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Articles

Intervalence Electron Transfer in Mixed Valence Diferrocenylpolyenes. Decay Law of the Metal−Metal Coupling with Distance

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A series of diferrocenylpolyenes of general formula $Fc(CH{=}CH)_nFc$ with $n = 1-6$ (Fc = ferrocenyl group) has been prepared and studied from the point of view of intervalence transitions in the mixed valence state. Well-resolved intervalence transitions are observed in dichloromethane upon partial electrolytic oxidation. Comproportionation constants have been determined from redox titration data and in some cases from electrochemical wave splitting. The corrected spectra of the mixed valence species have been deconvoluted to extract the parameters (position, intensity, width) of the intervalence bands, which allowed the determination of the metal−metal coupling (V_{ab}) through the bridging unit using Hush's formula. The decay of V_{ab} with distance is close to an exponential law with an exponent of 0.087 $Å^{-1}$, constituting one of the smallest attenuations reported so far. A small deviation to the exponential law is detected.

Introduction

Intervalence electron transfer can be detected and quantitatively studied from the characteristics of the intervalence band of mixed valence complexes. Basically, the intervalence transition is considered as a special case of charge transfer transition, the reduced site (Red) being the donor group, while the oxidized site (Ox) is the acceptor group. The mixing of the two electronic states Red−Ox and Ox−Red is due to an electronic coupling term V_{ab} which is also responsible of the intensity of the intervalence transition. Thus, V_{ab} can be determined by the following formula[1]

$$V_{ab} = 2.05 \times 10^{-2}(\epsilon_{max}\bar{\nu}_{max}\Delta\bar{\nu}_{1/2})^{1/2}/R_{MM} \qquad (1)$$

where V_{ab} is the coupling (cm^{-1}), ϵ_{max} is the maximum extinction coefficient, $\bar{\nu}_{max}$ is the band position (cm^{-1}), $\Delta\bar{\nu}_{1/2}$ is the full width at half-maximum (cm^{-1}), and R_{MM} is the metal−metal distance (Å). This simple approach due to the former Hush treatment[1] has been recently questioned in particular for relatively strongly coupled systems,[2] but for weakly coupled systems (which are considered here) there is no indication of a general problem with the Hush analysis. This treatment allows the evaluation of V_{ab} from experimental results only and is well-suited for making comparisons on a series of homologous compounds.

In a previous study involving bis(pentaammineruthenium) complexes of α,ω-bipyridylpolyenes, we have determined the electronic couplings for a series a complexes in which the polyene part contained one to four double bonds.[3] However, this study suffered from a relatively poor resolution of the intervalence transition which overlapped partially with a nearby metal-to-ligand charge transfer transition. In the present study, we have used mixed valence compounds obtained by partial oxidation of diferrocenylpolyenes; they exhibit intervalence transitions at a markedly lower energy than in the previous case, so that a much better resolution is obtained. In the following, these compounds of general formula $Fc(CH{=}CH)_nFc$ containing two ferrocene units (Fc) linked by *n* conjugated double bonds will be denoted Fc-*n*-Fc.

Although a number of studies have been devoted to mixed valence ferrocene systems,[4−7] in most of the cases the ferrocene units are directly linked without a bridging unit ($n = 0$). For $n = 1$, the intervalence band has been observed by Cowan *et al.*,[8] but only the valence delocalization coefficient was computed. A substituted compound corresponding also to $n = 1$ has been mentioned by Dong *et al.*[9] Apart from an isolated work on 1,6-diferrocenyl-2,5-dicyanohexa-1,3,5 triene,[10] no systematic study has been reported for the longer systems although the

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starting compounds are known from the work of Schlögl and Egger[11,12] for up to five double bonds.

In the present work, long diferrocenylpolyenes with up to 6 conjugated double bonds have been prepared using improved procedures, the mixed valence compounds have been generated, and the intervalence transitions have been recorded using a systematic procedure already described.[3] Thus, the present series offers an unique opportunity to study accurately intervalence electron transfer and the decay law of the electronic interaction with distance.

Experimental Section

Preparations. Compounds Fc-1-Fc and Fc-2-Fc have been provided by B. Bildstein, P. Jaitner, and H. Schottenberger (University of Innsbruck). The others were prepared at NIU as described below.

Elemental analyses were performed by Paulanne Rider using a Perkin-Elmer Model 240 CHN analyzer. NMR spectra were obtained on a Bruker Model 200 SY spectrometer and were determined as solutions in $CDCl_3$ relative to tetramethylsilane (Me_4Si). Melting behavior was determined by modulated differential scanning calorimetry (DSC) with a TA Model 2920 differential scanning calorimeter. All diferrocenylpolyenes decomposed immediately after melting.

