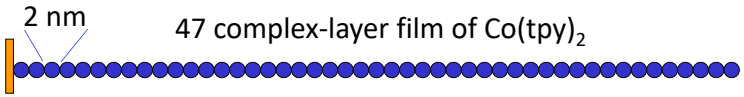


Sakamoto et al., *Chem. Soc. Rev.* **2015**, *44*, 7698.

SEM Images of the Molecular Wire Film

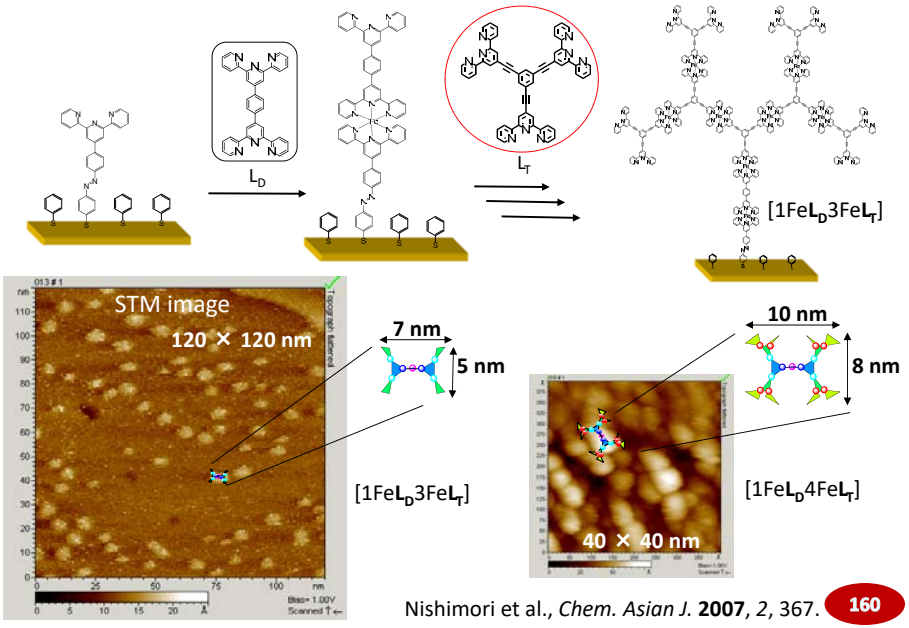


Top view Side view

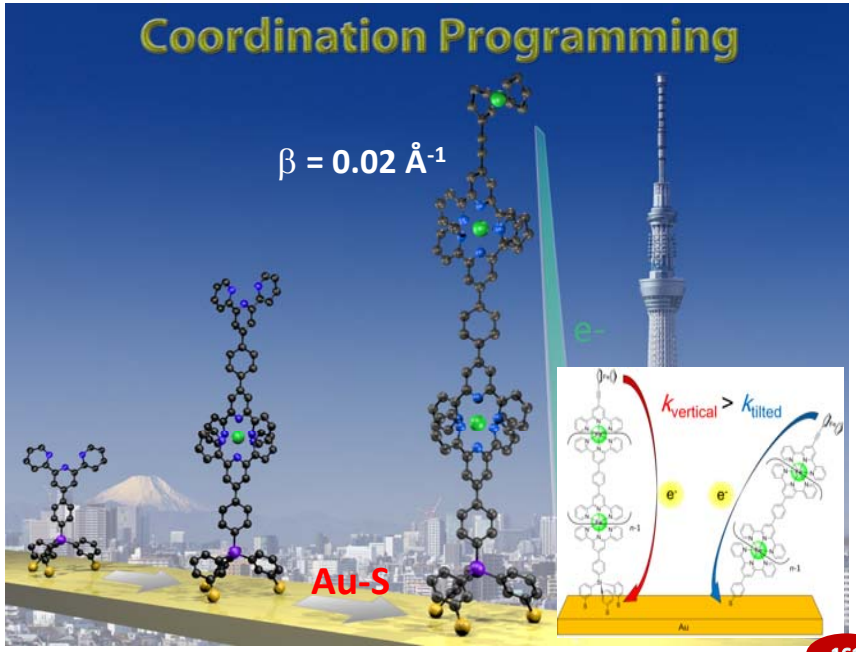


Kanaizuka et al., *Chem.Lett.* **2005**, *34*, 534.

Loosely Distributed Dendritic Molecular Wires



Nishimori et al., *Chem. Asian J.* **2007**, *2*, 367.



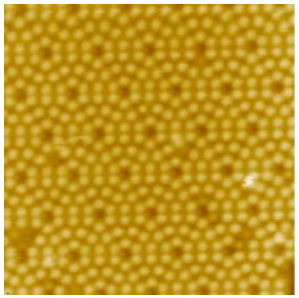
Sakamoto et al., *Chem. Commun.* **2013**, *49*, 7108.

Construction of Molecular Wires on Silicon Surface

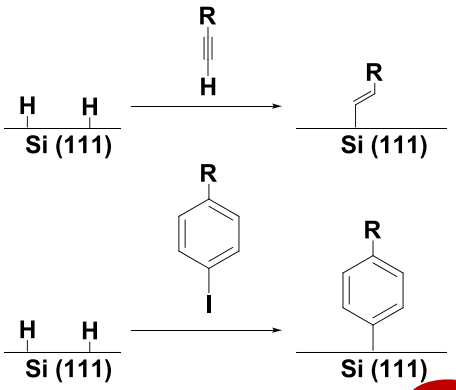
Si–CR

·Si–C bonds are more stable than Au–S bonds.
(Si–C: 347 kJ/mol, Au–S: 167 kJ/mol)

- Atomically flat surface
- Photo-responsive

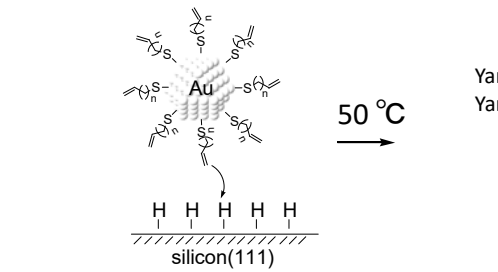


7 × 7 Reconstruction of Si(111)

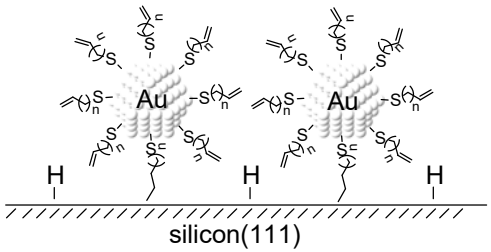


Chemical Immobilization AuNP at Si(111) Surface

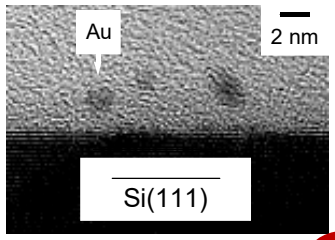
Alkenethiol-stabilized AuNP



Yamanoi et al., *Langmuir* **2004**, *20*, 1054.
Yamanoi et al., *Chem. Eur. J.* **2006**, *12*, 314.

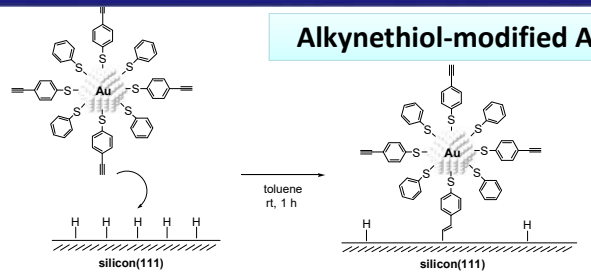


Side-view TEM



Room-Temperature Immobilization of AuNP on Si(111) Surface and Their Electron Behaviour

Alkynethiol-modified AuNP



Uchida et al., *Phys. Chem. Chem. Phys.* **2008**, *10*, 6925.

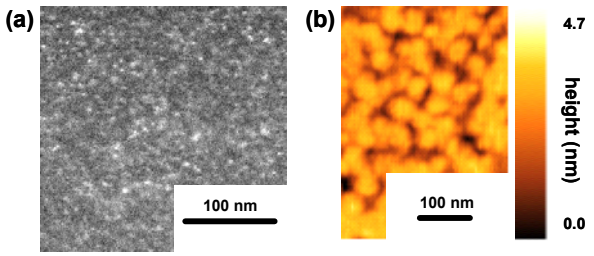
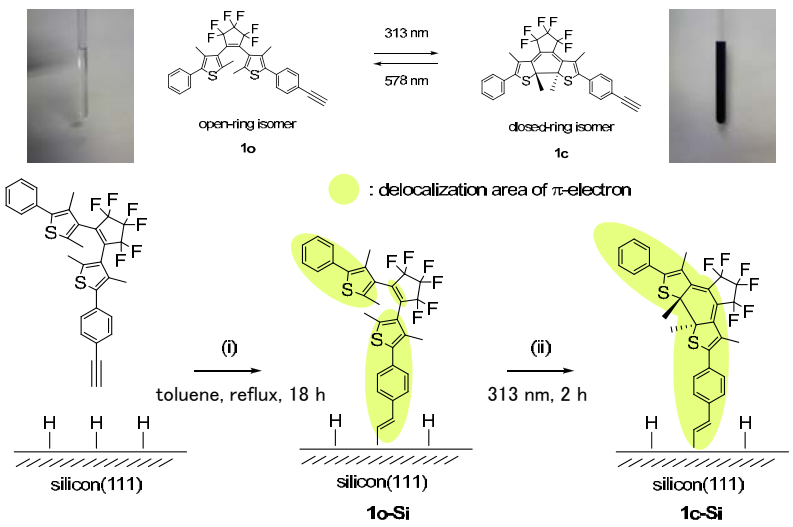


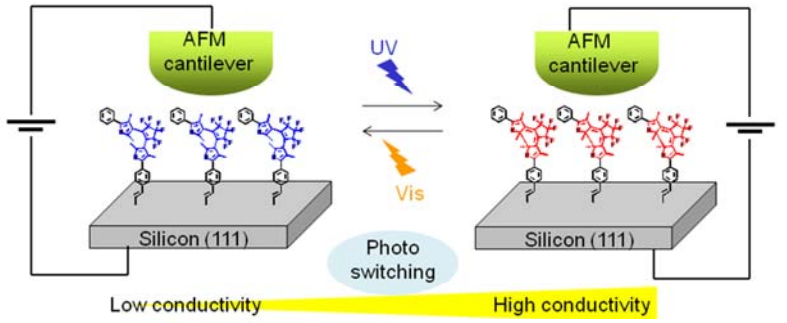
Fig. (a) HR-SEM and (b) AFM images.

