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Accounts

Redox and Optical Properties of Conjugated Ferrocene Oligomers

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Internuclear electronic interactions in conjugated ferrocene oligomers display unique redox and optical properties. I describe here recent research on the dependence of such properties on the number of ferrocene nuclei and on the structure of conjugated spacers. The neighboring-site interaction model explains the redox properties of oligo(ferrocene-1,1′-diyl)s. The infrared (IR) spectra of carbonyl complex-bound biferrocene and terferrocene enlighten the electronic structure in the mixed-valence states. Energy shifts of intervalence transfer (IT) in the mixed-valence states of oligo(ferrocene-1,1′-diyl)s resulting from changes in the oxidation state are rationalized by taking into account the change in neighboring-site combination by photo-electron transfer, which delivers extra energy due to the strain in internuclear distance. Oligo- and poly-(ferrocene-1,1′-diyl)s oxidized partially by tetracycanoethylene (TCNE) exhibit near-IR photoconductivity. Conjugated spacer groups between ferrocene nuclei involving metal complex moieties affect the redox properties of ferrocene dimers significantly. The azo group acts as a distinctive spacer of which conjugation ability is changeable photochemically.

The research field of transition metal organometallic chemistry started to investigate the compound ferrocene a half century ago.[1] Interest in ferrocene and its family has continued, mostly because of the compounds' high stability, good solubility, versatility in the synthesis of derivatives using a reactivity similar to that of benzene, and reversible redox property, that is, the easy electrochemical and chemical handling of the oxidation state.[2] Among the numerous known ferrocene derivatives, ferrocene oligomers in which the ferrocene units electronically interact with each other are part of a novel group exhibiting a formation of mixed-valence states where Fe(II) (ferrocene) and Fe(III) (ferrocenium ion) coexist within a molecule.[3–5] Biferrocene is the simplest conjugated ferrocene dimer. Its monocation is a typical example of Robin and Day Class II mixed-valence complexes,[6] and its derivatives have been frequent targets of study of internuclear electronic interaction not only in solution but also as a crystalline solid. [7–9]

A variety of other ferrocene dimers[10–23] with conjugated spacer groups have also been investigated. It has been shown that the chemical structure of the conjugated spacer group and its length dramatically affect the electronic interaction between the ferrocene moieties. Discussion of the electron-exchange mechanism for the mixed-valence complexes of such conjugated ferrocene dimers has been largely based on the Marcus–Hush theory.[24] In these studies, electrochemical and optical properties are the most important means to measure the magnitude of internuclear electronic interaction in the mixed-valence complexes. Various other tools to measure the electron exchange rate with different time windows in the mixed-valence complexes, such as Mössbauer, IR, NMR, and ESR, have been also developed. A new method recently developed by Ito and his co-workers is the analysis using coalescence of ν(CO) bands in the IR spectra of conjugated dimers of Ru trinuclear complex units with carbonyl ligands.[25] This technique gives quantitative kinetic information about internuclear electron exchange rates at $10^9 - 10^{13}$ s^{-1}.

Reports on conjugated ferrocene trimers and higher polymers have also been available since the 1960s, but recently there has been intensive research aimed at developing electronically and magnetically functional materials.[4,5,20–27] We have been studying two aspects of the synthesis and properties of π-conjugated ferrocene oligomers and polymers. One is the recognition of the physical property sequence that occurs in the change from dimer to polymer, and the other is the combination of unique physical properties of conjugated ferrocene oligomers with other functional molecules or materials. In this report I hope to present some of the research on these topics and compare the results with those of related studies.

1. Redox Properties of Oligo(ferrocene-1,1′-diyl) and the Neighboring-Site Interaction Model

In electrochemical measurements, thermodynamic stability of a mixed-valence dinuclear complex, which is denoted as a combination of reduced (Red) and oxidized (Ox) sites, Red–

Ox, is exhibited as the difference in redox potentials $\Delta E^0 = E^0(\text{Ox–Ox/Red–Ox}) - E^0(\text{Red–Ox/Red–Red})$. This relates to the comproportionation constant, K_c, defined in Eq. 1:

$$K_c = \exp(\Delta E^0 F/RT) \qquad (1)$$

The free energy of comproportionation, ΔG_c involves several factors, as given in Eq. 2 by Sutton and Taube:

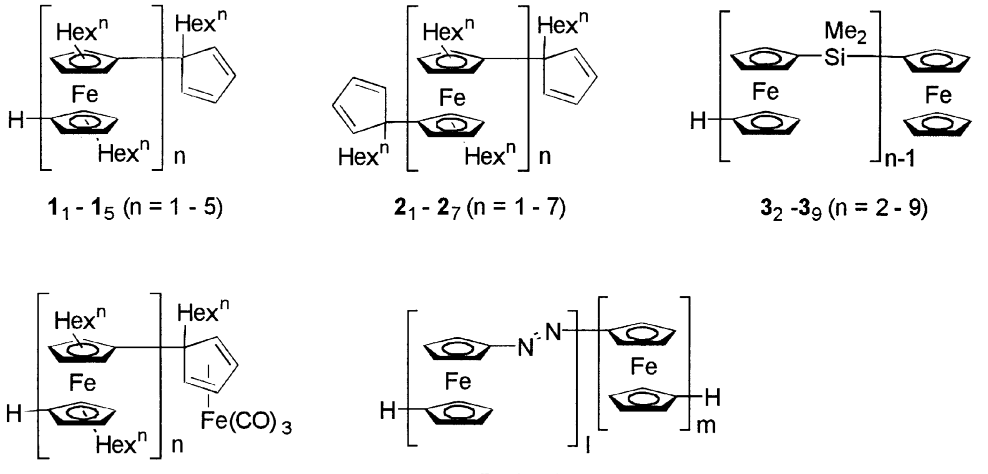
$$\Delta G_c = \Delta G_s + \Delta G_e + \Delta G_i + \Delta G_r \qquad (2)$$

where ΔG_s reflects the statistical distribution of the comproportionation equilibrium, ΔG_e accounts for the electrostatic repulsion of the two like-charged metal nuclei, ΔG_i is an inductive factor dealing with competitive coordination of the bridging ligand by the metal nuclei, and ΔG_r is the free energy of resonance exchange–the only component of ΔG_c that represents actual metal-metal coupling.[28] A recent paper of Crutchley et al. noting the involvement of an extra parameter, ΔG_{ex}, which concerns the stabilization of one of the reactants in ΔG_c, was presented by Sutin as a private communication.[29] This approach has been employed for various mixed-valence complexes, but the analysis has been restricted to mostly dinuclear species.