3-Ferrocenyl-2-propenal (1). Ferrocenecarboxaldehyde (Aldrich Chemical Co., 10.7 g, 0.05 mol) and 1,3-dioxan-2-yl methyltributylphosphonium bromide[13] (0.05 mol, 41.7 mL, 1.2 M solution in dimethylformamide (DMF)) were dissolved in DMF (200 mL) and heated with magnetic stirring to 80−90 °C. A solution of sodium ethoxide (0.055 mol, 55 mL, 1 M solution in EtOH) was then added dropwise over a period of 1 h, after which the reaction was heated at 90 °C for 48 h. The resulting mixture was poured into H_2O (ca. 1 L) and then extracted with ethyl ether (6 × 350 mL) and the combined extract dried ($MgSO_4$). After filtration the ether was removed under vacuum. The crude acetal was obtained as a dark red oil and was not purified further. It was dissolved in tetrahydrofuran (THF) (125 mL) to which a 5% aqueous solution of H_2SO_4 was then added (125 mL). After being stirred at 25 °C for 2 h, the mixture was poured into H_2O (*ca.* 1 L), extracted with ethyl ether (4 × 350 mL), and then washed with brine (2 × 250 mL) and dried ($MgSO_4$). After filtration and removal of the ether, crude **1** was obtained. The crude product was purified by chromatography over silica gel (Aldrich 70−230 mesh, 60 Å), eluting with 3% EtOAc in hexane. The product was obtained as dark red crystals (6.5 g, 54%); mp = 92−4 °C. ^{1}H NMR: δ 4.15(s, 5H, C_5H_5); 4.51 (m, 4H, C_5H_4), 6.26−6.38 (m, 1H, −C*H*CHO), 7.36−7.41 (d, J = 15.6, 1H, −C*H*═CH−), 9.53 (d, J = 7.7, 1H, CHO). Anal. Calcd for $C_{13}H_{12}OFe$: C, 65.03; H, 5.04. Found: C, 65.09; H, 5.03.

1,6-Diferrocenylhexa-1,3,5-triene, Fc-3-Fc (2). Ferrocenecarboxaldehyde (2.14 g, 0.01 mol) and (*E*)-but-2-ene-1,6-diylbis(tributylphosphonium) dichloride[14] (0.005 mol, 17.5 mL, 0.286 M EtOH solution) were placed in a round bottom flask (200 mL) and dissolved in DMF (75 mL). A solution of sodium ethoxide in ethanol (0.011 mol, 11 mL, 1.0 M solution) was added dropwise with magnetic stirring, and the resulting mixture, stirred at 25 °C for 48 h and then at 90 °C for 2 h. After cooling to room temperature, the mixture was cooled at 0 °C for several hours and filtered, yielding a red-orange product which was purified by solvent extraction with EtOH for several hours followed by vacuum drying. Pure **2** was of metallic copper color; 1.81 g, 81%, mp = 190 °C (dec). UV−vis (λ_{max} (CH_2Cl_2)): 368 nm (ϵ_{max} = 49 100 M^{-1} cm^{-1}). Anal. Calcd for $C_{26}H_{24}Fe_2$: C, 69.17; H, 5.36. Found: C, 69.7; H, 5.4%.

1,8-Diferrocenylocta-1,3,5,7-tetraene, Fc-4-Fc (3). Ferrocenecarboxaldehyde (2.14 g, 0.01 mol) and (*E,E*)-hexa-2,4-diene-1,6-diylbis(tributylphosphonium) dibromide[15] (0.005 mol, 13.3 mL, 0.375 M DMF solution) were dissolved in DMF (75 mL), and a solution of sodium ethoxide in ethanol (0.011 mol, 11 mL, 1.0 M solution) was added dropwise. The reaction mixture was treated as described for **2**, and crude **3** was obtained as a red-brown solid. The product was boiled in toluene, filtered, and purified by solvent extraction with EtOH followed by vacuum drying. Pure **3** was obtained as a bronze metallic solid; mp = 285 °C (dec). UV−vis (λ_{max}): 388.5 nm (ϵ_{max} = 53 500 M^{-1} cm^{-1}). Anal. Calcd for $C_{28}H_{26}Fe_2$: C, 70.86; H, 5.48. Found: C, 70.9; H, 5.5%.