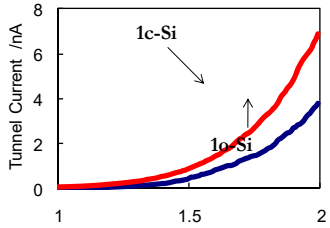
Reversible On/Off Conductance Switching of Single Diarylethene Immobilized on a Silicon Surface

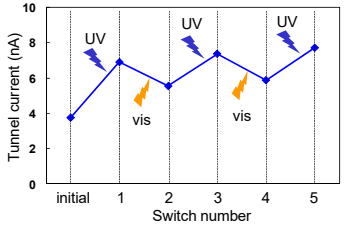


Uchida et al., *J. Am. Chem. Soc.* **2011**, *133*, 9239.

Reversible On/Off Conductance Switching of Single Diarylethene Immobilized on a Silicon Surface

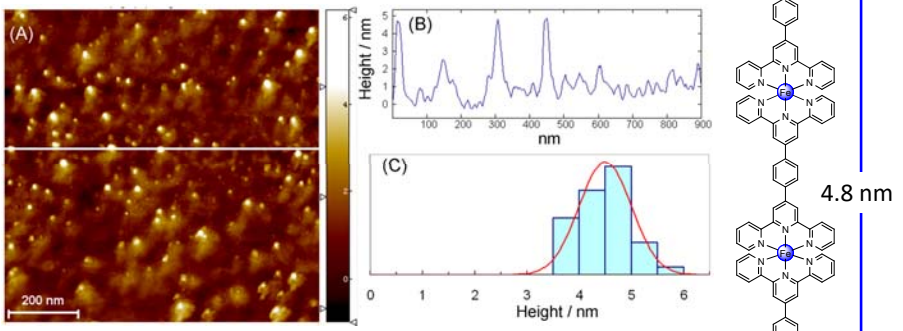






Uchida et al., *J. Am. Chem. Soc.* **2011**, *133*, 9239.

AFM image of n-Si-A(FeL^1)$_3$



Si-**A**[FeL^1]$_3$

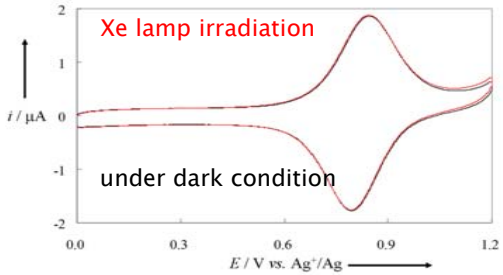
Fig. (A) AFM image of n-Si-**A**(Fe**L^1**)$_3$ (**A**:**eBz**=1:12). (B) Cross-section analysis of white line in (A). (C) Histogram of height of the height analysis.

Maeda et al., *Chem. Commun.* **2011**, *47*, 8644.

Photoresponse of Si-Fe(tpy)$_2$ oligomer electrodes

n$^+$–Si–**A**(FeL^1)$_2$

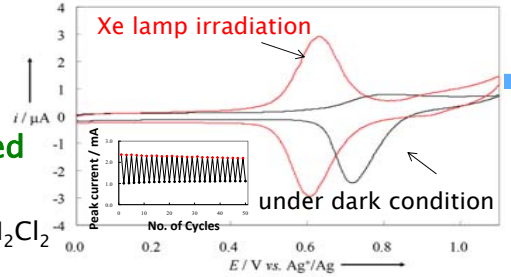
Highly doped

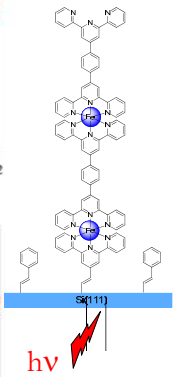


n–Si–**A**(FeL^1)$_2$

Moderately doped

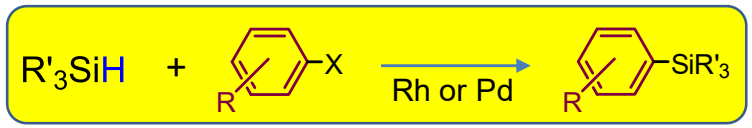
in 1M Bu_4NClO_4/CH_2Cl_2 at 100 mV/s



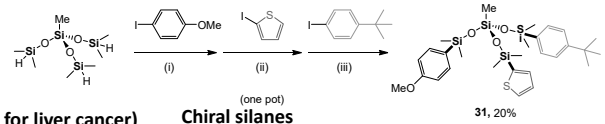


Maeda et al., *Chem. Commun.* **2011**, *47*, 8644.

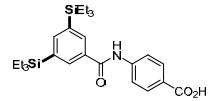
New Arylation Reactions of Hydrosilanes



Stepwise arylation

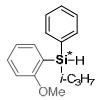


TAC-101 (drug for liver cancer)

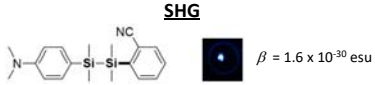


Chiral silanes

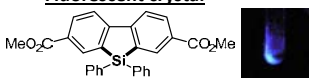
(one pot)



SHG

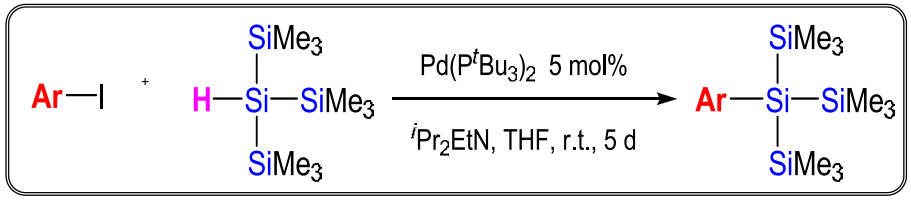


Fluorescent crystal



AIEE Fluorescence

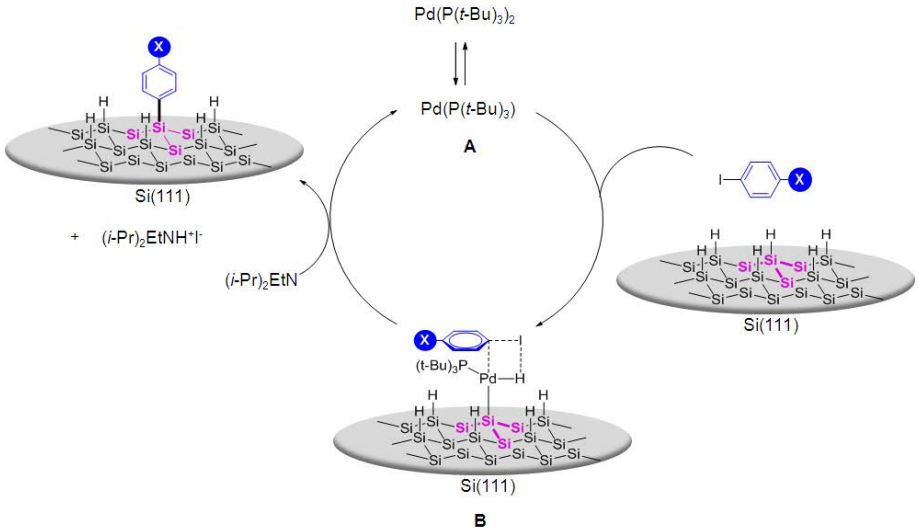
Yamanoi et al., *J. Org. Chem.* **2005**, *70*, 9607. *Tetrahedron Lett.* **2006**, *47*, 7157. *Org. Lett.* **2007**, *9*, 4543. *J. Org. Chem.* **2008**, *73*, 6671. *Chem. Eur. J.* **2010**, *16*, 5581. *Chem. Commun.* **2010**, *46*, 7784. *Chem. Eur. J.* **2010**, *16*, 13519. *Chem. Commun.* **2012**, *48*, 11564. *Chem. Commun.* **2013**, *49* 134. *Chem.Commun.* **2013**, *49*, 11275. *J. Org. Chem.* **2014**,*79*, 2974. *J. Am. Chem. Soc.* **2015**, *25*, 140. *Angew. Chem. Int. Ed.* **2016**, *55*, 3022. *J. Org. Chem.* **2017**, *82*, 6108 *J. Am. Chem. Soc.* **2017**, *139*, 11214.*ACS Appl. Mater. Int.* **2018**, 10, 12164



Entry	Ar	Yield (%)	Entry	Ar	Yield (%)
1	H_2N	28	6	Me_2N	47
2	^tBu	29	7	MeO	47
3	^{i}Pr	31	8	S	48
4	MeS	39	9	Bu_2N	78
5	MeO	41	10	S	81

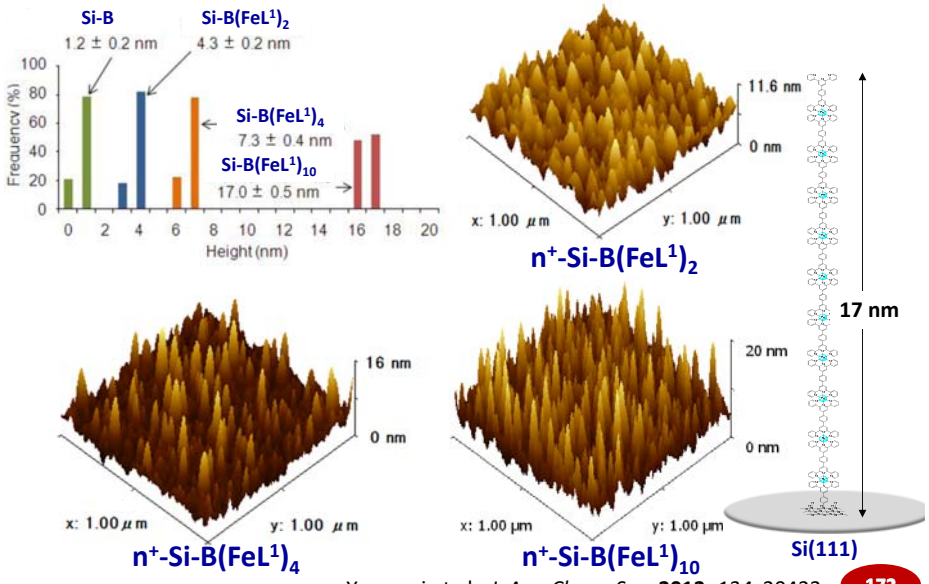
Lesbani et al., *Chem. Commun.* **2010**, 46, 7784.

