Macromol. Symp. ***156****, 21–27 (2000)*

Electron Transfer of Conjugated Polymeric Ferrocenes

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SUMMARY: This paper describes three topics on the π-conjugated ferrocene oligomers and polymers; the first is the dependence of intervalence-transfer bands for mixed-valence oligo(1,1'-dihexylferrocenylene)s on the oxidation number and the number of ferrocene units, the second is synthesis of azo-bridged ferrocene oligomers and a polymer and electrochemical and optical analysis of internuclear electronic interactions in their mixed-valence states and the third is synthesis, redox behaviors and electrodeposition of oligoferrocenylene-modified gold clusters.

Introduction

We have been investigating synthesis and physical properties of π-conjugated ferrocene oligomers because they are valuable examples of redox-conjugated linear systems exhibiting a variety of intriguing physical properties strongly dependent of the structure, the number and the oxidation state of redox nuclei, and the structure of π-conjugated spacers$^{1)}$. It is important to understand how to control such properties by adjusting the combination of molecular units and the environmental conditions.

In the previous studies, we have recognized the dependence of redox properties of oligoferrocenylenes on the number of ferrocene units based on the neighboring-site interaction model$^{2-4)}$, the charge localization and distribution in the mixed valence states using iron carbonyl attached oligoferrocenylenes$^{5)}$, and NIR photoconducitvity of polyferrocenylene-TCNE charge-transfer complex polymers$^{6)}$.

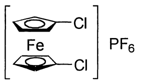
In this paper we present three further topics concerning π-conjugated ferrocene oligomers. The first topic shows how the intervalence transfer (IT) bands changes with increasing the number of ferrocene units and also with the oxidation number for

CCC 1022-1360/00/$ 17.50+.50/0

oligoferrocenylenes. Preliminary results have been reported in a communication$^{7)}$. This study denotes that the internuclear distance is the important factor to explain the red shift of the IT band with increasing the oxidation number for each oligoferrocenylene$^{8)}$. The second topic shows the synthesis and physical properties of new azo-bridged ferrocene oligomers and a polymer, of which preliminary results are presented in a communication$^{9)}$. We present a strong dependence of the redox and optical properties for azoferrocene and azo-bridged trimers on the properties of solvent and their photoisomerization reactions causing changes in physical properties in the mixed-valence state(s)$^{10)}$. The third topic denotes the hybrid system comprising both oligoferrocenylenes and Au clusters. We have found that the electrodeposition of Au clusters occur by oxidizing the Au-surface attached oligoferrocenylenes, resulted in a formation of electroactive Au cluster films$^{11)}$.

IT bands of Oligoferrocenylenes

IT bands at all of the mixed-valence states of oligo(1,1'-dihexylferrocenylene)s from the dimer to the hexamer, **2** - **6**, were determined by the analysis of the absorption spectra of the oligomers oxidized quantitatively with 1,1'- dichloroferrocenium



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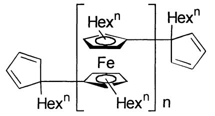


2: n = 2
3: n = 3
4: n = 4
5: n = 5
6: n = 6

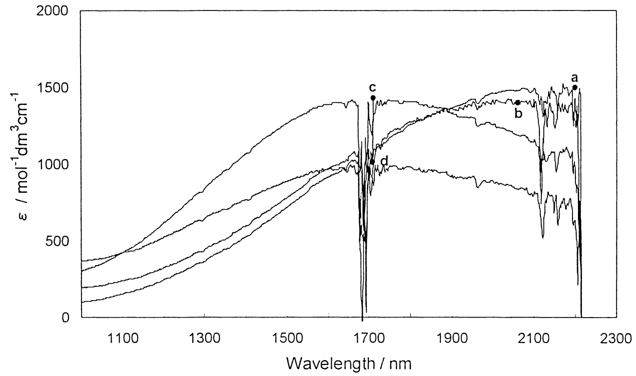


Fig. 1: Near-IR spectra of $\mathbf{5}^+$ (*a*), $\mathbf{5}^{2+}$ (*b*), $\mathbf{5}^{3+}$ (*c*), $\mathbf{5}^{4+}$ (*d*) in CH_2Cl_2-acetone.

hexafluorophosphate, **1**, in CH_2Cl_2-acetone[7]. Figure 1 shows the spectra of **5** in four mixed-valence states as an example. Characteristic features of the IT bands are a higher energy shift in ν_{max} as the oxidation number for each oligomer increases and a lower energy shift in ν_{max} for the monocationic form of the oligomers as the number of ferrocene units increases. We made a simple analysis of the shift in ν_{max} of IT bands based on a model assuming that the mixed-valence states are a linear combination of reduced (Red) and oxidized (Ox) nuclei[12]. It is qualitatively rationalized by taking into account the change in neighboring-site combination, especially between Red-Ox and Ox-Ox, formed by photo-electron transfer, which delivers extra energy, u_{ex}, due to the strain in internuclear distance as shown in Fig. 2 [8].

