

Dependence of intervalence-transfer bands for mixed-valence oligo(1,1'-dihexylferrocenylene)s on the oxidation number and the number of ferrocene units from two to six

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Intervalence-transfer (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 analysis of the absorption spectra of the oligomers oxidized quantitatively with 1,1'-dichloroferrocenium hexafluorophosphate, **1**, in CH₂Cl₂-acetone. 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 forms of the oligomers as the number of ferrocene units increases. A simple analysis of the shift in ν_{\max} of IT bands was made based on a model assuming that the mixed-valence states are a linear combination of reduced (Red) and oxidized (Ox) nuclei. It is qualitatively rationalized by taking into account the change in neighboring-site combination, especially between Red–Ox and Ox–Ox, formed by photoelectron transfer, which requires extra energy due to the strain in internuclear distance.

Spectroscopic investigation of mixed-valence complexes has been of continuing interest for a few decades, ever since the appearance of the pioneering theoretical work by Hush.¹ Creutz *et al.*² presented a theory on the relation of metal–ligand and metal–metal coupling elements, and experimental support of this theory has recently been presented by Crutchley and co-workers.³

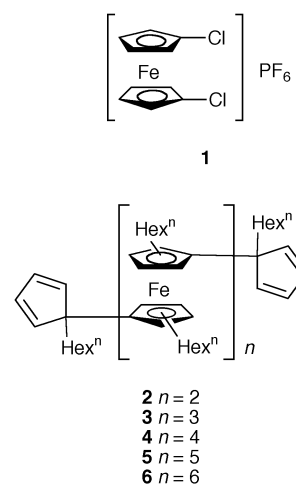
Most analyses on mixed-valence states have been focused on binuclear complexes such as the monocation of biferrocene, which is a typical example of a Robin and Day class II mixed-valence complex.^{4,5} There is continuing interest in studying its internuclear electronic interaction.^{6–11} A variety of other ferrocene dimers^{12–17} and some trimers¹⁸ with conjugated spacer groups have also been investigated. In these investigations electrochemical and spectroscopic methods are powerful tools to rule out the effect of internuclear distance on the magnitude of internuclear electronic interaction.

The effects of intervalence transfer (IT) bands on the number of nuclei have not been well recognized. The spectroscopic properties of oligo(1,1'-ferrocenylene) have been reported up to the tetramer (only the IT band of the dicationic form has been identified for the tetramer).¹¹ It should be noted that the poor solubility of unsubstituted oligo- and poly-(1,1'-ferrocenylene) is a problem in studying its fundamental properties. Manners and his co-workers¹⁹ have isolated oligo(ferrocenyldimethylsilane)s from the dimer to the nanomer, of which the electrochemical and optical properties have been systematically studied. In this series of ferrocene oligomers, however, IT bands at all the oxidation states could not be defined, since not all the redox potential differences are large enough to form the given mixed-valence state separately due to weaker internuclear interaction through the dimethylsilylene moiety compared with that of oligo(1,1'-ferrocenylene).

We have recently synthesized oligo- and poly-(1,1'-dihexylferrocenylene), soluble derivatives of oligo- and poly-ferrocenylene, and determined their redox potentials concerning all steps of one-electron transfer up to the heptamer.^{20,21} The dependence of the redox potentials on the number of ferrocene units can be interpreted based on a modification of the theory by Aoki and Chen²² that assumes partly oxidized oligo(ferro-

cenylene) as a sequence of reduced (Red) and oxidized (Ox) sites and uses first and second neighboring site interaction energies.²³ The second neighboring site interaction is important to separate the oxidation reactions into 1e⁻ electron transfer steps for oligomers with more than five units.²³

In the present study we have generated all the oxidation states of oligo(dihexylferrocenylene)s from the dimer to the hexamer (**2–6**) by a chemical oxidation method using 1,1'-dichloroferrocenium hexafluorophosphate **1** and measured their electronic spectra to recognize how the IT band changes as the oxidation stage and the number of ferrocene units increases. Preliminary results were reported in a previous communication.²⁴ A simple attempt to analyse the change in ν_{\max} of the IT bands with the oxidation number has been carried out based on the theory assuming the mixed-valence state as a linear combination of Red and Ox as given below.