Proposed Reaction Mechanism at Si(111) Surface



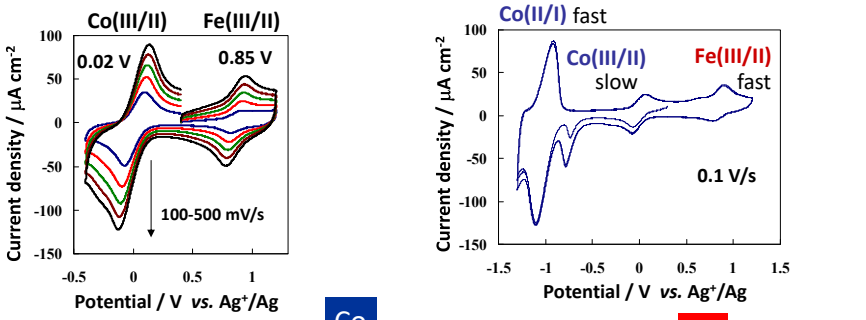
σ-bond metathesis intermediate

Arylation of H-terminated Si(111) Surface Using Pd Catalyst



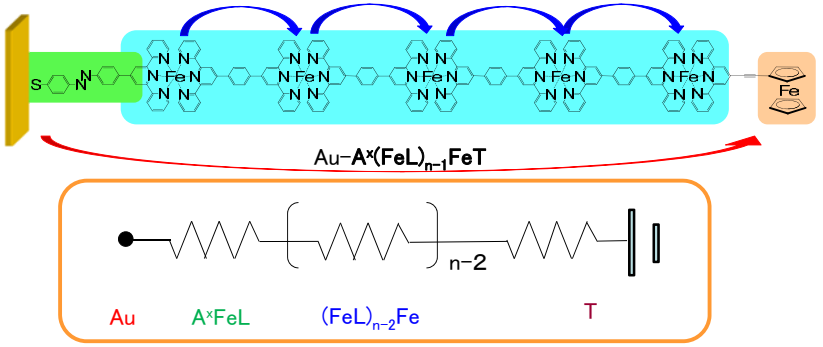
Yamanoi et al., *J. Am. Chem. Soc.* **2012**, *134*, 20433.

Construction of Hetero-structure, Co(10)-Fe (5)



Kanaizuka et al., *Chem.Lett.* **2005**, *34*, 534.

ET Issues for π-Conjugated Redox Moleculer Wires



1. Mechanism of molecular wire redox conduction
2. Superior long-range electron transport ability
3. Surface junction effects
4. Terminal redox site effects
5. Electron transport dynamics in branched wires

Polymer-coated electrode

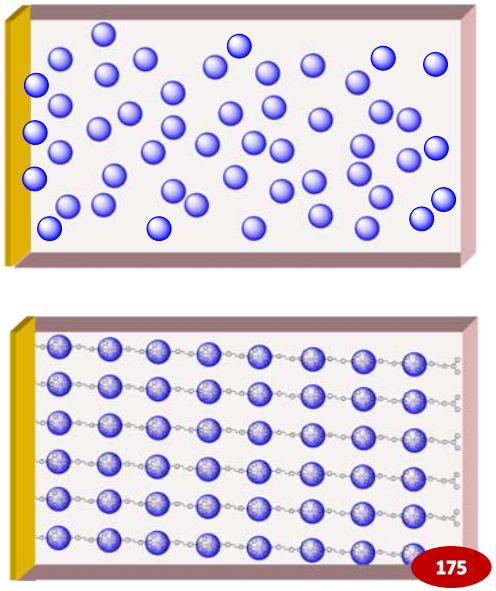
(Conventional polymer films)

Redox units are randomly distributed in a polymer film.

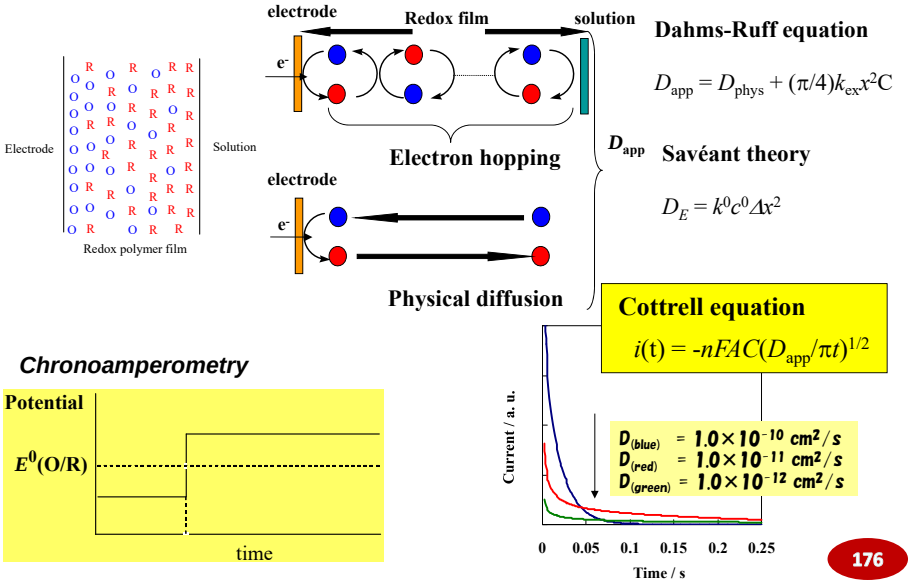
Difference in the electron transport behavior?

(New approach)

Redox units are aligned in linear polymer chains perpendicular to the electrode surface.



Redox conduction based on diffusional motion for a randomly distributed redox sites in a film



Cottrell equation $i(t) = -nFAC(D_{app}/\pi t)^{1/2}$

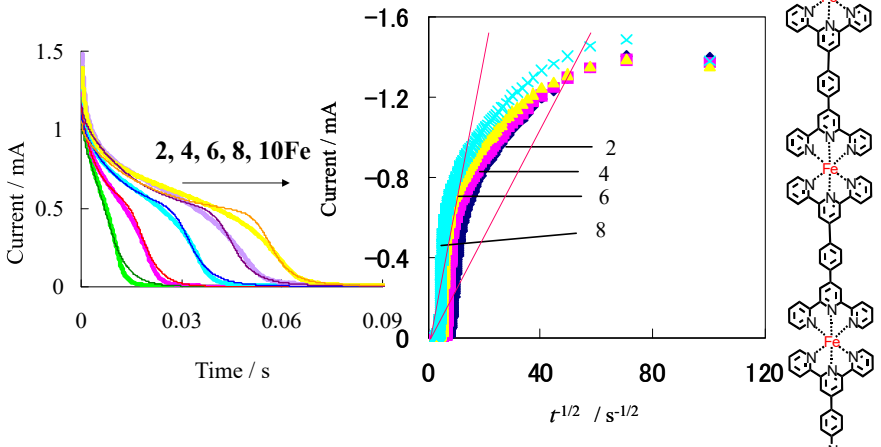
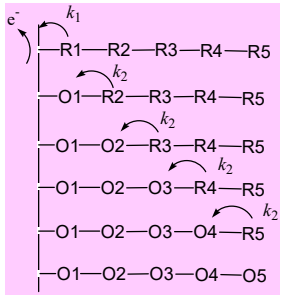
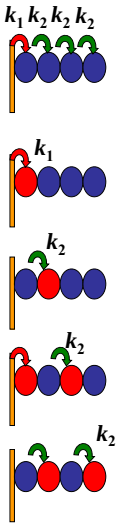


Figure. Cottrell plots of the current after the potential step from 0.96 to 0.36 V vs. Fc^+/Fc to reduce the Fe^{III} complex moieties in [nFe$\mathbf{L}_1$] (n = 2, 4, 6, and 8) with t_1 = 5 min in 1 M Bu_4NClO_4-CH_2Cl_2. The numbers in the figure refer to n.

A new model of redox conduction in a single molecular wire connected to electrode surface

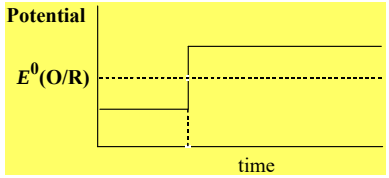




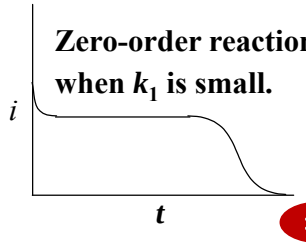
O_1 + e → R_1	k_1
R_1 + O_2 → O_1 + R_2	k_2
R_2 + O_3 → O_2 + R_3	k_2
R_3 + O_4 → O_3 + R_4	k_2

$dO_1/dt = -k_1O_1 + k_2(1-O_1)O_2$
$dO_2/dt = -k_2(1-O_1)O_2 + k_2(1-O_2)O_3$
$dO_3/dt = -k_2(1-O_2)O_3 + k_2(1-O_3)O_4$
$dO_4/dt = -k_2(1-O_3)O_4$

Chronoamperometry

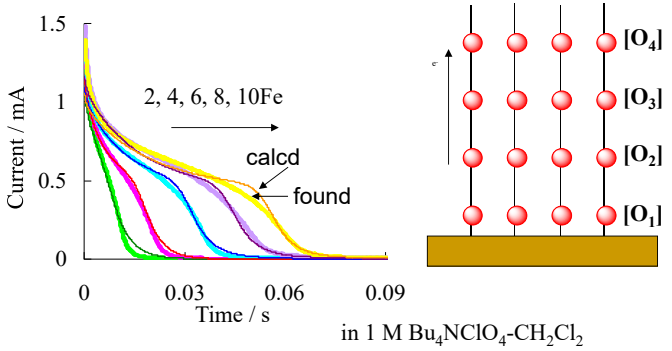


Zero-order reaction when k_1 is small.