An approach that gives a general theoretical insight on the redox properties of a linearly combined multi-redox system was presented by Aoki and Chen in 1995.[30] The theory is constructed based on the interaction energies between neighboring redox sites, u_{OR} u_{OO} and u_{RR}, where OR, OO, and RR denote combinations of Ox and Red, Ox and Ox, and Red and Red, respectively. Each interaction energy involves all the parameters given in Eq. 2, but we can assume that u_{OR} and u_{OO} mainly consist of resonance exchange energy (ΔG_r) and electrostatic repulsion energy (ΔG_e), respectively, when the internuclear electronic interaction is strong and the oxidized site is positively charged such as in conjugated ferrocene oligomers. Namely, u_{OR} is negative, u_{OO} is positive, and u_{RR} is less important than the others. An interesting forecast of this theory is that a system with an odd number of redox nuclei, $n = 2m + 1$ ($m \geq 1$), gives three redox waves with m, 1, and m electrons, and the system with an even number of redox nuclei, $n = 2m + 2$ ($m \geq 1$), gives four redox waves with m, 1, 1, and m electrons. Consequently, it is predicted that the number of waves converges into two when m approaches infinity.

A series of oligo- and poly-(ferrocene-1,1′-diyl)s are a representative linearly combined multi-redox system; their redox properties can be compared with the prediction of Aoki's theory. Brown et al. have reported that electrochemical properties of unsubstituted oligo(ferrocene-1,1′-diyl)s, which have been examined up to a tetramer, exhibit the same number of one-electron oxidation waves as those of ferrocene units in a molecule due to formation of mixed-valence states.[31] There is one report on the redox property of poly(ferrocene-1,1′-diyl) by Oyama et al. that notes that the cyclic voltammetry of low molecular weight poly(ferrocene-1,1′-diyl) (M_w = ca. 900) dissolved in CH_2Cl_2 or electrodeposited on Pt gives a broad redox wave with two (or three) peaks between 0.2 and 0.8 V vs. SSCE.[32] However, the low solubility of unsubstituted oligo(ferrocene-1,1′-diyl) and poly(ferrocene-1,1′-diyl) prevents the detailed analysis of their redox properties using Aoki's theory. The first experimental recognition of the dependence on the redox nuclei in the linearly combined multi-redox system was carried out by the author and co-workers, using alkylated oligo(ferrocene-1,1′-diyl)s up to a heptamer, **1_1–1_5** and **2_1–2_7**,[33,34] which are soluble in common organic solvents. Their redox behavior is subjected to the study based on the neighboring-site interaction model.[33–35]

The redox potentials of oligo(dihexylferrocene-1,1′-diyl)s **1** and **2** in Scheme 1, estimated by Osteryoung square-wave voltammetry, are given in Fig. 1. All the oligomers exhibit one-electron oxidation processes clearly. Simulation of the redox potentials of the oligo(ferrocene-1,1′-diyl)s by the theory based on the interaction between neighboring centers noted above has indicated that the redox potential dependency of the oligomers up to the tetramer on the number of redox nuclei (i.e., ferrocene units) can be explained, but the separation of redox potentials for each one-electron oxidation step for pentamers, a



1_1 - 1_5 (n = 1 - 5)

2_1 - 2_7 (n = 1 - 7)

3_2 -3_9 (n = 2 - 9)

4_1 - 4_3 (n = 1 - 3)

5_2: l = 1, m = 1
5_{3a}: l = 2, m = 1
5_{3b}: l = 1, m = 2

Scheme 1.

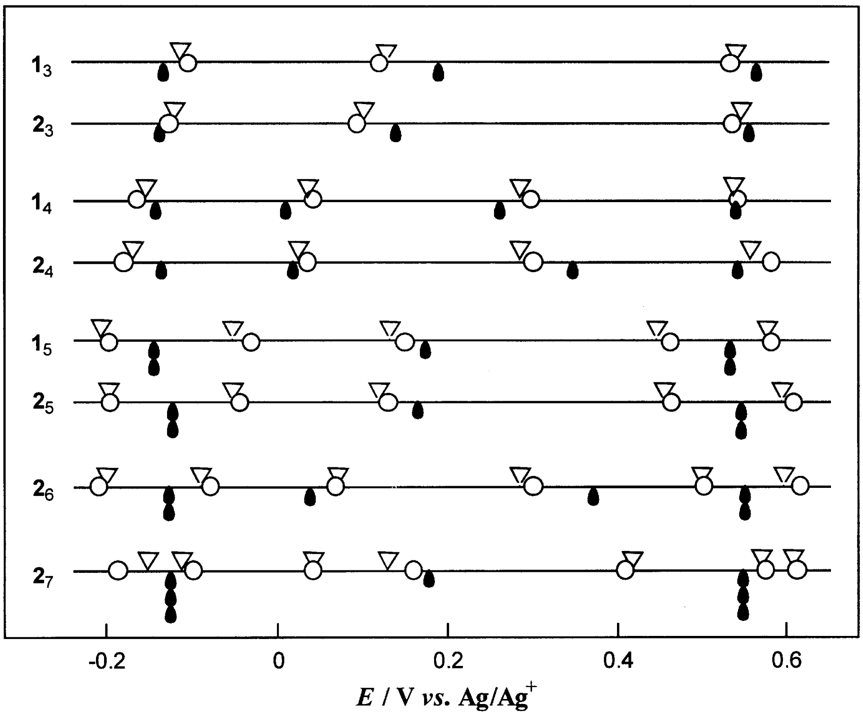


Fig. 1. Formal potentials of oligo(dihexylferrocene-1,1′-diyl)s **1** and **2**, obtained by Osteryoung square-wave voltammetry (○), those calculated from the first neighboring site interaction energies (▲) with u_1 = 15 kJ mol^{-1} an u_2 = 4.5 kJ mol^{-1}, and those calculated from both the first and second neighboring site interaction energies (▽) with u_1 = 15 kJ mol^{-1}, u_2 = 4.5 kJ mol^{-1}, and u_{OXR} = −3.8 kJ mol^{-1}.

hexamer, and a heptamer cannot be interpreted (see Fig. 1). The separation is reasonably interpreted by the introduction of an additional parameter, u_{OXR}, denoting the donor-acceptor interaction over three redox centers (Fig. 1). The simulation indicates that $u_1 = (u_{OO} + u_{RR})/2 - u_{OR}$ = 15 kJ mol^{-1}, $u_2 = (u_{OO} - u_{RR})/2$ = 4.5 kJ mol^{-1}, and u_{OXR} = −3.8 kJ mol^{-1}. Assuming u_{RR} = 0 because there is no electrostatic interaction or electron delocalization between Red and Red, we obtain u_{OO} = 9 kJ mol^{-1} and u_{OR} = −10.5 kJ mol^{-1}. The fact that the magnitude of u_{OXR} is only one-third of that of u_{OR} suggests that the positive charge in the molecule is considerably localized on the "Ox" sites.