1,10-Diferrocenyldeca-1,3,5,7,9-pentaene, Fc-5-Fc (4). 3-Ferrocenyl-2-propenal (2.4 g, 0.01 mol) and (E)-but-2-ene-1,6-diylbis-(tributylphosphonium) dichloride (0.005 mol, 17.5 mL, 0.286 M EtOH solution) were dissolved in DMF (100 mL), and a solution of sodium ethoxide in ethanol (0.011 mol, 11 mL, 1.0 M solution) was added dropwise. The reaction mixture was treated as described for **2**, and crude **4** was obtained as a red-brown solid. The product was refluxed overnight in 95% EtOH (200 mL) and filtered hot. The procedure was repeated with DMF (100 mL), yielding **4** (2.1 g, 85%); mp = 288 °C (dec). UV−vis (λ_{max} (DMF)): 405 nm (ϵ_{max} = 27 700 M^{-1} cm^{-1}). After vacuum drying at 50 °C and 1 Torr, elemental analysis indicated residual solvent contamination. Anal. Calcd for $C_{30}H_{28}Fe_2$: C, 72.03; H, 5.64. Found: C, 71.5; H, 5.45.

1,12-Diferrocenyldodeca-1,3,5,7,9,11-hexaene, Fc-6-Fc (5). 3-Ferrocenyl-2-propenal (2.4 g, 0.01 mol) and (*E,E*)-hexa-2,4-diene-1,6-diylbis(tributylphosphonium) dibromide (0.005 mol, 13.3 mL, 0.375 M DMF solution) were dissolved in DMF (100 mL), and a solution of sodium ethoxide in ethanol (0.011 mol, 11 mL, 1.0 M solution) was added dropwise. The reaction mixture was treated as described for **2**, and crude **5** was obtained as a red-brown solid. The product was refluxed overnight in a 50:50 mixture of EtOH/DMF (200 mL) and filtered hot, yielding crude **5** (1.6 g, 63%); mp = 292 °C. UV−vis (λ_{max} (DMF)): 414.5 nm (ϵ_{max} = 24 000 M^{-1} cm^{-1}). After vacuum drying at 50 °C and 1 Torr, elemental analysis indicated residual solvent contamination. Anal. Calcd for $C_{32}H_{30}Fe_2$: C, 73.03; H, 5.75. Found: C, 70.9, H, 5.6.

Physicochemical Measurements. Cyclic voltammetry was performed with an Electromat 2000 system (ISMP Technologie), using a platinum wire as working electrode and a satured calomel electrode as reference electrode. The solvent was dichloromethane containing 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte.

UV−vis and near IR were recorded using a Shimadzu UV-PC 3101 spectrophotometer.

Oxidations were performed by electrolysis in a two compartment cell using dichloromethane as solvent and 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte. The progress of the oxidation was followed coulometrically. A series of *ca.* 15 spectra was recorded and the curve giving the optical density (OD) as a function of x (average number of electrons removed, $0 < x < 2$) was used to determine the comproportionation constant as already described.[3]

For the longer systems ($n = 4-6$) a difficulty arose due to the weak solubility and the presence of impurities. Thus, to prepare the electrolysis solutions, the compounds were chromatographed on a SiO_2 column with CH_2Cl_2 as eluent. The mobile fraction was collected, the supporting electrolyte was added, and the diferrocenylpolyene concentration was determined by spectrophotometry (see below). The concentrations used for electrolyses were in the range 3×10^{-4} to 7×10^{-4} for $n = 1-3$ and 5×10^{-5} to 9×10^{-5} for $n = 4-6$.

Extinction coefficients of the starting products were determined straightforwardly for the shorter compounds ($n = 1-3$): a known quantity was dissolved in chloroform or dichloromethane using sonication if necessary (ϵ were found to be the same in both solvents) and the spectrum recorded. For the longer compounds (particularly Fc-5-Fc and Fc-6-Fc) dissolution was generally incomplete, so that the two following procedures were used to measure the concentration and hence the extinction coefficient: (i) following Schlögl, a suspension in chloroform or dichloromethane of the desired compound was heated in the presence of a small quantity of *p*-toluenesulfonic acid (typically 50 μL of a saturated solution of *p*-toluenesulfonic acid in chloroform for 10 mL of diferrocenylpolyene solution), with sonication if necessary, to convert all the material into the more stable *all-E* isomer; (ii) the diferrocenyl polyene was stirred in chloroform or dichloromethane and the solution was filtered. Then the concentration in the filtrate was determined by chronoamperometry using a rotating platinum disk

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Table 1. Electrochemical Data[a] (from Cyclic Voltammetry) for the Compounds Fc-*n*-Fc

compound	$E°_1$	$E°_2$	$\Delta E°$ [b]	K_c [c]
Fc-1-Fc	290	460	170	700
Fc-2-Fc	294	423	129	150
Fc-3-Fc	366	≈460	≈100	≈50
Fc-4-Fc	405 (2e)			
Fc-5-Fc	400 (2e)			
Fc-6-Fc	402 (2e)			

[a] Obtained in CH_2Cl_2 containing 0.1 M NBu_4BF_4. $E°$ (mV) are the arithmetic averages of anodic and cathodic peak potentials. Scan rate 0.1 V· s^{-1}. [b] $\Delta E° = E°_2 - E°_1$. [c] From $\Delta E° = (RT/F) \ln K_c$.