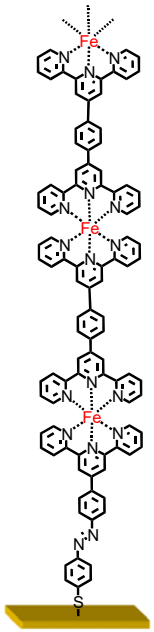
Experimental results and simulation of PSCA

Linear molecular wires

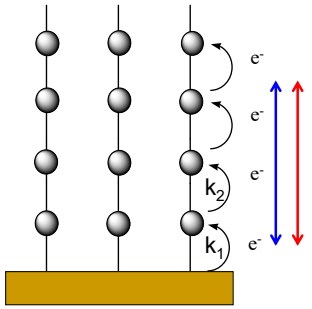


in 1 M Bu_4NClO_4-CH_2Cl_2

$k_1 = 220 \pm 20\ s^{-1}$
$k_2 = 1.4 \pm 0.3 \times 10^{13}\ cm^2mol^{-1}s^{-1}$
$C_{dl} = 25 \pm 15\ mC\ cm^{-2}$

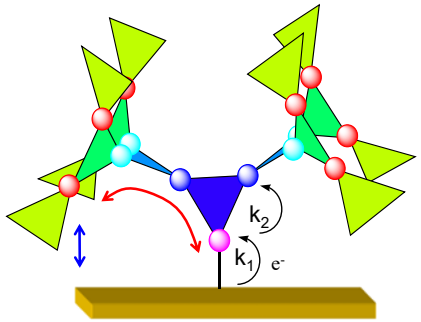


Linear molecular wire



Distance from electrode to redox active species

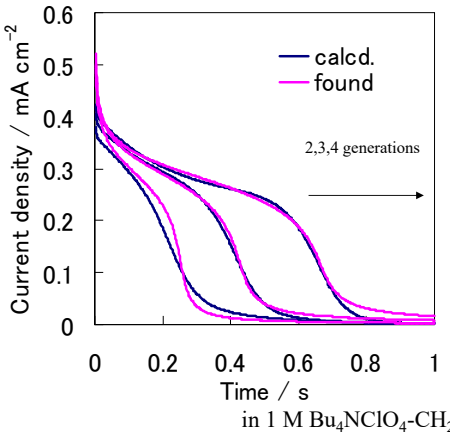
Branched molecular wire

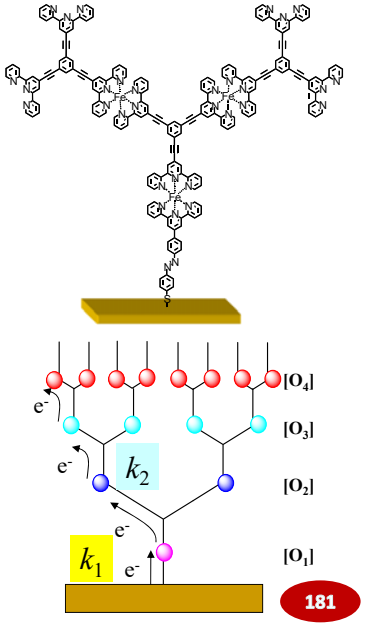


Distance of through bond electron transfer

Experimental results and simulation of PSCA

Branched molecular wires



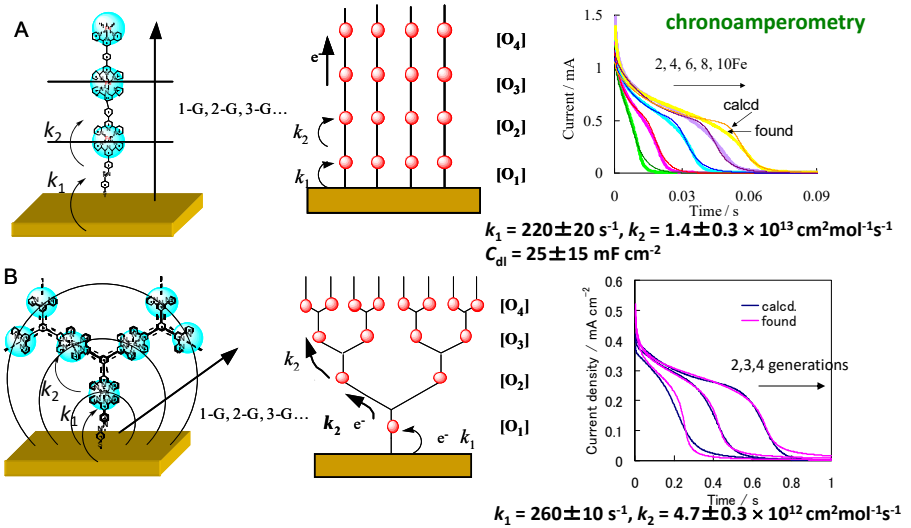


$k_1 = 260 \pm 10\ s^{-1}$

$k_2 = 4.7 \pm 0.3 \times 10^{12}\ cm^2mol^{-1}s^{-1}$

$C_{dl} = 22 \pm 4\ mC/cm^2$

Electrochemical Observation of Redox Conduction along Molecular Wires



$k_1 = 220 \pm 20\ s^{-1}$, $k_2 = 1.4 \pm 0.3 \times 10^{13}\ cm^2mol^{-1}s^{-1}$

$C_{dl} = 25 \pm 15\ mF\ cm^{-2}$

$k_1 = 260 \pm 10\ s^{-1}$, $k_2 = 4.7 \pm 0.3 \times 10^{12}\ cm^2mol^{-1}s^{-1}$

$C_{dl} = 22 \pm 4\ mF\ cm^{-2}$

Nishimori et al., *Chem. Asian J.* **2007**, *2*, 367.

Rapid Electron Tunneling Through Oligophenylenevinylene Bridg

Hadley D. Sikes,[†] John F. Smalley,[2e] Stephen P. Dudek,[†] Andrew R. Cook,[2] Marshall D. Newton,[2e] Christopher E. D. Chidsey,[1e] Stephen W. Feldberg[2e]

23 FEBRUARY 2001 VOL 291 SCIENCE

Exceptionally Small Attenuation Factors in Molecular Wires

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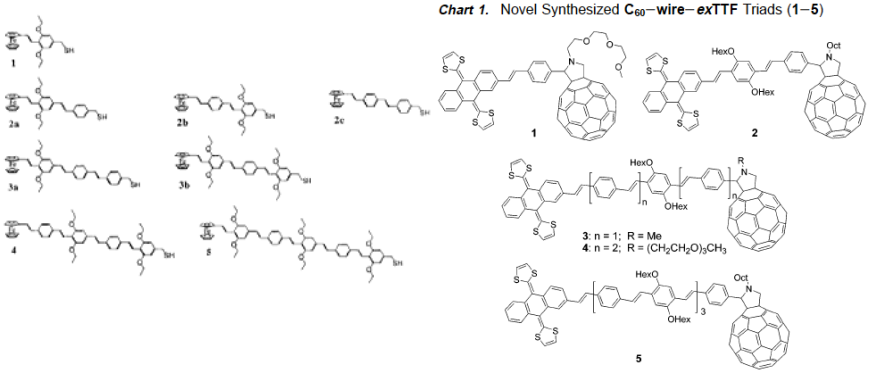
Received December 19, 2003; E-mail: nazmar@quim.ucm.es

Chart 1. Novel Synthesized C_{60}–wire–*ex*TTF Triads (**1**–**5**)