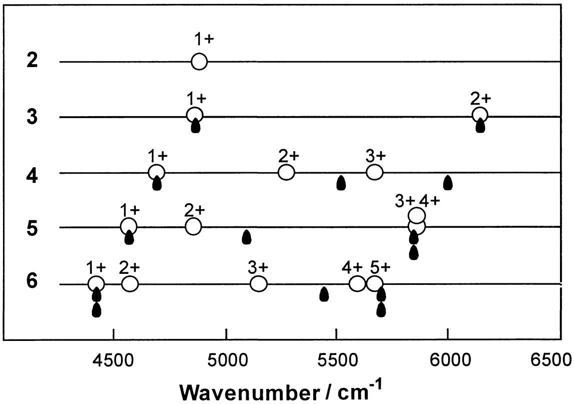
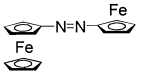


Fig. 2: Experimental (open circles) and theoretical (filled triangles) values of ν_{max} of IT bands using u_{ex} = 13 kJ mol^{-1} for **2** – **6**.

Azo-bridged Ferrocene Oligomers and a Polymer

New azo-bridged ferrocene trimers, Fc-Fc'-N=N-Fc (**8**) and Fc-N=N-Fc'-N=N-Fc (**9**), where Fc and Fc' refer to $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4\text{-})$ and $Fe(\eta^5\text{-}C_5H_4\text{-})_2$, respectively, were obtained in the reaction of a mixture of lithioferrocene and 1,1'-dilithioferrocene in THF with N_2O [9,10]. The reaction of 1,1'-dilithioferrocene and N_2O gives a polymer composed of $[\text{-}(Fc'\text{-}N{=}N\text{-}Fc')_{0.6}\text{-}(Fc'\text{-}Fc')_{0.4}\text{-}]_n$. (**10**) [10].



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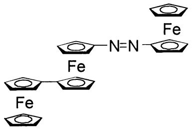

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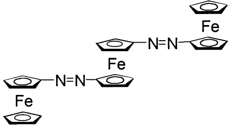

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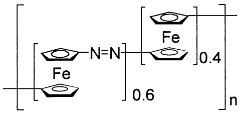

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X-ray crystallography of azoferrocene (**7**) has determined that the Fe-Fe distance is 6.80 Å in the *trans* form. Cyclic voltammograms of **9** in aprotic solvents such as CH_2Cl_2 or THF exhibit reversible 2e$^-$ and 1e$^-$ oxidation waves, indicating that the positive charge in the monocation is localized mostly on the terminal ferrocene unit (correspondingly, Fc$^+$-N$_2$-Fc’-N$_2$-Fc) due to a strong electron-withdrawing effect of the azo group. This charge distribution in the mixed-valence state is supported by the characteristics of intervalence-transfer (IT) bands. An asymmetrical complex, **8**, undergoes a three-step 1e$^-$ oxidation, and the two mixed-valence forms can be roughly expressed as Fc$^+$-Fc’-N$_2$-Fc and Fc$^+$-Fc’-N$_2$-Fc$^+$.

The redox potentials and IT band characteristics of **7**$^+$, **8**$^+$, and **8**$^{2+}$ depend markedly on the solvent. The solvent effect of the IT band on ν_{max} cannot be interpreted only by the parameters in the Marcus-Hush theory, indicating that the nature of the solvent as donor or acceptor should be taken into account in the electron-exchange process in the mixed-valence states. More donating solvent affords higher IT and LMCT energy, indicating the hole-transfer mechanism (Fig. 3)$^{13,14)}$.

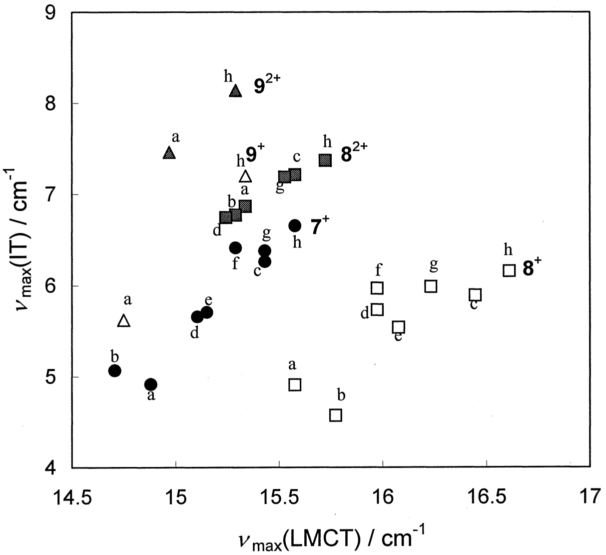
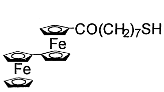


Fig. 3: Plots of ν_{max}(IT) *vs.* ν_{max}(LMCT) for mixed-valence states of **7-9** in CH2C12 (*a*), 1,2-dichloroethane (*b*), nitromethane (*c*), nitrobenzene (*d*), PhCN (*e*), MeCN (*f*), acetone (*g*) and THF (*h*).