Table 2. UV−Vis Spectra[a] of the Diferrocenylpolyenes in CH_2Cl_2

compound	$\pi-\pi^*$ band	ferrocene band
Fc-1-Fc	314 (15 700)	458 (1450)
Fc-2-Fc	330 (26 500)	466 (2800)
Fc-3-Fc	367 (42 800)	470 (5800)
Fc-4-Fc	388 (55 300)	465 (9500)
Fc-5-Fc	406 (73 100)	500 (sh)
Fc-6-Fc	409 (86 100)	500 (sh)

[a] Wavelength in nanometers; molar extinction coefficient in parentheses; sh = shoulder.

electrode, the calibration having been performed with Fc-3-Fc which dissolves completely. A correction was applied to take into account the variation in diffusion coefficients due to the difference in sizes.[16] Both methods gave essentially similar results.

The obtained values are reported on Table 2 and are consistent with the ones reported by Schlögl[12] up to Fc-5-Fc.

Results and Discussion

General Properties of the Diferrocenylpolyenes. The shorter compounds are stable and relatively soluble, but difficulties arose for the longer ones ($n = 4$ or more). It was found in particular that the dissolution was never complete even when very small quantities were used. In addition, thin layer chromatography on SiO_2 (eluent dichloromethane) revealed two spots: a mobile one (assigned to the all-*E* isomer) and a fixed one, attributed to an impurity. Purification by column chromatography failed, the impurity reappearing upon solvent evaporation. The nature of the impurity could not be determined (according to Schlögl, it could be a mixture of various geometrical isomers[11]). Thus, as described in the Experimental Section, the electrolysis solutions were prepared from the column output, *without solvent evaporation*.

Electrochemistry. The shorter compounds (Fc-1-Fc to Fc-3-Fc) exhibit two more or less resolved oxidation peaks in cyclic voltammetry. The difference in peak potentials decreases with the number of double bonds, and for Fc-4-Fc to Fc-6-Fc a single peak is observed. This is the expected trend for weakly coupled mixed valence systems.[17] From the wave splitting, the comproportionation constant K_c relative to the equilibrium

$$\text{Fc-}n\text{-Fc} + \text{Fc}^+\text{-}n\text{-Fc}^+ \rightleftarrows 2\text{Fc-}n\text{-Fc}^+$$

can be computed and is reported on Table 1 for the first three compounds.

UV−Vis Spectra of the Starting Diferrocenylpolyenes. Spectra in CH_2Cl_2 are collected in Table 2. As mentioned in the Experimental Section, the case of the longer compounds ($n = 4-6$) was plagued by solubility problems. They were finally solved by recording the spectra of the output of the chromatography column. Identical spectra were obtained with samples heated in the presence of *p*-toluene sulfonic acid (see Experimental Section), the latter case allowing a determination of the extinction coefficient. The spectra are in good agreement with the ones reported by Schlögl. Two main bands are observed: one in the UV (300 to *ca*. 400 nm), corresponding to the polyene part, and one in the visible (440 to *ca*. 600 nm), corresponding to the ferrocene chromophore. Curiously the extinction coefficient increases not only for the polyene band but also for the ferrocene band, showing that the ferrocene moiety is not an independent chromophore but is strongly electronically coupled to the bridge.

Chart 1

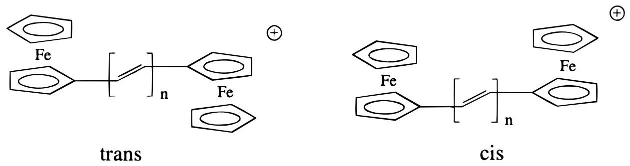

Table 3. Metal−Metal Distances, According to PC Model, for the Two Possible Dispositions of the Ferrocene Groups

compound		Fc-1-Fc	Fc-2-Fc	Fc-3-Fc	Fc-4-Fc	Fc-5-Fc	Fc-6-Fc
R_{MM}, (Å)	trans	7.03	9.21	11.54	13.87	16.29	18.71
	cis	6.19	8.59	11.05	13.46	15.94	18.41

Metal−Metal Distance Problem. The metal−metal distance is the main parameter of this study, and in addition it plays a role in the determination of the V_{ab} coupling through Hush's equation. Since no systematic crystallographic results are available, we have estimated the metal−metal distance using PC Model.[18] As stated above, the compounds are considered to be all-*E* isomers as far as the polyene chain is concerned, but there remains two possibilities corresponding to the two ferrocene units either cis or trans with respect to the polyene plane[19] (Chart 1).