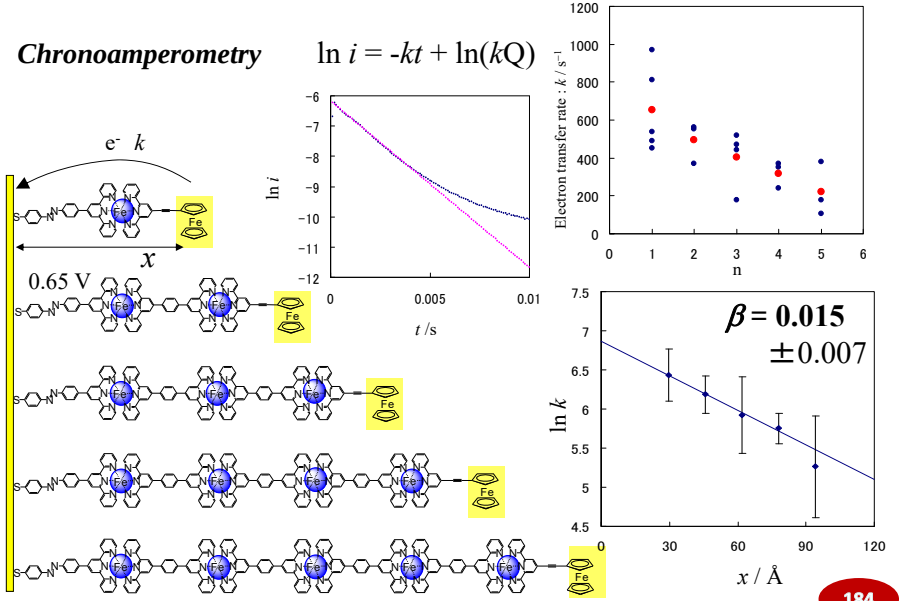


β = 0.06

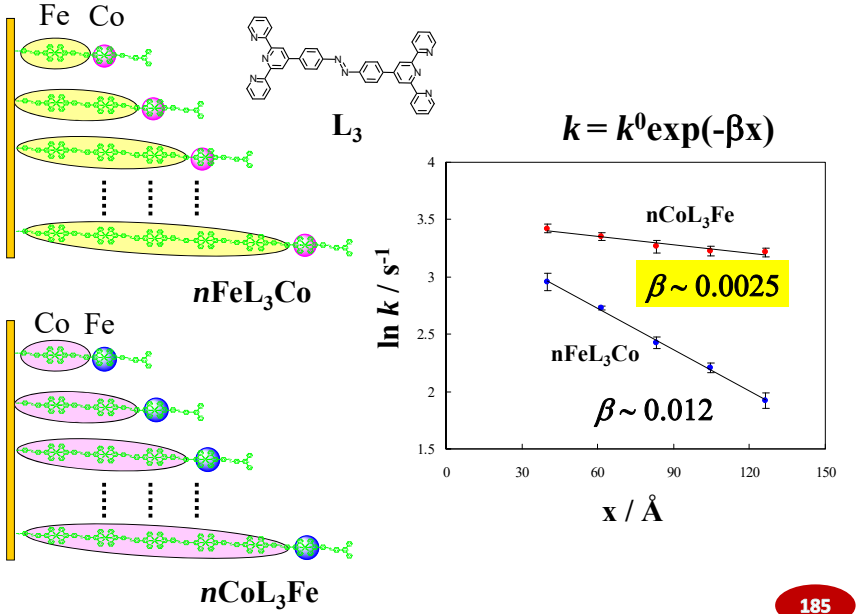
β = 0.01

β of the π-conjugated metal complex oligomer spacer I

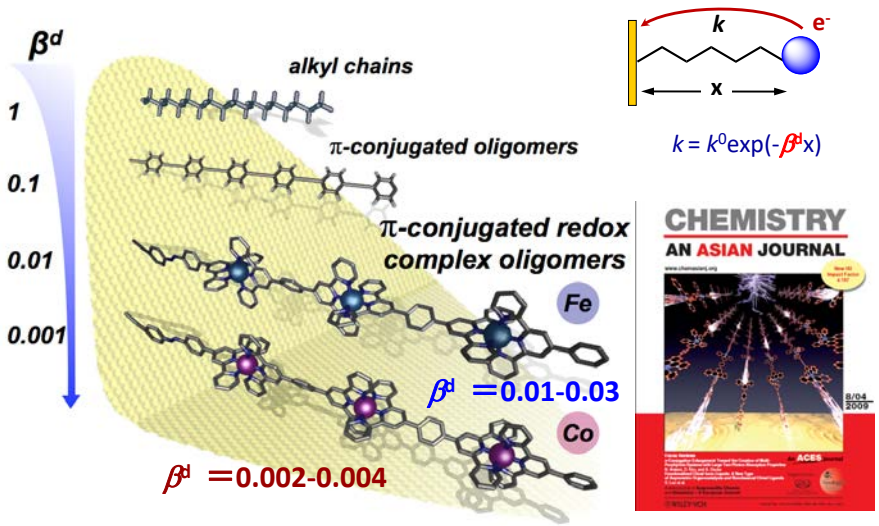
Chronoamperometry $\ln i = -kt + \ln(kQ)$



β of the π–conjugated metal complex oligomer spacer II

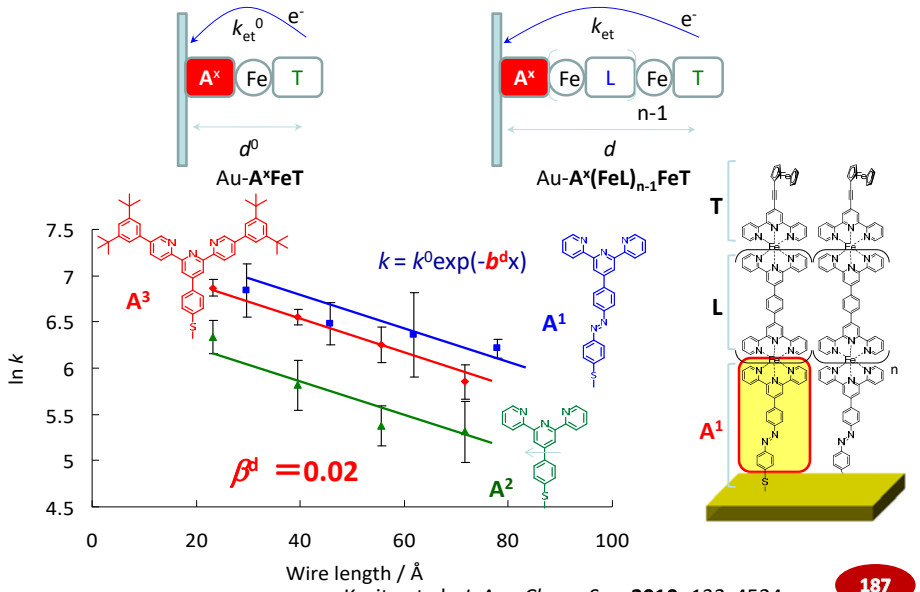


Superior Long-range Electron Transport Ability



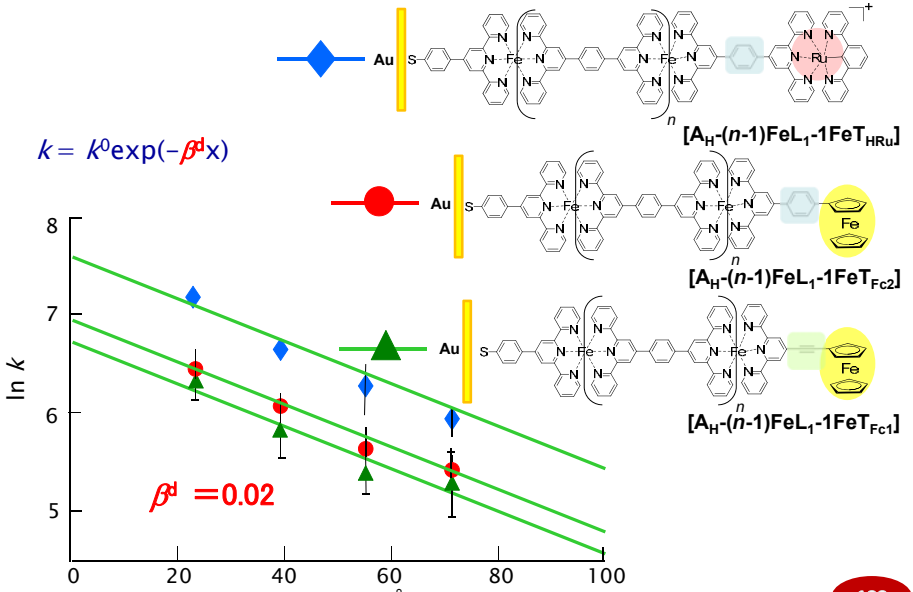
Nishimori et al., *Chem. Asian J.* **2009**, *8*, 1361 (Front cover)

Surface Junction Effects on Electron Transfer



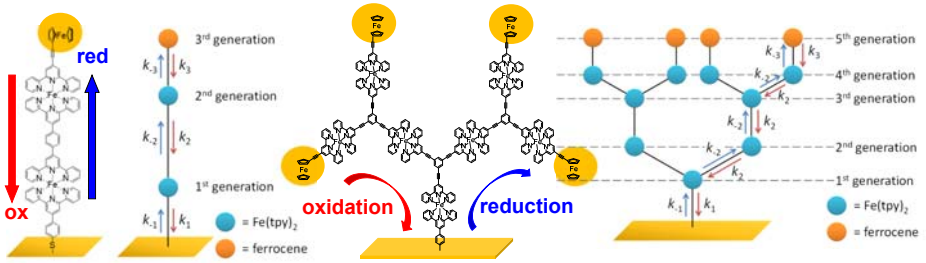
Kurita et al. *J. Am. Chem. Soc.* **2010**, *132*, 4524.

Terminal Redox Site Effects on Electron Transfer

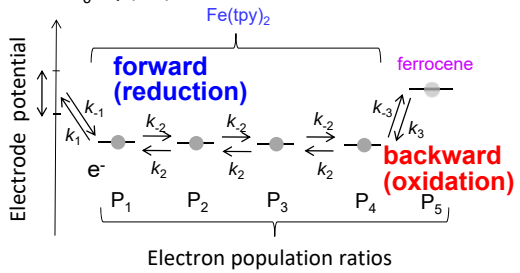


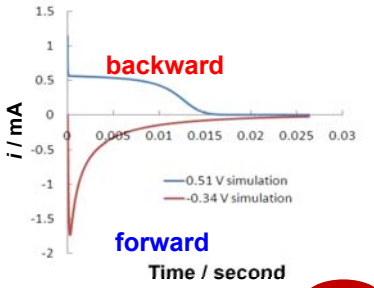
Katagiri et al., *Chem. Eur. J.* **2013**, *19*, 5088.

樹状形分子ワイヤの電子移動ダイナミクス



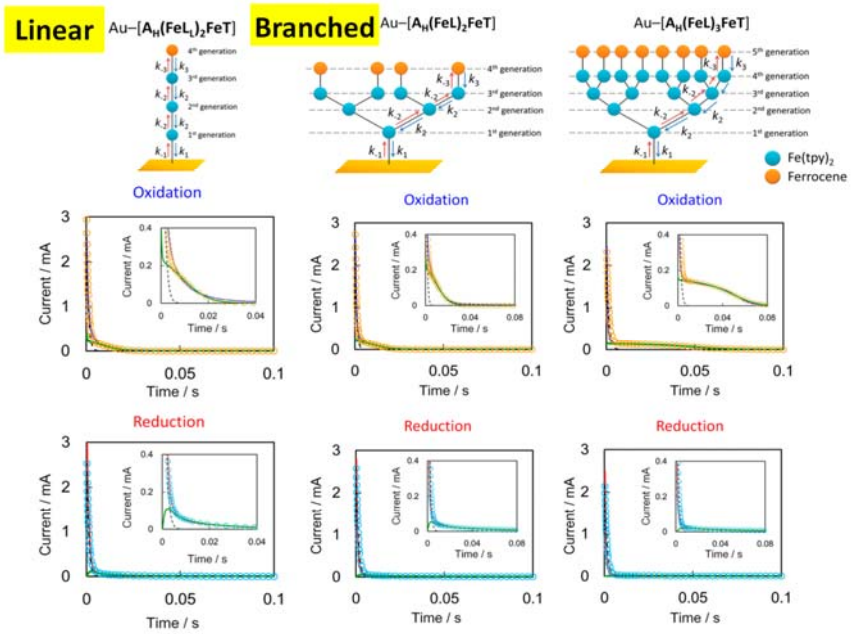
$i = i_0 \exp(-kt)$





Sakamoto et al., *J. Am. Chem. Soc.* **2015**, *137*, 734.