Another system of linear ferrocene oligomers of whose redox properties are systematically examined is oligo(ferrocenyldimethylsilane) from dimer to nanomer, **3**$_2$–**3**$_9$, reported by Rulkens et al.[36] Although all the redox potential differences are not large enough to form the given mixed-valence state separately due to weaker internuclear interaction through the dimethylsilylene moiety compared with that of oligo(ferrocene-1,1′-diyl), odd-number and even-number dependency of the redox property is observed. In the case of "odd" oligomers, where the number of nuclei is $2n + 1$, two redox steps with $(n + 1)e^-$ and ne^- are observed, and "even" oligomers with $2n$ nuclei exhibit three steps with ne^-, $1e^-$, and $(n - 1)e^-$. Analysis of the redox potentials of **3** in the reference based on the neighboring site interaction model gives u_1 = 7 kJ mol^{-1}, u_2 = 3 kJ mol^{-1}, and u_{OXR} can be neglected. This indicates that u_{OO} = 6 kJ mol^{-1} and u_{OR} = − 4 kJ mol^{-1} when we assume u_{RR} = 0. The difference in u_{OO} between **2** and **3**, 3 kJ mol^{-1}, can be ascribed to the stronger electrostatic repulsion of the smaller internuclear distance in **2** compared with that in **3**. The significantly higher u_{OR} value of **2** compared with that of **3** indicates the decrease in charge delocalization by the insertion of dimethylsilylene between ferrocene nuclei.

2. IR Sensing of the Electronic Structure in the Mixed-Valence States of Iron Carbonyl-Attached Oligo(ferrocene-1,1′-diyl)s

Electron delocalization between the two nuclei in the monocationic forms of biferrocene and its derivatives has been investigated using several methods: near-IR, IR, far-IR, Mössbauer, and ESR spectroscopy in addition to the electrochemical measurements.[3,5,10a,31,37,38] In IR spectroscopy, the presence of bands of perpendicular C–H bending mode is a diagnosis of the oxidation state of ferrocene units, and the analysis of this band is a powerful tool for examining the electron-transfer rate against the IR time scale.[8b,13,36,38]

Recently, the author and co-workers employed the IR spectra to recognize the charge localization in the mixed-valence states of oligo(ferrocene-1,1′-diyl) derivatives.[39] Biferrocenium monocation has a single form when the mixed-valence state is expressed as a combination of Red and Ox, whereas mixed-valence states of the higher oligo(ferrocene-1,1′-diyl) possess electronic isomers. For example, the monocation of terferrocene has two electronic isomers: Red–Ox–Red and Ox–Red–Red. In the neighboring-site interaction model, it is important to estimate the thermodynamically favorable form in order to simulate the redox potentials.[30] When all the nuclei have similar chemical potentials, the thermodynamically most favorable electronic isomers in the mixed-valence states are determined mainly by the total u_{OR} value. Thus, we determined that Red–Ox–Red is thermodynamically more favorable than Ox–Red–Red and that Ox–Red–Ox is a better candidate than Ox–Ox–Red for a redox trimer.[30]

An approach to determining the electronic structure of the favorable electronic isomers in the mixed-valence states of terferrocene as noted above has been carried out using IR spectroscopy of the ferrocene, biferrocene, and terferrocene derivatives $\mathbf{4_1}$–$\mathbf{4_3}$ involving an iron tricarbonyl moiety.[39] In this structure, the infrared absorption of CO can sense the oxidation state of the terminal ferrocenyl group attached to the (η^4-cyclopentadiene)$Fe(CO)_3$ moiety, as the CO stretching vibration of metal carbonyls responds to even slight changes in the electronic state of metal centers. In $\mathbf{4_1}$–$\mathbf{4_3}$, all the oxidation of ferrocene units occurs at potentials more negative than that of the iron carbonyl unit, so that the changes in the electronic structure of ferrocene units are observed without oxidative decomposition of the iron carbonyl unit.

The infrared spectra of $\mathbf{4_1}$–$\mathbf{4_3}$ show two ν(CO) absorption peaks typical of (η^4-diene)$Fe(CO)_3$ complexes; one is strong and sharp at ca. 2040 cm^{-1} (A′(1)), and the other is medium and broad at ca. 1965 cm^{-1} (A′(2) and A″).[40] In Table 1 are summarized the wavenumbers of the ν(CO) peaks of $\mathbf{4_1}$–$\mathbf{4_3}$ in each oxidation state generated electrochemically with $\Delta\nu_{\mathrm{CO}}$, which is the shift of ν_{CO} from the neutral form to a given oxidized form, and $\theta(\Delta\nu_{\mathrm{CO}})$, which denotes the ratio of $\Delta\nu_{\mathrm{CO}}$ for a given oxidation state to $\Delta\nu_{\mathrm{CO}}$ for a fully oxidized state. In the infrared refraction absorption spectra of the monomer $\mathbf{4_1}$, a wavenumber shift of the CO stretching mode to higher wavenumbers is observed according to the 1e$^-$ oxidation. A reversible shift upon oxidation and reduction in the magnitude of 12 to 15 cm^{-1} takes place (see Table 1) around the formal potential. This direction of wavenumber shift is reasonable because the positively charged ferrocenium site withdraws electrons from Fe(II) in the (cyclopentadiene)$Fe(CO)_3$ moiety and, consequently, the back-donation from Fe to CO must be lessened. A similar wavenumber shift to higher energy by 4–6 cm^{-1} has been reported by Wolf and Wrighton for a ruthenium carbonyl complex of poly(5,5′-di-2-thienyl-2,2′-bithiazole) when the polythiophene backbone is oxidized.[41]

Table 1. ν_{CO} at Different Oxidation States of $\mathbf{4_1}$–$\mathbf{4_3}$

Complex	Wavenumber/cm^{-1}		$\Delta\nu_{\mathrm{CO}}$/cm^{-1}		$\theta(\Delta\nu_{\mathrm{CO}})$
$\mathbf{4_1}^{0}$	2039	1965	—	—	0
$\mathbf{4_1}^{1+}$	2051	1980	12	15	1
$\mathbf{4_2}^{0}$	2038	1965	—	—	0
$\mathbf{4_2}^{1+}$	2047	1976	9	11	0.6–0.7
$\mathbf{4_2}^{2+}$	2051	1982	4	6	1
$\mathbf{4_3}^{0}$	2038	1964	—	—	0
$\mathbf{4_3}^{1+}$	2041	1970	3	6	0.2–0.3
$\mathbf{4_3}^{2+}$	2050	1979	9	9	0.8–0.9
$\mathbf{4_3}^{3+}$	2052	1982	2	3	1