The distances in the two hypotheses are reported on Table 3. In the case of Fc-1-Fc[20] and of 1,6-diferrocenyl-2,5-dicyanohexa-1,3,5-triene[10] (which is a substituted derivative of Fc-3-Fc), X-ray crystallography shows a trans disposition. However, this result is not necessarily valid for the geometry in solution. In addition, for long systems, it is very likely that the two possibilities are energetically equivalent since there is no longer steric interaction through space. This is indeed suggested by energy calculations through PC Model.

In the following, the results will be analyzed in the two hypotheses, except in the case of Fc-1-Fc for which steric hindrance favors clearly the trans arrangement.

Comproportionation Constants. Comproportionation constants can be obtained from the wave splitting when the waves are sufficiently resolved, or from the results of the redox titration, i.e. the OD *vs x* plots.[3] Then, the proportion of mixed

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(16) This correction used Perrin's formula for the diffusion coefficient of ellipsoidal molecules: Perrin, F. *J. Phys. Radium* **1936**, *7*, 1. This gave a decrease of 17% in the diffusion coefficient from Fc-3-Fc to Fc-6-Fc, leading to a correction of 8.5% on diffusion currents (which are proportional to $D^{1/2}$).

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(18) PC Model: Serena Software, Bloomington, IN.

(19) For long systems, the weak solubility and the complexity of NMR spectra precluded a reliable determination of the isomer. However the all-*E* nature of the compounds is suggested by the following: (i) a large number of polyenes have been obtained by the present Wittig method and they revealed always to be all-*E* isomers;[15] (ii) when crystal structures are available, they show an all-*E* isomer with a "trans" disposition of the terminal ferrocene sites,[10, 20] (iii) the evolution of the UV−vis spectra in the series Fc-*n*-Fc shows a regular increase of the conjugation length. It is true that in solution some rotation is conceivable around essentially single bonds of the polyene chain ("bicycle pedal" motion), but molecular modeling shows that the consequences on the metal−metal distance are very small. Thus the present molecules are considered relatively rigid.

(20) Bildstein, B. Private communication (structure of Fc-1-Fc).

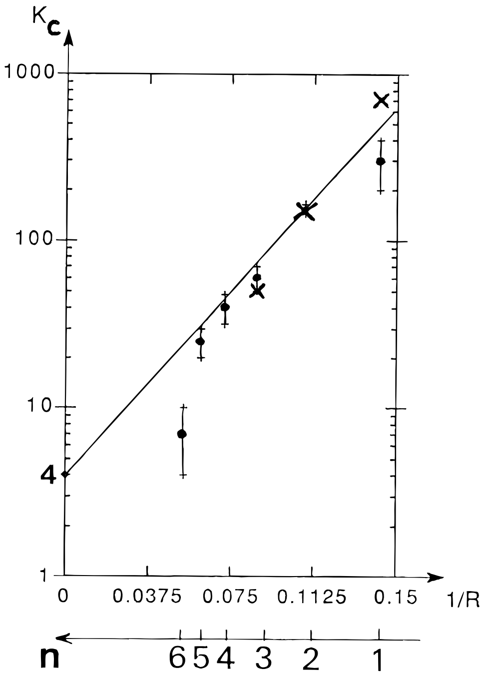

Figure 1. K_c (log scale) as a function of $1/R_{MM}$. (●) from redox titation, with error bar; (×) from wave splitting. The straight line has been drawn to pass through the statistical limit $K_c = 4$ for $R_{MM} \rightarrow \infty$.

valence species at half-oxidation

$$P = K_c^{1/2}/(2 + K_c^{1/2}) \tag{2}$$

is used to compute corrected spectra. The electrochemical method is more accurate for high K_c values (shorter compounds) because in this case the OD *vs* x plot is weakly dependent on K_c. Conversely, for small K_c values (longer compounds), the OD *vs* x plot is easier to use because the waves are too merged for a simple determination of $\Delta E°$. Thus, for Fc-1-Fc, we take $K_c = 700$, from electrochemistry (fortunately, for these high values of K_c, P being close to 100% depends very little on K_c). For Fc-2-Fc, the two methods are in good agreement, giving $K_c = 155$. For the longer compounds, the values from the redox titration have been used.

The dependence of K_c on metal−metal distance has been discussed by Reimers and Hush,[21] in the frame of a simple model considering that the deviation with respect to the statistical limit $K_c = 4$ is due to the electrostatic interaction between the added charges. This is certainly the major effect in the present compounds where the metal centers are separated by a large distance (7−18 Å). Thus, a plot of ln K_c *vs* $1/R_{MM}$ (R_{MM} = metal−metal distance) should be linear and pass through $K_c = 4$ for $1/R_{MM} \rightarrow 0$. As shown on Figure 1, this is the case, except for compound Fc-6-Fc which is clearly out of the plot. This comes probably from a lack of resolution of the intervalence band in this case. In addition, for Fc-6-Fc, the fully oxidized species absorbs notably in the near IR, which could have perturbed the spectra.