189



Sakamoto et al., *J. Am. Chem. Soc.* **2015**, *137*, 734.

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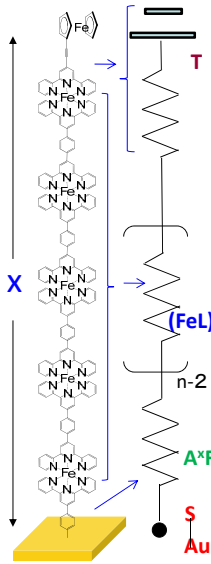
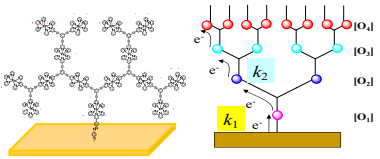
π共役レドックス錯体ワイヤの電子移動・輸送機構



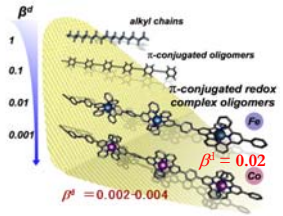
1. 分子鎖レドックス伝導



Chem. Asian J. **2007**,*2*, 367.

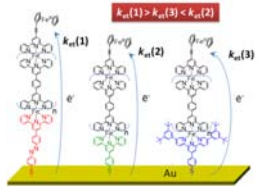
2. 超長距離電子輸送能

$k = k^0 \exp(-\beta^d x)$



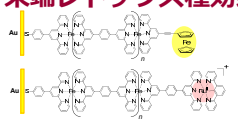
Chem. Asian J. **2009**,*4*, 1361. (Front cover)
Chem. Commun. **2013**, *49*, 7108. (Front cover)

3. 表面ジャンクション効果



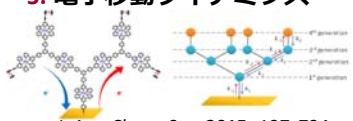
J. Am. Chem. Soc. **2010**, *132*, 4524

4. 末端レドックス種効果



Chem. Eur. J. **2013**, *19*, 5088.
Chem. Lett. **2013,** *42*, 553.

5. 電子移動ダイナミクス



J. Am. Chem. Soc. **2015**, *137*, 734
***Chem. Soc. Rev.* 2015, *44*, 7698 - 7714**

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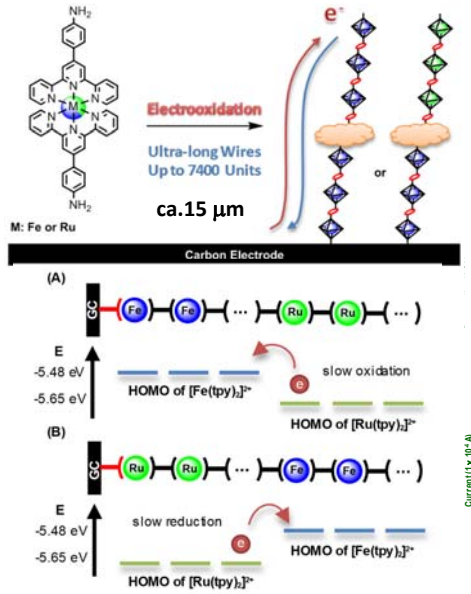
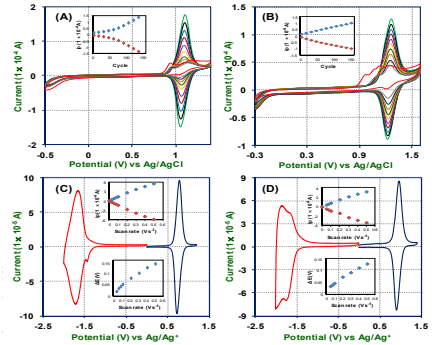
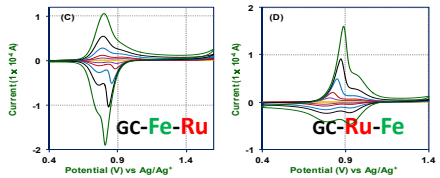
Ultra-long π-Conjugated Redox Molecular Wires





Redox diode behavior



Wu et al., unpublished

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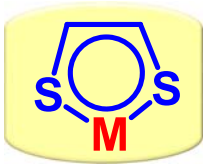
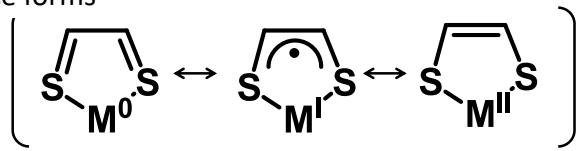
Metalladithiolene



Resonance forms

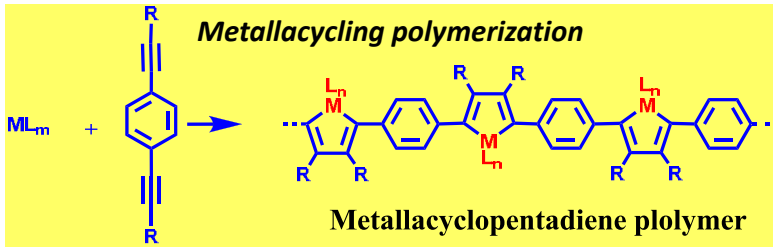


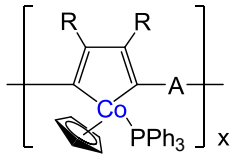
i) Quasi-aromaticity
ii) Unsaturation of the metal

⇨

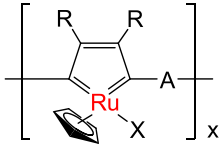
·Redox activity
·Photofunction
·Chemical reactivity

π–Conjugated Organometallic Polymers

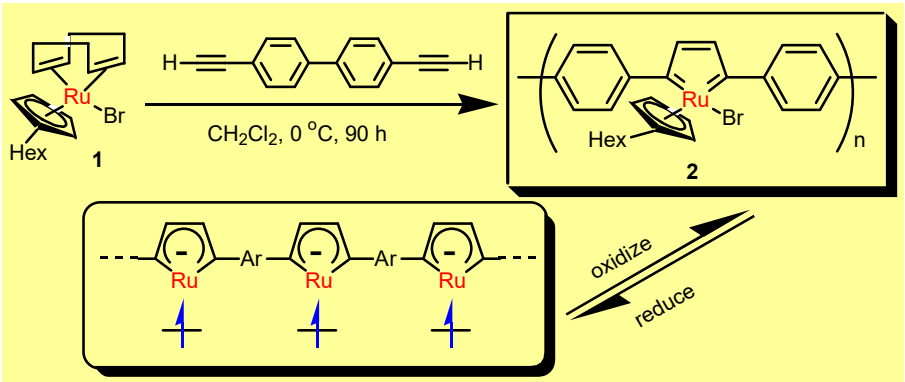




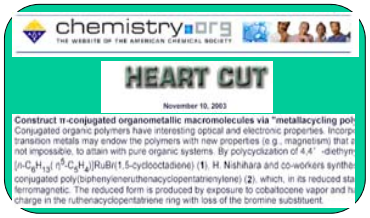
J.C.S. Chem. Commun. **1992,** *Chem.Lett.* **1993**, *Adv. Mater.* **1993**, *Inorg. Chim. Acta* **1995**, *Synth. Met.* **1995**, *Acta Cryst. C* **1995**, *Chem. Mater.* **1996**, *Mol. Cryst. Liq. Cryst.* **1996**, *J.C.S. Dalton Trans.* **1998,** *Synth. Met.* **1999**, *J. Inorg. Organomet. Polym.* **2000.**



J. Am. Chem. Soc. **2003**, *125*, 12420.

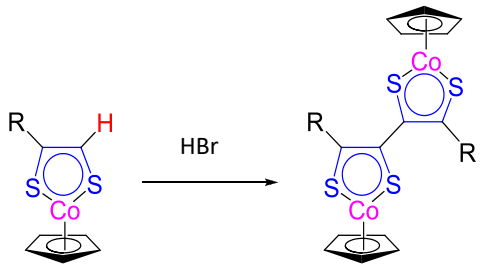


Ferromagnetic interaction between ruthenacycle units



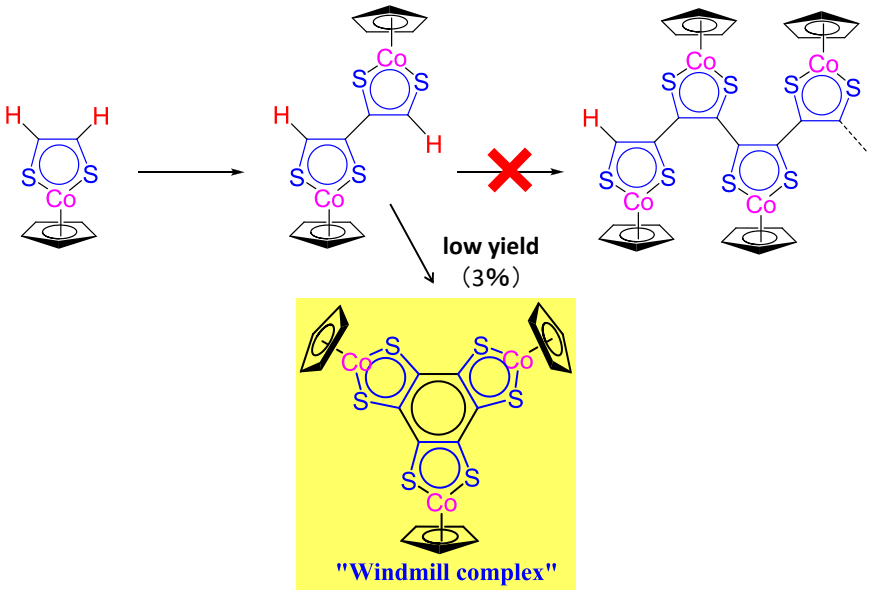
J. Am. Chem. Soc. **2003**, *125*, 12420.