In the case of the biferrocenium cation, **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, **3**⁺, of which

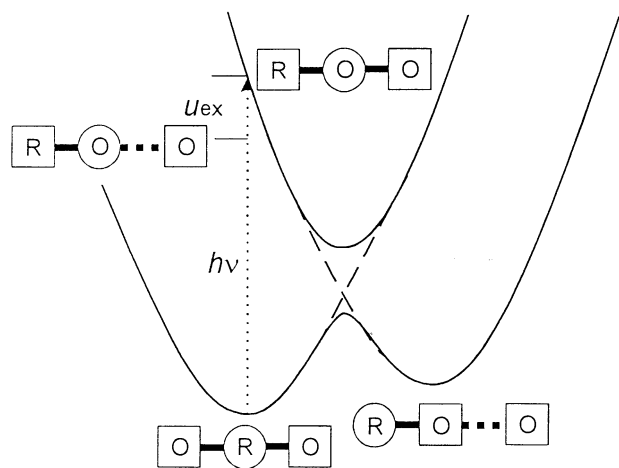


Fig. 1 Schematic illustration of the energy diagram for the photochemical intervalence-transfer process of the second mixed-valence state of the trimer.

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, 3^{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.^{22,23}

Judging from the situation noted above, it is clear that the photochemical intervalence transfer of Red–Ox–Red (or Ox–Red–Ox) requires more energy compared with the case of ferrocene not only due to the energy difference between unequal ground states before and after photoelectron 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. 1). As we can deduce 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.

Experimental

1,1'-Dichloroferrocenium hexafluorophosphate **1** was prepared by the oxidation of 1,1'-dichloroferrocene²⁵ with sulfuric acid, followed by the addition of NH_4PF_6 , similar to the preparation of ferrocenium hexafluorophosphate.²⁶ Oligo(1,1'-dihexylferrocenylene)s **2–6** and poly(1,1'-dihexylferrocenylene) with $M_w = 4005$ (corresponding to 10 ferrocene units) and $M_w/M_n = 1.6$ were prepared as reported previously.²⁰ Dehydrated dichloromethane (Kanto Chemicals) and acetone (Kanto Chemicals, a guaranteed grade) redistilled from KMnO_4 were used for the measurements. UV-VIS-NIR spectra were monitored with a JASCO V-570 spectrometer.

Electrochemical measurements

A glassy carbon rod (outside diameter 3 mm, Tokai Carbon GC-20) was embedded in Pyrex glass, and the cross-section used as a working electrode. Cyclic voltammetry was carried out in a standard one-compartment cell under an argon atmosphere equipped with a platinum-wire counter electrode and a Ag–Ag⁺ reference electrode ($10 \text{ mmol dm}^{-3} \text{ AgClO}_4$ in $0.1 \text{ mol dm}^{-3} \text{ NBu}_4\text{ClO}_4\text{-MeCN}$, E° (ferrocenium–ferrocene in $0.1 \text{ mol dm}^{-3} \text{ NBu}_4\text{ClO}_4\text{-CH}_2\text{Cl}_2$) = $0.214 \text{ V vs. Ag-Ag}^+$) with a BAS CV-50W voltammetric analyzer.

Table 1 Formal potentials of compounds **1–6**^a

Substrate	E°_1	E°_2	E°_3	E°_4	E°_5	E°_6
1	0.472					
2	–0.137	0.197				
3	–0.162	–0.009	0.353			
4	–0.193	–0.062	0.178	0.399		
5	–0.183	–0.075	0.072	0.362	0.489	
6	–0.158	–0.113	0.018	0.218	0.418	0.465

^a E/V vs. Ag–Ag⁺ in $0.1 \text{ mol dm}^{-3} \text{ NBu}_4\text{ClO}_4\text{-CH}_2\text{Cl}_2$ + acetone.