Finally, in this simple electrostatic model, the slope of the ln K_c *vs* $1/R_{MM}$ plot should be given in SI units by $N_A e^2/4\pi\epsilon_O\epsilon_R RT$, where N_A is the Avogadro constant, e the unit charge, ϵ_O the dielectric constant of vacuum, and ϵ_R the relative dielectric constant of the medium. Taking $\epsilon_R(CH_2Cl_2) = 9$ would give a slope of 62.2 at room temperature (R_{MM} being in angstroms), while the observed value from Figure 1 is 34. This discrepancy is certainly due to the difficulty of defining the dielectric constant at this scale, particularly in a low dielectric constant solvent (dichloromethane) containing a supporting electrolyte, i.e. a medium prone to ion-pairing effects. The experimental slope could be reproduced by taking an effective dielectric constant of 16.4, which seems reasonable for such a medium.

Mixed Valence Compounds: Corrected Intervalence Spectra and Metal−Metal Couplings. Spectra of the mixed valence species (corrected from comproportionation) are shown on Figure 2 with the deconvolution into gaussian components (Gaussian meaning that $\epsilon/\bar{\nu} = f(\bar{\nu})$ is a gaussian function, not $\epsilon = f(\lambda)$ of course). The vertical lines are artifacts coming from solvent absorption exceeding the compensation capability of the double beam spectrophotometer. As can be seen, excellent resolution is obtained for $n = 1-4$. The band is perfectly exploitable for $n = 5$. Only $n = 6$ raises a problem as the band is only a shoulder and the spectrum has been obtained after an important correction from the absorbance of the oxidized form Fc^+-6-Fc^+. Anyway, even if we restrict it to $n = 1-5$, *this is an unique series of compounds allowing the accurate determination of the decay law of the electronic interaction.*

Spectral deconvolution was usually performed with three bands:

(i) The first is an intense band located mainly in the visible but with a tail extending in the near IR. It corresponds to absorption coming from the ferrocene (*ca* 600 nm) and the ferrocenyl (Fc^+) chromophore[22] (*ca.* 850 nm). Ideally two different bands should have been introduced for this part of the spectrum, but the deconvolution process converged more efficiently with one band encompassing the two absorptions.

(ii) The second is the intervalence band, developing in the near IR.

(iii) The third is an additional band near 1000 nm which proved necessary for good spectral fits. This band is barely detectable for Fc-1-Fc^+ and Fc-2-Fc^+, but its intensity increases with n. Its nature is unknown; however, it was noticed that, during the oxidation of a given compound, it increases continuously and, thus, is maximum for the fully oxidized species. These characteristics show that it is not an intervalence transition but rather a new transition specific to the ferricinium chromophore. Consequently it should not be introduced in the V_{ab} calculations.

Finally, for $n = 6$, it was necessary to fit with four bands, since the ferrocene band and the normal ferricinium band could no longer be encompassed under the same gaussian. The “1000 nm band” occurred in fact at 1100 nm. Only the band occurring at highest wavelengths was considered as the intervalence transition.

The intervalence band parameters coming from the deconvolution are gathered in Table 4. For each compound, several independent determinations (3−5) have been performed, allowing an empirical determination of the uncertainty. The uncertainty on ϵ takes into account the uncertainty on K_c. Finally, for Fc-6-Fc, calculations have also been made for $K_c = 20$, which seems a more realistic value than $K_c = 7$ (see Figure 1).

Decay of the Metal−Metal Coupling with Distance. Figure 3 shows the variation of V_{ab} (in logarithmic scale) with distance. Strictly speaking, the values depend on the structural hypothesis (cis or trans as defined in Chart 1) but as shown on Figure 3, the difference is very small and lower than the experimental uncertainty. In the following we discuss the results in the “trans” hypothesis.