Heart Cut article
on the Web page of ACS



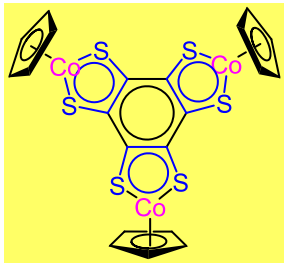
R = Me, $SiMe_3$, Ph

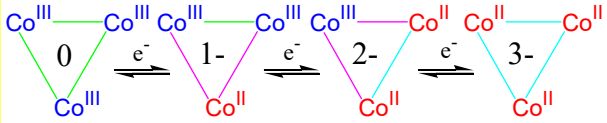
M. Kajitani *et al*.
42nd Symposium of Japan Society of Coordination Chemistry (1992)
Bull. Chem. Soc. Jpn. **1998**, *71*, 2351.



Chem. Lett. **1995**; *J. Electroanal.Chem.* **1997**; *J. C. S. Dalton Trans.* **1998**

Windmill complex

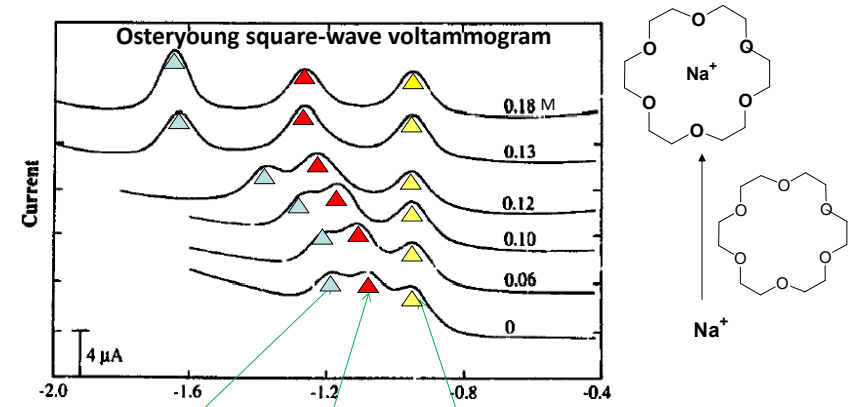




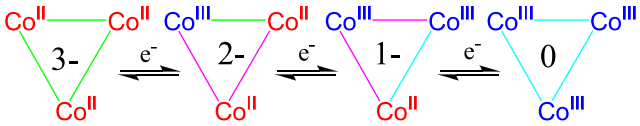
◎Matrix effect on the stability of mixed-valence states

◎Matrix effect on the stability of magnetic properties in the $Co^{II}Co^{II}Co^{II}$ state

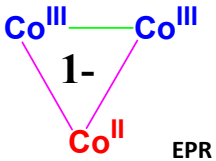
Matrix effect on the stability of mixed-valence states

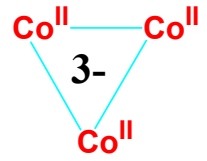


0.1 M $NaBPh_4$-THF



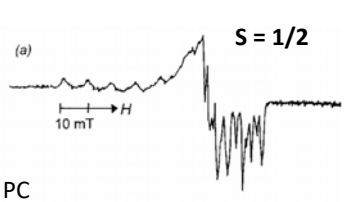
Matrix effect on the stability of magnetic properties

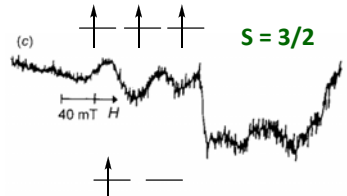




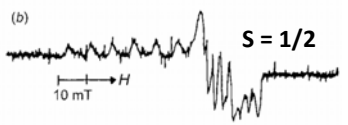
EPR spectra at 77K

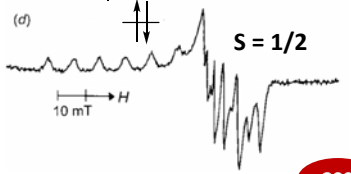
Na^+ in THF





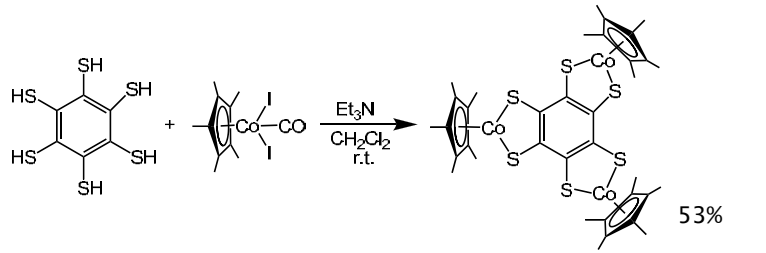
$[CoCp^*_2]^+$in PC

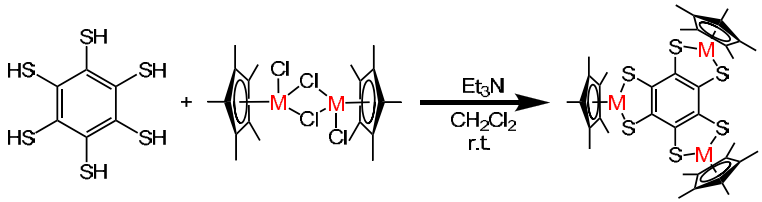




Chem. Lett. **1995**; *J. Electroanal.Chem.* **1997**; *J. C. S. Dalton Trans.* **1998.**

New Synthetic Method of Windmill Complexes



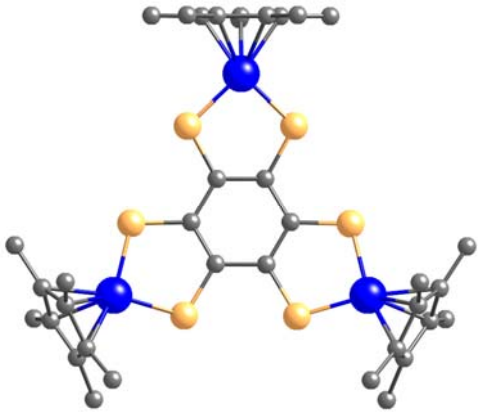


M = Rh: 71%
M = Ir: 90%

Y. Shibata et al., *Dalton Trans.* **2009**, 1939.

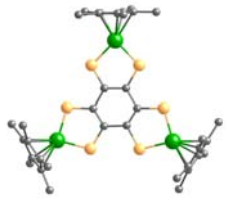
X-ray crystallography

Cp*Co



Cp*Rh

Cp*Ir



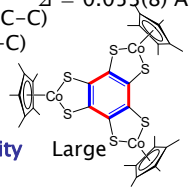
Y. Shibata et al., *Dalton Trans.* **2009**, 1939.

Dependence on the metal

Cp*Co

Δ = 0.053(8) Å

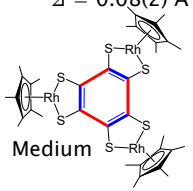
Δ = (long C–C) – (short C–C)