The wavenumber shift from the fully reduced form to the fully oxidized form for the dimer $\mathbf{4_2}$, is by 13–17 cm^{-1}, similar to the shift of the monomeric complex (see Table 1). The monocationic form gives the peaks at wavenumbers between those for the neutral form and the dicationic form, and the peak width is broadened. This is attributed to the rate of electron exchange between two electronic isomers, Red–Ox–$Fe(CO)_3$ and Ox–Red–$Fe(CO)_3$, where $Fe(CO)_3$ refers to a [(η^4-cyclopentadiene)$Fe(CO)_3$] moiety, is slower than or comparable to the time scale of IR (10^{11}–10^{13} s^{-1}).[25] This is in accordance with the expectation that the (cyclopentadiene)$Fe(CO)_3$-attached ferrocene unit can be either Red or Ox if the attached ferrocene and the non-attached ferrocene are electronically similar.

In the case of the trimer $\mathbf{4_3}$, the consideration based on neighboring site interaction indicates that the three-step oxidation pathway is composed of Red–Red–Red–$Fe(CO)_3$ → Red–Ox–Red–$Fe(CO)_3$ → Ox–Red–Ox–$Fe(CO)_3$ → Ox–Ox–Ox–$Fe(CO)_3$ and thus the (cyclopentadiene)$Fe(CO)_3$-attached ferrocene site should change from Red to Ox at the second oxidation step from monocation to dication. This prediction is roughly correct, as it can be seen in the IR spectra that the most significant wavenumber shift is 9 cm^{-1} at the second step. Small wavenumber shifts are observed even at the first and the third oxidation steps. A simple evaluation is that the shifts at the first and the third steps correspond to about 20% and 80% oxidation of the (cyclopentadiene)$Fe(CO)_3$-attached ferrocene site if the total wavenumber shift (14–18 cm^{-1}) corresponds to the full change in charge density of the ferrocene site from 0 to 1. The values of partial charge density can be regarded as the degree of electron delocalization.

3. Intervalence-Transfer Bands for Mixed-Valence Oligo(ferrocene-1,1′-diyl)s

Examining the electronic spectra of mixed-valence complexes is very helpful in allowing us to elucidate the magnitude of internuclear electronic interaction directly. Ever since the appearance of the pioneering theoretical work by Hush[24] in the 1950s, theoretical investigation of the intervalence-transfer (IT) band (or MMCT band) in mixed-valence complexes has been of continuing interest. The regular method of analyzing IT bands is to converge their parameters into the mixing coefficient, α, and resonance energy, H_{AB}, according to Eqs. 3 and 4, respectively:

$$\alpha^2 = (4.2\times10^{-4}/m_{\mathrm{d}}m_{\mathrm{a}})\varepsilon_{\mathrm{max}}\Delta\nu_{1/2}\nu_{\mathrm{max}}^{-1}r^{-2} \qquad (3)$$

$$H_{\mathrm{AB}} = \nu_{\mathrm{max}}\alpha \qquad (4)$$

where m_{d}, m_{a}, and r are the number of donor sites, the number of acceptor sites, and the donor-acceptor distance, respectively. The value of $\Delta\nu_{1/2}$ for a homonuclear mixed-valence dimer at 300 K is given as Eq. 5:

$$\Delta\nu_{1/2} = (2310\ \nu_{\mathrm{max}})^{1/2} \qquad (5)$$

One of the recent advances is the theory of Creutz, Newton, and Sutin (CNS) on the relation of metal–ligand and metal–

metal coupling elements.[42] The role of the bridging ligand between the metal nuclei on the electron exchange process is distinctly comprehended by this CNS theory. Experimental support for the CNS model has been presented for some mixed-valence complexes other than ferrocene oligomers.[29,43]

Morrison and Hendrickson have reported that the IT band of biferrocenium monocation has two peaks at 77 K.[38a] The analysis by Dong et al. on IT bands of biferrocene observed at room temperature was carried out assuming one broad peak, and it was reported that Eq. 5 was applicable for biferrocene derivatives.[8b] As for the IT bands of higher unsubstituted oligo (ferrocene-1,1′-diyl)s in the mixed-valence states, only one report by Brown et al. on the IT bands of monocation and dication of terferrocene and dication of quaterferrocene (tetramer) has been published .[31]

The first systematic study on the effects of IT bands on the number of nuclei and the oxidation number was carried out for oligo(dihexylferrocene-1,1′-diyl)s, $\mathbf{2_2}$–$\mathbf{2_6}$.[44] All the oxidation states of $\mathbf{2_2}$–$\mathbf{2_6}$ were generated by a quantitative chemical oxidation method using 1,1'-dichloroferrocenium hexafluorophosphate as the oxidizing agent in CH_2Cl_2–acetone. The $\Delta\nu_{1/2}$ values obtained for the oligo(ferrocene-1,1′-diyl)s are in the range of 3100–4000 cm^{-1}, which is similar to the range of the values calculated by Eq. 5, 3200–3800 cm^{-1}. Figure 2 displays the dependence of ν_{max} values of the IT band on the oxidation state and the number of ferrocene units. Characteristic features in the figure 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.

The shift in ν_{max} of IT bands can be analyzed based on a model assuming that the mixed-valence states are a linear combination of Red and Ox as follows. In the case of the biferrocenium cation, $\mathbf{2_2}^+$, photoexcitation of Red–Ox yields Ox–Red and thus no alteration in the internuclear distance is necessary during the relaxation process. On the other hand, the terferrocenium monocation, $\mathbf{2_3}^+$, of which the ground and electron-transferred excited states are Red–Ox–Red and Ox–Red–Red, respectively, needs a change in the internuclear distance in the relaxation process, since the appropriate distance for Red–Ox is different from that for Red–Red. Similar internuclear distance alteration occurs for the terferrocenium dication, $\mathbf{2_2}^{2+}$, of which the ground and excited states are Ox–Red–Ox and Red–Ox–Ox, respectively. In this case the combination Red–Ox changes into Ox–Ox, resulting in the largest distance alteration, as the Red–Ox distance is the shortest due to the attractive interaction by the electronic delocalization and the Ox–Ox distance is the longest due to the electrostatic repulsion.[34,35]

The consideration noted above leads to a conclusion that the photochemical intervalence transfer of Red–Ox–Red (or Ox–Red–Ox) requires more energy compared with the case of biferrocene not only due to the energetic difference between unequal ground states before and after photo–electron transfer but also due to a strain derived from the difference in internuclear distance between Red–Ox and Red–Red (or Ox–Ox) combinations (see Fig. 3). As it can be deduced that the extra energy for the change from Red–Ox to Ox–Ox is the largest, this energy, u_{ex}, is employed as the factor for rationalization of the ν_{max} shift due to the change in oxidation number of the higher oligomers. The dependency of the ν_{max} on the number of ferrocene units and the oxidation states is qualitatively rationalized by taking into account u_{ex} = 13 kJ mol^{-1} as shown in Fig. 2.