Preparation of mixed-valence states of oligo(dihexylferrocenylene) and measurement of their spectra

For spectroscopic measurements we used a $10 \times 10 \text{ mm}$ quartz cell connected to a Pyrex glass tube with six branched spaces to keep the oxidizing material. Set-up of the samples in the cell was carried out in an argon-filled dry-box. A given volume of an acetone solution of compound **1** was put in each branch of the cell, and the solvent carefully evaporated, leaving a solid residue. A CH_2Cl_2 –acetone solution of oligo(dihexylferrocenylene)s was put in the cell, and the cell closed with a stopcock. The cell was removed from the dry-box, and the spectrum measured before and after the sample solution was mixed stepwise with the oxidant in the six branches. This manipulation was repeated to get a series of successive changes in the spectrum of each oligomer with increasing amount of oxidant.

Analysis of IT bands in the mixed-valence states

Using the redox potentials of compound **1** and oligo(dihexylferrocenylene)s and the Nernst equation, we calculated the dependence of the ratio of the species with different oxidation numbers on the mole ratio of **1** to oligo(dihexylferrocenylene) using Mathematica software, Wolfram Research, on a personal computer. Genuine IT bands for each oxidation state of the oligomers were extracted by taking the ratio of the oxidation states into account. Deconvolution of the spectra was carried out using Grams/386 software, Galactic Industries, on a personal computer.

Results

The oxidizing agent that we used to generate all the mixed-valence states of oligo(dihexylferrocenylene)s have two to six ferrocene units, **2–6**, is 1,1'-dichloroferrocenium hexafluorophosphate, **1**. Formal potentials of **1–6** obtained by cyclic voltammetry as $E^{\circ} = (E_{\text{pa}} + E_{\text{pc}})/2$ are in Table 1. This oxidant was chosen because, first, its reduction potential is positive enough to form all the mixed-valence states even for the hexamer, **6**, and second the counter ion of the oxidized oligo(dihexylferrocenylene)s is PF_6^- with no possibility to form charge-transfer complexes that may interfere with the IT bands of mixed-valence complexes appearing in the near-IR region. The wide optical windows of 1,1'-dichloroferrocenium ion ($>700 \text{ nm}$) and 1,1'-dichloroferrocene ($>500 \text{ nm}$) can display the IT bands distinctly.

In an actual experiment a given amount of compound **1** was mixed stepwise with a solution of oligoferrocenylene under argon. A mixed solvent, CH_2Cl_2 –acetone (1 : 1 in volume), was used in order to dissolve the samples in all oxidation states. A typical example of observed spectra for the trimer **3** is displayed in Fig. 2. When the oxidant **1** is added at a mole ratio to **3**, x , of 0.73 : 1, a broad peak appears around 2000 cm^{-1} . Its intensity increases at $x = 1.1$, then shifts to a shorter wavelength until $x = 2.2$, and finally decreases with increasing values of x . Each spectrum is due to mixtures of four oxidation states, 3^0 , 3^+ , 3^{2+} and 3^{3+} , and the IT bands of mixed-valence species, 3^+ and 3^{2+} , are the origin of the absorption peak. Pure spectra of 3^+ and 3^{2+} were extracted using the mole ratios of the four species

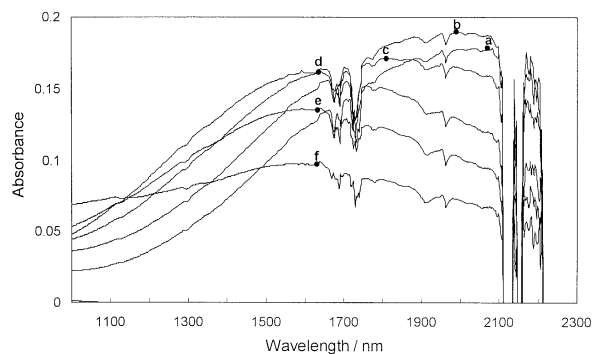


Fig. 2 Near-IR spectra of compound **3** oxidized stepwise with **1** in CH_2Cl_2 -acetone. The mole ratio of **1** to **3** is 0.73, 1.10, 1.46, 2.19, 2.92 and 4.38:1 for (a)–(f), respectively.