aromaticity Large

Cp*Rh

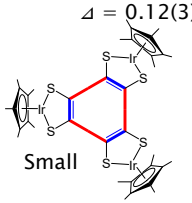
Δ = 0.08(2) Å



Medium

Cp*Ir

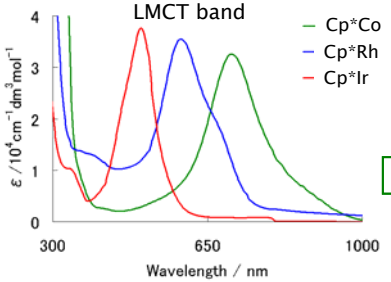
Δ = 0.12(3) Å

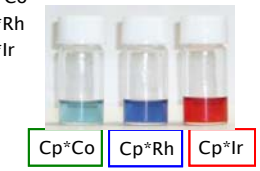


Small

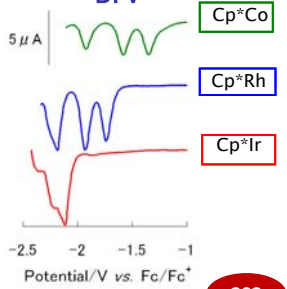
UV-vis

LMCT band



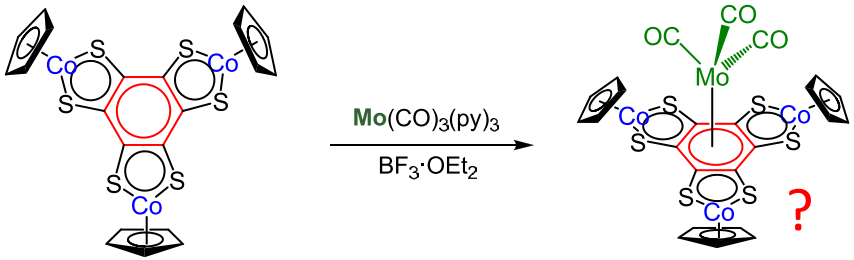


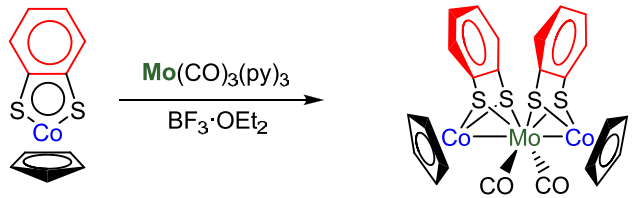
DPV



Y. Shibata et al., *Dalton Trans.* **2009**, 1939.

Metal-metal bond formation reaction



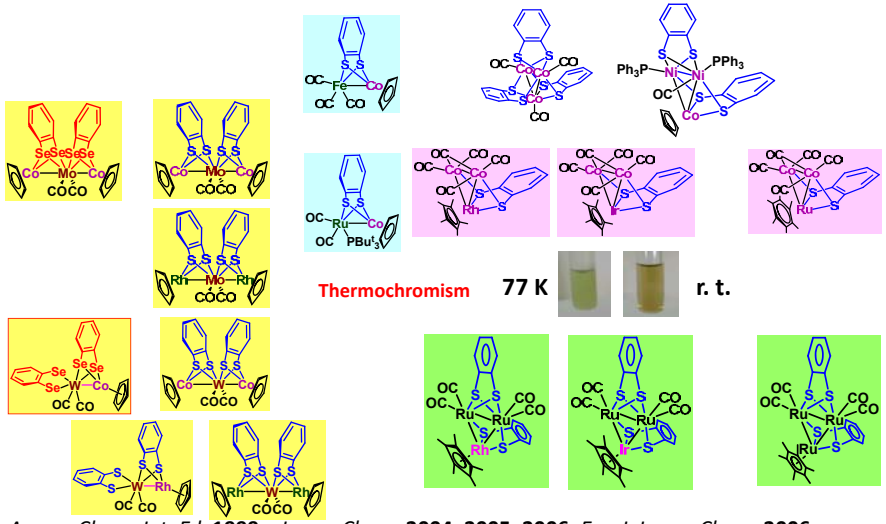


The first metal-metal bond formation reaction of metalladithiolene complexes

M. Nihei et al., *Angew. Chem. Int. Ed.* **1999,** *38*, 1098.

Metalladithiolene Cluster Complexes

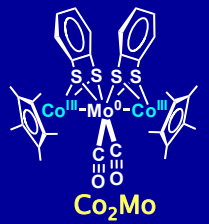
9-6-Se | 9-6-S | 9-8-S | 9-9-S | 9-10-S | 8-9-S



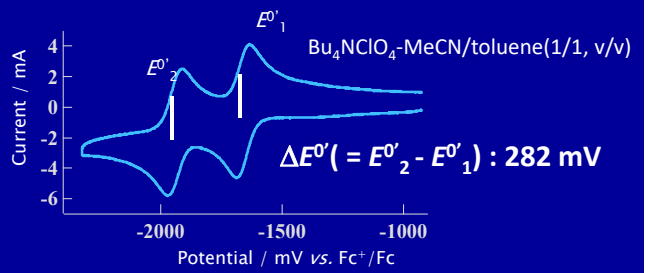
Angew.Chem. Int. Ed. **1999**. *Inorg. Chem.* **2004**, **2005**, **2006**. *Eur. J. Inorg. Chem.* **2006**. *J. Am. Chem. Soc.* **2009**, *Chem. Sci.* **2011**, *Chem. Lett.* **2012**

Difference in Redox properties of CoMoCo and RhMoRh

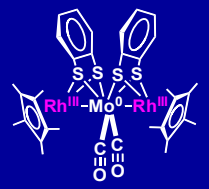
2-step 1e⁻ reduction



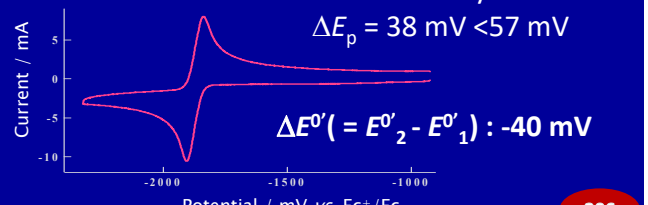
Co_2Mo



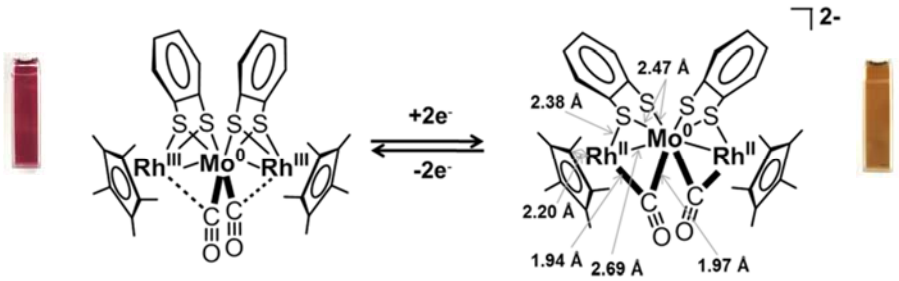
1-step 2e⁻ reduction



Rh_2Mo



Two-electron Reduction Associated with a Change in CO Coordination Mode



Rh_2Mo^0
Two semibridging COs
S = 0

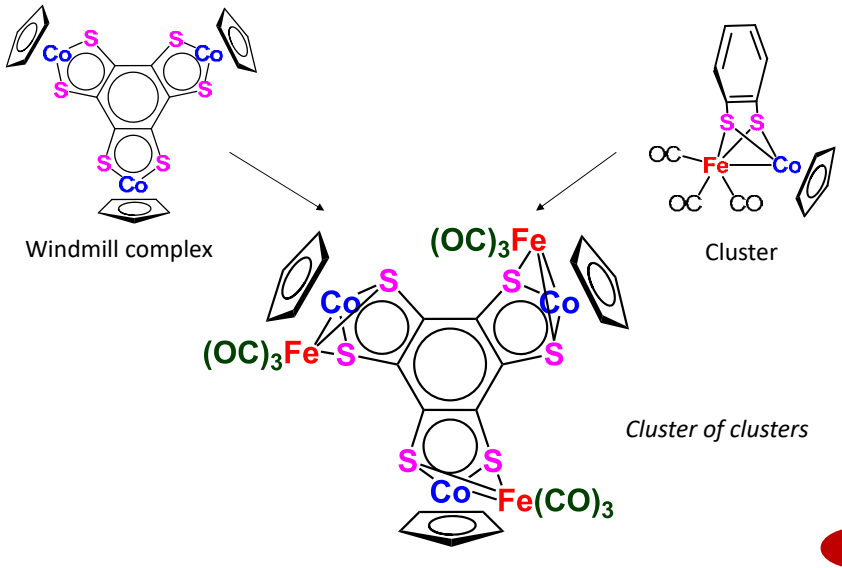
Rh_2Mo^{2-}
Two bridging COs
S = 1

Intramolecular ECE system

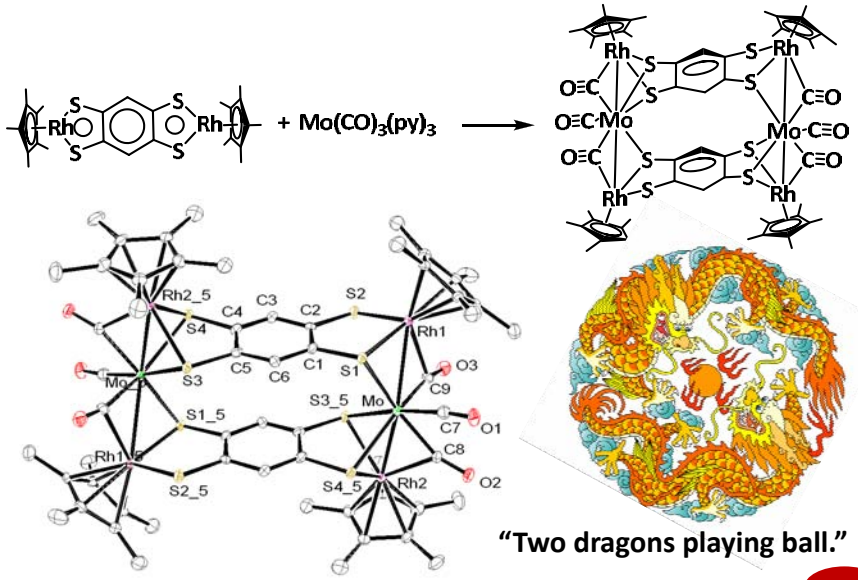
S. Muratsugu et al., *J. Am. Chem. Soc.* **2009**, *131*, 1388.
Chem. Sci. **2011**, *2*, 1960.

Multi-clusterization

Rational design of metal cluster complexes



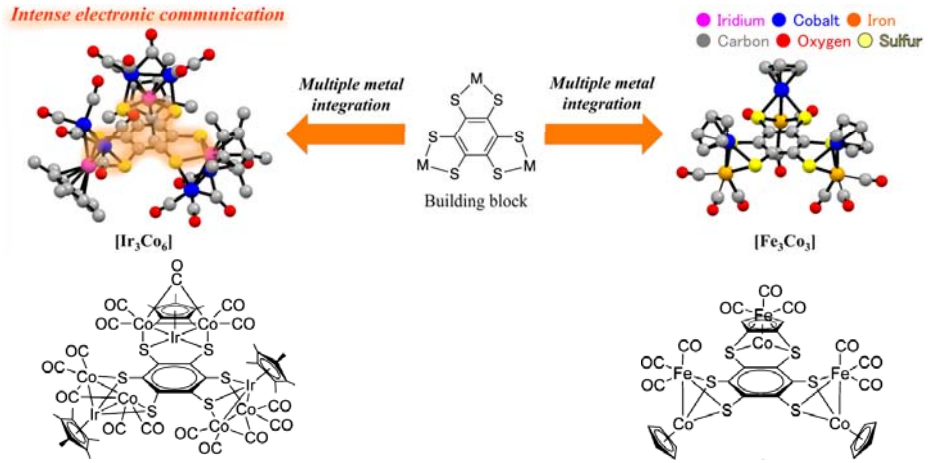
Metalladithiolene Cluster Complexes : Rh_2Mo_4



"Two dragons playing ball."

B. H. Zhu et al., *Angew. Chem. Int. Ed.* **2009**, *48*, 3858.

Metalladithiolene Cluster Complexes : Ir_3Co_6 and Co_3Fe_3



S. Tsukada et al., *Inorg. Chem.* **2012**, *51*, 1228.

The Metalladithiolene Family