4. Electrical Conductivity and Photoconductivity of Mixed-Valence Oligo- and Poly(ferrocene-1,1′-diyl)

Conductivity of the mixed-valence polymer complexes has been studied for both conjugated and non-conjugated systems. Poly(ferrocene-1,1′-diyl) is insulating ($\sigma = 10^{-12}$,[3] 0.4–8 × 10^{-10} S cm^{-1} [45]) in the neutral sate, but its conductivity increases dramatically when it is partially oxidized (doped). Pittman et al. have reported the conductivities of ca. 10^{-6} and 10^{-8} S cm^{-1} for I_2 and TCNQ doped complexes, respectively.[46] Sanechika et al. have presented higher values, 1 × 10^{-4} and 4 × 10^{-2} S cm^{-1}, for I_2 and TCNQ doped complexes, respectively, for the polymer samples with higher molecular weight (M_n = 5

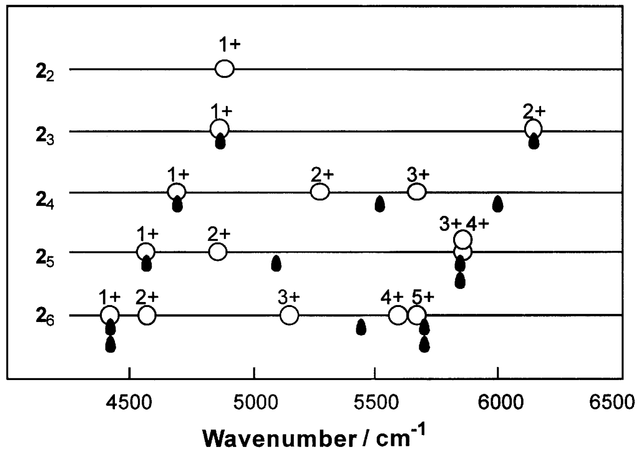


Fig. 2. The ν_{max} values of IT bands for the mixed-valence states of $\mathbf{2_2}$–$\mathbf{2_6}$; measured in CH_2Cl_2–acetone (1:1 in volume) (○), and calculated with u_{ex} = 13 kJ mol^{-1} (▲). The numbers in the figure refer to oxidation numbers.

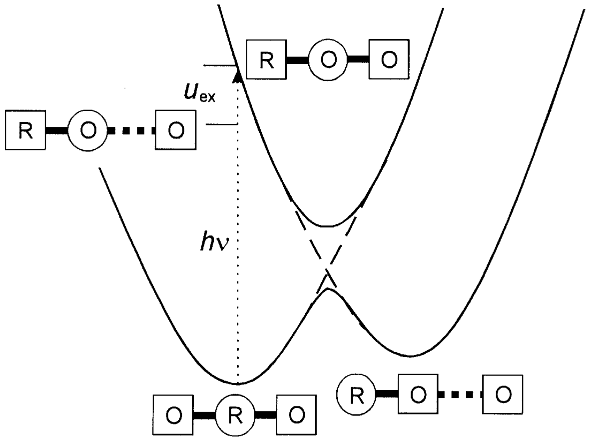


Fig. 3. Schematic illustration of the energy diagram on the photochemical intervalence-transfer process of the second mixed-valence state of the trimer.

× 10^3).[45] These lower conductivities compared with those of π-conjugated organic conducting polymers such as polyacetylene, polypyrrole, polythiophene, and polyaniline in the doped state occur because the charge is considerably localized at the metal sites in the conjugated ferrocene polymers where the ferrocene units are involved in the main chain.

Although poly(ferrocene-1,1′-diyl) in the partially oxidized valence state has an intrinsic semiconducting nature, as noted above, photoconductivity has been found for the complexes of oligo(dihexylferrocene-1,1′-diyl)s, $\mathbf{2}_2$–$\mathbf{2}_6$, and poly(dihexylferrocene-1,1′-diyl) ($\mathbf{2}_\mathrm{p}$) with TCNE.[33,47] The complexes exhibit both charge-transfer (CT) and intervalence-transfer (IT) bands in the near-IR region. Mössbauer spectra of $\mathbf{2}_3$–TCNE and $\mathbf{2}_4$–TCNE with $x = 2$ at low temperatures (50–293 K) give both a singlet peak due to $\mathrm{Fe^{III}}$ and a doublet one due to $\mathrm{Fe^{II}}$. The parameters obtained are IS = 0.42 mm $\mathrm{s^{-1}}$ for the former and IS = 0.51 mm $\mathrm{s^{-1}}$, QS = 2.25 mm $\mathrm{s^{-1}}$ for the latter. This appearance of both $\mathrm{Fe^{II}}$ and $\mathrm{Fe^{III}}$ species indicates that the charge is localized at the time scale of Mössbauer spectroscopy (10^{-8} s). The ratio of $\mathrm{Fe^{III}}$ to total Fe estimated from the peak area and intensity of the spectra depends on the temperature in a range of 0.4–0.5. This dependence is almost coincident with the one theoretically evaluated from the formal potentials of $\mathbf{2}_3$, $\mathbf{2}_4$ and TCNE, and the Nernst equation. Photoirradiation of the $\mathbf{2}_\mathrm{p}$–TCNE CT complex with near-IR light gives higher electronic conductivity than does irradiation with visible light. A positive dependence is observed between the near-IR photoconductivity and the number of ferrocene units in oligo- and poly-(dihexylferrocene-1,1′-diyl)s (Fig. 4). These results indicate that both IT and CT band excitation cause photoconductivity. The CT band excitation would alter the charge distribution on the poly(ferrocene-1,1′-diyl) chain, and IT band excitation would accelerate the intra-chain charge-transport rate.