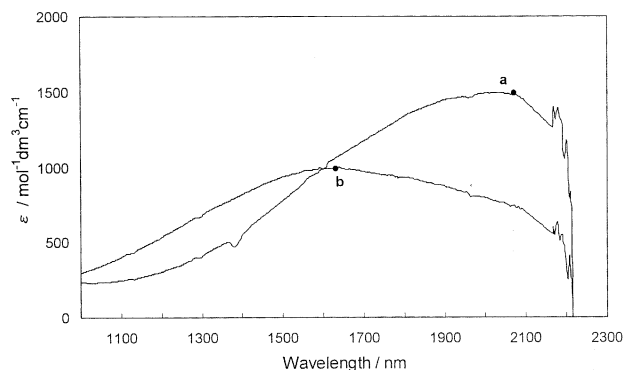


Fig. 3 Near-IR spectra of complexes **3⁺** (a) and **3²⁺** (b) in CH_2Cl_2 -acetone.

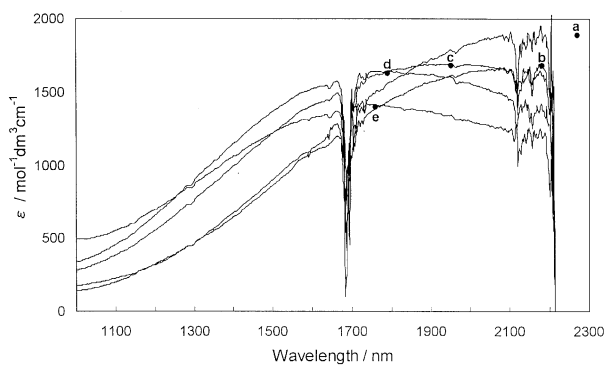


Fig. 4 Near-IR spectra of complexes **6⁺** (a), **6²⁺** (b), **6³⁺** (c), **6⁴⁺** (d) and **6⁵⁺** (e) in CH_2Cl_2 -acetone.

evaluated from redox potentials of **3** as reported¹⁸ and **1** ($E^{0'} = 0.472$ V in 0.1 mol dm^{-3} NBu_4ClO_4 - CH_2Cl_2 + acetone (1:1 in volume) vs. $\text{Ag}-\text{Ag}^+$) and the Nernst equation. The spectra thus obtained are displayed in Fig. 3. It can be seen that ν_{max} is higher and ϵ_{max} is smaller for **3²⁺** than for **3⁺**.

Similar procedures were carried out to attain genuine IT bands for all the mixed-valence states of compounds **4**, **5** and **6**, and the results for **6** are given in Fig. 4. Morrison and Hendrickson⁶ have reported that the IT band of biferrocene has two peaks at 77 K. The analysis by Dong *et al.*⁹ on IT bands of biferrocene observed at room temperature was carried out assuming one broad peak. We have also analysed each IT band with a single Gaussian curve (see Fig. 5 for **3⁺** and **3²⁺**). Our trials of deconvolution analysis resulted in a conclusion that the fitting of IT bands with multiple Gaussian curves gave no significant advances in accuracy over fitting them with a single curve, even for higher oligomers. We thus present the parameters of a single band ν_{max} , ϵ_{max} and the half-peak width, $\Delta\nu_{1/2}$,