Oligoferrocenylene-modified Au Clusters

Au clusters stabilized with alkanethiols were created and have developed a new research area on the metal-molecule interface15-18). We have synthesized biferrocene- and terferrocene-terminated alkanethiols, **11** and **12** and used for the modification of Au surface18). Biferrocene and terferrocene-attached Au clusters (2.2 ± 0.3 nm in diameter), **13** and **14**, were prepared by substitution reactions of octanethiol-modified Au cluster with **11** and **12**, respectively.



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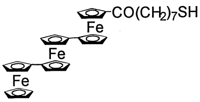

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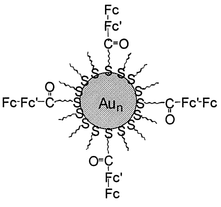

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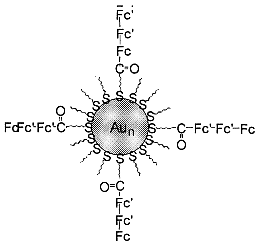

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The modified Au clusters, **13** and **14** undergo quasi-reversible two-step and three-step $1e^-$ oxidation reactions in NBu_4ClO_4-CH_2Cl_2, respectively. When the consecutive potential scans are carried out in the potential range to form fully oxidized states in the same electrolyte solution, redox-active Au cluster films are formed gradually on electrode surface. Namely, the second oxidation process of biferrocene (Bfc^{2+}/Bfc^{+}) and third one of terferrocene (Tfc^{3+}/Tfc^{2+}) are necessary for the electrodeposition. We suppose that the charge accumulation on the cluster plays the key role of the cluster aggregation.

Spectro-electrochemical measurements of the electrodeposited film of **13** formed at ITO indicate that the absorption at 520 nm decreases according to the oxidation of redox active sites in the film. This spectral change occurs reversibly with the potential shift. The molar absorption coefficient based on the number of $1e^-$ redox active units estimated form the change in absorbance and the amount of charge passed during the oxidation is 4×10^4 mol^{-1} dm^3 cm^{-1}, much larger than ε for the d-d transition of ferrocene appearing around 450 nm (10^2). It is thus reasonable to adjudge that the spectral change is not attributed to the absorption of the redox active units attached to the cluster surface but due to the surface plasmon19). These results demonstrate that the electronic properties of Au clusters can be controlled by the oxidation states of the surface-attached redox-active molecules.

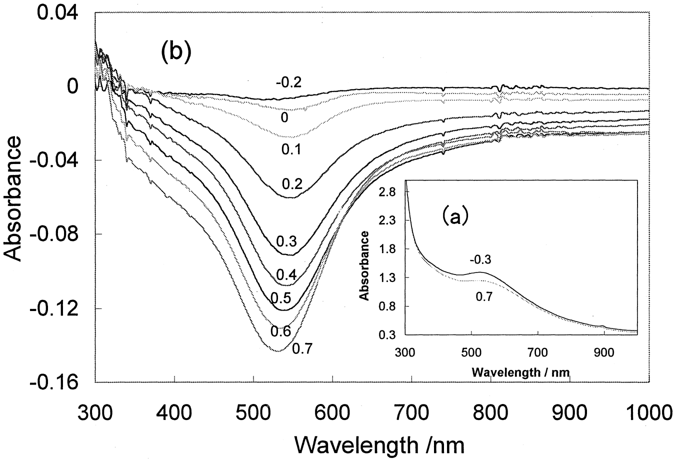

Fig. 4: (a) UV-VIS-NIR spectra of the electrodeposited film of **13** at ITO at –0.3 V (reduced state) and 0.7 V (oxidized state) *vs*. Ag/Ag$^+$ in 0.1 mol dm^{-3} Bu_4NClO_4-CH_2Cl_2. Electrodeposition was carried out in a solution of **13** (6.1 μmol dm^{-3}) in 0.1 mol dm^{-3} Bu_4NClO_4-CH_2Cl_2 at an ITO plate for consecutive potential scans at 0.1 V s^{-1}.for 200 cycles. (b) The differences in the spectra at given potentials from the one at –0.3 V *vs*. Ag/Ag$^+$ in 0.1 mol dm^{-3} NBu_4ClO_4-CH_2Cl_2. Numbers in the figure refer to the potentials *vs*. Ag/Ag$^+$.

Acknowledgements

This research was supported in part by a Grant-in-Aid for Scientific Research (No. 09237101, No. 09238101, No. 11136027 and No. 11309003) from the Ministry of Education, Science, Sports and Culture, Japan, and by the Asahi Glass Foundation.

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