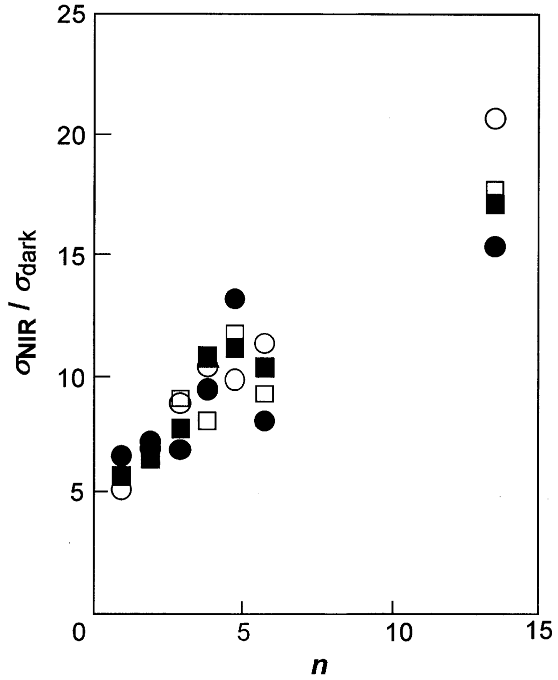


Fig. 4. Plots of near-IR photoconductivity of **2**–TCNE complexes given by the ratio of conductivity under near-IR irradiation to that in the dark ($\sigma_\mathrm{NIR}/\sigma_\mathrm{dark}$) vs. the number of ferrocene units in **2** (n). The molar ratios of TCNE to the ferrocene units in **2** were 0.4 (●), 0.5 (■), 0.6 (○), and 0.75 (□).

5. Dependence of Redox Properties on the Spacers in Conjugated Ferrocene Oligomers

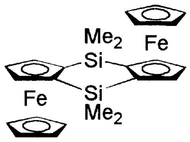
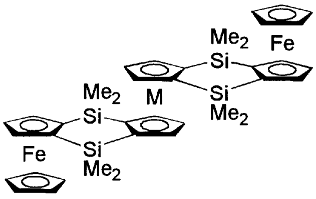
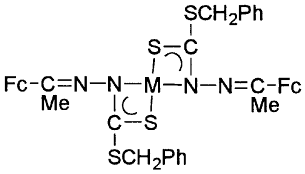
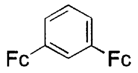
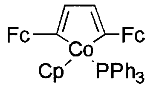
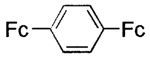
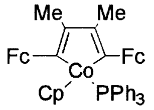
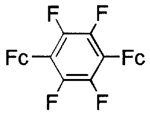
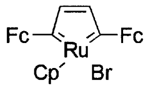
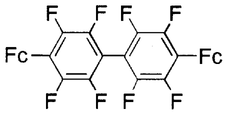
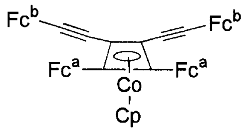
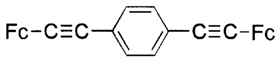
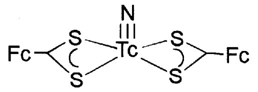
Effects of the spacer group on the formation and properties of the mixed-valence state of the conjugated ferrocene dimers have been extensively studied by both the electrochemical and spectroscopic methods. It should be noted that a characteristic feature in the electronic spectra of ferrocene dimers with conjugated spacer groups is an appearance of metal-to-ligand charge transfer (MLCT) bands in the neutral form besides IT bands in the mixed-valence state. Fc–CH=CH–Fc, where Fc refers to (η^5-$\mathrm{C_5H_5}$)Fe(η^5-$\mathrm{C_5H_4}$–), has an MLCT band at 458 nm with ε = 1450 $\mathrm{M^{-1}\,cm^{-1}}$ in $\mathrm{CH_2Cl_2}$,[16] and Fc–C≡C–Fc has a band at 453 nm with ε = 820 $\mathrm{M^{-1}\,cm^{-1}}$ in $\mathrm{CHCl_3}$.[11a] Fc–N=N–Fc ($\mathbf{6}_2$) has a band at 533 nm with ε = 4170 $\mathrm{M^{-1}\,cm^{-1}}$ in $\mathrm{CH_2Cl_2}$.[48] In this section, only redox properties of conjugated ferrocene dimers are appraised.

Table 2 summarizes redox potentials of conjugated ferrocene dimers with a single bridge. The difference between the two redox potentials, $\Delta E^{0'}$, is given as $u_\mathrm{OO} + u_\mathrm{RR} - 2u_\mathrm{OR}$ in the neighboring site interaction model. This equation is an alternative expression of Eq. 2 and indicates that both electrostatic repulsion included in u_OO and electron delocalization involved in u_OR are the main factors dominating $\Delta E^{0'}$. As noted above, comparison of the u_OO and u_OR values for oligo(ferrocene-1,1′-diyl) (**2**) and oligo(ferrocenyldimethylsilane) (**3**), assuming $u_\mathrm{RR} = 0$, shows that the difference in $\Delta E^{0'}$ between $\mathbf{2}_2$ and $\mathbf{3}_2$, 0.30 – 0.14 = 0.16 V, is composed of the difference in $-2u_\mathrm{OR}$, 13 kJ $\mathrm{mol^{-1}}$ in the main part, and that in u_OO, 3 kJ $\mathrm{mol^{-1}}$ as a small contribution. The difference in u_OO can be ascribed to the nearer internuclear distance in $\mathbf{2}_2$ compared with that in $\mathbf{3}_2$. It is not possible to separate the u_OO and u_OR values just from the redox potentials of dimers, but the consideration above indicates that the relative evaluation on the degree of electron delocalization in the mixed-valence state is possible using $\Delta E^{0'}$ when the internuclear distances are similar to each other.

There are several reports on the quantitative estimation of the structural factor that affects the internuclear electron delocalization. Ribou et al. have reported the dependence of internuclear electron transfer on the metal–metal distance using $\mathrm{Fc(CH{=}CH)}_n\mathrm{Fc}$ (n = 1–6), by both $\Delta E^{0'}$ and IT bands.[16] The $\Delta E^{0'}$ decreases with increasing n, and it is almost zero when n = 4. Patoux et al. have shown the topological effects of *m*-phenylene-bridged ferrocene dimers.[17] Compared with *o*- and *p*-phenylene-bridged dimers, *m*-phenylene-bridged dimers exhibit smaller $\Delta E^{0'}$, that is, a weak internuclear interaction. By introducing the electron-withdrawing substituents on the 5-position of *m*-phenylene (1,3-phenylene), both $E^{0'}_1$ and $E^{0'}_2$ shift in the positive direction, but the $\Delta E^{0'}$ values remain constant in the range of 80–100 mV.