Table 2 Parameters of IT bands for oligo(dihexylferrocenylene)s

Substrate	$\nu_{\text{max}}/\text{cm}^{-1}$	$\epsilon_{\text{max}}/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$	$\Delta\nu_{1/2}/\text{cm}^{-1}$	$\epsilon_{\text{max}}\Delta\nu_{1/2}/\nu_{\text{max}}/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$	$10^{-10} \epsilon_{\text{max}}\Delta\nu_{1/2}\nu_{\text{max}}/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$
2⁺	4870	1060	3740	814	1.93
3⁺	4830	1490	3850	1188	2.77
3²⁺	6140	990	3910	630	2.38
4⁺	4700	1730	4000	1472	3.25
4²⁺	5280	1500	3880	1102	3.07
4³⁺	5680	1250	3570	786	2.53
5⁺	4550	1500	3750	1236	2.56
5²⁺	4860	1400	3550	1023	2.39
5³⁺	5860	1430	3550	866	2.97
5⁴⁺	5860	1010	3340	576	1.98
6⁺	4410	1890	3800	1629	3.17
6²⁺	4580	1680	3940	1445	3.03
6³⁺	5140	1680	4010	1311	3.46
6⁴⁺	5600	1630	3820	1112	3.49
6⁵⁺	5680	1400	3570	880	2.84

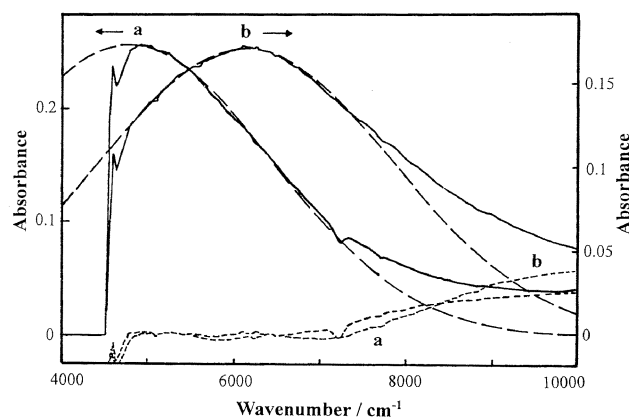


Fig. 5 Curve-fitting results of IT bands for complexes **3⁺** (a) and **3²⁺** (b) with a single Gaussian curve, displaying experimental (—), fitted (---) and residual (----) curves.

for the bands in Table 2. It should be noted that ν_{max} and ϵ_{max} are accurate but some error in $\Delta\nu_{1/2}$ (ca. 10%) may exist because of the broadness of the IT band and overlapping of the transition ${}^2\text{E}_{2g} \rightarrow {}^2\text{E}_{1u}$ for the ferrocenium ion.¹¹ The parameters for a band without a distinct peak maximum such as **6⁺** were estimated from the fitted Gaussian curve.

The parameters of IT bands of complexes **3⁺** and **3²⁺** are similar to those for unsubstituted terferrocene reported previously.¹¹ However, the values reported for the IT band of quaterferrocenium(2+), $\tilde{\nu}_{\text{max}} = 5590$ cm^{-1} and $\epsilon_{\text{max}} = 1720$ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$,¹¹ are different from those for **4²⁺**, $\tilde{\nu}_{\text{max}} = 5280$ cm^{-1} with $\epsilon_{\text{max}} = 1500$ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$, obtained in this study. This is probably due to the difference of the solvent employed for the measurement (CH_2Cl_2 -acetonitrile was used in ref. 11).

The ν_{max} dependence on the number of ferrocene units and the oxidation number is displayed in Fig. 6. A general tendency is that ν_{max} shifts to higher wavenumbers and ϵ_{max} to lower values according to an increase in the oxidation number. Rulkens *et al.*¹⁹ have also reported the shift of IT bands to higher wavenumbers according to the increase in the oxidation degree for oligo(ferrocenyldimethylsilane)s). The ν_{max} for the monocation shifts to lower wavenumbers as the number of ferrocene units increases, and the differences in ν_{max} are small between **5³⁺** and **5⁴⁺**, **6⁺** and **6²⁺** and **6⁴⁺** and **6⁵⁺**, as seen in Fig. 6.