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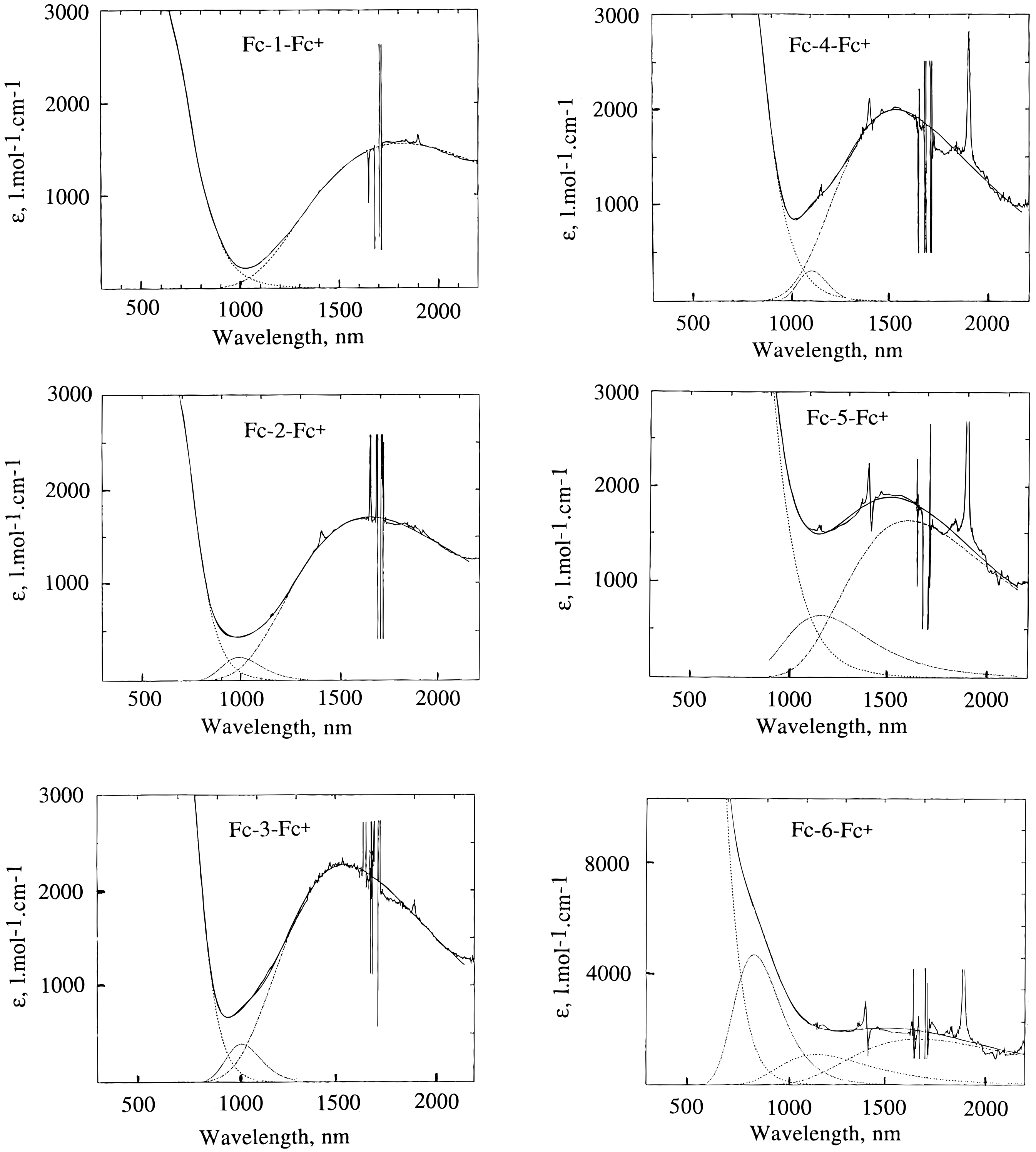

Figure 2. Spectra of the mixed valence species (corrected from comproportionation) with deconvoluted bands.

For the compound Fc-1-Fc, our V_{ab} value (0.061 eV) is in good agreement with the results of Cowan *et al.*[8] They report a delocalization factor of 0.09, which, after multiplication by the optical energy,[1] gives $V_{ab} = 0.063$ eV.

For the compounds with $n = 5$ and 6, the uncertainty increases due to the lack of resolution of the intervalence band and the residual absorption of the fully oxidized species. Fortunately the consequences on V_{ab} are buffered by the fact that V_{ab} depends upon the square root of the extinction coefficient of the intervalence transition. This is also why changing K_c from 7 to 20 for Fc-6-Fc has only very limited consequences on V_{ab}.

The plot of ln $V_{ab} = f(R_{MM})$ is almost linear, showing that, as a first approximation, V_{ab} decays exponentially with distance. The slope is 0.087 Å^{-1}, corresponding to a decrease of a factor 2 for each 8 Å. Curiously, this is almost the same law as for bipyridylpolyenes linked to terminal pentaammineruthenium groups.[3] In fact, the average decay coefficient reported here is one of the smallest reported so far.[23]

When looking in more detail, a significant deviation to the exponential law appears. Thus, the compound $n = 3$ is definitely above the line, taking into account the experimental uncertainty. We have reproduced several times this measurement and are reasonably confident about it, because, in this case,

Table 4. Comproportionation Constants, Intervalence Band Parameters, and Metal−Metal Couplings in the Series Fc-*n*-Fc