Recently, several systems where a transition metal is in-

Table 2. Differences between Two Redox Potentials Due to Ferrocene Moieties, $\Delta E^{0'}$, for Conjugated Ferrocene Dimers

Complex	$\Delta E^{0'}$/V	Ref.	Complex	$\Delta E^{0'}$/V	Ref.
Fc–Fc	0.35	12			
$\text{Fc–C}{\equiv}\text{C–Fc}$	0.13	12		0.21	20a
$\text{Fc}(\text{C}{\equiv}\text{C})_2\text{Fc}$	0.10	12			
Fc–CH=CH–Fc	0.17	16		0.065 (M = Cr$^{\text{III}}$) ca. 0 (M = Co$^{\text{III}}$)	20c
$\text{Fc}(\text{CH=CH})_2\text{Fc}$	0.13	16			
$\text{Fc}(\text{CH=CH})_3\text{Fc}$	0.09	16			
$\text{Fc}(\text{CH=CH})_4\text{Fc}$	ca. 0	16		0.04 (M = Mn) ca. 0 (M = Cu)	18
Fc–N=N–Fc	0.18	48			
	0.13	18			
	0.09	18		0.39	49a
	0.10	18		0.47	49b
	ca. 0	19		0.24	49c
	ca. 0	19		0.23$^{\text{a)}}$	50
	0.07	50		ca. 0	51

a) Due to Fc^{a}–Fc^{a} interaction.

volved in the spacer have been reported.[18,20,49–51] Atzkern et al. have reported that $\Delta E^{0'} = 65$ and ca. 0 mV when the incorporated metal is Cr, and Co, respectively, in the trinuclear metallocenes which are η^5-cyclopentadienyl-bridged by two adjacent Me_2Si groups.[20c] Yu et al. have reported that a Ni complex of *S*-benzyl-3-(1-ferrocenylethylidene)dithiocabazate shows redox potential separation, 44 mV, but no separation occurs for the Cu complex.[18] These results indicate the important role of d-orbitals of the metals involved in the spacer group. The author and co-workers have studied ferrocene dimers with conjugated metallacyclic spacers such as cobaltacyclopentadiene and ruthenacyclopentatriene.[49] It is noteworthy that $\Delta E^{0'} = 0.39 - 0.47$ V, larger than the separation of biferrocene, 0.35 V, when cobaltacyclopentadienylene is inserted, while most of the dimers with singly bridged spacers between ferrocene nuclei have $\Delta E^{0'}$ values smaller than that of biferrocene. This is ascribed to the strong assistance of the electron exchange between ferrocene nuclei via cobalt, since the cobaltacyclopentadiene unit has an aromatic nature and the HOMO of cobaltacyclopentadiene locates at a similar energy level of ferrocene.[52]

Redox potential data are limited for the ferrocene oligomers higher than dimers. Barlow et al. have reported that a single-carbon bridged ferrocene trimer, $\text{FcCMe}_2\text{Fc}'\text{CMe}_2\text{Fc}$, where Fc′ refers to $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{–})_2$, exhibits three-step 1e^- oxidation at $E^{0'} = -0.14, 0.00$, and 0.20 V vs. ferrocenium/ferrocene.[26] This affords $u_{\text{OR}} = -7$ kJ mol^{-1} and $u_{\text{OO}} = 3$ kJ mol^{-1}, assuming $u_{\text{RR}} =$

0, indicating stronger delocalization in the mixed-valence state than the isostructural single–silicon bridged oligomers, oligo(ferrocenyldimethylsilane)s, **3**, as noted above.

A series of cumulene-bound ferrocene tetramers, $(Fc)_2C_n(Fc)_2$, have been synthesized and their electrochemical properties examined by Bildstein et al.[22] The redox properties are as follows: $n = 2$, four separate $1e^-$ oxidations; $n = 3$, two separate $1e^-$ oxidations followed by a further $2e^-$ oxidation; $n = 4$, two $2e^-$ oxidations separated by $\Delta E^{0'} = 0.16$ V; $n = 5$, two $2e^-$ oxidations separated by $\Delta E^{0'} = 0.09$ V; and $n = 6$; one $4e^-$ oxidation. Maclachlan et al. have reported that $SiFc_4$ is oxidized with $1e^-$ stepwise at –0.03, 0.15, 0.29, and 0.39 V vs. ferrocenium/ferrocene.[23]

6. Redox and Optical Properties of Azo-Bridged Ferrocene Oligomers

Azoferrocene $\mathbf{5_2}$, is one of the π-conjugated ferrocene dimers discussed in the previous section and also one of the simplest analogues of azobenzene with two redox–active metal complex units. Synthesis of azoferrocene, $\mathbf{5_2}$, was first reported by Nesmeyanov et al. in 1961.[53] Although $\mathbf{5_2}$ is an intriguing complex since the azo group has been known as the representative photoisomerizable unit, only a few studies have been reported on azoferrocene. The IT band of its monocationic form in the mixed-valence state is reported by Delgado–Pena et al.[37c] X-ray crystallography of an azoferrocene crystal obtained in ambient conditions has determined that the azo moiety is in the *trans* form and the two cyclopentadienyl rings of two ferrocene units and the azo moiety are almost on the plane best for the π-conjugation.[48a] The ferrocene moieties are on the opposite side of the plane, and the Fe–Fe distance is 6.80 Å, indicating little through-space interaction between the ferrocene nuclei. Syntheses of higher azo-bridged ferrocene oligomers such as trimers, Fc–N=N–Fc′–N=N–Fc ($\mathbf{5_{3a}}$) and Fc–Fc′–N=N–Fc ($\mathbf{5_{3b}}$), and a polymer composed of $[-(Fc'-N{=}N-Fc')_{0.6}-(Fc'-Fc')_{0.4}-]_n$ were carried out by a reaction of dihexylfulvalene dianion with $FeCl_2(THF)_2$.[48]

The *trans*-azo bridge acts as a spacer assisting the electron exchange between ferrocene moieties, as in the example given for azoferrocene in Table 2. The trimer $\mathbf{5_{3a}}$ in aprotic solvents such as CH_2Cl_2 or THF exhibits a cyclic voltammogram showing reversible $2e^-$ and $1e^-$ oxidation waves, contrary to the behavior of terferrocene (three $1e^-$ waves) as noted above. Analysis based on the neighboring site interaction model indicates that the behavior of $\mathbf{5_{3a}}$ can be rationalized by the assumption 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.[48a] Similar two-step $2e^-$ and $1e^-$ oxidation is observed in a perfluorobiphenylene-linked ferrocene trimer in which the spacer group does not assist the internuclear electronic interaction but gives a strong electron-withdrawing effect.[19c] It is thus valuable to emphasize that even if there is a considerable internuclear electronic interaction, two-step oxidation is observed when the terminal site is oxidized first as $\mathbf{5_{3a}}$. This charge distribution in the mixed-valence states of $\mathbf{5_{3a}}$ is supported by the characteristics of IT bands.[48a] An asymmetrical complex, $\mathbf{5_{3b}}$, undergoes a three-step $1e^-$ oxidation, and the two mixed-valence forms can be roughly expressed as $Fc^+-Fc'-N_2-Fc$ and $Fc^+-Fc'-N_2-Fc^+$.