The IT bands of poly(dihexylferrocenylene) **7** for which the average number of ferrocene units is 10, were also measured upon oxidation using the dichloroferrocenium salt. An absorption peak appears at 2280 nm (4390 cm^{-1}) when a small portion

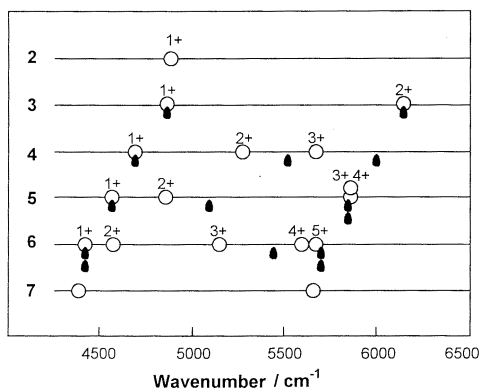


Fig. 6 Experimental (open circles) and theoretical (filled triangles) values of ν_{\max} of IT bands for compounds 2–7. As for 7, only the lowest and highest ν_{\max} obtained experimentally are given.

of the oxidant is added, and shifts to 1770 nm (5650 cm^{-1}) as the amount of oxidant increases. These lowest and the highest ν_{\max} values are marked in Fig. 6.

Discussion

It is intriguing to understand the IT bands of oligomers with more than three redox nuclei based on the Red–Ox linear combination model. In the case of the trimer, the ground state of the monocation can be expressed as Red–Ox–Red and the excited state is solely Ox–Red–Red. In the case of the tetramer monocation, the ground state is given as Red–Ox–Red–Red,^{21–23} and two forms, Ox–Red–Red–Red and Red–Red–Ox–Red, can be expected as the excited state. Consequently, there is a strong possibility of having more than two IT bands. It is, however, hard to separate the IT bands of higher oligomers into more than two peaks experimentally, as noted above. We therefore carried out the analysis of the IT bands as an averaged single peak involving several transitions.

The usual method to analyse IT bands is to converge their parameters into the mixing coefficient, a , and resonance energy, H_{AB} , according to eqns. (1) and (2), respectively,¹ where m_d , m_a

$$a^2 = (4.2 \times 10^{-4} / m_d m_a) \epsilon_{\max} \Delta\nu_{1/2} \nu_{\max}^{-1} r^{-2} \quad (1)$$

$$H_{AB} = \nu_{\max} a \quad (2)$$

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 by eqn. (3).

$$\Delta\nu_{1/2} = (2310 \nu_{\max})^{1/2} \quad (3)$$

It has been reported that eqn. (3) is applicable for ferrocene derivatives.⁹ If we apply eqn. (3) to examine $\Delta\nu_{1/2}$ for all oligomers, the calculated values are in the range $3200\text{--}3800 \text{ cm}^{-1}$, which is similar to the range of the obtained values, $3300\text{--}4000 \text{ cm}^{-1}$ (Table 2). In Table 2 are also given $\epsilon_{\max} \Delta\nu_{1/2} \nu_{\max}^{-1}$ and $\epsilon_{\max} \Delta\nu_{1/2} \nu_{\max}$ values that are proportional to a^2 and H_{AB}^2 , respectively, when m_d , m_a and r are constant in eqns. (1) and (2). The evaluation of m_d , m_a and r for higher oligomers is not meaningful at this stage, but we did observe a tendency of $\epsilon_{\max} \Delta\nu_{1/2} \nu_{\max}^{-1}$ to decrease monotonously as the oxidation number increased for each oligomer and that $\epsilon_{\max} \Delta\nu_{1/2} \nu_{\max}$ is higher for even-number oligomers, 4 and 6, than for odd-number oligomers, 3 and 5.