					V_{ab}, cm^{-1}		
compound	K_c[a]	$\bar{\nu}$,[b] cm^{-1}	ϵ,[b] mol^{-1}·L·cm^{-1}	$\Delta\bar{\nu}_{1/2}$[b]	trans[c]	cis[d]	V_{ab},[e] eV
Fc-1-Fc	300 ± 100	4910 ± 10	1340 ± 100	4360 ± 100	495 ± 25		0.061 ± 0.003
Fc-2-Fc	155 ± 10	5500 ± 10	1570 ± 80	4340 ± 100	430 ± 15	460	0.053 ± 0.002
Fc-3-Fc	60 ± 10	6010 ± 10	2100 ± 100	3800 ± 100	390 ± 15	405	0.048 ± 0.002
Fc-4-Fc	40 ± 8	6070 ± 30	1670 ± 200	3700 ± 100	290 ± 20	293	0.035 ± 0.002
Fc-5-Fc	25 ± 5	5860 ± 30	1600 ± 300	3600 ± 100	230 ± 25	234	0.028 ± 0.003
Fc-6-Fc	7 ± 3	5565 ± 30	1600 ± 400	3600 ± 100	195 ± 25	200	0.024 ± 0.003
			1320 ± 400[f]		177 ± 25[f]	180[f]	0.022 ± 0.003[f]

[a] Comproportionation constant, from the spectrophotometric titration. [b] From spectral simulation. The uncertainty on ϵ incorporates the uncertainty on K_c. [c] Computed with R_{MM} corresponding to the trans disposition. [d] Computed with R_{MM} corresponding to the cis disposition. [e] Value for the trans disposition. [f] Assuming $K_c = 20$ (see text).

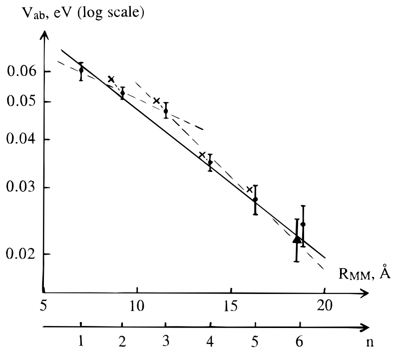

Figure 3. Decay of the metal−metal coupling (log scale) with distance: (●) values in the hypothesis of a trans configuration of terminal ferrocene groups, with error bars; (▲) for Fc-6-Fc with $K_c = 20$; (×) values in the hypothesis of a cis configuration; (—) straight line corresponding to the gross exponential decay; (- -) lines corresponding to the two different regimes (see text).

there was no problem with solubility and calibration. Thus, a more accurate description of the decay law involves two slopes: for Fc-1-Fc to Fc-3-Fc, the decay factor is 0.054 Å^{-1}, while for Fc-3-Fc to Fc-6-Fc, it is 0.113 Å^{-1}(see Figure 3). Deviations with respect to a simple exponential law are predicted by theoretical treatments[21,24] and are more likely to occur in systems for which the decay is slow with distance, which is the case here.

Finally, it is interesting to compare Fc-3-Fc with the case of 1,6-diferrocenyl-2,5-dicyanohexa-1,3,5 triene.[10] For this latter compound an analysis similar to the present one gave a value of 0.017 eV for V_{ab}, i.e., 2.8 times less than for Fc-3-Fc. Experimentally, this large difference comes mainly from a spectacular change in extinction coefficients (*ca.* 2000 for Fc-3-Fc *vs ca.* 200 for 1,6-diferrocenyl-2,5-dicyanohexa-1,3,5-triene). This is certainly due to the presence of cyano groups which drains some electron density from the polyene chain, thus lowering the effective overlap between diabatic orbitals. This effect has indeed been predicted theoretically.[25]

Conclusion

Diferrocenylpolyenes are for the moment the best systems to study long distance intervalence electron transfer and the decay law of the electronic interaction with a distance of up to 6 conjugated double bonds. The synthesis of more soluble compounds could increase this limit. The decay law is very close to an exponential law, and the rate of decay is the smallest established so far.

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(23) The metal−metal coupling through a bridging ligand has been discussed in a number of papers (see refs 1 and 17 and references cited therein). More recently, for bis(pentaammine)ruthenium complexes linked by bipyridylpolyenes, we have found theoretically (Joachim, C.; Launay, J.-P.; Woitellier, S. *Chem. Phys.* **1990**, *147*, 131) and experimentally[3] a decay coefficient of 0.087 Å^{-1}, although Reimers and Hush[21] give for this series a higher value, 0.13 Å^{-1}. For bis(terpyridyl)ruthenium complexes with phenyl groups as spacers, the decay coefficient is 0.084 Å^{-1} (computed from: Collin, J.-P.; Lainé, P.; Launay, J.-P.; Sauvage, J.-P.; Sour, A. *J. Chem. Soc., Chem. Commun.* **1993**, 434).

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