Significant solvation effects on the IT bands of the conjugated ferrocene dimers have been recognized, and the effects of solvents on the electron exchange rates have been analyzed for biferrocene and Fc–C≡C–Fc, based on the Marcus–Hush theory.[54] Azo-bridged ferrocene oligomers also show a marked dependence on the redox potentials and IT band characteristics of the solvent. A detailed analysis by the author and co-workers have verified that the solvent effect on $\nu_{\max}$ of the IT band of $\mathbf{5_2}^+$, $\mathbf{5_{3b}}^+$, and $\mathbf{5_{3b}}^{2+}$ cannot be interpreted using only the parameters in the Marcus–Hush theory, and 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.

The absorption of the MLCT band at 534 nm diminishes and a new band appears and increases at 672 nm with the oxidation to $\mathbf{5_2}^+$. The new band can be assigned to a ligand-to-metal charge transfer (LMCT) band with an electron transfer from the π orbital of the azo group to a Fe(III) d orbital. Similar LMCT bands appear in the mixed valence state of $\mathbf{5_{3a}}$ and $\mathbf{5_{3b}}$. More donating solvent affords higher IT and LMCT energy of $\mathbf{5_2}$, $\mathbf{5_{3a}}$, and $\mathbf{5_{3b}}$ in the mixed-valence states, as shown in Fig. 5, indicating the hole-transfer mechanism.[42]

The author and co-workers recently found that a photoisomerization reaction of azoferrocene proceeds in polar solvents such as benzonitrile and DMSO through both π-π* transition of the azo-group with a UV light (365 nm) and metal–to-ligand charge transfer (MLCT) transition with a green light (546 nm).[55] The *cis*-azoferrocene shows one-step $2e^-$ oxidation waves at a potential less positive than that of *trans*-azoferrocene by 0.3 V. The considerable shift of the oxidation potential to the negative potential by the conversion from the *trans* form to the *cis* form indicates that the electron-withdrawing nature of the azo group is retarded in the *cis* form. The diminishment of $\Delta E^{0'}$ (see Table 2) denotes that the internuclear electronic interaction decreases drastically by the conversion. We deduced that the twisted structure of the *cis* form results in loss of π-conjugation ability.

7. Concluding Remarks

In this account, recent studies on the fundamental properties of conjugated ferrocene oligomers were presented. The results indicate that the simple method based on the neighboring-site electronic interaction is useful to analyze redox and optical properties of the oligomers. It should be emphasized that this method would be generally applied to other systems involving multiple redox nuclei with internuclear electronic communication.

Although mixed-valence complexes have been studied for decades, interest in both basic and applied researches on the ferrocene oligomers and polymers has continued to increase. Some attempts to combine the unique physical properties of the conjugated ferrocene oligomers and polymers with other functional materials to construct molecular systems responsive

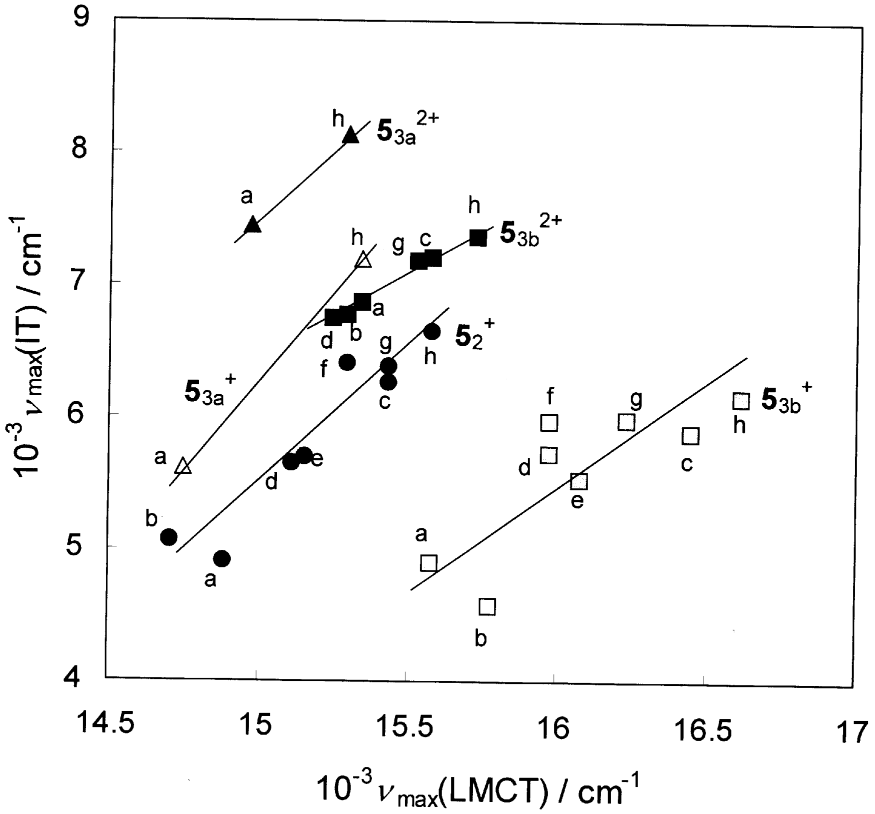


Fig. 5. Plots of ν_{max}(IT) vs. ν_{max}(LMCT) for mixed-valence states of **5**$_2$, **5**$_{3a}$, and **5**$_{3b}$ in CH$_2$Cl$_2$ (a), 1,2-dichloroethane (b), nitromethane (c), nitrobenzene (d), PhCN (e), MeCN (f), acetone (g), and THF (h).

to additives or outer fields have been also started. Dong et al. have reported on crown ether-bound biferrocene, in which the redox potentials are shifted by capturing metal ions within the crown ether.[8e] The author and co-workers have synthesized oligo(ferrocene-1,1′-diyl)-modified Au clusters and found electrochemical deposition of the clusters to form redox active cluster films.[56] Manners et al. have reported the synthesis of shaped ceramics with tunable magnetic properties by thermal cracking of poly(ferrocenylsilane)s.[57] These studies present possibilities of creating molecularly functional materials by the arrangement of original functionality of conjugated ferrocene oligomers and polymers.

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