Here we attempt to rationalize the dependence of ν_{\max} values on the oxidation number displayed in Fig. 6 using the neighboring-site interaction model as mentioned in the introduction (Fig. 1). Our proposal that the extra energy for the

change from Red–Ox to Ox–Ox is the largest is actually seen in Fig. 6 where the difference in ν_{\max} between 2^+ and 3^+ is small but that between 2^+ and 3^{2+} is large. The extra energy for the change from Red–Ox to Ox–Ox, u_{ex} , is roughly estimated from the difference in ν_{\max} between 3^+ and 3^{2+} , that is 13 kJ mol^{-1} assuming that the extra energy for the change from Red–Ox to Red–Red is negligible. Only the change from Red–Ox to Ox–Ox is taken into account for higher oligomers in order to simplify further discussion.

The oxidation pathway of compound 4 is assumed to be Red–Red–Red–Red \rightarrow Red–Ox–Red–Red \rightarrow Red–Ox–Red–Ox \rightarrow Ox–Ox–Red–Ox \rightarrow Ox–Ox–Ox–Ox, as has been reported previously.^{20,21} As mentioned above, the photo-excited state of 4^+ can be Ox–Red–Red–Red or Red–Red–Ox–Red by the neighboring-site electron transfer, neither of which involves the change from Red–Ox to Ox–Ox.

The excited state of complex 4^{2+} , Red–Ox–Red–Ox, can be Ox–Red–Red–Ox, Red–Red–Ox–Ox or Red–Ox–Ox–Red in the transition probability ratio of $1/\sqrt{2}:1/2:1/\sqrt{2}$ provided that the energy difference between the two excited forms is not taken into account. As the changes to Red–Red–Ox–Ox and Red–Ox–Ox–Red involve u_{ex} , the overall extra energy is given as $\{(1 + \sqrt{2})/(1 + 2\sqrt{2})\}u_{\text{ex}}$. As for 4^{3+} , all the extra energies for the changes from Ox–Ox–Red–Ox to Ox–Red–Ox–Ox and Ox–Ox–Ox–Red are u_{ex} , so that the overall extra energy for Ox–Ox–Red–Ox is u_{ex} .

The extra energy of each mixed-valence state for compounds 5 and 6 is evaluated in a similar manner and given in Table 3. Using these parameters and $u_{\text{ex}} = 13 \text{ kJ mol}^{-1}$ estimated from the ν_{\max} values of 3 as noted above, the magnitudes of the wavenumber shifts are calculated and given in Fig. 6, where the ν_{\max} value for the monocationic form of the oligomers is adjusted as the reference.

These theoretical values are qualitatively consistent with the experimental ones involving small shifts between 5^{3+} and 5^{4+} , 6^{1+} and 6^{2+} and 6^{4+} and 6^{5+} . The discrepancy between the calculated and experimental values should be due to the considerable simplification of the model which takes into account only the change from Red–Ox to Ox–Ox for the extra energy, which neglects the contributions of possible photo-excited forms created by longer-range electron transfer to the second neighboring site, which may make too simple an estimation of the transition probability, and so on. Moreover, it should be noted that the expression using just the Red–Ox combination has limitations in manifesting the accurate nature of mixed-valence states of oligoferrocenylenes because there exist longer-range internuclear interactions as demonstrated by electrochemical study^{21,23} and because the full charge is not located at Ox sites as ascertained by IR study.²⁷ We also neglected the solvation effects which might be significantly different when the charge on the oligomers changes. It is important, however, to recognize how the theoretical approach using a simple Red–Ox combination model can explain the experimental results such as those we have obtained from the analysis of redox potentials. The result given in Fig. 6 is not unsatisfactory as the first step.

There remain some general tendencies to be interpreted depending on the number of nuclei. The most significant one is the shift of ν_{\max} to lower wavenumbers as the number of ferrocene units increases, especially from compound 3 to 6. We deduce that this is caused by the effect of longer-range internuclear interactions, because the second neighboring site interaction exists when the number of nuclei is more than 4. The analysis of redox potentials gives the second neighboring site interaction energy, u_{OXR} , as 3.7 kJ mol^{-1} , which is four or five times smaller than the first neighboring site interaction energy, implying that the interaction is not extended to further nuclei.²³ This seems to be supported by the result that the ν_{\max} value for the lightly oxidized form of 7 is not much lower than that of 6^+ , as shown in Fig. 6.

Table 3 Analysis of extra energy due to the change of neighboring site combination^a

Substrate	Initial state	Excited state	Probability	Extra energy	Total extra energy
2 ⁺	R-O	O-R	1	0	0
3 ⁺	R-O-R	O-R-R	1/√2	0	0
		R-R-O	1/√2	0	
3 ²⁺	O-R-O	O-O-R	1/√2	u_{ex}	u_{ex}
		R-O-O	1/√2	u_{ex}	
4 ⁺	R-O-R-R	O-R-R-R	1/√2	0	0
		R-R-O-R	1/√2	0	
4 ²⁺	R-O-R-O	O-R-R-O	1/√2	0	$\{(1 + \sqrt{2})/(1 + 2\sqrt{2})\}u_{ex}$
		R-R-O-O	1/2	u_{ex}	
		R-O-O-R	1/√2	u_{ex}	
4 ³⁺	O-R-O-O	R-O-O-O	1/√2	u_{ex}	u_{ex}
		O-O-R-O	1/√2	u_{ex}	
5 ⁺	R-R-O-R-R	R-O-R-R-R	1/√2	0	0
		R-R-R-O-R	1/√2	0	
5 ²⁺	R-O-R-O-R	O-R-R-O-R	1/√2	0	$\{\sqrt{2}/(1 + \sqrt{2})\}u_{ex}$
		R-R-O-O-R	1/2	u_{ex}	
		R-O-O-R-R	1/2	u_{ex}	
		R-O-R-R-O	1/√2	0	
5 ³⁺	O-R-O-R-O	R-O-O-R-O	1/√2	u_{ex}	u_{ex}
		O-O-R-R-O	1/2	u_{ex}	
		O-R-R-O-O	1/2	u_{ex}	
		O-R-O-O-R	1/√2	u_{ex}	
5 ⁴⁺	O-O-R-O-O	O-R-O-O-O	1/√2	u_{ex}	u_{ex}
		O-O-O-R-O	1/√2	u_{ex}	
6 ⁺	R-R-O-R-R-R	R-O-R-R-R-R	1/√2	0	0
		R-R-R-O-R-R	1/√2	0	
6 ²⁺	R-O-R-R-O-R	O-R-R-R-O-R	1/√2	0	0
		R-R-O-R-O-R	1/2	0	
		R-O-R-O-R-R	1/2	0	
		R-O-R-O-R-R	1/√2	0	
		R-O-R-R-R-O	1/√2	0	
6 ³⁺	R-O-R-O-R-O	O-R-R-R-O-O	1/√2	0	$\{(3 + \sqrt{2})/(3 + 2\sqrt{2})\}u_{ex}$
		R-R-O-O-R-O	1/2	u_{ex}	
		R-O-O-R-R-O	1/2	u_{ex}	
		R-O-R-R-O-O	1/2	u_{ex}	
		R-O-R-O-O-R	1/√2	u_{ex}	
6 ⁴⁺	O-R-O-O-R-O	R-O-O-O-R-O	1/2	u_{ex}	u_{ex}
		O-O-R-O-R-O	1/2	u_{ex}	
		O-R-O-R-O-O	1/2	u_{ex}	
		O-R-O-O-O-R	1/√2	u_{ex}	
6 ⁵⁺	O-O-R-O-O-O	O-R-O-O-O-O	1/√2	u_{ex}	u_{ex}
		O-O-O-R-O-O	1/√2	u_{ex}	

^a Red and Ox given in the text are expressed as R and O in this table for simplification.

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